A Specialist Periodical Report

Photochemistry
Volume 1

A Review of the Literature Published between July 1968 and June 1969

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SBN: 85186 005 2
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The Chemical Society
Burlington House, London, W1V 0BN
Organic formulae composed by Wright's Symbolset method

PRINTED IN GREAT BRITAIN BY JOHN WRIGHT AND SONS LTD., AT THE STONEBRIDGE PRESS, BRISTOL
Introduction

This volume inaugurates what is hoped will be an annual series of comprehensive reports on the progress of photochemistry. In compiling the work, the authors have adopted as a guiding principle the need to present as unified a treatment as possible; and although various Chapters stress, say, the more ‘physical’ or ‘organic’ aspects of the subject, in reflection of the emphasis in the original papers, the aim has been to produce a work which as a whole will be of value to both physical and organic chemists, and even, with the inclusion of a section on Inorganic Photochemistry, to inorganic and organometallic chemists. Only the more biochemical aspects have been omitted, though with reluctance, partly because of the need to keep the work to a manageable length; but consideration will be given to the inclusion of a section covering the more chemical aspects of photobiology in future reports. It is hoped that the section on photopolymerisation will be of special use to the growing number of chemists interested in the industrial applications of photochemistry, although the authors are aware that many interesting developments lie hidden in the growing patent literature on the subject, which they have not found it feasible to cover. References to work in borderline areas will sometimes be found in more than one Chapter.

This report is concerned with the twelve months July 1968 to June 1969, inclusive. The authors have attempted to achieve both a report and a critical commentary, as far as possible; but the aim to have an edited manuscript at the printers only two and a half months after the end of the period under review has inevitably restricted the desirable element of commentary. The name of the author principally responsible for compilation is given for each Chapter, although the authors accept Cabinet responsibility for the work as a whole.

Until about ten years ago, photochemistry was largely a branch of physical chemistry, and organic chemists relied almost wholly on the Bunsen burner or its equivalent, and/or catalysts, for making and breaking bonds. The advent of gas-chromatography and the development of new spectroscopic tools made it feasible for organic chemists to study the often small quantities of compounds which are formed by chemical transformations of electronically excited molecules, and it soon came to be realised that a whole new branch of chemistry was easily accessible, having its own rules, and often providing structurally interesting molecules. The good news has also reached the inorganic and organometallic chemists, but is only just beginning to make an impact. There are numerous signs of industrial interest in photochemistry, most evidently in Japan, the United States, and Germany.

The year under review has seen solid progress in many areas, and a lot
of enthusiastic 'wildcatting' (to borrow a term from the petroleum industry) in others. Quite often one finds that apparently arbitrarily chosen complicated molecules are studied long before their structural parents have been looked at. Such approaches are probably relatively inefficient in promoting a greater understanding of the subject as a whole.

A greater awareness of the importance of chemical quenching processes for luminescence phenomena appears to be growing, and it is no longer expected that the quantum yields for photophysical processes such as fluorescence and phosphorescence should total unity. Kasha, Jortner, and Ting have independently developed some stimulating new ideas relevant to 'radiationless' transitions between electronically excited states. The whole basis of earlier theories has been questioned. It had previously been thought that such transitions are time-dependent and require some perturbation influence possibly connected with failure of the Born–Oppenheimer approximation. Kasha in particular has now argued that the transitions may be time-independent, and that intermolecular perturbation may occur prior to interaction with the external field. This approach would require replacement of the hallowed term 'intersystem crossing' with a new term 'intersystem mixing'. Future work may clarify the degree of difference implied by this distinction. The related new ideas developed by Jortner are specially relevant to the mechanism of bond-breaking processes which occur consequent upon initial electronic excitation.

Until recently, upper excited singlet and triplet states were thought to cascade down so rapidly to the lowest excited states \( (S_1 \text{ and } T_1) \) that, except in the special case of azulene, all luminescence emission phenomena, energy transfer processes, and chemical transformations must proceed from these lowest excited states. This viewpoint is being modified in the light of clear evidence for energy transfer from \( T_2 \) anthracene, and indications that some photoadditions of olefins to cyclopentenone proceed via the \( T_2 \) state of the enone. It seems possible that some phenomena now attributed to 'non-vertical' energy transfer may actually involve higher excited states. Cases of \( T \rightarrow T \) fluorescence in arylcarbenes have been claimed, and a valuable new technique involving simultaneous monitoring of an e.s.r. signal has made it possible to use \( T \rightarrow T \) absorption spectra to provide a quantitative measure of triplet state populations.

Contrary to previous belief, the position of \( \lambda_{\text{max}} \) for fluorescence is not necessarily independent of the wavelength of the exciting radiation, for example in the case of quinine which is often used as a reference standard.

Energy-transfer phenomena in photochemistry have previously been thought largely to involve triplet species, but cases of singlet energy transfer are now being reported, sometimes for systems hitherto supposed to involve energy transfer between triplets. The formation of singlet and triplet excimers and exciplexes in fluid solutions continues to attract interest, although the precise nature of the bonding and geometry in such complexes is still less clear than one would like.
Introduction

The fallacious assumption is still occasionally being made that the ability of triplet sensitisers such as benzophenone to sensitise a process implies that the unsensitised process proceeds via triplet intermediates. It is still much easier to establish a triplet pathway for a reaction than to exclude the possibility of a contribution from excited singlet intermediates. Triplet processes are often thought to be non-stereospecific, but one or two substantially stereospecific examples are beginning to appear. More reliable and unambiguous diagnostic tests for triplet intermediates have long been needed: there is some hope that lanthanide ions may provide sensitive probes for such intermediates, particularly those of $\pi\pi^*$ type.

Studies of photochemical transformations are generally most conveniently carried out in fluid media; but more cases are becoming known where photoreactions follow substantially different courses in the gas and liquid phases. Several workers have pointed out the importance of temperature effects in photoreactions, but temperatures are still frequently unspecified in publications. There is increasing interest in the effects of acid media, since it is now recognised that molecules have acid–base characteristics in excited states different from those in the electronic ground state, and that proton-transfer can be rapid in comparison with excited state lifetimes. Protonation of excited states can produce carbonium ions and lead thereby to isomerisation and other reactions typical of these species. Solvent effects are often loosely attributed to the solvent ‘polarity’, but it is rarely made clear whether the property referred to is related to the dielectric constant or to the solvating (e.g. hydrogen bonding) character.

Previous discrepancies concerning the quantum yield for photodecomposition of water at 1849 Å have been largely resolved, and evidence has been obtained for the formation of solvated electrons at shorter wavelengths. Studies of inorganic phosphors have been stimulated by the ability of such systems to show laser action, but much remains to be done here, and also on the use of inorganic oxide-type semiconductors as photosensitisers. There is growing interest in the photochemistry of co-ordination compounds in solution.

Many may feel that work published during the year in the more organic regions of photochemistry has been impressive for its quantity rather than its overall quality; but significant advances have certainly been made in several areas. The Woodward–Hoffmann orbital symmetry rules continue to be valuable in rationalising many varieties of photochemical behaviour, but have occasionally been applied without analysis to systems, e.g. anthracene, where their relevance is uncertain.

Among numerous new photoisomerisations, Zimmermann’s transformation of cyclo-octetraene into semibullvalene is specially interesting, as is Anet’s report that bond-inversion in cyclo-octetraenes is promoted by light. White and his co-workers have described an extraordinary mono-
trans isomer said to be formed from the irradiation of 1,2,4,7-tetraphenyl-
cyclo-octetraene.
Introduction

Interest in enone and dienone photochemistry continues at a high level: this rich seam shows few signs of being exhausted. The mechanism of the preparatively-useful isomerisation of \( \alpha\beta \)-enones to the \( \beta\gamma \)-isomers has been considerably clarified.

Mechanistic studies on the photochemical \emph{cis–trans} isomerisation of ethylenes have suggested that both singlet and triplet processes can occur. The direct isomerisation of stilbenes increasingly appears to be a singlet process, although doubts persist in the cases of certain substituted stilbenes. There may even be some small contribution from singlet intermediates in the benzene-sensitised isomerisation of but-2-ene, especially at high olefin concentrations, although the process is often used to measure the triplet yields of aromatic hydrocarbons.

Work continues on the photochemistry of benzene and its derivatives. The photoisomerisation of \( o \)- to \( m \)-xylene has been shown to be a singlet process, in accordance with previous predictions based on orbital and state symmetry considerations. It has been suggested that the unusually short lifetimes of aromatic triplet species may be due in part to the formation of triplet excimers. Past discrepancies concerning the solid-state photo-dimerisation of anthracene have been resolved, and attributed to a hitherto-unrecognised wavelength dependence.

The photo-Fries reaction has received continued attention. Previous studies had identified free-radical intermediates, but it now seems possible that the \emph{ortho}-Fries rearrangement in \emph{para}-blocked phenyl esters can be viewed as a concerted process. Some interesting effects of solvent viscosity and ‘polarity’ have been observed for this reaction.

Applications of photochemical procedures continue to be made in the synthesis of natural products, \emph{e.g.} thyroxine, and interesting reports have appeared on the photochemistry of purines and pyrimidines, a topic of importance in connection with the effects of u.v. radiation on nucleic acids.

D. B-S.
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Part I

PHYSICAL ASPECTS OF PHOTOCHEMISTRY
Spectroscopic and Theoretical Aspects

This chapter is devoted to those spectroscopic and theoretical aspects of the subject which will be of immediate interest to photochemists. Since absorption of light by a molecule necessarily precedes the photochemical and photophysical processes of interest, mention will be made of the absorptive act where this provides useful information. Theoretical treatments of the factors influencing the photophysical properties of excited states, including luminescence and radiationless transitions, and attempts to account for observed behaviour of excited molecules are considered here in detail. The rationalisation of the mechanisms of both photochemical and thermal reactions by orbital symmetry considerations will be considered only briefly in this chapter. Discussion of these rules with reference to particular organic molecules is to be found in those chapters dealing with the photochemistry of the relevant compounds.

1 Absorption and Energy Level Calculations

Absorption spectroscopy can provide much useful information concerning the nature of the excited states studied. In general, molecular orbital calculations have not been precise enough to predict exact energies of excited electronic states of most complex molecules, but the results are often useful in the characterisation of the states. All mono-olefins exhibit a single strong optical transition whose absorption maximum falls between 7.6 and 6.2 eV, with $\varepsilon_{\text{max}}$ of ca. 10$^4$. Many substituted olefins show a lower-energy transition with $\varepsilon_{\text{max}}$ of ca. 1000, which is incompletely characterised. S.C.F. calculations have been performed on ethylene and trans-cyclo-octene in an attempt to determine which orbitals are involved in these transitions. The conclusions reached are that the strong absorption observed is due to the $\pi_s \rightarrow \pi_s^*$ transition, as was known before, but in the case of trans-cyclo-octene, another transition, the $\pi_s \rightarrow \pi_g^*$ must also be available in the 5—7 eV region to account for the observed rotational strength of the transition. The transition with $\varepsilon_{\text{max}} \sim 1000$ can only be assigned to the $\pi_s \rightarrow 4a_g$ (3so*) transition. Thus at least three excited singlet states of simple olefins lie in the 5—7 eV region. Data on the electronic spectra of a large number of conjugated compounds in the u.v. and

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visible region of the spectrum have been compared with calculations of
energy levels by use of Hückel molecular orbitals in a recent review.²
Pariser–Parr–Pople calculations on the excited states of some aromatic
molecules yield results for the energies of singlet states in good agreement
with experiment.³ ⁴ An interesting fact arising from the calculations is that
the non-bonding electrons on the fluorine atom in fluorobenzene have no
effect on the ring in the lower energy transitions. Appreciable effect would
only be noticed on the \( E_{sa} \) state of benzene, transformation to which is in an
inaccessible part of the spectrum and has not been observed experimentally.

The electronic absorption spectra of carbonyl compounds have been the
subject of several studies.⁵ ⁷ While there is no doubt that the lowest lying
excited singlet state of carbonyl compounds is the \( nn^* \) state, controversy
exists over the assignation of the second singlet. In aromatic ketones, there
seems little doubt that this arises from a \( \pi \rightarrow \pi^* \) transition, and a similar
transition has also been assumed in the case of aliphatic ketones. However,
a polarisation study of crystalline heptadecan-9-one and the changes
observed upon melting of the sample seem to indicate unequivocally that
the second singlet in this compound arises from the \( n \rightarrow \sigma^* \) transition.⁵
Since the second singlet in acetone has been assigned to this transition by
some authors, the implication is that in aliphatic ketones the second excited
singlet state is of a nature different from that in aromatic compounds.
Though the second singlet is considered to be of the \( \pi\pi^* \) configuration,
extended Hückel molecular orbital calculations were performed on a
variety of substituted alky and aryl carbonyl compounds, and a rationale
obtained for the observed red and blue shifts of transitions to both first and
second excited states.⁶ Substitution clearly affects the \( n \rightarrow \pi^* \) transition
more than the transition to the second excited state.

The forbidden \( S_0 \rightarrow T_1 \) transition in benzophenone can be seen in absorp-
tion in the crystalline state. A polarised high-field Zeeman study reveals
that the triplet state reached by such absorption is the symmetry analogue
of the \( ^3A_d (C_{2v}) \) state of formaldehyde.⁷ The transition gains its intensity \( \text{via} \)
spin–orbit coupling with the \( ^1A_1 \) and \( ^1B_2 \) states. Since the \( \text{C}=\text{O} \) and aryl
moieties are non-planar, there is the possibility of strong vibronic coupling
between the \( ^1\pi\pi^* \) states and carbonyl \( ^1\sigma \rightarrow \pi^* \) transitions. Since the \( ^1\sigma\pi^* \)
states are already strongly spin–orbit coupled to the \( nn^* \) states, the net
effect of twisting is to intensify the \( S \rightarrow T \) transition. The second triplet state
of benzophenone⁸ has never been located experimentally, although it has
been convenient to assume that it lies in energy between the lowest singlet
\( 1nn^* \) state and the lowest triplet \( 3\pi\pi^* \). In this position the \( \pi\pi^* \) triplet can

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Spectroscopic and Theoretical Aspects

be used to account for the observed high rates of intersystem crossing from the $^1n\pi^*$ to $^3n\pi^*$ states. Theory shows that transitions between these states should be of much lower probability than transitions between states of different configurations. However, if it is assumed that the $^3n\pi^*$ state lies just lower in energy than the $^1n\pi^*$, ready intersystem crossing between these levels could occur, followed by internal conversion to the $^3n\pi^*$ state.

There is evidence now, however, that this explanation is unsatisfactory, since a search for singlet–second triplet absorption in crystals of benzophenone and 4,4’-di-iodobenzophenone has failed to show the existence of this state in the expected energy region. Experimentally, the technique of phosphorescence excitation$^9,10$ was used to overcome the difficulties of detecting the very weak absorption. Both compounds exhibited singlet–triplet absorption attributable to the $S \rightarrow T_{n\pi^*}$ transition, but neither showed any absorption between this wavelength region and the onset of the strong singlet–singlet absorption. The conclusions to be drawn from this study are that the $^3n\pi^*$ state in these compounds lies higher in energy than the $^1n\pi^*$ singlet, or at least is nearly degenerate with it. This inference, if correct, has the important implication that the rapid intersystem crossing observed in benzophenone between the $^1n\pi^*$ and $^3n\pi^*$ states occurs without the intermediacy of the $^3n\pi^*$ state, despite theoretical predictions to the contrary.$^{11}$ However, an indirect involvement of this state via second-order vibronic mixing cannot be excluded.

Calculations using a modified version of the Pariser–Parr–Pople method on the electronic spectra of unsaturated ketones yield results in good agreement with experiment for the $\pi-\pi^*$ transition, but results of varying success when the method is applied to $n-\pi^*$ transitions.$^{12}$

Detailed calculations of Franck–Condon factors and their effect upon the rates of radiationless processes in molecules are considered in the next section. Brief mention will be made here only of calculations pertaining to small molecules. Calculations on Lyman bands of hydrogen have shown that hitherto neglected vibration–rotation interaction effects are appreciably large for a number of the bands.$^{13}$ For the Schumann–Runge bands in the $^{16}O_2$ and $^{18}O_2$ isotopes, and the Lyman H$_2$ bands, Franck–Condon factors were also found to vary considerably with rotation quantum number.$^{14}$ A simple method of obtaining structural data from vibrational intensities has been applied to molecules in which there is a large change in shape in going from the ground state to the excited state.$^{15}$ The transitions considered are the 1500 Å system of ammonia, the 1600 Å system of PD$_3$, the $\alpha$-X system of HCN, the 2400 Å system of acetylene, and the 3500 Å

system of formaldehyde. For a transition from a linear ground state to a bent excited state it is possible to decide whether the transition correlates with an allowed or forbidden transition in the linear–linear configuration.

Absorption spectra can provide data on the physical properties of excited states also. Thus a special technique has been developed to measure the change in dipole moment of molecules on going from the ground to excited states, using a strong electric field.\textsuperscript{16} For a mixed crystal of azulene in naphthalene, the dipole moments of azulene in its first two excited states have been measured. The direction of the dipole changes in both states from that in the ground state. The changes in dipole moment of the singlet state of naphthalene and substituted naphthalenes in different solvents have been measured.\textsuperscript{17} From an extension of the theory of solvent shifts based on the Onsager model of dielectrics, it is possible to derive equations which include the change of polarisability, $\Delta \alpha$, from the ground state to an excited state.\textsuperscript{18} For some aromatic molecules $\Delta \alpha$ in the excited state is calculated to be appreciably smaller than in the ground state. However, solvent shift methods have failed to detect any measurable polarisability change. The reason for this failure may lie in the fact that in the presence of the very large field due to the solvent shell, the assumption that the magnitude of the induced dipole moment is still proportional to the field may not be valid, owing to a saturation effect.

### 2 Radiationless Transitions

The term radiationless transition refers to processes in which molecules change from one electronic state to another without emission of radiation. If no change in multiplicity is involved, the process is termed an internal conversion, whereas transitions between states of different multiplicity are referred to as intersystem crossings. If the final state is dissociative, the transition is deemed predissociation. Any successful theoretical treatment of radiationless processes must be able to explain the vast amount of experimental data which has been accumulated in the literature and which may be summarised into the following general observations.

- (a) With the exception of azulene and its derivatives, only the lowest electronically excited levels of polyatomic organic molecules emit radiation, implying rapid radiationless transitions between higher excited states.

- (b) Radiationless transitions are first-order processes, as far as can be determined experimentally.

- (c) As the energy gap between the electronic terms of the initial and final states increases, the rates of radiationless processes decrease.

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Spectroscopic and Theoretical Aspects

(d) Deuteration of molecules containing C—H bonds greatly reduces the rates of radiationless transitions, leading to an increase in observed radiative lifetimes.

(e) Generally, as the temperature of a system is raised, radiationless transitions become more important, or at least, radiative processes are quenched.

(f) Molecules of high enough complexity (see Chapters 2 and 3) appear to undergo radiationless transitions in the absence of perturbing collisions, i.e. the phenomenon is a strictly intramolecular one. For small molecules this is not the case.

A number of theoretical approaches,\textsuperscript{19–39} have appeared in the literature attempting to explain the above experimental observations, and some of these have been briefly reviewed in an article purporting to show cases of transitions which do not fall into the categories above.\textsuperscript{40} More recently, there has appeared an excellent and critical evaluation of the main theories to date,\textsuperscript{38} and it is worthwhile summarising the salient features of the most important here.

Gouterman.\textsuperscript{19, 36}—This treatment will be considered first, since it differs from all subsequent theories in that a perturbation external to the molecule undergoing the radiationless transition is essential to the mechanism. The case of a solute molecule embedded in a crystalline host is treated by postulating interactions of the molecule with the crystal phonon field. By analogy with photon-induced radiative transitions, an expression is obtained for the spontaneous radiationless transition rate $A_{\nu \rightarrow \nu}^r$,

$$A_{\nu \rightarrow \nu}^r = \frac{4\omega^3}{3\hbar c_0^2} |M_{\nu \nu}^r|^2$$

(1)

\textsuperscript{18} M. Gouterman, \textit{J. Chem. Phys.}, 1962, 36, 2846.
\textsuperscript{19} P. Seybold and M. Gouterman, \textit{Chem. Rev.}, 1965, 65, 413.
\textsuperscript{20} H. Sponer, \textit{Radiation Res.}, 1959, 1, 658.
\textsuperscript{24} G. W. Robinson and R. P. Frosch, \textit{J. Chem. Phys.}, 1962, 37, 1962; G. W. Robinson and R. P. Frosch, \textit{ibid.}, 1963, 38, 1187.
\textsuperscript{26} W. Siebrand, \textit{J. Chem. Phys.}, 1966, 44, 4055; 1967, 46, 440.
\textsuperscript{34} J. Jortner and R. S. Berry, \textit{J. Chem. Phys.}, 1968, 48, 2757.
\textsuperscript{38} C. H. Ting, \textit{Photochem. and Photobiol.}, 1969, 9, 17.
where $c_s$ is the velocity of sound, $\omega/2\pi c = E_i - E_f$ (cm$^{-1}$) and $M_{ij}$ is the matrix element coupling the two states. This latter term includes the vibrational overlap integral, and from a consideration of how this factor varies with energy gap, deuterium substitution $\text{etc}$., observed experimental behaviour can be explained. However, the theory implies that for a single isolated molecule in the gas phase which is not subjected to a phonon field, radiationless processes should not occur, whereas data are available to show that the contrary is true. For this reason the theory may be discounted.

Franck and Sponer.$^{21,22}$ Initially Sponer considered that crossing of potential surfaces was a necessary condition for radiationless transitions such as predissociation and internal conversion to occur, although since then it has become apparent that quantum mechanical tunnelling can satisfactorily explain such processes where no crossing occurs. Franck and Sponer$^{22}$ suggested that intramolecular radiationless transitions might be caused by radiative transfer of excitation energy from one state of a molecule to another state of the same molecule, in a manner analogous to radiative transfer of energy between two different molecules, which is a well-defined process. The rate of intramolecular transfer from the zeroth vibrational level of state $S_i$ to the isoenergetic vibrational level of state $S_f$ is then some function of the transition moments for absorption from the ground state to states $S_i$ and $S_f$. The theory was rejected because it is incapable of accounting for observed transitions from the lowest singlet and triplet excited states to the ground state, since the ground state would be incapable of absorbing the emitted radiation, the transition not being electronic in nature. However, the approach has recently been revived and remarkable data presented to support the concept of radiative transfer (see later).

Ross and Co-workers.$^{23,24}$ In the early approach of these workers, transitions from the zeroth vibration level of the upper state to the isoenergetic vibrational level of the lower excited state were considered to occur $\text{via}$ tunnelling between the potential surfaces of the two states. Polyacenes were considered as diatomics, and potential surfaces could be constructed as functions of a single parameter $R$, given by

$$R = \left( \sum_{i} \Delta r_{ij}^2 \right)^{\frac{1}{2}}$$

(2)

Here $\Delta r_{ij}$ denotes the change in length of the $j$th bond when a molecule goes from ground to excited state. The bond lengths considered to be changing are only the C--C bonds associated with the 1400 cm$^{-1}$ vibration of aromatic hydrocarbons. By constructing curves for different excited states, the 'barrier width', or distance between curves along a line drawn through the zero-point energy of the upper state, can then be correlated with the experimental radiationless transition rate constant $k$. The correlation obtained was

$$\log_{10} k = 13.6 - 42.5 \text{ (barrier width in } \AA)$$

(3)
The expression is useful qualitatively in that it correctly predicts that most aromatics will not undergo radiative transitions from higher excited states.

A later paper $^{24}$ extends these results by use of the theory of Robinson and Frosch,$^{25}$ although instead of calculating barrier widths, Franck-Condon factors are determined. These factors, $F$, are represented as the sum of vibrational overlaps for three types of vibration, CH stretches, skeletal stretches, and skeletal bends, thus:

$$F = \sum S_{\text{CH}}^2 \ S_{\text{skeletal}}^2 \ S_{\text{bend}}^2$$

(4)

where $S$ represents the vibrational overlap and the sum is over all possible values of $n$ giving degeneracy. For a given value of the energy separation $\Delta E$, a maximum value of $S^2$ can be found, and it is found that upon deuteriation, $S_{\text{max}}^2$ is lowered, in agreement with observation.

Robinson and Frosch.$^{25, 26}$—The immediate success of this theory has caused it to dominate discussion on radiationless transitions ever since its appearance. In the original treatment,$^{25}$ dilute solid solutions were considered in which there were no solute-solute interactions, but in which the solvent provided an energy sink to enable nearly degenerate states to couple. The treatment was limited to cases where transitions were slow in comparison with vibrational relaxation, and is thus limited to $S_1 \rightarrow S_0$, $S_1 \rightarrow T_1$, $T_1 \rightarrow S_0$ transitions. The perturbation $H'$, which causes multiplicity-allowed transitions, arises from coulombic interactions among the electrons and nuclei of the system, and this is considered to be a property of the isolated molecule. Thus the transition is allowed in the free molecule, and does not depend upon the medium for its existence, unlike the Gouterman treatment. For intersystem crossings, the perturbation is spin-orbit in character, modified by the Franck-Condon overlap integral between the low vibrational levels of the initial state and the high vibrational levels of the isoenergetic final state. It should be noted that transitions occur between non-stationary states of the overall system.

The initial non-stationary state of the system $\psi'$ and the final state $\psi''$ separated by electronic energy $\Delta E$, are made degenerate by the addition of molecular vibrational energy and small amounts of lattice vibrational energy. The energy of coupling between the initial state and any directly coupled final state is $\beta_n$, where

$$\beta_n = \langle \psi' \mid H' \mid \psi'' \rangle$$

(5)

These directly coupled final states are in turn coupled to indirectly coupled final states which differ only in the amount and distribution of the vibrational energy among the modes of the solvent. If there are $N-1$ such indirectly coupled final states, they are coupled to the directly coupled final state and to each other by a matrix element $\alpha$. Since it has been assumed that electronic transitions are much slower than vibrational relaxation, $\alpha \gg \beta_n$. 
The radiationless transition probability, summed over all directly coupled final states is given by

$$\frac{\omega(t)}{t} = \frac{2\pi \beta_{el}}{\alpha \hbar} \sum_n \langle \Phi''_n | \Phi'_n \rangle^2$$

(6)

where using the Born–Oppenheimer approximation,

$$\psi(x, z) = \mathcal{H}(x, z) \Phi(z)$$

(7)

and therefore

$$\beta_n = \beta_{el} \langle \Phi''_n | \Phi'_n \rangle$$

(8)

$$\langle \Phi''_n | \Phi'_n \rangle$$ is the vibrational overlap factor, and quantitative estimation of \(\beta_{el}\) and the Franck–Condon factors show that the theory is in agreement with observation. For singlet–triplet transitions, using an arbitrary but reasonable value of \(\beta_{el}\) of 0.01 cm\(^{-1}\), an expression relating \(\langle \Phi''_n | \Phi'_n \rangle\) to \(\Delta E\) was obtained

$$\langle \Phi''_n | \Phi'_n \rangle_{\text{total}} = 10^{-0.109\Delta E_n^{0.44}}$$

(9)

Thus for large separation, the Franck–Condon factors become very small, leading to slow radiationless transitions. The lengthening of triplet state lifetimes upon deuteration can be explained since more quanta of C—D vibrations are required than the corresponding C—H vibrations to cover the same energy gap, thus leading to reduced overlap.

The values given to Franck–Condon integrals for C—H stretching vibrations have been criticised on the grounds that since these are large, they should appear strongly in the absorption and emission spectra of molecules considered. In fact, these vibrations appear only very weakly in the spectra of most molecules, and intensity data enable a calculation of Franck–Condon integrals between the lowest triplet and ground state of benzene. The values obtained are of the order of \(10^{-38}\), instead of \(10^{-16}\) used by Robinson and Frosch. Although combinations of C—H stretching and C—C stretching vibrations may improve matters by a factor of ca. 100, a real discrepancy remains.

The effect of molecular size on the probability of radiationless transitions in polyatomic molecules has also been considered by Robinson. As stated before, the transition occurs from a sharply defined energy level to a quasicontinuum of molecular vibrational levels. In the solid, the quasi-continuum is affected by interaction with the environment, but in the gas phase at pressures such that collisions are unimportant, the molecule must be of sufficient complexity that the vibrational levels become so closely spaced that it provides its own quasicontinuum. Molecules of complexity such that they satisfy this condition are referred to as being in the \(\omega\) limit. In contrast, small molecules with widely spaced vibrational levels have no quasicontinuum. This is referred to as the \(\alpha\) limit. Intermediate cases, of which benzene is cited as an example, are termed \(\mu\) cases, where electronic relaxation occurs only after a slight external perturbation of the system. This may be long range, of the order of 50 Å, and thus the ordinary concept of molecular collisions is inapplicable.
Spectroscopic and Theoretical Aspects

The concepts in this paper have been criticised on two grounds: firstly, the fact that Franck-Condon factors have been ignored, and secondly, the necessity of a continuum as a physical as opposed to mathematical prerequisite for the occurrence of radiationless transitions. It is pointed out that as $\Delta E$, the energy separation of the electronic states is decreased, the Franck-Condon overlap increases, whereas the density of final states is decreased. These two factors operate in opposite directions in influencing the rate of the processes under consideration.

Siebrand.27, 28—The calculations undertaken by this author are essentially concerned with the Franck-Condon factors associated with the Robinson and Froesch theory. An empirical relationship between the radiationless transition rate for the $T_1 \rightarrow S_0$ transition and the electronic energy separation was first obtained, and then Franck-Condon factors were calculated using harmonic oscillator functions. The effect of temperature on the system was considered, and the most recent calculations have described the effect of anharmonicity upon the rates of radiationless transitions.

If a natural triplet lifetime of 30 sec. is assumed for all aromatic hydrocarbons, the rate constant $k$ for the radiationless transition $T_1 \rightarrow S_0$ was given by an expression of the type

$$\log k = \log k_0 - f(E - E_0)/\eta$$

(10)

where $E$ is the electronic energy difference between the states, and $\eta = N_H/(N_H + N_C)$, where $N_i$ is the number of atoms of type $i$: a best fit with data is obtained if $E_0^R$ is taken as 4000 cm$^{-1}$ for C-H aromatics. This empirical relationship can be explained in terms of the Robinson and Froesch theory and calculations of Franck-Condon factors.

The transition probability per unit time is given by $W$, where

$$W = \left(\frac{2\pi \rho \rho}{\hbar}\right) J^2 F$$

(11)

$\rho E$ is the density of final states, and $J$ is the electronic transition matrix element. Assuming changes in $F$ are dominant in causing changes in $k$, and thus that $J$ and $\rho$ are constant, the relationship may be rewritten in terms of $F$:

$$\log F(E) = \log F(E_0) - f(E - E_0)/\eta$$

(12)

For small values of $E$, $F(E)$ can be obtained from the ratio of intensities of vibrational peaks in phosphorescence spectra, as mentioned earlier. Thus $F(E)$ for small values of $E$ can be constructed, and empirical $F(E)$ lines for hydrocarbons and deuterated hydrocarbons obtained. In this way the value of $E_0^R$ was verified and a value of $E_0^D$ of 5500 cm$^{-1}$ obtained.

Now, $F$ can be written as

$$F = \sum_{\nu} \left[ \sum_{n=1}^{N} \left| \langle \chi_n^0(\nu) | \chi_n(0) \rangle \right|^2 \right]$$

(13)

where $\chi_n$, $\chi_n^0$ are vibrational wavefunctions of mode $n$ in their initial and final states respectively. In calculating $F$, it is assumed that the molecules
are composed of harmonic oscillators, and furthermore, that normal modes can be divided into groups of quasidegenerate oscillators. Expressions are presented for the calculation of $F(E)$ for an $N$-fold degenerate displaced oscillator, a degenerate distorted oscillator, and the case where the $N$-fold degenerate oscillators undergo both displacement and distortion upon absorption.

The efficiency of the oscillators taking up electronic energy is measured by

$$F'(E) = \left[ \frac{\partial \log F(E')}{\partial E} \right]_E$$

(14)

and from the theoretical expressions given in ref. 27, it is possible to show that for small $E$, $F'(E)$ is greatest for displaced oscillators, but for larger $E$, distorted oscillators represent the dominant modes into which the electronic energy goes. Thus the energy will first flow into the quasidegenerate group $\alpha$ with the largest $F'_\alpha (0)$, which are probably displaced oscillators. At a particular energy $E_\alpha$, the efficiencies of two different groups of oscillators will be equal.

$$F'_\alpha = \left[ \frac{\partial \log F_\alpha(E)}{\partial E} \right]_{E_\alpha} = \left[ \frac{\partial \log F_\beta(E-E_\alpha)}{\partial E} \right]_{E_\alpha}$$

(15)

For energies $E > E_\alpha$, group $\beta$ will provide the major contribution to $F$. $E_\alpha$ can thus be identified in expression (10), as the energy at which two groups of oscillators are equally effective. Below $E_\alpha$, the C—C stretching modes seen in phosphorescence are dominant, whereas above $E_\alpha$, the C—H modes dominate the $F(E)$ function. The deuterium isotope effect may thus be satisfactorily explained because of the involvement of the C—H modes, and also because of the appearance in the expression of $\eta$, which is the fraction of H atoms in the molecule. However, although the calculated Franck-Condon factors can explain qualitatively the experimental curve obtained from equation (10), difficulties are encountered when these calculated values are used to attempt a matching of the curves.

Some of these difficulties are removed when the anharmonicity of the oscillators is taken into account. An expression is derived for $F(E)$ in terms of the anharmonicity of the form

$$F(E) = F(E_\alpha) \left( \frac{\lambda_0}{N_\alpha} \right)^v \frac{\Gamma(N_H + v)}{\Gamma(N_H) \Gamma(v+1)}$$

(16)

where $v = E - E_\alpha/\hbar \omega_\alpha$, and $\omega_\alpha$ is the C—H or C—D stretching frequency. $\lambda$ is a parameter which depends upon the effective difference in vibrational energy between the two vibronic states involved in the transition, and is governed by the anharmonicity of the C—H stretching modes in the final state $S_\alpha$. An attempt was made to measure $F(E)$ spectroscopically and thus determine $\lambda$ in order to see if the values obtained are in agreement with those assumed to give a fit to data for rates of radiationless transitions. The study involved a quantitative study of the long wavelength region of the fluorescence spectrum of anthracene and [2H16]anthracene in crystalline form and dispersed in methyl methacrylate glass. The results obtained are summarised in Table 1.
Table 1  Values of \( \lambda \) for \( T_1 \rightarrow S_0 \) transition*

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Anthracene</th>
<th>0.08</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(^2\text{H}_{10})Anthracene</td>
<td>0.13</td>
</tr>
<tr>
<td>Single crystals</td>
<td>Anthracene</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>(^2\text{H}_{10})Anthracene</td>
<td>0.074</td>
</tr>
<tr>
<td>Empirical</td>
<td>Anthracene</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>(^2\text{H}_{10})Anthracene</td>
<td>0.051</td>
</tr>
</tbody>
</table>

* Adapted from Table 1, ref., *J. Chem. Phys.*, 1968, 49, 1860.

The experimental uncertainties in the solution work were great enough to make the values obtained subject to considerable error, and it is pointed out that the value for crystals may be smaller than that for solutions because electronic coupling is stronger. Thus the crystal values should be considered as lower limits. The values for the deuteriated hydrocarbons are dismissed since theoretical arguments show that the values of \( \lambda \) for these species should be lower than those of the hydrocarbon, not higher as observed. Thus the assumption that C—D stretching modes take up most of the electronic energy in the radiationless transition appears to break down. It has since been shown that equation (16) must be modified further. When originally derived, a constant \( \xi \) was obtained instead of \( \lambda \nu \). The substitution of \( \lambda \nu \) for \( \xi \) amounted to an *ad hoc* introduction of anharmonicity, but left \( v \) defined as for a harmonic oscillator. If the equation is re-derived starting with Morse potential functions, it can be shown for a one-dimensional oscillator that

\[
F(v) = F(0) \left( \frac{\nu}{K_2} \right)^v
\]

(17)

where

\[
K_2 = \frac{\omega_s}{x_s} \omega_e
\]

(18)

This is directly comparable to equation (16) reduced to a one-dimensional form, so that

\[
\lambda = \frac{e}{K_2}
\]

(19)

\[
= \frac{e x_s \omega_e}{\omega_e}
\]

(20)

Approximate values of \( \omega_s \) and \( x_s \) can be obtained from the C—H stretch overtone spectrum of benzene, and substitution of these values into equation (20), yields a value for \( \lambda \) of 0.0507, in agreement with that derived semi-empirically.

The rate constants \( \alpha \) for the internal conversion \( S_1 \rightarrow S_0 \) in many molecules can be obtained and compared with the few available experimental values by rewriting equation (16) as

\[
\alpha(E) = \frac{\alpha(E_0) \left( \frac{\lambda \nu}{N_2} \right)^v \Gamma(N_H + \nu)}{\Gamma(N_H) \Gamma(v + 1)}
\]

(21)

\( \lambda \) is taken as 0.051, and \( E_0 \) as 4000 cm\(^{-1}\) as before. Thus only one adjustable parameter remains, \( \alpha(E_0) \), and if a single value for all hydrocarbons is assumed, reasonable correlation with experiment is obtained. It is of
interest to note that the value of $\alpha(E_0)$ for $S_1 \rightarrow S_0$ transitions when compared with the value of $\beta(E_0)$ for the $T_1 \rightarrow S_0$ transitions implies a spin prohibition factor of $10^8$ for radiationless processes, which is two orders of magnitude greater than the values quoted by Kasha.\textsuperscript{33} It is felt that the new value is appropriate when comparing $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions, but that Kasha's value of $10^8$ is to be preferred for the $S_1 \rightarrow T_1$ transition which may well occur via an intermediate $T_2$ triplet, although this mechanism has been disproved in the case of benzophenone.\textsuperscript{8} A rationalisation is also given of the anomalous $S_2 \rightarrow S_0$ fluorescence of azulene in terms of values of $\alpha(E)$. Since the energy separation between $S_2$ and $S_1$ and $S_1$ and $S_0$ is approximately equal, the rates of the radiationless processes $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ process must be comparable. However, the oscillator strength for the radiative $S_0 \rightarrow S_2$ process is much greater than that of $S_0 \rightarrow S_1$, and thus the ratio of radiative to radiationless rates for the state $S_2$ must also be greater than that for $S_1$. Hence fluorescence is observed preferentially from $S_2$.

A method of evaluating Franck–Condon factors for the radiationless $S_1 \rightarrow T_1$ transition has been described recently.\textsuperscript{29} The results obtained give order of magnitude agreement with experimental data.

Measurement of anharmonicities in benzene and deuteriated benzenes from near-i.r. spectra have produced results in essential agreement with those of Siebrand.\textsuperscript{39} It should be noted that Siebrand's work is based upon the theory of Robinson and Frosch, but only discusses the behaviour of the Franck–Condon factors. As Kasha has pointed out, from such a consideration, it can be shown that as the number of degenerate oscillators in a group increases, Franck–Condon factors tend to decrease. Thus a consideration of Franck–Condon factors alone leads to the prediction that radiationless transitions should become less important in large molecules. On the other hand, Robinson and Frosch predict that as the density of final states increases, or in other words, as the complexity of the molecule increases, there should be an increase in the rate of radiationless transitions. Clearly the two effects ought to be considered together. Kasha has also pointed out that all of the theories so far considered, and that of Lin below, apply only to transitions where vibrational relaxation is much more rapid than the transition itself. They are therefore restricted to the relatively slow $S_1 \rightarrow S_0$, $S_1 \rightarrow T_1$, and $T_1 \rightarrow S_0$ transitions. Siebrand's theory suffers from the additional restriction that only aromatic molecules can be considered.

Lin.\textsuperscript{31, 32}—This theory uses Born–Oppenheimer wavefunctions for the initial and final states, and considers the transitions to arise from deviations of the true stationary-state wavefunctions from the Born–Oppenheimer functions. The perturbation causing radiationless transitions can be written as

$$H' \psi_{av} = T \phi_a \Theta_{av} - \phi_a \Theta_{av}$$

(22)
where $T$ is the kinetic energy operator for all nuclear motions; $\psi_{av} = \phi_a \Theta_{av}$ is the Born–Oppenheimer wavefunction, $\phi_a$ is the vibrational wavefunction for a fixed internuclear distance, and $\Theta_{av}$ is the vibrational wavefunction. From time-dependent perturbation theory, the transition probability for a transition from state $bv'$ to state $av''$ is given by

$$W_{(bv'\rightarrow av'')} = \frac{2\pi}{\hbar} \left| \langle av'' | H' | bv' \rangle \right|^2 \delta(E_{av''} - E_{bv'})$$

(23)

This transition probability is averaged over all thermally available initial vibrational states, and is then summed over all final vibrational states consistent with energy conservation. The vibrational wavefunctions are taken as harmonic-oscillator wavefunctions. The treatment leads to predicted rates for intersystem crossings of $10^{-2} - 10^4$ and for internal conversions rates of $10^4 - 10^8$ sec$^{-1}$, which are clearly too low. In a recent report, Lin states that because of a lack of knowledge of the normal co-ordinates and frequencies of local modes between the two electronic states in which the non-radiative transition occurs, upon which the rates depend, precise calculation of the probability is difficult. It is suggested that the difficulty can be resolved if an analysis of absorption or emission of the molecule dissolved in a crystalline solvent is undertaken, and a method is presented of determining the absorption coefficients of overlapping bands.

Following the above summary (due largely to Kasha$^{33}$) of previous theories, three new approaches can be considered.

Kasha.$^{35}$—In addition to particular criticisms of the theories considered above, Kasha questions the whole basis of the major theories of Ross et al., Robinson and Frosch, and Siebrand and Lin. In every case the transition is considered as due to a time-dependent intramolecular perturbation, and it is implicit throughout, although not always stated, that a set of zeroth order states is considered which are not true stationary states of the system. Thus the perturbation causing the transition may be related to the very reason that the states are not stationary, which in every case can be traced to a failure of the Born–Oppenheimer approximation. Thus the perturbation is due to the dependence of the electronic state upon nuclear displacement. Because this dependence may not always be apparent, it is worthwhile quoting from ref. 33 and identifying the perturbation used in each theory. In Lin's theory, the perturbation is explicitly stated to be the deviation from the Born–Oppenheimer approximation. Robinson and Frosch identify the perturbation as that part of the Hamiltonian which causes the zeroth order states to be non-stationary. The form of the purely electronic perturbation is never disclosed, but the perturbation clearly identified is that arising from departure from Born–Oppenheimer normalcy. In the early work of Ross, the mechanism of the transition is considered to be quantum-mechanical tunnelling between potential
surfaces. Kasha maintains that quantum mechanical tunnelling arises because of the inadequacy of potential surfaces to describe a physical system, and therefore accounts for the perturbation in terms of a failure of Born–Oppenheimer separability. The later work of Ross, and that of Siebrand, is based on the assumptions of Robinson and Frosch. It is the use of non-stationary zeroth-order states of the molecule which is called into question by Kasha. Thus if the Born–Oppenheimer approximation does not hold, it is artificial to postulate initial states which are Born–Oppenheimer states of the molecule. An alternative steady-state, time-independent, approach is proposed. In this approach, any mixing of states due to an intramolecular perturbation will occur before interaction with any external radiation field, in contrast to the time-dependent theories.

![Diagram](image)

**Figure 1** Conventional (a) and Kasha (b) formulation for absorption and emission in molecule

(Based on Figure 3, B. R. Henry and M. Kasha, Ann. Rev. Phys. Chem., 1968, 19, 161)

The treatment is illustrated with reference to a molecule which absorbs radiation to produce the second excited singlet state $S_2$ of the molecule. It is experimentally well determined, azulene excepted, that any emission observed is characteristic of the first excited singlet state of the molecule, in a vibrationally excited state. This is true even under conditions such that collisions cannot be important during the radiative lifetime of the states involved. On the time-dependent basis, this would be explained as absorption to state $S_2$, followed by rapid internal conversion to states $S_1$ in a vibrationally excited level, followed by emission of radiation from this level to reach an excited vibrational level of state $S_1$. This sequence is illustrated in Figure 1(a).
According to the treatment of Kasha and Henry,\textsuperscript{23} absorption will produce a manifold of stationary states of the system, each one of which consists mainly of a vibrationally excited $S_1$ state and a small amount of $S_2$ [Figure 1(b)].

$$\psi_j = S_{1j} + \delta_j S_2$$  \hfill (24)

The absorptive act will be almost unchanged from the time dependent theory since the matrix element for absorption is:

$$\langle S_0 | \sum_k e r_k | S_{1j} + \delta_j S_2 \rangle$$  \hfill (25)

But because of low Franck–Condon factors for the transition of $S_0$ to a high vibrational level of $S_1$,

$$\langle S_0 | \sum_k e r_k | S_{1j} \rangle \approx 0$$  \hfill (26)

Thus the transition gains its intensity from the $S_2$ character in the state. When summed over $j$, the square of the complete matrix element is non-zero.

$$\sum_j \langle S_0 | \sum_k e r_k | S_{1j} + \delta_j S_2 \rangle |^2 \neq 0$$  \hfill (27)

The radiative transition probability of absorption to any particular state is small because of the small amount of $S_2$ character in each state, implying that the emission radiative probability $S_2 \rightarrow S_0$ is similarly small. However, the probability of the radiative transition from vibrationally excited $S_1$ to vibrationally excited $S_0$ is not small, because of larger Franck–Condon overlap, and thus one might expect to see emission corresponding in the time-dependent case to $S_1 \rightarrow S_0$ transitions. Few details of the treatment are at present available, but it is evident that in it radiationless transitions do not in fact occur at all, since mixing of states is achieved before interaction with the photon field. For this reason, the terms ‘internal mixing,’ and ‘intersystem mixing’ have been proposed to cover the terms ‘internal conversion’ and ‘intersystem crossing’ used in the non-stationary approach.

Jortner and Co-workers.\textsuperscript{34}—Independently of Kasha, Jortner and co-workers have arrived at similar conclusions concerning the applicability of the use of Born–Oppenheimer states as non-stationary states describing molecules undergoing radiationless transitions. As these authors point out, it is well known that the Born–Oppenheimer approximation is only valid if the energy difference between the Born–Oppenheimer states is large relative to the vibronic matrix element connecting these states. When there are near-degenerate or degenerate zero-order vibronic states belonging to different configurations the Born–Oppenheimer approximation fails completely, as is evidenced in the Jahn–Teller effect, and also in pre-dissociation. The first paper in this series considers the case of intramolecular radiationless transitions in an isolated molecule. The Born–Oppenheimer zero-order states are not considered to be pure, because of configuration interaction between the nearly degenerate zero-order states.
The optically excited state considered is described in terms of a superposition of molecular eigenstates. The conventional method of calculating molecular structures is traced as far as the introduction of the Born–Oppenheimer adiabatic approximation, and it is then demonstrated that this will not hold in cases where vibronic levels of different electronic states lie close in energy. The interaction of Born–Oppenheimer levels constructed from two electronic states $A$ and $B$ is then considered. Suppose $\psi_s$ represents the vibronic state corresponding to the electronic state $A$ which is reached by the allowed excitation from the ground state, with energy $E_s$, and $\{\psi_i\}$ is the set of vibrationally excited vibronic states corresponding to electronic state $B$ which are quasidegenerate with $\psi_s$. The manifold of states $\{\psi_i\}$ becomes more densely spaced with increasing energy gap between the electronic states $A$ and $B$. In view of the small energy denominations which determine the vibronic coupling matrix elements, an appreciable mixing of $\psi_s$ with the background manifold $\{\psi_i\}$ will be expected. Since an exact solution to the problem is impossible, assumptions are introduced to simplify the calculation. These are that the states $\{\psi_i\}$ are uniformly spaced, with an energy difference $\varepsilon$ between the consecutive states. The value $i = 0$ is given to the nearest state to $\psi_s$. If $\alpha = E_A - E_0$, the energy of state $\psi_i$ is $E_i = E_s - \alpha + i\varepsilon$ ($i = 0, \pm 1, \pm 2, \text{ etc.}$). The second assumption is that the matrix elements of the complete Hamiltonian between the states $\psi_s$ and $\psi_i$, $v_i = \langle \psi_i | H | \psi_s \rangle$ are independent of $i$, although in reality $v_i$ is a function of energy and will strongly decrease with increasing $|E_s - E_i|$. A new set of eigenvalues $E_n$ is generated because of interactions in which each value of $E_n$ falls between a pair of the zero-order Born–Oppenheimer levels. The probability $a_n^2$ of finding the vibronic state $\psi_s$ in the new states is given by the relationship.

$$a_n^2 = v^2 \left[ (E_n - E_s)^2 + v^2 + \left( \frac{mv^2}{\varepsilon} \right)^2 \right]^{-1}$$  

(28)

This equation gives a Lorentzian envelope for the values of $a_n^2$ as a function of $E_n$. The probability of light absorption into the new states is proportional to $a_n^2$, and thus the Lorentzian envelopes a series of absorption lines centred around $E_s$. Thus absorption lines should be broadened, yielding a half-line width which is given by

$$\Delta E = [v^2 + (\pi v^2/\varepsilon)^2]^{1/2}$$  

(29)

or simplifying, since $\nu \varepsilon^{-1} \gg 1$

$$\Delta E = \pi v^2/\varepsilon$$  

(30)

Because of rotational broadening, the above effect will be manifested experimentally only if the linewidths exceed 0.5 cm$^{-1}$, corresponding to a radiationless transition lifetime shorter than $10^{-11}$ sec. Thus the effect is only to be expected in internal conversions between excited states, and in fact the absorption lines of higher-excited singlet states of aromatic molecules are known to be diffuse.
Spectroscopic and Theoretical Aspects

The time dependence of the system upon irradiation is treated, and it is found that if a broad optical source is used, the excited state will show an exponential non-radiative decay, characterised by a lifetime \( \tau \), where

\[
\tau = \frac{eh}{2\pi\nu^3}
\]  

(31)

This is provided \( \varepsilon \ll v, \tau \ll h/\varepsilon \).

It is also shown that the rate of a radiationless process will be enhanced if more than two electronic levels are involved, e.g. if the second excited triplet state is situated just below the first excited singlet.

It is easily seen from the treatment that apart from the interaction matrix element, the other parameter determining the rate of radiationless processes is the spacing of the vibronic states \( \varepsilon \), or alternatively, the density \( \rho \), where \( \rho = \varepsilon^{-1} \). Provided the density of intramolecular vibrational states around \( E_v \) is large enough, i.e. \( v \gg \varepsilon \), the treatment shows that intramolecular radiationless transitions can occur in isolated molecules. Thus a critical number of intramolecular vibrations are necessary. For example, for an energy gap of 1 ev, Franck-Condon factors have been estimated as \( F = ca. 10^{-4} \). For an internal conversion, \( v \) can be taken as \( v = 10^8 \times F = 0.1 \) cm\(^{-1} \). Thus to satisfy the condition \( \varepsilon \ll v \), at least 100 states per cm\(^{-1} \) are necessary to observe this transition. For a spin-forbidden intersystem crossing, \( v \) can be taken as \( 10^{-4} \) cm\(^{-1} \), so that \( \rho \) must be much greater than \( 10^4 \) cm. Now for polyatomic molecules with equal vibrational frequencies of \( 10^8 \) cm\(^{-1} \), the density of states obtained is as shown below.

\[
\begin{array}{ccc}
\text{Triatomic} & \rho = \varepsilon^{-1} \text{ cm} & \text{Six atoms} & \rho = \varepsilon^{-1} \text{ cm} \\
& 0.06 & & 400 \\
Four \text{ atoms} & 4 & Ten \text{ atoms} & 4 \times 10^5 \\
Five \text{ atoms} & 50 & & \\
\end{array}
\]

(Data from ref. 34)

Thus this order of magnitude calculation shows that whereas a molecule with five atoms is approaching the limit of exhibiting internal conversion, at least ten atoms are required before an intersystem crossing could be seen in an isolated molecule (for the same energy gap of 1 ev, of course).

The problem is treated in a slightly different way later. Here a molecule is excited from its ground state \( \Phi_0 \) to a member of the set of eigenfunctions of the molecular Hamiltonian \( \Phi_K \) which is adequately represented as a superposition of Born-Oppenheimer vibronic states \( \phi_j \).

\[
\Phi_K = \sum_j \phi_j \langle \phi_j | \Phi_K \rangle
\]

(32)

Supposing that a single zero-order vibronic state carries the bulk of the transition amplitude for optical excitation, which is a similar proposal to that of Kasha,

\[
| (\Phi_0 | \mu_\varepsilon | \phi_j) | \gg | (\Phi_0 | \mu_\varepsilon | \phi_i) | \hspace{1cm} j \neq i
\]

(33)
The fluorescence intensity of the system under conventional conditions following narrow-band excitation is:

\[ F = | \langle \Phi_0 | \mu_e | \phi_i \rangle |^2 \sum_{K} | \langle \phi_i | \Phi_K \rangle |^2 \]  

(34)

where the sum over the limited set \( \{K\} \) is taken only over the narrow excitation range. If the density of Born–Oppenheimer states is sufficiently large (\( \Phi_K \) is large), and the vibrational interaction is sufficiently strong, then \( F \) is considerably smaller than \( | \langle \Phi_0 | \mu_e | \phi_i \rangle |^2 \). In this case, the intensity is spread over a moderately wide spectral region, and a narrow band excitation reduces drastically the fluorescence intensity relative to what one would infer from a pure Born–Oppenheimer state. This reduction occurs as an intramolecular property, and molecules exhibiting it are referred to as examples of the ‘statistical case’.

Alternatively, the states mixing in a small molecule with only a few degrees of freedom can reduce the fluorescence rate below that expected for the pure Born–Oppenheimer state \( \phi_i \) only by a small amount. This limiting case of low density of states is referred to as the ‘resonant case’. Here, an external perturbation, usually a collision, will be required to induce a radiationless transition. The requirement for the ‘statistical case’ has already been given. Rough numerical estimates show that \( S_1 \rightarrow T_1 \) transitions in anthracene are in the statistical limit, in \( \text{SO}_2 \) are in the resonant limit, and are intermediate in benzene. A treatment is presented of the type of behaviour observed during an experimental measurement of fluorescence yields and radiative lifetimes. It is shown that in a small molecule such as \( \text{SO}_2 \), \( \text{NO}_2 \), etc., the pure radiative component in the decay rate is ‘diluted’ as a consequence of the static mixing of zero-order levels and the redistribution of the oscillator strength within the inhomogeneously broadened band. This can lead to an anomalously long radiative lifetime in the resonant limit. In the statistical limit, the interference effects between the large number of densely spaced levels are manifested by the appearance of an intramolecular decay process which reduces the quantum yield and lifetime of the state. Thus in the resonant limit for small molecules, quantum-beat signals between closely spaced eigenstates should be observable, whereas in the statistical limit these should disappear. The effect of molecular size on rates of radiationless transitions has been treated in a different manner recently.\textsuperscript{38}

Jortner’s earlier treatments have been extended and generalised in two later papers.\textsuperscript{36, 37} This treatment of the breakdown of the Born–Oppenheimer approximation is general and does not depend upon any explicit assumptions about the level spacing in the statistical limit. The theory predicts that the mixing of Born–Oppenheimer states in the true molecular eigenstate leads to a lengthening of the radiative lifetime of each molecular eigenstate, as did the previous approach. The conclusions regarding lifetimes of the states are also similar. Whereas it has hitherto been assumed that the radiative and non-radiative decay processes are independent in
molecules, the present treatment shows in fact that the radiative decay time is altered by the existence of inhomogeneously broadened lines. Thus the radiative decay time depends upon the number of states within the half-line width. The correct relationship between the observed decay time $\tau_{\text{obs}}$, the non-radiative decay time $\tau_{\text{nr}}$, and the apparent radiative decay time $\tau_r$ (determined from the oscillator strength in the usual way) is

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{B \tau_r} + \frac{1}{\tau_{\text{nr}}}$$

(35)

in the limit where $\tau$ is small. $B$ is given by $(\pi v/\epsilon)^2$. If the widths of two states exceed their separation, as can occur, then the decay rate should become non-exponential, although this prediction is not yet amenable to experimental testing.

Use can be made of the theory developed for radiationless transitions in providing an explanation of photochemical decompositions. Two phenomena are required to be explained. Firstly, that localised excitation such as $n \rightarrow n^*$ absorption in ketones can lead to breakage of bonds some distance removed from the site of excitation, and secondly, that as a bond stretches and breaks, there is established a continuous connection between the translational co-ordinate along which fragmentation occurs and the vibrational motions of the molecule. It is necessary to understand how the vibrational modes can be combined to give the decomposition mode. Suppose as before, that in the zeroth approximation in the energy region of interest the spectrum of states consists of one discrete state overlapping a dense but discrete set of vibrational levels belonging to a different electronic state, but that these vibrational levels in turn overlap the translational continua corresponding to molecular fragmentation. Now the discrete level is coupled to the vibrational set, and the vibrational set are coupled to the continuum, but the discrete level is not directly coupled to the continuum (see Figure 2). Assuming that the ground state is adequately represented by a Born–Oppenheimer state, and that this is coupled via a dipole transition matrix element only to the discrete state $\psi_a$ and not to $\{\phi_n\}$ or $\xi_E$, absorption of a photon will produce a non-stationary state $\psi_E$. If $\psi_E$ is an eigenfunction of the complete Hamiltonian $\mathcal{H}$, and $\psi_a$, $\{\phi_n\}$, $\xi_E$ are eigenfunctions of the zeroth-order Hamiltonian $\mathcal{H}_0$ corresponding to the single discrete state, the set of vibronic levels of another state, and the fragmentation continuum respectively, then

$$\mathcal{H} = \mathcal{H}_0 + V$$

(36)

and

$$\psi_E = a(E) \psi_a + \sum_n b_n(E) \phi_n + \int dE' C_{\mathcal{H}'}(E) \xi_{E'}$$

(37)

Making the assumption, as before, that the states $\phi_n$ are uniformly spaced, and also that

$$\langle \psi | \mathcal{H} | \phi_n \rangle = v_1 = \text{const., all } n$$

(38)

$$\langle \phi_n | \mathcal{H} | \xi \rangle = v_2 = \text{const., all } n,$$

(39)
the values of $a(E)$, $b_n(E)$, and $C_E (E')$ can be evaluated, and a number of predictions made from equation (37). These are that the lifetime of the state will appear as a consequence of mixing the continuum into the exact eigenstates and because of interference between coherently excited states. By analogy with previous work, two lifetimes should appear, proportional to $\nu_1^2$ and $\nu_2^2$. Provided $\rho_1\nu_1^2 \approx \rho_2\nu_2^2$ are of comparable magnitude ($\rho_1 = \rho_{\nu \nu}$ and $\rho_2 = \rho_{\text{cont}}$) the rate of decay of the molecule will depend on both

\[ \nu_1 \text{ and } \nu_2. \]

If $\rho_1\nu_1^2 \gg \rho_2\nu_2^2$, the molecule behaves like a state of a long-lived vibrationally hot molecule, whereas if $\rho_1\nu_1^2 \ll \rho_2\nu_2^2$ the state is like an excited molecular state which decomposes directly to fragments. In the former case, the Rice–Ramsperger–Kassel–Marcus theory can be applied to consider the decomposition of the molecule. In the second limiting case, the molecule clearly dissociates as rapidly as the non-stationary wave packet localised in $\psi_n$ can disperse into the non-stationary states $\{\phi_n\}$. This paper was intended as a preliminary formal analysis of the primary act of photodissociation, and provides a challenge for both theoretician and experimentalist.

Ting. As was stated earlier, the Franck and Sponer mechanism of radiative transfer of energy from one excited state of a molecule to another excited state of the same molecule has been revived by Ting. The main
Obscure to the earlier theory has also been stated, namely, that transitions from first excited states to the ground states of molecules would not be allowed since the oscillator strength of the transition from the ground state to a high vibrational level of the same state would be zero. Ting in fact shows that this is not the case, and that overtone C—H stretching vibrations extend well into the near-i.r. and visible regions with diminishing intensity. Oscillator strengths $f$ for this vibration were measured in many compounds, and reported on a $p_f$ scale, where

$$p_f = -\log_{10} f$$

From selected data from the literature, $p_k$ values were obtained where

$$p_k = -\log_{10} k$$

and $k = \text{rate of radiationless transition considered in sec}^{-1}$. A remarkable correlation between $p_k$ and $p_k'f'$ is then shown, where $p_k'f'$ is the sum of the $p_f'$ values for transitions from the ground state to the initial state and final state respectively. The plot is linear over a wide range of values, and can be represented by the following linear equation.

$$p_k = -13.0 + 0.56p_k'f'$$

An equation similar to the empirically obtained (42) can be readily derived from theoretical considerations of a three-level system, consisting of a ground state $\Phi_0$, and two isoenergetic excited states $\psi_a$ and $\psi_b$ which are not directly coupled to one another, but can both be reached from the ground state by the first-order radiative process. To simplify the calculation, it has been assumed that once $\psi_b$ is reached there is a rapid deactivation which prevents reverse transfer from occurring.

The Hamiltonian for the molecular system and radiation field is

$$\mathcal{H} = \mathcal{H}_{\text{mol}} + \mathcal{H}_{\text{rad}} + V$$

where $V$ is the interaction operator connecting the molecule and radiation field. Since $\psi_a$ and $\psi_b$ are not directly coupled, they can interact only through a second-order perturbation with interaction energy

$$(\psi_a | \mathcal{H} | \psi_b) = C(\psi_a | V | \Phi_0)(\Phi_0 | V | \psi_b)/(E_i - E_0)$$

where $(\psi_a | V | \Phi_0)$ and $(\Phi_0 | V | \psi_b)$ are the matrix elements determining the radiative processes between the ground state and the excited states, $C$ is a geometrical factor depending upon polarisations of excited states, and $E_i - E_0$ is the energy gap between the ground and excited states.

The matrix elements can be evaluated according to Heitler, and related to oscillator strengths $f$, as follows:

$$(\psi_a | \mathcal{H} | \psi_b) = -1.9 \times 10^{-5} C(f_a \cdot f_b) \nu V_0$$

where $\nu$ is the frequency at which the transition occurs, and $V_0$ is the volume of the molecule.
If the coupling corresponds to a strong coupling case, the rate of the transition is proportional to the interaction energy.

\[ k_{a\rightarrow b} = 1.2 \times 10^{28} \frac{C(f_a f_b) \nu}{\nu V_0} \]  \hspace{1cm} (46)

where \( \nu \) is in units of \( \text{cm}^{-1} \), \( V_0 \) in \( \text{Å}^3 \).

Taking \( \nu \) as 30,000 \( \text{cm}^{-1} \), and \( V_0 \) as 100 \( \text{Å}^3 \), equation (46) can be expressed in the \( p \) scale as

\[ pk \approx -15.6 + 0.50pff' - \log_{10} C \]  \hspace{1cm} (47)

This equation is close to the empirically derived (44).

The success of this simple approach is somewhat surprising; but because it appears to yield valid results, the treatment must be included. A comparison is now possible between the new theories of Kasha, Jortner, and Ting. In the first, mixing of the upper excited state level with the vibrational manifold of the lower level occurs before absorption of radiation, and thus radiationless transitions do not occur as such. In the second, the vibrational manifold is coupled to the upper excited state but not directly to the ground state, via vibrational interaction terms and spin–orbit terms for transitions involving a change in multiplicity. In Ting’s theory, the upper excited state and vibrational manifold are coupled only indirectly in that both states are radiatively coupled to the ground state. In the latter two cases, absorption thus produces both upper states, whereas in Kasha’s case a state is produced which has the character of both upper states. Thus the three approaches have some features in common.

Recent Relevant Experimental Evidence.—In addition to the data already alluded to, and reviewed many times in the references given already, more recent experimental evidence has been obtained concerning the effects of deuteration, temperature, and the state of the sample on radiative lifetimes and radiationless processes. For the first time, direct measurements on ultra-fast (10^{-10}—10^{-11} sec) spectroscopic transitions have become possible with the development of a picosecond pulsed laser.\textsuperscript{41,42} The possibilities of this kind of work are exciting, and it is worthwhile considering the experimental set-up briefly.\textsuperscript{41} The apparatus consisted of two lasers, one neodymium in glass, the other ruby, which generated pulses varying in duration from 1 to 15 psec. The pulses were separated by a time interval of \textit{ca.} 7 \times 10^{-4} sec; thus each pulse arrived after the relaxation process to be studied had occurred and did not interfere with the previous measurement. The beam, consisting of two pulses, one from each laser with \( \omega_1 = 1060 \text{ nm} \) and \( \omega_2 = 530 \text{ nm} \) passed through filters to remove the pumping light and fundamental or second harmonic as required, and then through a dispersive cell before entering the fluorescence cell. A 3 \times 10^{-3} \text{ M} \text{ solution of diphenylcyclopentadiene in tetrahydrofuran was used as the fluorescing medium for the measurement of the size of the pulse. Neither of the pulses alone}
induced fluorescence from this solution, since $\omega_1$ has insufficient energy to reach the first excited state of fluorescer (365 nm) even by a biphotonic process, and $\omega_2$ was attenuated so that its intensity was such that the fluorescence induced was undetectable. As the laser beam passed through the dispersive cell, the two pulses were separated by a distance determined by the group velocity of each pulse in the dispersive medium, and the cell length. The $\omega_1$ pulse entered the fluorescence cell first, and when the two pulses collided, an intensive fluorescence spot was recorded whose length is correlated to the size of the pulse. This technique and variations of it have been used to investigate vibrational relaxation,\textsuperscript{41} intersystem crossing, and internal conversions in azulene.\textsuperscript{42}

![Energy levels for azulene](image)

Figure 3  \textit{Energy levels for azulene}

(Based on Figure 3, P. M. Rentzepis, \textit{Chem. Phys. Letters}, 1968, 2, 117; and Figure 1, E. Drent, C. M. van der Deijl, and P. Zandstra, \textit{Chem. Phys. Letters}, 1968, 2, 526)

As is well known, azulene exhibits anomalous fluorescence in that it is the $S_2 \rightarrow S_0$ transition which is radiative. Now the pulse $\omega_1$ has insufficient energy to populate $S_2$ even by a biphotonic process, and thus cannot induce fluorescence. However, $\omega_2$ has sufficient energy to populate a high vibrational level of $S_1$, which is non-radiative, and absorption of a second photon of $\omega_1$ energy then populates the radiative $S_2$ level (Figure 3). Biphotonic processes involving two quanta of $\omega_2$ are avoided by attenuation of their intensities. Thus whenever two pulses travelling in opposite directions collide, azulene is induced to fluoresce. One of the pulses is made to travel in the opposite direction by reflection from the back surface of the fluorescence cell. After the pulses have separated, the fluorescence should
cease to be omitted if the level initially populated by $\omega_2$ is a virtual level, but in this case a state of finite lifetime is produced. Thus $\omega_1$ on its path will excite to the fluorescent level all molecules remaining in excited vibrational levels of $S_1$. Consequently, the longer fluorescence spot from the azulene solution compared with the diphenylcyclopentadiene solution is a direct measure of the vibrational relaxation time from the initially excited $S_1$ molecules. The vibrational relaxation time from the $S_1$ ($v = 4$) to $S_1$ ($v = 0$) level was found to be $7.5 \times 10^{-12}$ sec.

A similar technique has been applied using single giant pulses from a ruby laser.\textsuperscript{42} In this case, the standard solution used was perylene in benzene, two-photon absorption causing a fluorescent spot as before. In azulene, the energy of the pulse (14,400 cm$^{-1}$) is sufficient to populate the $V = 1$ level of the $S_1$ state ($\omega_3$, Figure 3). Absorption of a second photon produces the $V = 4$ level of the $S_2$ state, from which fluorescence occurs. As before, the broadening of the collision spot is a measure of the relaxation time from the $S_1$ ($V = 1$) state to some level from which the second $\omega_3$ photon cannot populate the $S_2$ level. Two possibilities exist; relaxation to $S_0$, or intersystem crossing to the lowest triplet state $T_1$. The use of heavy atom solvents such as carbon tetrachloride strongly affected the relaxation times measured, which indicated that intersystem crossing was an important mode of relaxation. It seems evident that the relaxation time measured in the two pulse experiments\textsuperscript{41} may not strictly be vibrational relaxation, but could include intersystem crossings also.

A method has been proposed of measuring rate constants for lowest excited singlet to lowest triplet intersystem crossings,\textsuperscript{43} based upon observation of optical densities of triplet–triplet absorptions. The optical density change $\rho(\lambda)$ due to triplet–triplet absorption from the lowest triplet state $T_1$ to a higher triplet state $T_n$ is

$$\rho(\lambda) = e_T(\lambda) I [T_1]$$

where $e_T(\lambda)$ is the molar extinction coefficient, $I$ the path length, and $[T_1]$ the concentration of triplet states. Assuming a steady state for both $S_1$ and $T_1$, and a long irradiation time compared with $\tau_p^b$, the experimentally observed phosphorescence lifetime, it can be shown that

$$[T_1]_{SS} = \tau_p^b \tau_F^a k_{inc}^a I_a$$

where $\tau_F^a$ is the experimental fluorescence lifetime $k_{inc}^a$ is the intersystem crossing rate constant, and $I_a$ is the rate absorption from $S_0$ to $S_1$.

Thus

$$\rho(\lambda)_{SS} = e_T(\lambda) \tau_p^b \tau_F^a k_{inc}^a I_a$$

and

$$k_{inc}^a = \frac{\rho(\lambda)_{SS}}{e_T(\lambda) \tau_p^b \tau_F^a I_a}$$

Thus provided $e_T(\lambda)$ and $\tau_F^a$ can be measured accurately, $k_{inc}^a$ may be determined. However, precise measurement of these quantities has proved

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to be very difficult, and some of the results quoted in ref. 43 have been drastically altered by the authors in the light of recent values for the quantities above.

Data concerning radiationless processes are usually obtained by observing variations in luminescence quantum yields and especially lifetimes under a variety of conditions. Great care has to be exercised in the interpretation of data obtained in this way because of the number of variables which can affect the measured quantity. Thus for example, a study of temperature effect upon the lifetime of phosphorescence of compounds in glasses at low temperatures can yield spurious results because of the effect of biomolecular quenching by impurities which have an increased mobility as the temperature is raised. The measured variation in lifetime in this case is not a true reflection of the effect of temperature. The data presented below are concerned with the effect of the medium upon radiative processes, the effect of temperature, and of partial and complete deuteriation of the molecule.

The role of the matrix in the deactivation of the triplet state of aromatic molecules dissolved in solid solutions at 77 K is not well understood. Conditions of this type are convenient, but the state is not uniquely defined, and a wide variety of structures is possible, such as single crystal, poly-crystalline, partially ordered and amorphous solids. Glasses such as ether–isopentane–ethanol (E.P.A.) are often used because of their transparency, but lifetime measurements are found to vary widely in glasses which undergo glass transitions in the neighbourhood of 77 K.\textsuperscript{44} For example, the phosphorescence lifetime of benzene in 3-methylpentane was determined at frequent intervals after the sample was immersed in liquid nitrogen, and the measured lifetimes were found to increase monotonically with time of immersion, until after \textit{ca.} 3 hr a constant value was reached. It was shown that this process applied to other solvents also, and was not dependent upon the time of illumination. Larger aromatic solute molecules having more than one conjugated ring did not show any change in $\tau_m$, although substituted benzenes such as toluene did. It was proposed that the variations are due to the relaxation of the glasses. Glasses can be considered to have an arbitrarily frozen configurational disorder which is established when the liquid is cooled quickly past its glass transition temperature $T_g$. The viscosity of a glass increases with time when held at around $T_g$, owing to configurational relaxation. Unfortunately, most of the glasses currently used in studies on phosphorescence decay have $T_g$ near 77 K, and therefore great care must be taken to allow the glass to relax fully before measurements are taken.

Non-exponential decay of the $^3B_{1u}$ state of benzene ($T_1$)\textsuperscript{45,46} and deuteriated benzenes\textsuperscript{45} has also been attributed to medium effects. The

\textsuperscript{44} T. E. Martin and A. H. Kalantar, \textit{J. Phys. Chem.}, 1968, 72, 2265.
\textsuperscript{46} J. D. Spangler and N. G. Kilmer, \textit{J. Chem. Phys.}, 1968, 48, 698.
aromatics studied were C₆H₆, C₆H₅D, 1,3,5-C₆H₃D₃, C₆HD₅, and C₆D₆ in different phases of cyclohexane and methylcyclohexane at 77 K.⁴⁵ The results show quite clearly that benzene molecules dissolved in cyclohexane at 77 K can lie in two different environmental sites. Cyclohexane can exist in two phases at 47 K, and thus the substitutional site associated with each phase gives rise to spectra with slightly different energy shifts, and also gives rise to two distinctly different lifetimes, one associated with each type of site. The different lifetimes are due to a change in $k_T$, the rate constant for the radiationless process rather than a change in $k_F$, the rate constant for the phosphorescence step. In other solvents which have very different sizes and shapes compared with benzene, such discrete sites will not occur, and any resolution of different lifetimes associated with such sites would be difficult. Any solvent similar in size and shape to benzene will show the effect, however, and methylcyclohexane falls into this category. The effect is to make the observed phosphorescence decay, non-exponential. A slowly frozen sample produces a monoclinic cyclohexane lattice,⁴⁶ whereas a quickly frozen sample gives a cubic cyclohexane lattice. The fluorescence and phosphorescence spectra of diphenylene sulphide and fluorene in n-paraffin solutions also show a marked dependence upon rate of cooling and concentration.⁴⁷ Three regions are distinctly separable, viz. spectra corresponding to the microcrystalline state, quasi-linear spectra, and diffuse molecular spectra. The onset of each particular region is determined by the rate of cooling and concentration. With n-aliphatic alcohol solvents, a change in the chain length of the solvent gives rise to changes in the local solute environment of the dissolved phosphor.⁴⁸ Similar results have been observed for coronene dissolved in normal paraffins at low temperatures.⁴⁹ This dependence of lifetime upon environment again demonstrates the necessity for care in the interpretation of data.

In fluid solutions, two additional modes of decay serve to decrease the phosphorescence lifetime of aromatic molecules⁵⁰ compared with that measured in glasses. These are bimolecular quenching by oxygen and other impurities, and triplet–triplet annihilation. Because of the former, vastly different results have been obtained for the same compound in different laboratories (see Table 1, ref. 50), depending upon the care taken to purify materials. A careful study has been carried out on naphthalene triplets in 3-methylpentane at −45 °C. It was shown that the lifetime of the aromatic was strongly dependent upon the care with which the material was purified. With the highest quality of solute and solvent, the result obtained for the lifetimes of C₁₀H₈ at −45 °C was 0.49 ± 0.07 sec, and for C₁₀D₈, 0.64 ± 0.07 sec. Both phosphorescence and triplet–triplet absorption were used to monitor decay of the triplet state. A decrease in

lifetime down to 18 msec was observed when the same sample was exposed to air at 10⁻² torr pressure. In fluid solutions the lifetimes are clearly shorter than those measured in glasses at lower temperatures. It seems likely therefore that the reduced lifetimes are due to the presence of quenching impurities, probably residual oxygen. If this is so, little deuterium effect would be expected, as is observed. The results here support the mechanism proposed by several authors for radiationless transitions, in which little or no temperature effect would be expected.²⁶, ²⁷, ³⁴, ⁵⁵

The effect of temperature upon lifetimes in rigid media is in some dispute. As stated above, theories predict that there should be little effect of temperature upon the rates of radiationless processes. For coronene and [²H₁₀]coronene in poly(methyl methacrylate) at 77—300 K this is apparently the case,⁶¹ whereas there is apparently a temperature-dependent internal conversion from $S_1$ to $S_0$ in the case of benzocoronene.⁵¹ The activation energy for this process is 514 cm⁻¹ (compare with benzene, ref. 69). However, for some organic solute molecules in rigid polymer matrices, triplet lifetimes do apparently vary with temperature, $\tau_{77}/\tau_{298}$ being of the order of 2. If this were due solely to diffusional quenching by some unknown impurity, then the ratio $\tau_{77}/\tau_{298}$ should be considerably larger for deuteriated compounds than for their protium analogues, since the lifetimes of the former are much longer. The ratio is independent of deuteration however. It has been shown that such results can be explained by questioning the assumption that transitions occur from only the zeroth vibrational level of the electronically excited state.⁶² At elevated temperatures the Boltzmann distribution predicts significant populations of higher vibrational levels. In this case, the rate of triplet decay would be better represented by

$$1/\tau_p = A_0 k_0 + \sum_i A_i k_i$$  \hspace{1cm} (52)

where $k_0$ is rate of triplet decay from the zeroth vibrational level, $k_i$ is the rate of decay from the $i$th level, and $A_i$ is the relative population of the $i$th level. By assuming values for the energy of the lowest vibrational levels in triplet naphthalene similar to those for the ground-state molecule, acceptable fit of equation (52) to the published lifetime data can be made by assuming reasonable values for the rate constants $k_0$ and $k_i$. Siebrand ⁶³ considers that a combination of this intramolecular effect and external diffusional quenching is necessary to explain the results. Smaller temperature dependences have been observed in polymers where considerable care has been taken to remove excess of monomer, and in this case normal and deuteriated hydrocarbons behave differently, as would be expected from theoretical considerations.

A study of the intersystem crossing rates in pyrene and [²H₁₀]pyrene ‘dissolved’ in poly(methyl methacrylate) as a function of temperature in the

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range 80—300 K leads to the conclusion that two mechanisms are operative. 64 Two different techniques were used; in one phosphorescence intensity measurements were made, and in the other an electron paramagnetic resonance (e.p.r.) signal from the triplet state was monitored. Results from the two methods were in excellent agreement. Rate constants for the intersystem crossing $S_1 \rightarrow T_1$ calculated from the data fit an equation of the type:

$$k_{10c} = k_{10c}^0 + k_{10c}' \cdot e^{-\Delta E/kT} \quad (53)$$

From this relation, $\Delta E = 450 \pm 15 \text{ cm}^{-1}$ for [H$_{10}$]pyrene, and $k_{10c}'/k_{10c}^0 = 44 \pm 3$. For [H$_{10}$]pyrene the corresponding values are $\Delta E = 560 \pm 30$ and $k_{10c}'/k_{10c}^0 = 29 \pm 5$. The term $k_{10c}^0$ may be interpreted as the intersystem crossing rate constant from the lowest vibrational level of $S_1$ direct to isoenergetic levels of the lowest triplet state $T_1$, whereas $k_{10c}'$ may be considered to be the rate constant for the same process from higher vibration levels of $S_1$, or for the crossing from these levels to a higher triplet state $T_2$, which then internally converts to $T_1$. Naphthalene, phenanthrene, and biphenyl have also been investigated with the same technique, producing similar results. 64

The phosphorescence lifetime of mesitylene in rigid solution is observed to be constant at temperatures below 150 K, but to decrease sharply between this temperature and 230 K. The reason for this behaviour is not clear, but above 150 K diffusional quenching of the triplet state may well be of importance. 65

The dramatic increase in lifetimes of the triplet states of aromatic molecules upon deuteration has been explained in theoretical terms by supposing that it is the C—H stretching modes which take up the vibrational energy when a radiationless intersystem crossing occurs. Deuteriation of a molecule requires that more quanta of C—D stretches are required for the same energy gap, and thus Franck—Condon factors are lower for deuteriated molecules. Hence there is a decrease in radiationless transition rate, and a corresponding increase in lifetime. Lim 66 has shown that in naphthalene, the lifetime of the triplet state increases upon deuteration, but that the number of deuterons is the sole criterion affecting the rate of radiationless processes, and not the position of substitution. This is to be expected from Lim's theoretical considerations. 66 There is much recent evidence to show that the contrary is the case. 57—61 The data obtained on deuterium-substituted naphthalenes, 57 biphenyls, 58 toluenes, 59 2-naphthaldehydes, 60 and benzenes 61 are summarised in Table 2.

Table 2  Effect of deuteriation on phosphorescent lifetimes at 77 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent*</th>
<th>Lifetime (sec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene $\text{C}_6\text{H}_6$</td>
<td>3MP</td>
<td>5.75</td>
<td>61</td>
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<td></td>
<td>Isopropanol</td>
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<tr>
<td></td>
<td>Cyclohexane</td>
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<td>61</td>
</tr>
<tr>
<td>$[^{13}\text{C}]\text{C}_6\text{H}_6$</td>
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<td>5.68</td>
<td>61</td>
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<td>61</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>4.75</td>
<td>61</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{D}$</td>
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<td>61</td>
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<td></td>
<td>Cyclohexane</td>
<td>14.10</td>
<td>61</td>
</tr>
<tr>
<td>Toluene $\text{C}_8\text{H}_8\text{CH}_3$</td>
<td>3MP</td>
<td>8.02</td>
<td>59</td>
</tr>
<tr>
<td>$\text{C}_8\text{H}_8\text{CD}_3$</td>
<td>3MP</td>
<td>8.03</td>
<td>59</td>
</tr>
<tr>
<td>$\text{C}_8\text{D}_8\text{CH}_3$</td>
<td>3MP</td>
<td>10.24</td>
<td>59</td>
</tr>
<tr>
<td>$\text{C}_8\text{D}_8\text{CD}_3$</td>
<td>3MP</td>
<td>10.54</td>
<td>59</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>E.P.A.</td>
<td>4.3</td>
<td>58</td>
</tr>
<tr>
<td>$[4,4'-^3\text{H}_2]\text{biphenyl}$</td>
<td>E.P.A.</td>
<td>5.7</td>
<td>58</td>
</tr>
<tr>
<td>$[3,3',5,5'-^2\text{H}_4]\text{biphenyl}$</td>
<td>E.P.A.</td>
<td>5.2</td>
<td>58</td>
</tr>
<tr>
<td>$[2,2',6,6'-^3\text{H}_3]\text{biphenyl}$</td>
<td>E.P.A.</td>
<td>6.4</td>
<td>58</td>
</tr>
<tr>
<td>$[2,2',4,4',6,6'-^2\text{H}_6]\text{biphenyl}$</td>
<td>E.P.A.</td>
<td>8.7</td>
<td>58</td>
</tr>
<tr>
<td>$[2,2',3,3',5,5',6,6'-^2\text{H}_6]\text{biphenyl}$</td>
<td>E.P.A.</td>
<td>7.2</td>
<td>58</td>
</tr>
<tr>
<td>$[^{13}\text{H}_1]\text{biphenyl}$</td>
<td>E.P.A.</td>
<td>10.3</td>
<td>58</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>3MP</td>
<td>2.51</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>2.6</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>2.47</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>2.94</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>3.03</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>2.9</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>2.75</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>2.85</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>2.6</td>
<td>59</td>
</tr>
<tr>
<td>$[1,2-^3\text{H}_2]\text{naphthalene}$</td>
<td>3MP</td>
<td>3.08</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>3.14</td>
<td>57</td>
</tr>
<tr>
<td>$[2,3-^3\text{H}_2]\text{naphthalene}$</td>
<td>3MP</td>
<td>3.61</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>3.74</td>
<td>57</td>
</tr>
<tr>
<td>$[\alpha-^3\text{H}_4]\text{naphthalene}$</td>
<td>3MP</td>
<td>~6</td>
<td>59</td>
</tr>
<tr>
<td>$[\beta-^3\text{H}_4]\text{naphthalene}$</td>
<td>3MP</td>
<td>~4</td>
<td>59</td>
</tr>
<tr>
<td>$[2,3,4,5,6,7,8-^3\text{H}_7]\text{naphthalene}$</td>
<td>3MP</td>
<td>11.08</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>11.07</td>
<td>57</td>
</tr>
<tr>
<td>$[1,3,4,5,6,7,8-^3\text{H}_7]\text{naphthalene}$</td>
<td>3MP</td>
<td>13.51</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>13.35</td>
<td>57</td>
</tr>
<tr>
<td>$[^6\text{H}_8]\text{naphthalene}$</td>
<td>3MP</td>
<td>21.73</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>21.82</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>21.0</td>
<td>59</td>
</tr>
</tbody>
</table>

* 3MP, 3-methylpentane; E.P.A., ether–isopentane–ethanol glass.
Table 2 (cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent*</th>
<th>Lifetime (sec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methylnaphthalene</td>
<td>3MP</td>
<td>2·45</td>
<td>59</td>
</tr>
<tr>
<td>2-methylnaphthalene</td>
<td>3MP</td>
<td>2·33</td>
<td>59</td>
</tr>
<tr>
<td>1-ethylnaphthalene</td>
<td>3MP</td>
<td>2·50</td>
<td>59</td>
</tr>
<tr>
<td>2-ethylnaphthalene</td>
<td>3MP</td>
<td>2·35</td>
<td>59</td>
</tr>
<tr>
<td>2-naphthaldehyde</td>
<td>E.P.A.</td>
<td>0·37</td>
<td>60</td>
</tr>
<tr>
<td>$[^\alpha\text{H}]$-2-naphthaldehyde</td>
<td>E.P.A.</td>
<td>1·35</td>
<td>60</td>
</tr>
<tr>
<td>$[^1,3,4,5,6,7,8-^2\text{H}]$naphthaldehyde</td>
<td>E.P.A.</td>
<td>0·46</td>
<td>60</td>
</tr>
<tr>
<td>$[^\text{H}_8]$naphthaldehyde</td>
<td>E.P.A.</td>
<td>4·80</td>
<td>60</td>
</tr>
</tbody>
</table>

* 3MP, 3-methylpentane; E.P.A., ether–isopentane–ethanol glass.

There is clear evidence that the position of the deuterium substituent is extremely important in its effect upon the rate constant for the radiationless transition. Lim’s data are very imprecise in that the purity of the deuterio-compounds used was very low. There is clearly a great difference between the $\alpha$- and $\beta$-positions in naphthalene, substitution in the ring or side chain in toluenes, and it is obvious that it is the aldehydic hydrogen which has the most marked effect on radiationless transitions in 2-naphthaldehyde. The benzene results can be taken to mean that it is the totally symmetrical C–H stretches which are predominant in determining the radiationless rate constant. The difference between the $\alpha$- and $\beta$-substituted naphthalenes may well be due to the different anharmonicities of the $\alpha$ and $\beta$ C–H bonds. It is also clear that changes in unconjugated alkyl C–H modes have no effect on the non-radiative decay process, as is evidenced by the toluene results. Enhancement of luminescence caused by deuteriation has also been observed in biacetyl.\(^{42}\) Both deuteriation of the biacetyl molecule itself, and the use of the deuteriated solvent, lead to an increase in the luminescence yield and lifetime of the ketone.

Further data relevant to theoretical approaches to radiationless transitions will be found in the next sections dealing with luminescence in solution.

### 3 Luminescence in Solution

A massive amount of data is published yearly on the emission properties of excited electronic states of molecules in solution, both in the fluid and solid states. The types of emission seen may be categorised as fluorescence (monomer singlet–singlet transition), phosphorescence (monomer triplet–singlet transition), excimer and exciplex emission (dissociative dimer transitions), delayed emission (both monomer and dimer transitions) and sensitised emission (intermolecular electronic energy transfer involved). An attempt is made here to evaluate the more significant contributions to this field under various sub-headings. The review of data is not intended to be comprehensive, and clearly some work falls into more than one category.

Fluorescence in Solution.—Work which is primarily of a spectroscopic nature is not considered here. The concern is quantitative estimation of fluorescence quantum yields of organic compounds, and the effect on these yields of such parameters as the solvent, temperature, concentration, and heavy atom substitution. Mention is also made of fluorescence from some novel compounds.

It is usually assumed that the position of the fluorescence emission spectrum of an organic molecule will be independent of exciting wavelength, and for many molecules this is the case. However, a group of molecules has been investigated in which a shift in the position of the emission spectrum, called the $B$ shift, is observed when the wavelength of the exciting radiation is varied. For example, for quinine bisulphate, a well-known fluorescence standard, the position of the fluorescence maximum shifts from 455 nm when excited at 350 nm to ca. 475 nm when excited at 430 nm. The nature of the spectrum is also shown to depend strongly upon the solvent used for this compound. Thus in pure dioxan, an additional long wavelength band appears which is absent in aqueous solution or water–dioxan mixtures. It is postulated that the $B$ shift occurs because the molecule which has a rotatable auxochromatic group can exist in two different average conformations each with its own distinct electronic energy transitions. These conformations can be considered to be stabilised by the interaction of the solvent with the molecule in both its ground and excited states. The $B$ shift results from different proportions of each conformer being excited as the wavelength of excitation is varied. Compounds exhibiting this behaviour in addition to quinine include 2-aminopurine, 2,2'-dihydroxybibenyl, 6-methoxyquinidine, 6-ethoxyquinidine, luminol, and 6-methoxyquinoline. It is important for investigators to recognise this phenomenon, especially in the cases of quinine, which is widely used as a fluorescence standard, and luminol, a well-known chemiluminescent material.

Since most workers attempting to measure quantum yields of luminescence in solution do so by comparison with a reference compound rather than making the tedious and experimentally difficult absolute measurements, it is necessary to have reliable data comparing the fluorescence yields of some of the compounds, such as quinine, used as such standards. These have hitherto been largely lacking, but a careful measurement of the fluorescence yields of 18 compounds on the same apparatus has done much to provide a consistent basis for the comparison of data. The authors conclude that fluorescein in 0.1-N NaOH and anthracene in ethanol are the best fluorescence standards. The widely used quinine in sulphuric acid suffers from the dependence of its fluorescence quantum yield upon the acid concentration and the exciting wavelength (see above). This, coupled with the solvent dependence already mentioned, means that this compound

---

should in future be disregarded as a reliable standard. The values obtained
for the various compounds are summarised in Table 3. Several compounds,
for example chrysene, show no variation in fluorescence quantum yield with
exciting wavelength, and are thus useful standards. The only complaint

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Excitation wavelength</th>
<th>$\Phi_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinine</td>
<td>1·0N-H$_2$SO$_4$</td>
<td>3655</td>
<td>0·54 ± 0·02</td>
</tr>
<tr>
<td>Quinine</td>
<td>0·1N-H$_2$SO$_4$</td>
<td>3655</td>
<td>0·50 ± 0·02</td>
</tr>
<tr>
<td>Perylene</td>
<td>Ethanol</td>
<td>2537-4358 average</td>
<td>0·94</td>
</tr>
<tr>
<td>Perylene</td>
<td>Benzene</td>
<td>3655</td>
<td>0·99 ± 0·03</td>
</tr>
<tr>
<td>Acridene</td>
<td>Ethanol</td>
<td>3655</td>
<td>0·72 ± 0·02</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Ethanol</td>
<td>3655</td>
<td>0·27 ± 0·01</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Benzene</td>
<td>3655</td>
<td>0·27 ± 0·01</td>
</tr>
<tr>
<td>Fluorene</td>
<td>Ethanol</td>
<td>2537</td>
<td>0·68 ± 0·04</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Ethanol</td>
<td>2537</td>
<td>0·205 ± 0·014</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Ethanol</td>
<td>2537-4358 average</td>
<td>0·125</td>
</tr>
<tr>
<td>Aminoacridine</td>
<td>Water</td>
<td>2537-4358 average</td>
<td>0·81 ± 0·02</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>0·1N-NaOH</td>
<td>2537-4358 average</td>
<td>0·87</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>Ethanol</td>
<td>2537</td>
<td>0·065 ± 0·006</td>
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<tr>
<td>Chrysene</td>
<td>Ethanol</td>
<td>2537-4358 average</td>
<td>0·17</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Ethanol</td>
<td>3131</td>
<td>0·53 ± 0·02</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Benzene</td>
<td>3131</td>
<td>0·60 ± 0·03</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Cyclohexane</td>
<td>3131</td>
<td>0·58 ± 0·01</td>
</tr>
<tr>
<td>Benzene</td>
<td>Hexane</td>
<td>2537</td>
<td>0·053 ± 0·008</td>
</tr>
<tr>
<td>9,10 Dichloroanthracene</td>
<td>Benzene</td>
<td>3655</td>
<td>0·71 ± 0·04</td>
</tr>
</tbody>
</table>

* Data from Table 1, ref. 64.

concerning the work here is that concentrations of solutions are not given
explicitly, and no extended investigation of the effect of concentration upon
fluorescence yields has been attempted. Nevertheless, the data are a very
valuable contribution to the field.

A novel approach to the problem of measuring accurately fluorescence
quantum yields has been devised. As has already been stated, precise
absolute determination of these yields is difficult, and problems arise
even when making photometric relative measurements. These can be
categorised as (1) anisotropy of emission, (2) constancy of the exciting
light, (3) refraction of emitted light, (4) detection geometry, (5) variation of
detector sensitivity with wavelength, and (6) medium effects such as
concentration, pH etc. A calorimetric method has been shown to produce
results in essential agreement with data obtained photometrically, which
eliminates some of these problems. The energy $E_0$ incident on a solution
of a luminophore may be represented as

$$E_0 = E_h + E_T + E_t$$  \hspace{1cm} (54)

---

Spectroscopic and Theoretical Aspects

where $E_h$ is the heat produced in the solution by radiationless processes, $E_f$ is the fluorescence energy, and $E_t$ the transmitted energy. The quantum yield of the radiationless process $Q_t$ is then given by

$$Q_t = \frac{E_h}{(E_0 - E_t)}$$  \hspace{1cm} (55)

and the fluorescence yield $\Phi_F$ as

$$\Phi_F = \frac{\nu_h (K_b - K_f)}{\nu_F (K_b - K_a)}$$ \hspace{1cm} (56)

where $\nu_h$ and $\nu_F$ are the average frequencies of the light absorbed and emitted respectively, $K_f$ is the rate of production of heat in the fluorescent sample, $K_a$ the rate of production of heat in the pure solvent, and $K_b$ the heating rate of a non-fluorescent sample absorbing the same fraction of radiation as the fluorescer. The non-fluorescer used was aniline blue-black in methanol, and heating rates were measured by the simple expedient of observing the expansion of the solution up a precision capillary tube. The method is a relative one, but the results obtained for many compounds were in excellent agreement with the photometric measurements mentioned, although these were based on the literature value of the fluorescein fluorescence quantum yield of 0.93, which is probably ca. 5% too high.\textsuperscript{64}

The effects of solvents upon the quantum yields of fluorescence of several aromatic molecules have been studied.\textsuperscript{64} From a study of the relative fluorescence intensity of $\alpha$- and $\beta$-naphthol in n-heptane as a function of the addition of aromatic hydrocarbons such as benzene, toluene, and xylene, it was concluded that there is $\pi$-hydrogen bond formation between the hydroxy-group of the naphthol and the $\pi$-electron system of the aromatic. The equilibrium constants obtained from such measurements were higher than those obtained from absorption data, a fact which can be explained on the basis of the increased proton donor character of the naphthol in the excited state compared with the ground state. For aromatics excited in various alcoholic solvents, quenching was observed to occur. The fluorescence yields were observed to decrease with choice of solvent in the order t-butyl > isopropyl > isobutyl > n-butyl > isopentyl alcohol. Again the quenching is probably due to the formation of a hydrogen bond between the $\pi$-system of the aromatic and the hydroxy-group of the alcohol. The results may be explained on the basis of a simple scheme.

$$A + h\nu \rightarrow A^*$$ \hspace{1cm} (57)

$$A^* \rightarrow A + h\nu_F$$ \hspace{1cm} (58)

$$A^* + S \rightarrow A + S$$ \hspace{1cm} (59)

where $A$ is the aromatic, $S$ the solvent. The Stern–Volmer relation predicted from this simple scheme was obeyed.

Anthraquinine itself does not fluoresce in propanol, but the β-fluro-, β-amino-, β-methyl-, α-fluoro-, 1,2,5,8-tetrahydroxy-, and α-amino-substituted anthraquinine dyes show fluorescence with an increasing quantum yield.\(^{67}\) The increase may be due to a suppression of the photo-reaction of anthraquinine with the alcohol upon increasing substitution, or an alteration in the rates of radiationless deactivation processes. The effect of structure of aqueous solutions on the luminescence yields of dyes is also important.\(^{68}\) In the presence of ionic materials which break down the bonds in the hydration shell of the dye, strong quenching of the fluorescence of the dyes is observed.

Benzene excited at \textit{ca.} 254 nm. in solution at 25 °C has a fluorescence quantum yield which is very much smaller than that in the vapour phase. However, as the temperature of the solution is reduced, the yield approaches that in the gas phase. This thermal quenching is due to oxygen,\(^{69}\) and it is shown that there is no direct relation between fluorescence quenching and the viscosity of the solvent. Excimer formation (concentration quenching, see later) is important only at intermediate temperatures (\textit{ca.} 175 K). From the temperature study, an activation energy of 2000 cm\(^{-1}\) is predicted for the quenching process. This corresponds well to the value of the excess of vibrational energy which benzene must have in the vapour phase to quench fluorescence. The competitive quenching process is not an intersystem crossing, and may well result from structural isomerisation, as proposed recently.\(^{40}\)

In many systems in the condensed phase, emission yields are independent of the exciting wavelength, or vibrational level reached upon excitation, because the high collision frequency ensures that the equilibrated vibrational level is reached before any other process occurs. In certain cases, however, where a chemical reaction may occur (as in benzene above), the amount of vibrational energy initially present in the excited molecule may be critical in determining the fate of the molecule. This is a well-studied phenomenon in the gas-phase (see Chapter 3), but so far little attention has been paid to the problem in condensed phases. A comparison of the fluorescence yields of 1,2-dihydronaphthalene and compounds (I) and (II) as a function of exciting wavelength has yielded interesting data concerning this problem.\(^{70}\)

\[\text{O} \quad \text{Et} \quad \text{Et} \]

(I)

\[\text{H} \quad \text{C} \quad \text{H} \quad \text{H} \]

(II)

---


\(^{68}\) A. V. Karyakin and C. C. Babicheva, \textit{Optics and Spectroscopy}, 1968, 24, 541.


It was found that the fluorescence quantum yield of the 1,2-dihydronaphthalene did not vary with wavelength, implying that vibrational relaxation dominates at all wavelengths; but in the case of compounds (I) and (II), which can undergo an isomerisation reaction of the type

\[ \text{[Diagram: } \text{Spectroscopic and Theoretical Aspects} \text{]} \]

fluorescence yields were found to decrease markedly as the frequency of exciting radiation was raised. However, the decrease was not uniform, as has been observed for benzene in the vapour phase.\(^{71}\) There are two electronic states in the region studied, and the sharply defined absorption bands permit a vibrational assignment to these. From the results it is obvious that particular vibrations favour the photochemical reaction and that relaxation will only occur via a particular vibrational manifold, as has been proposed for molecules in the gas phase.\(^{71}\)

For some time, azulene has been one of the few compounds known to show \(S_2 \rightarrow S_0\) fluorescence (see Figure 3). Some substituted azulenoid systems have now been shown to exhibit similar behaviour.\(^{72}\) The substituted Hafner's hydrocarbons (III), (IV), and (V) were all observed to emit from a state higher than \(S_1\), as did the naphthazulene (VI).

\[ \text{[Diagram: } \text{Spectroscopic and Theoretical Aspects} \text{]} \]


Upon protonation of compounds (III), (IV), and (V), only (V) retains its anomalous fluorescence, the first two then exhibiting normal $S_1 \rightarrow S_0$ fluorescence. Compound (VI) behaved similarly to (V) in that the protonated species retained its anomalous emission. From results on other substituted azulenes, it is apparent that protonation will destroy the radiative capacity of the upper excited states, except in peri-condensed systems containing four rings.

The emission properties of some perfluorinated aromatics \(^{73}\) in cyclohexane solution at 25 °C and in E.P.A. at 77 K are in good agreement with those determined for perfluorobenzene.\(^ {74}\) In every case perfluorination drastically reduces the fluorescence quantum yield, and also the phosphorescence yield at 77 K. The compounds studied were perfluorobiphenyl, perfluoronaphthalene, and perfluorotoluene.

The term fluorescence refers to a radiative transition between two electronic states of a molecule without change in multiplicity. For almost all molecules this means a singlet $\rightarrow$ singlet transition. However, for diphenylmethylene (diphenylcarbene) and substituted compounds of the same nature, the emission observed has been assigned to a $T_1 \rightarrow T_0$ transition on the basis of e.s.r. measurements. Since in general transitions involving a change in multiplicity have much longer lifetimes than those between states of a like spin state, a check on the fluorescence lifetime of diphenylmethylene would provide information as to whether the assignment is correct. The lifetime has been measured to be of the order of 100 nsec,\(^ {75}\) and it seems likely that the emission indeed arises from a triplet–triplet fluorescence transition. An emission of lifetime ca. 150 nsec has been observed from a related compound $m$-phenylenebisphenylmethylene \(^ {76}\) (VII) excited at 485 nm, again implying that the transition is not violating spin selection rules. Since compound (VII) is known to exist in its ground state as a quintet, the implication from the emission data is that the first excited state is also a quintet. Thus we have here two examples of fluorescence which do not occur by the radiative transition between singlet states.

**Concentration Quenching and Excimer Formation**—Excited electronic states of molecules in condensed phases may be quenched by a number of processes. Solute–solvent interactions of both a physical and chemical nature have been mentioned briefly already, and electronic energy transfer to accepting species will be dealt with in a later section. The remaining major influence upon the emissive properties of excited electronic singlet states of molecules is the effect of the concentration of the species in the solution. At high concentrations interaction between the excited state and a ground state molecule may lead to the formation of excited dimers, excimers, or mixed complexes, exciplexes, which lead to a reduction in the normal


fluorescence yield of the molecule. Delayed fluorescence of both monomeric and dimeric character arising through triplet–triplet annihilation is a related phenomenon. Thus, for example, monomer emission from solutions of 2-phenylindole and its derivatives is observed to decrease with increasing concentration of solute.\textsuperscript{77} Simultaneously, long-wavelength excimer emission bands are observed. However, since excimer emission is not observed in every case where self-quenching is present, there may be a common pathway for these processes.

\[
\begin{align*}
M^* & \longrightarrow M + h\nu_M \text{ monomer fluorescence} \\
M^* + M & \longrightarrow M^* + M \longrightarrow 2M + \text{heat} \\
M^* & \longrightarrow 2M + \text{heat} \\
2M + h\nu_D & \text{ excimer emission}
\end{align*}
\] (61)

(62)

This type of concentration quenching is to be contrasted with that due to the formation of solute aggregates in solution\textsuperscript{78} in the latter case, the absorption spectrum of the solution also changes with concentration.

Pioneering work on excimer formation was done on the pyrene system, and this molecule continues to be investigated in detail.\textsuperscript{79–81} Pyrene is of interest in that it displays all the possible types of luminescence categorised earlier, but discussion of this molecule is considered with that of others exhibiting delayed fluorescence later in this section. Aromatic molecules generally show excimer and exciplex luminescence. Thus excimer fluorescence has been observed recently in toluene,\textsuperscript{82, 83} benzene,\textsuperscript{83} p-xylene,\textsuperscript{83} mesitylene,\textsuperscript{83} 2-methylnaphthalene, 1,6-dimethylnaphthalene, naphthalene, fluorobenzene, and fluoronaphthalene in cyclohexane solution.\textsuperscript{84} In the latter study, the fluorescence excitation spectra of these compounds were taken. The observed dependence of the relative fluorescence yield upon excitation wavelength and concentration was analysed in terms of a model kinetic scheme involving the formation of higher excimer states D\textsuperscript{**} from higher excited molecular states X\textsuperscript{**}. The scheme used is

\[
\begin{align*}
X + h\nu & \longrightarrow X^{**} \\
X^{**} & \longrightarrow X^*
\end{align*}
\] (63)
(64)


\textsuperscript{82} J. R. Greenleaf, M. D. Lumb, and J. B. Birks, \textit{J. Phys. (B)}, 1968, 1, 1157.


\[
\begin{align*}
X^{**} & \rightarrow X' \text{ quenching or dissociation} \\
X^{**} + X & \rightarrow D^{**} \\
D^{**} & \rightarrow D^* \\
D^{**} & \rightarrow 2X' \\
D^{**} & \rightarrow X^{**} + X \\
X^* & \rightarrow X + h\nu_X \\
X^* & \rightarrow X' \\
X^* + X & \rightarrow D^* \\
D^* & \rightarrow 2X + h\nu_D \\
D^* & \rightarrow 2X' \\
D^* & \rightarrow X^* + X
\end{align*}
\]

In this scheme, \(X\) is the aromatic, \(X^*\) and \(X^{**}\) are the aromatics in first excited and higher excited singlet states respectively, \(D^*\) and \(D^{**}\) the excimer in its first and higher excited states respectively. A comparison of the fluorescence yields for excitation into a higher state with that into the first excited state yields the expression:

\[
\frac{\Phi_F}{\Phi_{F_1}} = \beta = \frac{k_{64} + k_{67} K_1[X]}{k_{70} + k_{73} + (k_{73} + k_{74}) K_2[X]}
\]

(76)

where

\(\Phi_F\) = total fluorescence yield (monomer + excimer) from excitation to higher state

\(\Phi_{F_1}\) = total fluorescence yield from excitation to first excitation to first excited state

\(K_1 = [D^{**}]/[X^{**}]\)

and

\(K_2 = k_{72}/(k_{73} + k_{74} + k_{75})\)

Expression (76) can be rearranged to be of the form

\[
\frac{1}{\beta} = \frac{1 + B[X]}{A(1 + C[X])}
\]

(76a)

Data obtained were found to fit expression (76a) satisfactorily. For all compounds except benzene, \(B > C\), whereas the reverse is true for the benzene case. In this case, \(\beta\) decreases upon dilution. The implications are that in benzene higher excited states, quenching, dissociation, or isomerisation (equation 65) compete effectively with internal conversion to \(X^*\) (process 64). However, internal conversion of \(D^{**}\) to \(D^*\) is more efficient in this case. In the other compounds, \(D^{**}\) is more liable to quenching than \(X^{**}\), so \(\beta\) decreases on increasing \([X]\).
Exciplex formation between excited aromatic molecules and various substrates have been reported. Thus, 1,2-benzanthracene will form an exciplex with disubstituted anthracenes, and mixed complexes between dimethylanthracene, diphenylanthracene, dipropylanthracene, dichloroanthracene, 9-chloro-10-methoxyanthracene, 9-methyl-10-methoxyanthracene, and 2-acetylanthracene, as well as complexes between these compounds and other species such as acridine, quinoline, etc., have all been observed. The kinetics of formation of the exciplex between substituted benzanthracenes and tetra-alkyldiaminophenylmethanes have been studied. However, excimer formation is by no means restricted to aromatic molecules; it has recently been observed in aliphatic ketones such as acetone, and in other comparably polar molecules.

Excimer formation and quenching of fluorescence in solution are processes whose rates will be diffusion controlled. Thus the quenching rate constants $k_q$ will be given by

$$k_q = \frac{8RT}{3000\eta} \text{ mole}^{-1}\text{sec}^{-1} \quad (77)$$

where $R$ is the gas constant, $T$ the absolute temperature, and $\eta$ the viscosity of the solvent. For many systems the rate constant predicted by equation (77) is found to be in good agreement with experiment, but systems have been described in which there is a deviation from this simple behaviour. Care must be taken to distinguish between the microscopic and macroscopic viscosity of the solvent. Thus different behaviour is observed in the rates of excimer formation between solutions of pyrene in hydrocarbon solvents of the same viscosity. With hexane and paraffin mixtures as solvent, the rate of excimer formation decreases strongly with increasing overall viscosity. With benzene solvent plus added dissolved polystyrene to give the same overall viscosity as the paraffin solutions, little change in rate of formation of excimers with macroscopic viscosity was observed. Clearly in the latter case, since the volume fraction occupied by the polymer in solution is small, there is no large variation in the path length for the diffusing pyrene molecules, and hence no change in rate.

Using time-resolved electronic spectroscopy, a test of the assumption that bimolecular quenching rates and excimer formation rates are diffusion controlled was made. It was found that the assumption is invalid for solvents of low viscosity. An apparatus was used in which fluorescence intensity measurements were made at nanosecond intervals using a simple exciting lamp of high intensity and very short flash duration. Assuming

---


excimers are formed by the reversible process

\[ A^* + A \rightleftharpoons AA^* \]  

(78)

then if the rates of these processes are fast compared with deactivation of
the excited species the position of the equilibrium is determined by them,
and the fluorescence efficiency is a non-perturbing measure of equilibrium.
This can be termed case \( \alpha \). If, on the other hand, the rates of the processes
are slow, then the concentration of excited species will appear to depend
upon viscosity of the solvent (case \( \beta \)). In normal solvents at 25 °C, naphtha-
lene was shown to exhibit \( \alpha \)-type behaviour, whereas pyrene approximated
to case \( \beta \). Each compound could be made to show the opposite effect by,
on the one hand, lowering the temperature and concentration of the
naphthalene, and on the other by raising the temperature and concentration
of the pyrene. The results can be interpreted as showing that the dissocia-
tion of the excimer requires an activation energy.

A correlation has been found between the electron affinity of a quenching
molecule and the rate constant for the quenching of monomer fluorescence
of anthracene, and both monomer and excimer fluorescence of pyrene in
solution.\(^90\) As the electron affinity increases, the rate constants for quenching
of both excited dimer and monomers also increases. A charge-transfer
mechanism is thus strongly suggested in which quenching may be inter-
preted in terms of the formation of an excited-state charge-transfer complex
due to the increased mixing of the locally excited (\( A^*Q \)) and charge transfer
(\( A^+Q^- \)) configurations upon approach of excited molecule \( A^* \) to quencher
\( Q \). Emission from the charge-transfer complexes was observed in several
systems as new long-wavelength bands. There was clear evidence that the
pyrene excimer was also quenched by the electron-accepting molecules. A
similar phenomenon has been observed in the perylene–NN-dimethyl-
aniline system,\(^91\) where the mechanism may be represented as follows:

\[
\begin{align*}
A & \rightarrow A^* \\
A^* + Q & \rightleftharpoons A^*Q \\
A + h\nu_P & \rightarrow A^* \\
A^*Q & \rightarrow \begin{cases} P + Q \\
p + Q \\
P^- + Q^+ \end{cases} \\
A + Q + h\nu_{CT} & \\
\end{align*}
\]

(79)

As predicted from this mechanism, linear Stern–Volmer plots were
obtained. The values of the quenching rate constants showed a marked
dependence upon the viscosity of the solvent, but little effect of dielectric
constant was noticed. A value of 8.1 kcal mole\(^{-1}\) for the dissociation
energy of the charge-transfer complex was obtained.

The heat of formation of the pyrene–NN-dimethylaniline exciplex is strongly dependent upon the polarity of the solvent used, as is the ground-state destabilisation energy. This behaviour is quite different from that in excimers, which are independent of polarity of the solvent. The difference is understandable in that exciplexes are considerably more polar in nature than excimers, and thus sensitive to solvent polarity.

A number of semiempirical molecular orbital calculations have been carried out in an attempt to account at least qualitatively for the occurrence and characteristics of excimer luminescence. In Lim’s treatment, the simplest case is taken in which the excimer is assumed to have the highest symmetry possible, i.e. the aromatic rings are considered to eclipse one another if viewed from above. Using this model, and considering configuration interaction among various states, it is possible to explain qualitatively the observed effects. The results also show that triplet states of most aromatic excimers are expected to be unstable with respect to dissociation into a monomer triplet and monomer ground state, which may be an explanation of why data on triplet excimers are scarce at present. A more complete treatment has been applied to the benzene excimer, in which ground and excited states have been calculated for a number of configurations, including the one of highest symmetry considered by Lim. Thus geometric conformations of C\(_{2h}\), S\(_2\), C\(_0\), S\(_{12}\), and C\(_{2v}\) symmetry have been considered in addition to the D\(_{6h}\) case. For the symmetrical case, the transition from excited state to ground state is dipole forbidden, but since excimer fluorescence lifetimes are observed to be short, the transition must borrow its strength from other states. This can be done in two ways, one through vibronic states in much the same way as the \(^1A\(_{1g}\) → \(^1B\(_{2u}\) transition of benzene becomes allowed, the second by supposing that the excimer possesses C\(_1\) or C\(_{2v}\) symmetry, in which case a relatively small tilting of the benzene planes can induce transition moments of the proper magnitude without invoking vibronic effects at all. The most stable excimer conformation was found to be one in which the rings are rotated about the D\(_{6h}\) axis and/or tilted with respect to one another. For all configurations, the ground state of the excimer was found to be dissociative, as it must be, whereas the E\(_1\) state was always stable. It is of interest to note that the calculations predict that the ground state of the excimer, though dissociative, should show diffuse absorption to both dissociative and stable upper states. The authors contend that many of the broad continua which underlie structured absorption spectra of solutions originate in ‘contact’ excimer absorption processes. ‘Contact’ here does not imply the formation of any stable ground-state dimer; rather it refers to a situation in which two monomers are sufficiently close for there to be some interaction, both attractive and repulsive between them. The temperature dependence of the

fluorescence spectra of excimer systems has been the subject of a short study.\textsuperscript{94}

As stated previously, there is but little evidence in the literature for the existence of triplet excimers. However, it has been reported that the quantum yield of formation of trans-but-2-ene from the cis-isomer sensitised by o-xylene in methylcyclohexane solution at 60 °C is strongly dependent upon the concentration of o-xylene.\textsuperscript{95} This phenomenon has been interpreted as showing that a strong self-quenching of the triplet aromatic by ground-state molecules to form a triplet excimer can occur. The process envisaged is

\[
\begin{align*}
\text{S} + \text{S} & \rightarrow (3\text{A}_2) \rightarrow \text{S} (\text{A}^+\text{A}^-) \rightarrow [\text{S} \text{A}^+ \text{A}^-] \\
& \quad \downarrow \text{A} + \text{A} \\
\end{align*}
\]

The arguments assume no chemical interaction between the solvent and o-xylene, and that quenching impurities are unimportant. Evaluation of the results is difficult since no details of the calculations are presented. Since the excited singlet state of o-xylene is self-quenched, and the singlet is the precursor of the triplet, singlet quenching must be considered in any calculation of triplet yields by the sensitisation method. Presumably this was done, although the fact is not stated.

The luminescence of pyrene in viscous solutions may be represented diagramatically in Figure 4. Excimer phosphorescence has been ignored here. A study of the normal and delayed monomer and excimer fluorescence and phosphorescence of pyrene in propylene glycol solution in the range 200—295 K has revealed interesting facts concerning the triplet-triplet annihilation process from which delayed emission arises.\textsuperscript{79} Two alternative models have been suggested. Birks proposed (see ref. 79) that T*—T* association resulted in a double excited state of the excimer D** which

\[
\begin{align*}
\text{T}^* + \text{T}^* & \rightarrow \text{D}^{**} \\
& \quad \uparrow \text{D}^* \\
& \quad \downarrow \text{M}^* + \text{M} \\
\end{align*}
\]

either rapidly internally converted to D* or dissociated into M* and M

Parker and Tanaka on the other hand proposed that

\[
\text{T}^* + \text{T}^* \rightarrow \text{M}^* + \text{M}.
\]


Spectroscopic and Theoretical Aspects

was a long-range interaction process, whereas

\[ T^* + T^* \rightarrow D^* \] (83)

was collisional in nature.

Figure 4 Radiative and radiationless processes in pyrene: upper diagram, under continuous illumination; lower diagram, delayed spectra. (A, absorption; F, fluorescence; IC, internal conversion; ISC, intersystem crossing; EF, excimer fluorescence; IQ, internal quenching; P, Phosphorescence; Ex, Excimer formation; Dis, excimer dissociation; TA, triplet–triplet annihilation)
(Based on Figure 1, J. B. Birks, B. N. Srinivasan, and S. P. McGlynn, J. Mol. Spectroscopy, 1968, 27, 266)

Present data indicate that above 250 K, process (82) is collisional and therefore diffusion controlled, but that below 250 K, a low constant value for the rate constant is obtained which is probably due to an electron exchange interaction. It thus appears meaningless to attempt to distinguish between two mechanisms above 250 K.

It is clear that the nature of the collisional interaction of the triplet excited pyrene molecules is complex. Possible states of the excimer formed \(^79\) are:

(a) doubly excited states \(^1D^{**}, \(^3D^{**}, \(^5D^{**}\);

(b) charge resonance states arising from interaction of positive and negative ions;

(c) exciton resonance states arising from various molecular excited states and ground states;
(d) various 'mixed' states arising from configuration interaction between the above states.

The effects of concentration and exciting wavelength upon the emission spectrum of the pyrene monomer have been described, and triplet–triplet interaction of other molecules in solution has been discussed.

Delayed fluorescence has also been observed in the aromatic ketone species benzil in perfluoromethylcyclohexane. Temperature studies show clearly that this is due to thermal reactivation of the singlet state, that is, the emission is E-type delayed fluorescence. The term 'activation-controlled delayed fluorescence' has been proposed to cover the emission observed under such conditions.

Flash photolysis using light pulses of short duration is proving to be a powerful tool in the investigation of the phenomenon of delayed fluorescence and associated processes. As a demonstration of the method, the efficiency of the triplet–triplet annihilation process in anthracene was determined. The quantities measured were: (i) the intensity of the delayed fluorescence as a function of time; (ii) the intensity of the normal fluorescence as a function of time; and (iii) the triplet state yield. Using direct or excitation sensitisation, the intensity of the delayed fluorescence, \( I_{DF} \), is given by:

\[
I_{DF} = \alpha \Phi_F \rho k_{TT}[T^*]^2
\]

where \( \Phi_F \) = normal fluorescence yield, \( k_{TT} \) = second order rate constant for triplet decay, and \( \alpha \) is a constant depending on the apparatus. To eliminate \( \alpha \), the normal fluorescence and triplet yields are measured.

Now

\[
\int I_F(t) \, dt = \alpha \Phi_F \int I_{ab}(t) \, dt
\]

where \( I_F(t) \) is the fluorescence at time \( t \), \( I_{ab}(t) \) is the light absorbed, and

\[
[T^*_T] = \Phi_T \int I_{ab}(t) \, dt
\]

where \( \Phi_T \) is the triplet quantum yield. \( [T^*_T] \) can be evaluated from an extrapolation of the decay of \( D_T \), the optical density of triplet anthracene, to \( t = 0 \).

Thus

\[
\frac{\int I_{DF} \, dt}{\int I_F \, dt} = k_{TT} \rho \Phi_T \frac{\int [T^*]^2 \, dt}{[T^*_T]} = \frac{k_{TT} \rho}{\epsilon_T I} \Phi_T \frac{\int (D_T)^2 \, dt}{[D_T]_0}
\]

The quantities \( \int I_F \, dt, \int I_{DF} \, dt, \int (D_T)^2 \, dt, \) and \( [D_T]_0 \) can be evaluated experimentally, as can \( k_{TT}/\epsilon_T I \) from the observed second-order decay constant

---

of the triplet state: \((\varepsilon_T\) is the extinction coefficient of the triplet–triplet absorption, and \(l\) the optical path length). Thus taking the literature value of \(\Phi_T\), the only assumed quantity, values of \(\rho\) may be determined. These are in excellent agreement with Parker’s values.\(^{98}\) The technique may also be used to distinguish between ‘\(P\)’ type and ‘\(E\)’ type delayed fluorescence. For \(P\) type:

\[
\begin{align*}
T^* + T^* & \xrightarrow{S^* + S} \frac{k_a}{k_b} \quad k_{TT} = k_a + k_b \\
\end{align*}
\]

(88)

Now \(\rho = k_a/k_{TT}\)

(89)

and

\[
I_{DF} = \alpha \Phi_F \rho k_{TT}[T^*]^2
\]

(90)

\[
= \alpha \Phi_F \rho k_{TT}[D_T/\varepsilon_T l]^2
\]

(91)

For \(E\) type:

\[
\begin{align*}
T^* & \xrightarrow{\Delta H} S^* k_i \\
I_{DF} & = \alpha \Phi_F k_i [T^*] \\
& = \alpha \Phi_F k_i \frac{D_T}{\varepsilon_T l}
\end{align*}
\]

(92)

(93)

(94)

Since the dependence of \(I_{DF}\) is different, the two types may be distinguished readily.

The same technique has been used to investigate mixed triplet–triplet annihilation between eosin and anthracene in ethanol, using \(\beta\)-acetonaphthone as a sensitizer. Of the possible processes:

\[
\begin{align*}
H^T + A^T & \longrightarrow E^* + A \\
E^T + A^T & \longrightarrow E + A^* \\
A^T + A^T & \longrightarrow A^* + A \\
E^T + E^T & \longrightarrow E^* + E
\end{align*}
\]

(95)

(96)

(97)

(98)

the second, (equation 96), does not apparently occur. However, the possibility that this is followed by the energy-transfer process

\[
A^* + E \longrightarrow E^* + A
\]

(99)

cannot be ruled out.

The growth of phosphorescence and delayed fluorescence in rigid glasses and in mixed crystals has a lifetime different from that of their decay.\(^{101, 102}\) The rise time is inevitably shorter than the decay. The explanation given is that in rigid glasses triplet–triplet absorption events contribute to the depopulation of the triplet state and thus decrease the rise time, whereas in


crystals triplet–triplet annihilations are of predominant responsibility. It is not clear however why the absorptive act should not also be important in crystals.

4 Further Aspects of the Triplet State

The triplet state has already featured largely in discussions of radiationless transitions and delayed emission in condensed phases. Some additional information concerning triplet states of organic molecules will be presented here.

The lowest triplet state of most organic molecules is populated generally via an intersystem crossing from the lowest excited singlet state, although higher triplets degenerate with or slightly lower in energy than the first singlet have been postulated as intermediates in some systems. The rates of such spin inversion processes may be influenced drastically by interaction of the nucleus of heavy atoms in either the molecule under consideration or solvent with the electronic system via spin–orbit coupling. However, the radiative spin inversion process, phosphorescence, and intersystem crossing from the triplet to ground state will also be influenced by the heavy atom. The criteria necessary to maximise the steady state concentration of triplet molecules have been considered.\(^\text{103}\) By measuring the triplet state population using triplet–triplet absorption spectroscopy, it can be shown that

\[
\frac{I'}{I} = \frac{\chi + 1}{a\chi + 1} \cdot \frac{a}{b}
\]

(100)

where \(I'\) is the intensity of triplet absorption in the presence of a heavy atom (in the solvent), \(I\) is the intensity of absorption in the absence of the heavy atom, and \(a = k'_{\text{ls}}/k_{\text{is}}, \ b = k'_{\text{p}}/k_{\text{p}},\) and \(\chi = k_{\text{ls}}/k_{\text{p}}\) where \(k_{\text{ls}}, \ k_{\text{is}}\) are the rate constants for the intersystem crossing process in the presence and absence of the heavy atom respectively, \(k'_{\text{p}}, \ k_{\text{p}}\) are the corresponding rate constants for the phosphorescence process, and \(k_{\text{p}}\) the rate constant for the fluorescence process. It is clear that for values of \(\chi \gtrless 1\) or of the order of unity, any increase in spin orbit coupling will serve to decrease the triplet state population. Only in the case where \(\chi \ll 1\) and \(a/b > 1\) will the proximity of a heavy atom cause a significant increase in the triplet state population. These conclusions apply only when the decay of the triplet state is principally via processes which depend upon spin–orbit perturbation. Clearly if the triplet state is deactivated by other processes such as bimolecular quenching in fluid solution, increase in spin–orbit coupling should serve to increase the triplet state yield in all cases. This is used to determine triplet state quantum yields of a number of aromatic hydrocarbons in solution, xenon being used as the heavy atom.\(^\text{104}\) Both fluorescence yields and triplet yields from triplet–triplet absorption spectra were measured in ethanolic solution, and


it was found that for all of the compounds studied, with the exception of coronene, the sum of triplet state yields and fluorescence yields was unity. The results are shown in Table 4. They are a useful complement to those

Table 4  Triplet state and fluorescence yields of hydrocarbons in solution*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\Phi_T$ (Triplet state yield)</th>
<th>$\Phi_F$ (Fluorescence yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorene</td>
<td>Ethanol</td>
<td>0.32 ± 0.02</td>
<td>0.68 ± 0.07</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Ethanol</td>
<td>0.80 ± 0.01</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>1-Methoxynaphthalene</td>
<td>Ethanol</td>
<td>0.82 ± 0.05</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>Acenaphthalene</td>
<td>Ethanol</td>
<td>0.58 ± 0.02</td>
<td>0.39 ± 0.04</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Ethanol</td>
<td>0.72 ± 0.02</td>
<td>0.30 ± 0.03</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Ethanol</td>
<td>0.85 ± 0.02</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>1,2-benzanthracene</td>
<td>Ethanol</td>
<td>0.82 ± 0.02</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Ethanol</td>
<td>0.77 ± 0.02</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Ethanol</td>
<td>0.38 ± 0.02</td>
<td>0.72 ± 0.07</td>
</tr>
<tr>
<td>Coronene</td>
<td>Ethanol</td>
<td>0.56 ± 0.1</td>
<td>0.23 ± 0.02</td>
</tr>
</tbody>
</table>

* Data from Table 3, ref. 103.

obtained for fluorescence only (Table 3). The effect of the heavy atom in ethyl bromide upon the absorption spectra (singlet–singlet and triplet–triplet) of naphthalene in cyclohexane and ethanol solution is complex in that in addition to the expected increase in spin–orbit coupling, the formation of a complex between the solute and heavy-atom solvent appears to occur.\(^{105}\)

Triplet states are conveniently detected by their emissive properties and also by their absorption spectra, when they undergo transitions to higher triplet states. Phosphorescence data in solid solutions have been obtained for the following molecules: phenanthrene,\(^{105}\) p-benzoquinone,\(^{106}\) phenoxazine,\(^{107}\) quinoxaline,\(^{108}\) formaldehyde,\(^{109}\) α-diketones,\(^{110}\) and acetophenone.\(^{111}\) It is generally necessary to use low-temperature glasses to observe phosphorescence in most compounds, since in fluid solutions radiationless deactivation of the triplet states is very rapid. However, it has been shown that for benzophenone in an inert fluorocarbon solvent,\(^{112}\) a high quantum yield of phosphorescence is possible. In hydrocarbon solvents the triplet state of the ketone may abstract hydrogen from the substrate, but in the fluorocarbon solution such a reaction is impossible, and thus more triplets decay radiatively.

---


Triplet–triplet absorption spectra, observed by flash techniques, have been obtained for naphthalene and some of its monosubstituted derivatives,113 perdeuterionaphthalene,114 9,10-diphenylanthracene,115 and NN-dimethylamline.116 Attempts to utilise triplet–triplet absorption as a quantitative measure of triplet state populations are difficult in that the extinction coefficients of the transitions are not usually available. However, these extinction coefficients can be obtained by simultaneously monitoring the e.s.r. signal from the triplet state and the triplet–triplet optical density. This technique has been applied to $[^1H_8]$naphthalene,117, 118 phenanthrene, $[^9H_{10}]$phenanthrene, triphenylene, chrysene, 1,2-benzanthracene, $[^9H_{10}]$pyrene, picene, and coronene.117 The values obtained are not in good agreement with previously used literature values, but are likely to be more accurate. The method has a general applicability and promises to be useful. Similar work has been performed on phenazine, chlorophyll B, and benzophenone.118

Although triplet–triplet absorption is by now a well-known phenomenon, fluorescence arising from a triplet–triplet transition is still a rarely seen event. The $T_1 \rightarrow T_0$ transition in diphenylmethylenes and its derivatives gives rise to fluorescence,78, 76 but there is recent evidence of a transition between excited triplet states of rubrene which gives rise to an emission with the characteristics of a fluorescence.119 Since the position of the spectrum is red-shifted from that of the triplet–triplet absorption, it seems not unreasonable to assign the emission to fluorescence from an excited triplet to lower excited triplet transition. This is the first recorded observation of such a transition. Triplet–triplet absorption is an easily observed phenomenon compared with excited-singlet to higher singlet transitions because the lifetimes of triplet states are long relative to those of singlets. However, the development of nanosecond pulsed lasers has permitted transitions of the latter nature to be observed in the case of naphthalene.120 Intersystem crossing between excited triplets and singlets has been observed.121 Thus many aromatic molecules (naphthalene, deuterionaphthalene, quinoline et al.) were excited with u.v. radiation to populate the triplet state, and the exciting radiation was then shut off. Photoexcitation with visible light then populated higher triplet states of the molecules. Under such conditions, fluorescence was observed, indicating that intersystem crossing from the higher triplet to singlet manifold is competitive with internal conversion to the lowest triplet. The participation of the

singlet manifold in relaxation from higher triplets is not seen in all molecules, however. A study similar to that of ref. 121 on Michler's ketone, 1,8-bibenzoylnaphthalene, chrysene, and coronene has failed to reveal any fluorescence. Thus in these compounds, the higher triplet states decay uniquely to the lowest triplet via internal conversion.

The nonradiative character of phthalazine in hydrocarbon solvents has been investigated by using electronic energy transfer (see later) to a naphthalene acceptor. The data show that the nitrogen compound is non-fluorescent because of a very rapid intersystem crossing to the triplet state, but that this state is non-phosphorescent because of a rapid intersystem crossing to the ground state.

5 Electronic Energy Transfer

Transfer of electronic excitation energy is well known to occur in the vapour, fluid solution, and solid phases, although the mechanism by which the process occurs is clearly dependent upon the conditions under which it is studied. In fluid solution and in the gas phase, the mechanism is predominantly collisional in nature. The rapid destruction of triplet states by molecular oxygen has been well known for a considerable period of time, and indeed, the quenching of reaction paths by oxygen is often used as a diagnostic method to detect triplet state intermediates: but note equation (102). However, the precise nature of the interaction has been the subject of only little attention. During a study of the sensitised photoperoxidation of unsaturated organic molecules, the involvement of \(1\Delta_g\) oxygen molecules has been proposed. These arise via quenching of the sensitisier triplet state by ground-state oxygen molecules.

\[
s^* + O_2 \rightarrow S^* + O_2^* \tag{101}
\]

This mechanism certainly operates in situations where the sensitisier has a low fluorescence yield. In cases where the fluorescence yield is high, the \(1\Delta_g\) \(O_2\) intermediate may arise by oxygen quenching of the singlet state, via the following mechanism:

\[
s^* + O_2 \rightarrow S^* + O_2^* \tag{102}
\]

Energy transfer has also been observed from \(1\Delta_g\) \(O_2\) to the dye methylene blues. It is worth mentioning in passing that oxygen will also quench triplet states of molecules in polymer matrices at room temperatures. If the material containing the triplet molecule is subjected to a pressure of ca. 12 Kbar, quenching by \(O_2\) ceases to be important.

Energy transfer in fluid solution is of great importance in that it is a technique widely used to excite acceptor molecules specifically to an
excited state of particular multiplicity; thereby distinctions can be made between the physical and especially the chemical properties of excited states of different multiplicity. This important area naturally continues to attract much attention. There are a few recent examples of transfer of singlet energy in solution. The quenching of fluorescence of pyrene and anthracene by electron-accepting substances has already been referred to.\textsuperscript{90} Biacetyl fluorescence may be sensitised by transfer of singlet electronic energy from 2-aminopyridine in cyclohexane solution at 25 °C,\textsuperscript{127} although this phenomenon does not occur in the case of 3-aminopyridine, for reasons which are not obvious. Singlet energy may be transferred from benzene to olefins in the liquid phase if the concentration is high enough,\textsuperscript{128, 129} but at moderate concentrations, triplet transfer is the predominant energy transfer process, reflecting the longer lifetime of the triplet species.\textsuperscript{129} In the gas phase, benzene fluorescence is quenched strongly by 1,3-dienes, but only weakly by mono-olefins: see chapter 2.

Triplet–triplet energy transfer is by far the most commonly observed phenomenon in solution. The process may be followed by monitoring spectroscopic properties of the donor and acceptor, or chemical properties. The spectroscopic properties are generally the phosphorescence of the donor, and sometimes of the acceptor also, but a recent novel investigation has used n.m.r. spectroscopy to follow the energy transfer process.\textsuperscript{130}

Eosin and anthracene provide an interesting pair of molecules in which to study triplet transfer in that the triplet states of these molecules are almost degenerate, and thus the transfer process is reversible. The data can be represented by a scheme

\[
\begin{align*}
\text{3E}^* + A & \xrightleftharpoons[ka]{k_d} \text{3A}^* + E \\
+ A & \xrightleftharpoons[k_c]{k_e} + E
\end{align*}
\]

(103)

where E is eosin and A is anthracene.\textsuperscript{131} This scheme would predict an equilibrium concentration of each triplet state given by

\[
\frac{\text{3E}^*}{\text{3A}^*} = \frac{k_d [E]}{k_b [A]^*}
\]

(104)

The relation is found to hold.

\textsuperscript{131} K. Kikuchi, H. Kokubun, and M. Koizumi, \textit{Z. Phys. Chem. (Frankfurt)}, 1968, \textbf{67}
Spectroscopic and Theoretical Aspects

Charge-transfer processes may be important in the quenching of triplet species in solution.\textsuperscript{138, 138} Thus in the latter study, eosin Y triplets produced by flash illumination were quenched by aniline, resorcinol, \( \beta \)-naphthol, \( p \)-sulphanilic acid, and bromophenol in an energy transfer process, but also underwent a slower electron transfer process. Triplet energy transfer is of enormous importance in biological systems, and is under active quantitative investigation.\textsuperscript{134}

Since the process under these conditions, in the absence of any long-range effects, is essentially collisional, the rate will be diffusion controlled. However, long-range (Förster) interactions may be important even in fluid solutions. Birks\textsuperscript{138} has discussed the kinetics of two extreme cases for donor D\(^*\), acceptor A, energy transfer. These are as follows:

(i) Stern–Volmer kinetics, in which there is a complete statistical ‘mixing’ of D\(^*\) and A due to diffusion and/or excitation migration. The energy transfer rate is independent of time, and D\(^*\) emission decays exponentially.

(ii) Förster kinetics, where D\(^*\) and A remain essentially stationary, apart from possible Brownian motion. The energy transfer rate decreases with time, and the decay of D\(^*\) is non-exponential.

Birks has shown that energy transfer from phenanthrene singlets to acridine in a range of solvents can be made to follow either of these two types of kinetics depending upon the viscosity of the solvent.\textsuperscript{135} Diffusion-controlled energy transfer has been observed in other systems.\textsuperscript{136} Intermediate cases where both long-range effects and diffusion-controlled transfer may be operative have also been studied recently.\textsuperscript{137} In this case, naphthalene was used as the donor and anthranilic acid as acceptor, in a variety of alcoholic solutions. It can be shown that the energy transfer yield \( f_{nr} \) due to Förster-type interaction is given by

\[
f_{nr} = 1 - \frac{q_{D^*}}{q_D} = \pi \frac{C_B}{C_0} \exp \left( \frac{C_B}{C_0} \right)^2 \left( 1 - \frac{\Phi C_B}{C_0} \right)
\]

(105)

where \( q_D \) and \( q_{D^*} \) represent quantum yields of donor emission in presence and absence of acceptor respectively, \( C_B \) is the concentration of the acceptor, \( \Phi \) is the Gaussian error integral, and \( C_0 \) a characteristic of the system given by:

\[
C_0 = \frac{3000}{2\pi^\frac{1}{4}} N_0 R_0^9
\]

(106)

in which \( N_0 \) is Avagadro’s number and \( R_0 \) is given by

\[
R_0^6 = \frac{9000 \ln 10 \chi^2 q_{D^*}}{128\pi^\frac{1}{4} N_0 \bar{n}^3} \int_0^\infty f_D(\nu) e_A(\nu) \frac{d\nu}{\nu^4}
\]

(107)

Here \( \chi^2 \) is an average orientation factor resulting from rapid rotatory
Brownian motion of donor and acceptor, $\bar{n}$ is the refractive index of the medium, $f_D(\nu)$ the normalised fluorescence intensity of the donor at wavenumber $\nu$, and $\varepsilon(\bar{\nu})$ is the molar extinction coefficient of the acceptor at the same wavenumber. The derivation and use of these equations have been reviewed many times, and a further brief review has appeared recently.\textsuperscript{138} Values of $f_{ac}$ calculated from, e.g. equation (105), are always smaller than the experimentally observed values for the naphtalene–anthranilic acid system, and the discrepancy is most marked in solvents of low viscosity. Clearly therefore the deviation from Förster's prediction is due to the influence of the diffusional collisional process, following Stern–Volmer kinetics. A theoretical model to cover this intermediate case has been presented.\textsuperscript{139} The effect of preventing the rotatory Brownian motion upon the non-radiative energy transfer process has also been considered.\textsuperscript{140} The average value of $\chi^5$ which appears in, e.g. equation (107), is normally taken to be $\frac{3}{2}$, in the situation in which rotatory Brownian motion is rapid. If this motion is suppressed, the time dependence of $\rho_t$, the probability of an excited molecule remaining after time $t$ in its excited electronic state, does not vary, but the extent to which energy transfer occurs is reduced. Förster-type energy transfer has been shown to occur in both singlet–singlet and singlet–triplet exchanges.\textsuperscript{141} The singlet–singlet system comprised pyrene donor and Sevron Yellow L acceptor in a cellulose acetate substrate at room temperature. The triplet–singlet system was $[\text{H}_{10}]$phenanthrene donor and Rhodamine B acceptor in cellulose acetate at 77 K. High polymer matrices have also been used to study singlet–singlet energy transfer between pyrene donor and perylene acceptor.\textsuperscript{142} In both poly(methylmethacrylate) and polystyrene matrices the excitation transfer clearly occurred as a result of weak dipole–dipole coupling, and Förster's equation was accurately obeyed. Transfer between the same molecules at high excitation intensities results\textsuperscript{143} in departure from normal behaviour of the energy transfer transition probability, owing to saturation of the excited states being formed. It has been proposed for many molecules that intersystem crossing from the $S_1$ to $T_1$ states occurs via the intermediacy of the second excited triplet state $T_2$, which in some molecules lies just below the first singlet in energy. This has been confirmed in the case of anthracene by energy transfer studies.\textsuperscript{144, 145} Spectroscopic studies on guest molecules of anthracene and $[\text{H}_8]$naphthalene in host crystals of dibenzofuran or biphenyl at 90 K show that absorption by the anthracene produces naphthalene phos-

\textsuperscript{138} A. A. Lamola, \textit{Photochem. and Photobiol.}, 1968, 8, 601.

\textsuperscript{139} I. Z. Steinberg and E. Katchalski, \textit{J. Chem. Phys.}, 1968, 48, 2404.

\textsuperscript{140} I. Z. Steinberg, \textit{J. Chem. Phys.}, 1968, 48, 2411.


phorescence. The energy levels are such (Figure 5) that the donor can only be the anthracene $S_1$ or $T_1$ states. The former can be discounted in that use of 9,10-diphenylanthracene, which has a fluorescence quantum yield of unity, as a donor greatly reduced the sensitised phosphorescence yield, indicating that the triplet $T_1$ in anthracene is the donor state. These findings were confirmed by a study of the anthracene-sensitised reactions of several molecules, which undergo specific triplet reactions. It is apparent

![Energy level diagram for anthracene and $[^3H_{10}]naphthalene$](image)

(Figure 5) Energy level diagram for anthracene and $[^3H_{10}]naphthalene$

(Based on Figures 1, R. S. H. Liu and R. E. Kellog, J. Amer. Chem. Soc., 1969, 91, 250)

from this work that anthracene can serve as a triplet sensitiser of energy 68–74 kcal mole$^{-1}$ from the $T_1$ state, and previous mechanisms involving 'non-vertical' triplet energy transfer, of the type described recently for carbonyl donor, olefin acceptor pairs, are unnecessary.

There have been many new reports of triplet energy transfer in rigid media.\textsuperscript{147--152} Triplet transfer was found to occur much more efficiently between benzophenone donor and naphthalene acceptor in the crystalline state than in a glass at 77 K.\textsuperscript{153} The principal effect in destroying the three-dimensional structure of the crystal is apparently to increase the cross-section for exciton trapping, thus significantly increasing the probability that

\textsuperscript{148} Y. A. Terskoi and V. G. Brudz, Optiks and Spectroscopy, 1968, 25, 877.
the excitation energy supply remains on the initially excited molecule. If the exchange mechanism of triplet energy transfer is operative, the rate of the process is dependent upon the overlap of the electronic wavefunctions of the participating molecules and hence there can be an optimum geometry for transfer to occur. Polarisation studies have shown that for the anthrone-[6H10]-phenanthrene pair maximum transfer occurred when the molecular planes of the donor and acceptor are parallel, but that there is no preferred angular orientation of the molecules in this parallel configuration. Similar results were obtained for the benzophenone-[6H10]-phenanthrene pair.

Effects in Crystals.—Many of the above phenomena observed in solution may also be manifested in crystals. Although the study of these phenomena in the crystalline state is not usually of primary interest to the preparative chemist, the data gleaned from such studies is of importance in that it assists in an understanding of the physical processes which may compete with photo-chemical reactions in organic molecules.

Thus singlet–triplet absorption and phosphorescence have been observed in pure crystalline naphthalene and benzophenone, and the luminescence of many molecules in the pure crystalline state has been studied. Singlet and triplet states in mixed organic crystals have gained attention and phenomena such as triplet–triplet annihilation, delayed fluorescence, and electronic energy transfer have been observed. The main differences between crystalline media and condensed randomly oriented media is that in crystals the excitation energy is not localised but travels effectively round the crystal as excitons. Singlet excitation energy has been known in this form for some time, but there is recent evidence of triplet exciton migration in crystals also. Finally, the effect of high

pressures upon the absorption spectra and fluorescence spectra of tetra-
cene, rubrene, anthracene, and coronene and on fluorescence lifetime and excimer emission of various aromatics has been discussed.

6 Orbital Symmetry Considerations

The interpretation of such concerted reactions of organic molecules as Diels–Alder addition, Cope rearrangement, Claisen rearrangement, etc., in terms of the symmetry properties of the molecular orbitals of the reactant and product has shed much light on previously puzzling aspects of these reactions. A rationale is now available for the thermal and photochemical control of these reactions and their high degree of stereospecificity. The bases for this approach are the rules widely known as the ‘Woodward–Hoffmann orbital symmetry rules’, which rest on the principle that concerted processes (which normally have a kinetic advantage) proceed with retention of orbital symmetry. The restrictions imposed by the symmetry requirement permit solid predictions covering the stereochemistry. State symmetries can also be correlated in suitable cases. Since their enunciation in 1965, these rules have been applied to many systems, and extensive reviews of the applications have appeared recently. In addition, many examples of the use of the rules will be found in the chapters of this volume dealing with organic photochemistry.

As an example of the different mechanisms occurring, one may consider the thermal and photochemical interconversion of butadiene and cyclo-
butene. Substitution shows that the thermal isomerisation proceeds via a conrotatory mechanism (108), whereas the photochemical reaction is disrotatory in nature (109):

![Diagram](image)

Although the photochemical cyclisation of butadiene undoubtedly obeys the rule, some aspects of the mechanism remain unexplained. Since the

ground state of cyclobutene is ca. 20 kcal mole\(^{-1}\) less stable than that of butadiene, and the spectroscopic singlet state of cyclobutene is 50—60 kcal mole\(^{-1}\) higher than that for butadiene, it thus appears unlikely that a spectroscopic excited singlet state of cyclobutene can be formed from that of the butadiene. In order to gain some insight into this problem, the energies of ground and excited states of butadiene and cyclobutene have been calculated for a number of configurations, resulting in potential surfaces from which a detailed discussion of the course of the reaction is possible.\(^{181}\) The energies were calculated as a function of three angles \(\phi\), \(\chi\), and \(\theta\), where \(\phi\) is the angle between C(2) and C(3), C(1) and C(2), and C(3) and C(4), \(\chi\) describes the rotation of the p orbitals on C(1) and C(4), and \(\theta\) is a measure of rotation about C(2)—C(3). The angle \(\phi\) was varied between 125° and 90°, \(\chi\) between 0° and 90°, and \(\theta\) between \(-90°\) and \(+90°\). For each combination of \(\phi\) and \(\chi\), the value of \(\theta\) giving the lowest energy for that combination was selected for the ground state, as well as the excited states, and thus \(\theta\) was eliminated as an independent variable. Two-dimensional graphs can then be drawn of energy against \(\phi\) and \(\chi\) for each state. Two excited states of butadiene were considered, the antisymmetric state, which is reached on absorption from the ground state, and a symmetric state, the transition to which is forbidden. The dependence of the energies of these states and the ground states upon rotation is shown in Figure 6. It can be seen clearly that in the ground state, the disrotatory process of ring closure is impossible, since an activation energy of ca. 100 kcal mole\(^{-1}\) is necessary, whereas the conrotatory process requires no activation energy. Upon u.v. irradiation, the antisymmetric excited state of butadiene is formed. At \(\phi = 116°\), the antisymmetric and symmetric energy levels intersect, and thus the molecule can pass into a symmetric state and initiate a disrotatory ring closure. The transition from the symmetric excited state to the ground state is not well understood. The authors have suggested that the following additional statement may be generally applicable.

If a conrotatory (disrotatory) process is unfavourable in the ground state, it implies the presence of a high potential barrier. From general principles it follows that there will be another potential surface of the same symmetry which has a well not far above this barrier. The photo-initiated reaction may profit from this energy well to bring about ring closure or opening by a conrotatory (disrotatory) process opposite to the reaction in the ground state.\(^{181}\)

Although the rules have generally been applied to the stereochemical aspects of a variety of chemical transformations, other effects may also be explained by them. Thus, the unexpected effect of neighbouring group substituents leading to the inertness towards maleic anhydride of certain trans–trans conjugated dienes can be accounted for in terms of the orbital

Figure 6  Potential energy surfaces for cyclobutene and butadiene
(Based on Figure 1, W. Th. A. M. van der Lugt and L. G. Oosterhoff, Chem. Comm., 1968, 1235)

symmetries of the molecule when mixing of the neighbouring group orbitals is considered.\textsuperscript{182} Although energy criteria are usually the most important in determining electronic energy transfer rates, it has been claimed that where there is a competition between different energy transfer processes, orbital symmetry control may be decisive.\textsuperscript{183}

In this chapter primary photophysical and photochemical processes which occur when molecules are excited in the vapour phase will be considered. Secondary reactions, such as those arising from free radicals generated photolytically, will not be included unless they are strictly relevant to the primary acts. Sections are devoted to the specialised techniques of vacuum u.v. photolysis and mercury and other metal photosensitisation, and a discussion of recent developments in flash photolysis is included.

1 Photophysical Processes in the Gas Phase

Many molecules are known to exhibit luminescence in the vapour phase. The radiation emitted is usually either resonance fluorescence or normal fluorescence depending upon the pressure region of the system observed, but with some molecules phosphorescence can be seen also. The theories of radiationless transitions (see Chapter 1) predict that transitions such as intersystem crossings are strongly dependent upon molecular size, among other factors. Thus isolated small molecules are incapable of undergoing radiationless transitions without some collisional perturbation. In the terminology of Robinson (see Chapter 1) this is the $\alpha$ limit, whereas in Jortner’s language the molecule is said to be in the resonant limit. Very complex molecules are capable of radiationless transitions without perturbation ($\omega$ limit or statistical case), and there are many intermediate molecules for which a perturbation will normally be required to induce a radiationless transition, but this need not be a collision in the strict gas-kinetic sense.

A mainly historical account has recently been given of the investigations carried out on luminescence in the gas phase in the laboratories of A. N. Terenin in the Soviet Union.\(^1\)

Sulphur dioxide is a molecule which clearly belongs to the $\alpha$ limit or resonant case, and the photophysical processes following excitation of this molecule have attracted attention lately.\(^2-5\) Absorption in the first allowed

\(^1\) N. A. Borisevich and B. S. Neoporent, Zhur. priklad. Spektroskopii, 1968, 8, 377.
transition produces the $^1B_1$ state, from which collision-induced intersystem crossing to the $^3B_1$ state occurs. Emission is observed from both states, and a preliminary study of the effect of temperature upon the emission intensities in the gas phase revealed that the phosphorescence has a negative temperature coefficient, i.e. the phosphorescence yield decreased with increasing temperature. Possible explanations are that increase in temperature favours collisional deactivation to the ground singlet state (reaction 2) rather than intersystem crossing (3); that the triplet state is destroyed by a temperature-dependent process; or that the vibrational relaxation of the triplet state to the lowest vibrational state, which is the one which phosphoresces, is less rapid when the collision partner is at a higher vibrational temperature. Although the second possibility is preferred, a study of the effect of temperature upon the luminescence of SO$_2$ in the solid phase between 4 and 100 K has shown a similar temperature dependence of the phosphorescence. However, in this case the solvent also affects the emission intensity, and it thus seems likely that the effect of temperature and change of solvent is to alter the rate of the excited singlet–triplet intersystem crossing. Three spectroscopic studies on the emission yields of SO$_2$ as a function of pressure and in the presence of added gases have shown that the photochemistry of this compound can be represented by the following mechanism:

\[
\begin{align*}
\text{SO}_2 + h\nu & \rightarrow ^1\text{SO}_2 \quad (1) \\
^1\text{SO}_2 + \text{SO}_2 & \rightarrow 2\text{SO}_2 \quad (2) \\
& \rightarrow ^3\text{SO}_2 + \text{SO}_2 \quad (3) \\
^1\text{SO}_2 & \rightarrow \text{SO}_2 + h\nu \quad (4) \\
& \rightarrow \text{SO}_2 \quad (5) \\
& \rightarrow ^3\text{SO}_2 \quad (6) \\
^3\text{SO}_2 & \rightarrow \text{SO}_2 + h\nu \quad (7) \\
& \rightarrow \text{SO}_2 \quad (8) \\
^3\text{SO}_2 + \text{SO}_2 & \rightarrow 2\text{SO}_2 \quad (9)
\end{align*}
\]

The scheme assumes that vibrational relaxation of the excited singlet state is unimportant, whereas that of the triplet state is very rapid. As would be expected from such a scheme, Stern–Volmer plots of reciprocal fluorescence yield against pressure of SO$_2$ give excellent straight lines. From the ratio of the slope to intercept of such plots, estimates can be made of the value of $k_2 + k_3$. Unfortunately, there is not good agreement between the different authors (Table 1). As has been pointed out, the main reason for these differences lies in the value of the intercept, since different authors produce lines with almost identical slopes. The value from ref. 5 is probably to be preferred, since it is also obtained by other methods independent of the one above.
All authors are in agreement that collisional deactivation of excited singlet SO₂ occurs at a rate which is within an order of magnitude of the collisional rate. This high rate has been rationalised by assuming that the excited singlet is a composite of excited singlet, excited triplet, and ground vibronic states, a treatment similar to Kasha's approach to radiationless transitions (Part I). Theory would predict that at low pressures of gas, the fluorescence quantum yield of SO₂ should approach unity, since collisions are required to induce radiationless processes [i.e. rate constants for reactions (5) and (6) are zero]. If the value of \( k_2 + k_3 \) in ref. 2 is accepted, the fluorescence yields do extrapolate to unity at zero pressure, but this is not the case in the other work.

Addition of CO₂ or O₂ to the SO₂ system causes quenching by the following additional processes:\(^5\)

\[
\begin{align*}
\text{\(^1\)SO}_2 + \text{O}_2 & \rightarrow (\text{SO}_2 - \text{O}_2) & (10) \\
\text{\(^1\)SO}_2 + \text{CO}_2 & \rightarrow (\text{SO}_2 - \text{CO}_2) & (12) \\
\text{\(^3\)SO}_2 + \text{O}_2 & \rightarrow (\text{SO}_2 - \text{O}_2) & (14) \\
\text{\(^3\)SO}_2 + \text{CO}_2 & \rightarrow (\text{SO}_2 - \text{CO}_2) & (15)
\end{align*}
\]

The values obtained for the relative rate constants for quenching are shown in Table 2. If the concept of the upper excited state as a composite level is accepted, the quenching rates would be expected to be related to the number of degrees of internal freedom of the colliding molecules. Thus

**Table 1** Values of \( k_2 + k_3 \) for SO₂ excited at 2850 Å

<table>
<thead>
<tr>
<th>(10^{16}(k_2 + k_3)) (l mole(^{-1})s(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2 ± 1.0</td>
<td>5</td>
</tr>
<tr>
<td>6.4 ± 1.1</td>
<td>4</td>
</tr>
<tr>
<td>14 ± 8</td>
<td>2</td>
</tr>
</tbody>
</table>

**Table 2** Relative quenching rates of \(^1\)SO₂ and \(^3\)SO₂ by CO₂ and O₂ (data from ref. 5)

\[
\begin{align*}
\text{Rate of } \text{\(^1\)SO}_2 \text{ with } \text{SO}_2 & = 3.18 ± 0.33 \\
\text{Rate of } \text{\(^1\)SO}_2 \text{ with } \text{O}_2 & = 1.36 ± 0.01 \\
\text{Rate of } \text{\(^1\)SO}_2 \text{ with } \text{CO}_2 & = 1.27 ± 0.26 \\
\text{Rate of } \text{\(^3\)SO}_2 \text{ with } \text{SO}_2 & = 1.62 ± 0.48 \\
\text{Rate of } \text{\(^3\)SO}_2 \text{ with } \text{O}_2 & = 1.36 ± 0.01 \\
\text{Rate of } \text{\(^3\)SO}_2 \text{ with } \text{CO}_2 & = 1.27 ± 0.26
\end{align*}
\]
little difference would be expected between SO$_2$ and CO$_2$, as is observed, and on this basis, O$_2$ would be expected to be less efficient, again in agreement with experiment. The effect of O$_2$ on the triplet state is somewhat surprising in that quenching rates for triplet states by O$_2$ are usually large. In this case the rate for O$_2$ is less than that for CO$_2$ or SO$_2$. Charge-transfer states may be very important in the deactivation of triplet states by O$_2$, and the absence of effect in the $^3$SO$_2$-O$_2$ system indicates little charge-transfer interactions between this pair of molecules.

The sensitisation of the phosphorescence of biacetyl has by now become a standard technique for the measurement of triplet state yields in the vapour phase. Thus in the case of SO$_2$, addition of biacetyl quenches the phosphorescence of SO$_2$ and gives rise to the phosphorescence spectrum of biacetyl. The photochemistry of biacetyl is thus of great importance and has been further studied recently. The fluorescence and phosphorescence spectra have been re-examined.

The following simple mechanism may be written to explain the photochemistry of biacetyl excited at wavelengths longer than 4000 Å:

$$\text{Bi} + h\nu \rightarrow ^1\text{Bi} \quad (16)$$
$$^1\text{Bi} \rightarrow ^3\text{Bi} + h\nu \quad (17)$$
$$^1\text{Bi} \rightarrow ^3\text{Bi} \quad (18)$$
$$^3\text{Bi} \rightarrow \text{Bi} + h\nu \quad (19)$$
$$^3\text{Bi} \rightarrow \text{Bi} \quad (20)$$
$$^3\text{Bi} + \text{Bi} \rightarrow \text{Bi} + \text{Bi} \quad (21)$$
$$^3\text{Bi} + \text{M} \rightarrow \text{Bi} + \text{M} \quad (22)$$

where Bi is a biacetyl molecule, and M a quenching molecule. Superscripts refer to the multiplicity of the excited state. It is normally assumed that the phosphorescence yield of biacetyl is independent of biacetyl pressure (i.e. $k_{31} = 0$). However, inclusion of step (21) leads to the overall expression for biacetyl phosphorescence yield of

$$\Phi_p = \frac{k_{18}k_{19}}{(k_{17} + k_{18})(k_{19} + k_{20} + k_{21}[\text{Bi}] + k_{22}[\text{M}])} \quad (23)$$

Thus in the absence of a quencher, a plot of reciprocal $\Phi_p$ against biacetyl pressure should yield a straight line. Such behaviour has been observed, and can be attributed to the importance of reaction (21). Other molecules are

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6 P. Longin, Compt. rend., 1968, 267, B, 128, 404.
similarly effective in quenching biacetyl triplets via (22): these include acetone, propylene, isopropanol, methyl chloride, acetylene, and triethylborane.

If excited at wavelengths shorter than 4000 Å, biacetyl may undergo reaction from the initially produced vibrationally excited singlet state. The reaction rate is such that collisional deactivation to the equilibrated singlet level is competitive with it and the system may be used to study the efficiency of vibrational–vibrational energy transfer.

Reactions of biacetyl have been studied in solution. The observed photo-enolisation of biacetyl irradiated at wavelengths which produce the second excited singlet state has been accounted for by the participation of the second triplet excited state. This conclusion is reached on the basis of evidence of observed energy transfer to molecules which have triplet states higher in energy than the first triplet state of biacetyl. The results indicate that care must be taken to consider the possible role of higher triplet states of biacetyl whenever energy transfer phenomena concerning this molecule are studied.

2 Photochemistry of Aromatics

The molecules considered in the foregoing section do not undergo any photochemical reactions in the gas-phase systems so far studied; energy dissipation seems to occur solely via photophysical processes. The molecules described below may also undergo photochemical transformations which must be considered in addition to the important photophysical phenomena encountered. For convenience, molecules will be grouped according to type: thus this section deals with aromatics in the vapour phase.

According to theory, benzene is an example of a molecule which lies between the \( \alpha \) and \( \omega \) limits, or statistical and resonant cases. It would be predicted therefore that some kind of perturbation would be required to induce radiationless transitions such as the \( ^1B_{\text{su}} \rightarrow ^3B_{\text{tu}} \) intersystem crossing in this molecule, and that, in the absence of any other competing processes such as chemical reaction, the fluorescence quantum yield should extrapolate to unity in the limit of zero pressure. Two independent studies of the variation of benzene fluorescence yield with pressure at very low pressures clearly demonstrate that such behaviour does not occur.

For benzene, \( [^2\text{H}_6]\)benzene, and \( [1,4-^3\text{H}_4]\)benzene excited at 2537 Å, the fluorescence yield is independent of pressure below 0.4 torr. The average values for the quantum yields are 0.39, 0.53, and 0.38 respectively. For benzene between 0.01 and 0.12 torr, the fluorescence yield was similarly independent of pressure. At higher pressures in excess of 0.4 torr, the character of the spectrum of \( [1,4-^2\text{H}_4]\)benzene changes and there is both

---

self-quenching and quenching by cyclohexane, as has been observed before. These observations clearly show that the theoretical predictions were in error. This may be due to the importance of chemical processes under these conditions (see later), or the capacity for benzene to undergo radiationless transitions in the absence of perturbations.

Since the $^3B_{1u}$ state of benzene formed by intersystem crossing from the $^1B_{2u}$ state does not phosphoresce, alternative methods must be used to estimate the quantum yield of its formation. The two most widely used techniques are those of the sensitisation of the phosphorescence of biacetyl and the sensitisation of the cis–trans isomerisation of olefins. The former is more convenient in that emission is measured, which is an immediate observation, whereas the second requires long irradiation times. However, since biacetyl has singlet states which lie lower in energy than the aromatic singlet, the technique may only be used if the aromatic triplet has a lifetime significantly longer than that of the singlet state, otherwise the system is complicated by energy transfer to the singlet biacetyl from the singlet aromatic. For some time cis–trans isomerisation of the olefin (Cundall’s technique) has been preferred because the olefin generally employed, but-2-ene, has its first excited singlet state higher in energy than that of the aromatic and thus is incapable of accepting the singlet energy of the aromatic. Indeed, only slight quenching of the fluorescence of benzene by certain mono-olefins has been observed.¹⁶ This study was at 2537 Å and took into account the variation in absorption coefficient of the aromatic with pressure. Since benzene is apparently self-quenched, results obtained for the quenching rate constants for added olefins are dependent upon benzene pressure. These will not be quoted here, but it can be stated that the conjugated dienes 1,3-pentadiene, isoprene, and 1,3-butadiene strongly quench the fluorescence of benzene, whereas tetramethylethylene, but-2-ene, and propylene quench this only slightly. Conventional singlet energy transfer processes to the mono-olefins and dienes should be markedly endothermic in each case. At a benzene pressure of 15 torr, paraffins can also cause a reduction in the benzene fluorescence yield. This effect appears to be entirely associated with vibrational relaxation of the molecule to the equilibrated level. The self-quenching of benzene observed here has previously been attributed to geometrical effects in the system. Despite the fact that absorption effects have been considered in the present study, the observed self-quenching may again be attributable to geometrical effects. For a real self-quenching, fluorescence lifetimes should also be pressure dependent; measurement of these recently has shown them to be independent of pressure.¹⁶ The mechanism of the quenching of excited benzene singlets by the olefinic species is not clear, although very close

physical contact or complex ('exciplex') formation is obviously necessary for it to occur. A two-step process may be proposed:\textsuperscript{15}

\[
\begin{align*}
{^1}\text{B} + \text{Q} & \rightarrow (1\text{B}. \text{Q}) \rightarrow \text{products} \quad (24)
\end{align*}
\]

in which \( {^1}\text{B} \) represents the benzene singlet, and Q the olefin quencher. As yet, one can only speculate about the bonding forces in such complexes; but there might be an element of charge-transfer. Similar quenching effects have been observed in solution (see Chapter 1).

It is clear from these results that care must be taken when \textit{cis}-but-2-ene is used as a triplet quencher for benzene and other aromatics, although the singlet quenching rate is small. A complete scheme incorporating such effects can be written:\textsuperscript{15, 16}

\[
\begin{align*}
\text{B} + \hbar \nu & \rightarrow {^1}\text{B} \quad (25) \\
{^1}\text{B} & \rightarrow \text{B} + \hbar \nu \quad (26) \\
{^1}\text{B} & \rightarrow \text{isomer} \quad (27) \\
{^1}\text{B} & \rightarrow \text{B} \quad (28) \\
{^3}\text{B} + \text{B} & \rightarrow \text{B} + \text{B} \quad (29) \\
{^1}\text{B} + \text{c-Bu} & \rightarrow \text{B} + \text{c-Bu} \quad (30) \\
{^1}\text{B} & \rightarrow {^3}\text{B} \quad (31) \\
{^3}\text{B} & \rightarrow \text{B} \quad (32) \\
{^3}\text{B} + \text{B} & \rightarrow \text{B} + \text{B} \quad (33) \\
{^3}\text{B} + \text{c-Bu} & \rightarrow \text{B} + {^3}\text{(c-Bu)} \quad (34) \\
{^3}\text{(c-Bu)} \xrightarrow{a} \text{b} \quad {^3}\text{(t-Bu)} \xrightarrow{c} \text{d} \\
\text{c-Bu} & \rightarrow \text{t-Bu} \quad (35)
\end{align*}
\]

where Bu refers to but-2-ene, and c and t the \textit{cis}- and \textit{trans}-isomers respectively.

Considerable controversy exists over reactions (34) and (35), and the corresponding case where \textit{trans}-but-2-ene is used as the starting material (36)

\[
\begin{align*}
{^3}\text{B} + \text{t-Bu} & \rightarrow \text{B} + {^3}\text{(t-Bu)} \quad (36)
\end{align*}
\]

It can be shown that if benzene-sensitised photoisomerisations were carried out under identical conditions using first \textit{cis}- then \textit{trans}-but-2-ene as acceptor, the ratio of rates of conversion of \textit{cis} to \textit{trans} and \textit{vice versa} is given by the following equation:

\[
R_{c\to t}/R_{t\to c} = k_{3\text{ss}}/k_{3\text{sd}}k_{3\text{sh}}/k_{3\text{sc}} \quad (37)
\]

The value previously obtained by Cundall for this ratio was \( 1.37 \pm 0.02 \),\textsuperscript{17} whereas the workers in ref. 16 obtained \( 1.03 \pm 0.02 \) for conditions which were identical except that in Cundall's work the wavelength spread was

Gas-phase Photochemistry

between 2400 and 2600 Å, compared with a single line at 2537 Å in the latter case.

If a reaction mixture is photolyzed to a photostationary state, the ratio of amounts of cis- and trans-butene at this point is given by

$$[\text{c}-\text{Bu}/\text{c}-\text{Bu}]_{\text{pss}} = \left( \frac{k_{\text{s}}}{k_{\text{as}}} \right) \left( R_{\text{c} \rightarrow \text{t}} / R_{\text{t} \rightarrow \text{c}} \right)$$

(38)

The value for this ratio obtained here was $0.92 \pm 0.02^{16}$ which compares well with the value of Sato et al. of $0.92^{16}$ but is in serious disagreement with the original value of Cundall of $1.37 \pm 0.01^{37}$. Since the earlier results on pyridine $^{17}$ have since been shown to be in serious error, $^{19}$ it seems likely that the values for ratios of rate constants and photostationary state values obtained more recently are to be preferred. $^{16}$

It should be noted that a number of mono-olefins have been found to undergo 1,3-photoaddition to benzene in the liquid $^{19a}$ and the gas $^{19b}$ phase under conditions where benzene is excited to the S₂ state, and that butadiene likewise adds both 1,3 and 1,4. $^{19e}$ These reactions will need to be considered in future photophysical studies.

The effect of deuterium substitution on an olefinic acceptor (ethylene) is similar when benzene and acetone are used as donors. $^{20}$ In each case, the quenching of the donor triplet state is less pronounced with the fully deuteriated acceptor than with the protio-compound. The relative rates are 1:7 and 1:9 for the benzene and acetone donors respectively. The isotope effects are observed because of the near degeneracy of the triplet levels ($E_T$ benzene = 84, $E_T$ ethylene = 82, $E_T$ acetone = 78, $E_T$ deuterio-ethyene ca. 0.7 kcal mole$^{-1}$ higher than that of ethylene).

There has been much speculation concerning reaction (27), the formation of valence isomers of benzene. At 2537 Å, fluorescence and triplet state formation account for all but a few (ca. 10%) of benzene molecules initially excited, but at shorter wavelengths the sum of these quantum yields is small, indicating that some other process is important. It has been shown that benzvalene (I) is formed in the gas-phase photolysis of benzene at 2537 Å. $^{21}$

Experimental difficulties encountered were that this compound (I) isomerised to fulvene (II) rapidly in freshly flamed quartz vessels. Upon irradiation of (I) at 2537 Å in 1 atmosphere of nitrogen, it was converted with high quantum yield to benzene and fulvene. Addition of benzene greatly accelerated this process, but addition of triplet quenchers to this system greatly reduced the rate again. Clearly benzvalene formed by the


irradiation of benzene at 2537 Å undergoes a triplet benzene-photo-sensitised isomerisation to benzene and fulvene. Addition of inert quenching gases increases the rate of benzvalene production, presumably by removing excess vibrational energy from initially produced 'hot' benzvalene. Photolysis at shorter wavelengths shows that benzvalene is also produced from higher vibrational levels of singlet benzene than the fluorescent level, and, in general, quantum yields for its formation increase with energy of incident photons. Although the chemical yields of benzvalene plus fulvene are never great enough to account for all the molecules not undergoing either fluorescence or triplet state formation, part or all of the deficiency may result from thermal isomerisation of benzvalene to benzene. A rationalisation of the formation of fulvene in the irradiation of benzene at 1849 Å, using orbital symmetry considerations, has been presented.\textsuperscript{22}

The above techniques for estimating triplet state yields have been used on aromatic molecules other than benzene. Fifteen sensitisers in solution have been investigated using the cis-but-2-ene technique,\textsuperscript{23} and it was found that the rate of isomerisation decreased rapidly with triplet energy of the donor, and photostationary state values for trans- and cis-isomers varied from 1·2 to 3 with change in triplet energy from 90 to 65 kcal mole\textsuperscript{-1}. For toluene excited to the lowest vibrational level of the $S_1$ state, fluorescence and intersystem crossing to the first triplet state are the only important processes.\textsuperscript{24} The respective quantum yields are 0·30 ± 0·07 and 0·70 ± 0·03 at 2668 Å excitation. As for benzene, as the exciting radiation frequency is increased, the quantum yields of these processes decrease. The nature of the process which competes at the shorter wavelengths is not revealed, but could of course be a valence isomerisation by analogy with the behaviour of benzene and other molecules.

Spectrofluorometric techniques have been used to investigate the photochemistry of ortho- and para-difluorobenzene and 1,2,4- and 1,3,5-trifluorobenzene in the vapour phase. Again, excitation at short wavelengths causes the sum of fluorescence and triplet state yields to be significantly less than unity, indicating the importance of some other route for energy dissipation under these conditions.\textsuperscript{25}

The photoisomerisation of ortho-xylene to the meta form has been shown to proceed in solution exclusively via the singlet state, and a presumed


benzvalene intermediate. The temperature dependence of the isomerisation shows that an activation energy of ca. 8 kcal mole\(^{-1}\) is required for this process.\(^{26}\) The observed singlet mechanism and temperature dependence are in accordance with the predictions made by Bryce-Smith and Louguet-Higgins\(^ {23b}\) on the basis of orbital and state symmetry considerations.

In the photochemistry of hexafluorobenzene, another valence isomer, the so-called 'Dewar' form (III) is important. A recent investigation of the

(III)

irradiation of hexafluorobenzene in the gas phase at 2537 Å\(^ {27}\) has confirmed earlier findings that the yields of Dewar hexafluorobenzene are small.\(^ {28}\) The mechanism suggested to account for the results involves two excited singlet states of the hexafluorobenzene molecule, as was proposed earlier:\(^ {29}\) cf. ref. 22b.

If flash photolysis is used to produce a high concentration of triplet species, triplet–triplet annihilation may be observed in the vapour phase as well as in solution.\(^ {30}\) Three molecules were studied, naphthalene, anthracene, and phenanthrene, and two processes were investigated (reactions 39 and 40).

\[
\begin{align*}
8A + 3A & \rightarrow 1A + A \\
& \rightarrow A + A + \text{heat}
\end{align*}
\]

(39)

(40)

The Stevens–Parker mechanism proposes that an intermediate excimer is first formed which may then decompose to \(^1A\) or be deactivated (see Chapter 1).

\[
\begin{align*}
3A + 3A & \rightarrow (1AA)
\end{align*}
\]

(41)

If \(c\) is the probability that molecules undergoing triplet–triplet annihilation give rise to singlet aromatics, and if \(\Delta E\) is defined as

\[
\Delta E = 2E_T - E_{S_1}
\]

(42)

where \(E_T\) is the energy of the triplet state and \(E_{S_1}\) that of the excited singlet, then \(c\) will be temperature dependent if \(\Delta E\) is smaller than the excimer binding energy; \(c\) has a constant saturation value close to unity. Anthracene exhibits the former behaviour, and naphthalene and phenanthrene the latter.

---

27 A. Bergomi and F. Gozzo, _Chimica e Industria_, 1968, 50, 743.
3 Photochemistry of Ketones

Acetone has been studied exhaustively over the past thirty or forty years, but studies on this molecule continue to appear.\textsuperscript{31} Excluding emission from this ketone, which is only of minor importance, the results may be interpreted on the basis of the following reaction scheme, where $A$ refers to acetone:

\[
\begin{align*}
A + h\nu & \rightarrow ^1A_n \quad (43) \\
^1A_n + A & \rightarrow ^3A_n + A \quad (44) \\
^3A_n & \rightarrow 2\text{Me} + \text{CO} \quad (45) \\
^3A_n + A & \rightarrow ^3\text{A}_0 + A \quad (46) \\
^3\text{A}_0 + A & \rightarrow 2\text{Me} + \text{CO} + A \quad (47) \\
^1A_n + A & \rightarrow ^1\text{A}_0 + A \quad (48) \\
^1\text{A}_0 & \rightarrow ^3A_n \quad (49) \\
\text{Me} + A & \rightarrow \text{CH}_4 + \text{CH}_2\text{COMe} \quad (50) \\
\text{Me} + \text{CH}_3\text{COMe} & \rightarrow \text{EtCOME} \quad (51) \\
2\text{Me} & \rightarrow \text{C}_2\text{H}_6^* \quad (52) \\
\text{C}_2\text{H}_6^* + A & \rightarrow \text{C}_2\text{H}_6 + A \quad (53) \\
2\text{MeCOCH}_3 & \rightarrow (\text{MeCOCH}_2)_2 \quad (54)
\end{align*}
\]

where $\text{C}_2\text{H}_6^*$ refers to a vibrationally excited ethane molecule.

Since the study was in the temperature range $121-298 \, ^\circ\text{C}$, decomposition to give methyl and acetyl radicals can be excluded. Also excluded are reactions giving rise to the minor products methyl vinyl ketone, biacetyl, mesityl oxide, 2,5-hexenedione, and 2,5-hexanedione. In the limit of high pressure of acetone, the mechanism predicts the following quantum yields of product formation,

\[
\Phi_M^0 + \Phi_{\text{MEK}}^0 = 2, \quad \Phi_{\text{H}_2}^0 = 0, \quad \Phi_{\text{HDO}}^0 = 1, \quad -\Phi_A^0 = 3
\]

where $M =$ methane, MEK = methyl ethyl ketone, E = ethane, HDO = 2,5-hexanodione, and $\Phi^0$ refers to the quantum yield at infinite pressure. The results obtained are in good agreement with this prediction.

At limiting low pressures, the predicted quantum yields would be

\[
\Phi_M^0 = 0, \quad \Phi_E^0 = 1, \quad \Phi_{\text{MEK}}^0 = 0, \quad \Phi_{\text{HDO}}^0 = 0, \quad -\Phi_A^0 = 1
\]

Again there is good agreement except in the case of methane formation, which is certainly non-zero and may be as high as unity. It therefore appears that an additional primary step (55) is required to explain the results adequately.

\[
^1A_n \rightarrow \text{CH}_4 + \text{CH}_2\text{CO} \quad (55)
\]

The fate of the ketene produced in (55) was not determined.

\textsuperscript{31} H. Shaw and S. Toby, \textit{J. Phys. Chem.}, 1968, 72, 2337.
Gas-phase Photochemistry

Hexafluoroacetone is often used as a 'clean' source of trifluoromethyl radicals,\textsuperscript{32} but the fundamental photochemistry of this molecule is still the subject of debate.\textsuperscript{33–35} Previous studies were complicated by the fact that systems containing mercury were used, and mercury has since been shown to quench the triplet state of the ketone. A mechanism has been proposed which considers promotion to an excited vibrational level of the singlet state,\textsuperscript{38} from which fluorescence and decomposition are competitive with collisional stepwise loss of vibrational energy. Each level formed this way may decompose or fluoresce until the equilibrated level is reached. From this, intersystem crossing to the triplet may also occur, but decomposition may not.

\[
\begin{align*}
A + h\nu & \longrightarrow {^1A}_n \quad \text{(56)} \\
{^1A}_n & \longrightarrow A + h\nu_f \quad \text{(57)} \\
{^1A}_n & \longrightarrow \text{CF}_3\cdot + \text{CF}_3\text{CO}\cdot \quad \longrightarrow 2\text{CF}_3\cdot + \text{CO} \quad \text{(58)} \\
{^1A}_n + A & \longrightarrow {^1A}_{n-1} + A \quad \text{(59)} \\
{^1A}_n + M, X, Y & \longrightarrow {^1A}_{n-1} + M, X, Y \quad \text{(60)} \\
{^1A}_{n-1} & \longrightarrow A + h\nu_f \quad \text{(61)} \\
{^1A}_1 & \longrightarrow A + h\nu_f \quad \text{(62)} \\
{^1A}_1 & \longrightarrow \text{CF}_3\cdot + \text{CF}_3\text{CO}\cdot \quad \longrightarrow 2\text{CF}_3\cdot + \text{CO} \quad \text{(63)} \\
{^1A}_1 + A & \longrightarrow {^1A}_0 + A \quad \text{(64)} \\
{^1A}_1 + M, X, Y & \longrightarrow {^1A}_0 + M, X, Y \quad \text{(65)} \\
{^1A}_0 & \longrightarrow A + h\nu_f \quad \text{(66)} \\
{^1A}_0 & \longrightarrow A \quad \text{(67)} \\
{^3A}_0 & \quad \text{(68)} \\
{^3A}_0 & \longrightarrow A + h\nu_p \quad \text{(69)} \\
{^3A}_0 & \longrightarrow \text{CF}_3\cdot + \text{CF}_3\text{CO}\cdot \quad \longrightarrow 2\text{CF}_3\cdot + \text{CO} \quad \text{(70)} \\
{^3A}_0 & \quad \text{(71)} \\
{^3A}_0 + X & \longrightarrow A + X \text{ (or } X^* \text{ etc.)} \quad \text{(72)} \\
{^1A}_n, {^1A}_0 + Y & \longrightarrow A + Y \text{ (or } Y^* \text{ etc.)} \quad \text{(73)}
\end{align*}
\]

Here A now refers to the hexafluoroacetone, superscripts to multiplicity, and subscripts to vibrational level. M is an inert gas, X is a triplet quencher, and Y a singlet quencher.

\textsuperscript{32} C. L. Kirby and R. E. Weston, \textit{J. Chem. Phys.}, 1968, 49, 4825.
\textsuperscript{34} J. S. E. McIntosh and G. B. Porter, \textit{J. Chem. Phys.}, 1968, 48, 5475.
As would be expected from the mechanism, the quantum yield of decomposition at infinite pressure was independent of the wavelength of excitation, but dependent upon temperature, reflecting the temperature coefficient of reaction (70). The ratio of phosphorescence to fluorescence yields was similarly independent of exciting wavelength at infinite pressure, being 6.1, and was zero at zero pressure, as expected. An absolute value of 0.018 for $\Phi_F^{\infty}$ (quantum yield of fluorescence at infinite pressure) was obtained, and thus $\Phi_P^{\infty}$ is 0.11. Since $\Phi_F$ did not become zero at zero pressure, it was necessary to postulate fluorescence from higher vibrational levels of the singlet state of the ketone.

A measure of the efficiency of reaction (68) can be obtained by use of the standard techniques for triplet state estimation, those of the sensitised cis–trans isomerisation of but-2-ene and the sensitisation of biacetyl phosphorescence. In both cases in this work, interpretation was complicated by the observance that both the singlet and triplet states of the ketone were quenched by the added olefin or biacetyl. Nevertheless, by using low pressures of acceptor molecules the effects of singlet transfer could be minimised, and a value obtained by both methods for the rate constant ratio:

$$\frac{k_{68}}{k_{66} + k_{67} + k_{68}} = 0.9 \pm 0.1$$

Since $\Phi_P^{\infty} = 0.02$ approximately,

$$\frac{k_{67}}{k_{66} + k_{67} + k_{68}} < 0.08 \text{ and may be zero.}$$

Energy transfer from the singlet and triplet states of hexafluoroacetone to hexafluorobiacetyl has also been observed. The bimolecular rate constant for the triplet–triplet energy transfer step (72) in this case was found to be $8.5 \pm 1.5 \times 10^{-8}$ l mole$^{-1}$ s$^{-1}$. For an effective collision diameter of 7 Å, this corresponds to a steric factor of ca. 0.03, which is similar to that found in the proto-compounds.

The nature of the quenching of the singlet state of hexafluoroacetone by olefins and biacetyl has been considered. From the effect upon fluorescence and decomposition yields, rate constants for the quenching steps, assuming the simple case where it is the equilibrated singlet which is quenched, are shown in Table 3, together with data from a study of the quenching of the fluorescence of hexafluoroacetone by various compounds. Except in the case of biacetyl, energy transfer can be ruled out as a quenching mechanism since the singlet levels of all quenchers lie higher than that of the hexafluoroacetone. Adduct formation (oxetanes) with the olefins may be occurring, or a charge transfer complex may be formed.

Tests used previously to decide whether vibrational relaxation occurred in large jumps (strong mechanism) or in a multistep cascade (weak mechanism) depended upon the assumption that only the equilibrated singlet level was fluorescent. Since this has been shown to be in error,
low-pressure plots of quantum yields no longer have diagnostic value. Evidence is provided from a consideration of the present low-pressure data concerning decomposition and emission yields that a weak mechanism of vibrational relaxation is operative.

Other substituted acetones have been the subject of investigations in the vapour phase.\textsuperscript{36, 37}

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Rate constant $k_{78}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-But-2-ene</td>
<td>$2.4 \times 10^{10}$</td>
<td>33</td>
</tr>
<tr>
<td>cis-But-2-ene</td>
<td>$3.5 \times 10^{10}$</td>
<td>35</td>
</tr>
<tr>
<td>Isobutene</td>
<td>$2.7 \times 10^{10}$</td>
<td>33</td>
</tr>
<tr>
<td>Isobutene</td>
<td>$3.5 \times 10^{10}$</td>
<td>35</td>
</tr>
<tr>
<td>Butyronitrile</td>
<td>$3.1 \times 10^{10}$</td>
<td>35</td>
</tr>
<tr>
<td>Piperylene</td>
<td>$8.0 \times 10^{10}$</td>
<td>35</td>
</tr>
<tr>
<td>Propylene</td>
<td>$1.6 \times 10^{10}$</td>
<td>35</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>$8.7 \times 10^{8}$</td>
<td>35</td>
</tr>
<tr>
<td>Benzene</td>
<td>$8.2 \times 10^{8}$</td>
<td>35</td>
</tr>
<tr>
<td>Ethylene</td>
<td>$4.1 \times 10^{8}$</td>
<td>35</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$7.6 \times 10^{7}$</td>
<td>35</td>
</tr>
<tr>
<td>Perfluoropropylene</td>
<td>Negligibly small</td>
<td>35</td>
</tr>
</tbody>
</table>

The photolysis of chloropentafluoroacetone at 3130 Å results primarily in the breakdown to trifluoromethyl and chlorodifluoromethyl radicals and carbon monoxide (74).\textsuperscript{37} At shorter wavelengths an alternative mode of decomposition occurs which gives rise to perfluoroacetonyl radicals and chlorine atoms (75). The subsequent reactions of these radicals are discussed.

\[
\text{CF}_3\text{COCF}_2\text{Cl} + \text{hv} \rightarrow \cdot\text{CF}_3 + \text{CO} + \cdot\text{CF}_2\text{Cl} \quad (74)
\]

\[
\text{CF}_3\text{COCF}_2\text{Cl} + \text{hv} \rightarrow \text{CF}_3\text{CO}\cdot\text{CF}_3 + \text{Cl} \quad (75)
\]

Free radical reactions consequent upon photoexcitation of diethyl ketone in the presence of oxygen,\textsuperscript{38} and nitric oxide and nitrogen dioxide,\textsuperscript{39} have also been investigated.

The photochemistry of 2-pentanone is of interest since it is the first in the homologous series of alkanones which can undergo the intramolecular elimination ‘Norrish Type II’ process (76). It has been evident for some time that both the singlet and triplet $n\pi^*$ states of this molecule are capable of this type of reaction,

\[
\text{MeCH}_2\text{CH}_2\text{COMe} + \text{hv} \rightarrow \text{MeCOMe} + \text{C}_2\text{H}_4 \quad (76)
\]

and further evidence has been provided by a gas phase study of the direct and benzene photosensitised reactions of the compound.\textsuperscript{40} The results

obtained indicated that the Norrish Type II quantum yield ($\Phi_{II}$) in pure 2-pentanone vapour is almost independent of exciting wavelength from 2537 to 3130 Å, being ca. 0.3. Addition of cis-but-2-ene had little effect on the quantum yields, but addition of butadiene or penta-1,3-diene quenched the type II yield at 3130 Å to ca. 0.4 of its value in the absence of diene. Clearly at this wavelength the triplet state of the ketone is responsible for ca. two-thirds of the total type II yield, the remainder arising from the singlet state. At shorter wavelengths (2654 and 2540 Å), addition of diolefin reduced the total type II yield to 0.8 of its value in the absence of diolefin; thus at this wavelength the singlet state is the principal precursor of the type II elimination.

In the benzene-sensitised reaction, addition of ca. 1 torr of 2-pentanone was required before a constant $\Phi_{II}$ was reached. This had the value of ca. 0.28. Addition of cis-butene under these conditions reduced the quantum yield by about half, presumably because the olefin quenched the triplet state of the aromatic leaving only those ketone molecules excited by singlet energy transfer from the aromatic to undergo the type II process.

Making reasonable assumptions, the data can be used to calculate the rate constants for the type II elimination from the singlet state and from the triplet state. The values obtained at 3130 Å were 0.34 and $1.2 \times 10^7$ s$^{-1}$ respectively. Similar differences in rate have been noticed for intramolecular reactions of alkanones in solution.41, 42 and it has been proposed that the mechanism of elimination reactions is different in the singlet and triplet manifolds.42 Reactions occurring from the triplet are assumed to involve biradical intermediates,41 whereas there is no evidence that this is so in the singlet manifold.44 However, deuterium substitution experiments have shown that the intramolecular transference of the γ-hydrogen necessary for the type II process is reversible, a fact which may account for the low quantum yields of the process via both singlet and triplet manifolds.43

Cyclic ketones were supposed in the past to decompose exclusively from their singlet states. Cyclobutanone however undoubtedly undergoes distinctly different photochemical reactions from both singlet and triplet states, as recent studies have shown.44, 45 Only two modes of decomposition occur to any large extent, leading to cyclopropane and carbon monoxide, and ethylene and ketene. While both reactions were earlier attributed to the singlet state,44 the use of benzene as a singlet and triplet sensitisier shows unequivocally that the reaction leading to cyclopropane and carbon monoxide arises from a triplet state precursor. Transfer of singlet energy from the benzene results largely in ethylene and ketene formation from the

decomposition of the singlet cyclobutanone, plus some cyclopropane which arises from the triplet state of the ketone formed by intersystem crossing from the singlet.

**Singlet sensitisation.** [Cf. reactions (25)—(29), and (31)—(33).]

\[
\begin{align*}
^3\text{B} + \text{C} & \rightarrow ^1\text{C} + \text{B} \quad (77) \\
^1\text{C} & \rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{CO} \quad (78) \\
^1\text{C} & \rightarrow \text{C} \quad (79) \\
^1\text{C} & \rightarrow ^3\text{C} \quad (80) \\
^3\text{C} & \rightarrow (\text{cyclo-C}_6\text{H}_6^*) + \text{CO} \quad (81) \\
^3\text{C} & \rightarrow \text{C} \quad (82) \\
(\text{cyclo-C}_6\text{H}_6^*) & \rightarrow \text{C}_6\text{H}_6 \quad (83) \\
(\text{cyclo-C}_6\text{H}_6^*) + \text{M} & \rightarrow \text{cyclo-C}_6\text{H}_6 + \text{M} \quad (84)
\end{align*}
\]

where \text{C} refers to cyclobutanone, and the asterisk refers to excess vibrational energy.

**Triplet sensitisation.** If pressures are used such that reaction (77) does not occur, the triplet state of the ketone may be populated exclusively via reaction (85).

\[
^3\text{B} + \text{C} \rightarrow ^3\text{C} + \text{B} \quad (85)
\]

The quenching cross-section of cyclobutanone and benzene singlets has been estimated to be 4 Å², whereas that of cyclobutanone and benzene triplets is smaller, 1 Å². Sensitised decomposition yields were close to unity.

The immediate precursor of the ethylene and ketene shown above as arising from reaction (78) has since been shown to be a highly vibrationally excited ground-state cyclobutanone molecule which is produced by an internal conversion from the excited singlet. Thus reaction (78) should be replaced by reactions (86), (87), and (88).

\[
\begin{align*}
^1\text{C} & \rightarrow \text{C}^{**} \quad (86) \\
\text{C}^{**} & \rightarrow \text{C}_2\text{H}_4 + \text{CO} \quad (87) \\
\text{C}^{**} + \text{M} & \rightarrow \text{C} + \text{M} \quad (88)
\end{align*}
\]

The equations demand that decomposition should then be competitive with vibrational relaxation (86), and this fact can be used to explain the observed data. The ratio of rates of the intersystem crossing step (80) to the internal conversion step (86) is wavelength dependent, changing from 0·4 at 3100 Å to 0·8 at 2500 Å. Such internal conversion steps have been postulated to occur via an intermediate valence isomer, but whether or not this is the case in cyclobutanone is open to question.

A qualitative study of the photochemistry of perfluoroalicyclic ketones in the vapour phase at 3130 Å has shown that the products observed may be interpreted on the basis of a diradical intermediate.\textsuperscript{46} Further support for

the involvement of diradicals in the photochemistry of cyclic ketones comes from an investigation in the liquid and vapour phases of the reactions following excitation of 2-methylecyclohexanone. Ketones higher than cyclobutanone undergo a rearrangement to give an unsaturated aldehyde, in addition to fragmentation reactions. If the internal hydrogen shift leading to the product were due to a molecular mechanism, stereospecificity in the product would be expected. If a diradical mechanism prevails, then several alternative products, (IV), (V), or (VI) might arise.

Of the possible products, (IV) and (V) were observed, but (VI) was absent, so the indicated alternative cleavage did not occur. The results clearly favour a diradical mechanism for the formation of the aldehydes.

![Diagram showing the reaction of a diradical to form aldehydes](image)

Ketene is widely used as a source of methylene (carbene). New details concerning its photochemistry, and the fate of the methylene, have appeared. Because of the proximity in energy of the singlet and triplet states of methylene produced by photolysis of ketene at various wavelengths, and the apparent difference in the chemical properties of the two states, the system will be considered in some detail. The photolysis of ketene at wavelengths longer than 3000 Å has been investigated by many groups of workers, but a recent careful study at 3660 and 3130 Å in the presence and absence of inert gases has been carried out. Absorption at 3660 Å results in the formation of excited singlet ketene having ca. 4 kcal mole⁻¹ of vibrational energy. This may decompose to form singlet methylene and carbon monoxide, intersystem cross to the triplet state of the ketene, or be vibrationally relaxed by collision with ketene or an added inert gas. The equilibrated triplet ketene can decompose to give triplet methylene, or intersystem cross to the ground state; and the equilibrated singlet ketene will undergo only internal conversion to the ground state. It is supposed that both singlet and triplet methylene may react with ground-state ketene to form ethylene and carbon monoxide. The scheme is summarised below.


Gas-phase Photochemistry

\[ \text{K} + h\nu \rightarrow ^1\text{K}_p \]  
\[ ^1\text{K}_p \rightarrow ^1\text{CH}_3 + \text{CO} \]  
\[ ^1\text{K}_p \rightarrow ^3\text{K}_u \xrightarrow{\text{M or K}} ^3\text{K}_0 \]  
\[ ^1\text{K}_p + \text{K} \rightarrow ^1\text{K}_0 + \text{K} \]  
\[ ^1\text{K}_p + \text{M} \rightarrow ^1\text{K}_0 + \text{M} \]  
\[ ^3\text{K}_0 \rightarrow ^3\text{CH}_3 + \text{CO} \]  
\[ ^3\text{K}_0 \rightarrow \text{K} \]  
\[ ^1\text{K}_0 \rightarrow \text{K} \]  
\[ ^1\text{CH}_3 + \text{K} \rightarrow \text{C}_4\text{H}_4 + \text{CO} \]  
\[ ^3\text{CH}_3 + \text{K} \rightarrow \text{C}_4\text{H}_4 + \text{CO} \]  

Here K refers to ketene, superscripts to multiplicity of state, and subscripts to vibrational energy content. On application of the usual steady-state approximation, expression (95) is obtained.

\[ 2/\Phi_{\text{CO}} = \frac{k_{91a} + k_{91b}k_{92a}/(k_{92a} + k_{92b})}{A} + \frac{k_{91c}[\text{K}]}{A} + \frac{k_{91d}[\text{M}]}{A} \]  

where \( A = k_{91a} + k_{91b}k_{92a}/(k_{92a} + k_{92b}) \). Results showed that at all temperatures studied (37, 150, 225, and 300°) the values of \( 2/\Phi_{\text{CO}} \) increased linearly with ketene concentration in the absence of added gas, and linearly with inert gas pressure at constant concentration of ketene. In addition the slopes for three different gases were all of similar magnitude, indicating that (91c) and (91d) occurred on every collision. At higher temperatures (225 and 300°) there was evidence that the inert gas \( \text{C}_4\text{F}_8 \) was much less efficient than ketene in removing vibrational energy from the excited ketene molecule. This observation is rationalised on the basis that at these temperatures the \( \text{C}_4\text{F}_8 \) is vibrationally excited, and collision with an excited ketene molecule may result in transfer of energy to the ketene rather than from it. This would be less likely to happen in collisions between ketene ground-state molecules and excited states, since the ketene has fewer vibrational modes than the \( \text{C}_4\text{F}_8 \).

Absorption at 3130 Å produces ketene molecules with \textit{ca.} 17 kcal mole\(^{-1}\) of vibrational energy. The carbon monoxide yield in this case is 2.0 at low pressures, and steadily decreases at pressures above 250 torr. The carbon monoxide yield of 2.0 implies that every molecule which absorbs a quantum ultimately decomposes. However, since not all methylenes formed at this wavelength are singlet, intersystem crossing (91b) must be followed at this wavelength by decomposition from a high vibrational level of the triplet ketene. At this wavelength, plots of \( 2/\Phi_{\text{CO}} \) against added gas pressure are linear, at least at the lowest temperatures, whereas those of \( 2/\Phi_{\text{CO}} \) against ketene pressure are not. It seems likely that the departure from linearity of the latter plot is due to multistage collisional deactivation, \textit{i.e.} the excited ketene does not lose all of its 17 kcal mole\(^{-1}\) of vibrational energy upon a
single collision with ground-state ketene. It still retains sufficient vibrational energy to decompose or intersystem cross, and only after one or more subsequent collisions does it lose all of its vibrational energy. The linearity of the plots with varying inert gas pressure reveals that for these compounds a single-stage deactivation is operative at 37°. At 100°, it seems probable that deactivation by $\text{C}_4\text{F}_8$ and $\text{SF}_6$ is becoming multistage. It can be shown that no significant change in $\alpha$, the fraction of singlet methylene formed, would be expected with change in pressure. While different values of $\alpha$ have been reported in the literature (see ref. 48), all authors agree on the invariance of this quantity with pressure.

When photolyzed at 2139 Å, ketene alone produces carbon monoxide with a quantum yield of 2.0 which is invariant with pressure.49 The other main product is ethylene with a quantum yield of ca. 0.8, and smaller yields of hydrogen, acetylene, ethane, and $\text{C}_3$ and $\text{C}_4$ hydrocarbons were observed. These last two types increased with increase in percentage decomposition, and are thus probably the result of reactions of methylene with the primary products. The experimental results are consistent with the conclusion that the primary decomposition of the ketene yields methylene and carbon monoxide. The similarity between the decompositions at this wavelength and at 3130 Å means that the same reaction mechanism may be assumed. At 2139 Å, it appears that ca. 70% of the methylene formed attacks ketene to give ethylene and CO. It seems likely that a small fraction of the ethylene so produced is 'hot' and dehydrogenates to give acetylene and hydrogen. The other 30% of the methylene formed abstracts hydrogen from ketene, giving methyl radicals and CHCO radicals. Subsequent reactions of these form ethane, ca. 60% of the acetylene observed, and ca. 17% of the ethylene. Although reactions such as these were ignored in the work at 3130 Å,48 since only the CO yield was monitored, and the net result of attack by singlet and triplet methylene is carbon monoxide formation, no alteration of the given scheme is necessary, except that (94b) should be rewritten.

\[
\begin{align*}
\text{CH}_2 + \text{CH}_2\text{CO} & \rightarrow \text{Me} \cdot + \text{CHCO} \cdot & (96a) \\
2\text{Me} \cdot & \rightarrow \text{C}_2\text{H}_4 & (96b) \\
2\text{CHCO} \cdot & \rightarrow \text{C}_2\text{H}_2 + 2\text{CO} & (96c) \\
\text{Me} \cdot + \text{CHCO} \cdot & \rightarrow \text{C}_2\text{H}_4 + \text{CO} & (96d) \\
\text{Me} \cdot + \text{CH}_3\text{CO} & \rightarrow \{ \text{unknown products, possibly polymer.} \} & (96e) \\
\text{CHCO} + \text{CH}_3\text{CO} & \rightarrow \{ \text{unknown products, possibly polymer.} \} & (96f)
\end{align*}
\]

Reactions (96e) and (96f) will be important only at low light intensities.

The above scheme requires quite different reactivities for singlet and triplet methylenes. These different reactivities are probably a reflection of the geometries and energies of the different electronic states of methylene. Extensive molecular orbital calculations have been carried out on methylene

in the $^3B_1$ ground state, and the $^1B_1$ and $^1A_1$ excited states, among others. Calculations show that the $H-C-H$ angle in these three states is $^3B_1$ (138°), $^1A_1$ (108°), and $^1B_1$ (148°). An estimate is made of the $^3B_1-^1A_1$ energy separation, which has the value 33.4 kcal mole$^{-1}$. This is much higher than usually accepted, and other calculations have given a value much nearer the accepted value. Calculations have also been performed on ways of stabilising singlet methylene.

The difference in reactivities and mode of reaction of $^3$CH$_3$ and $^1$CH$_3$ is evidenced by a number of studies with added substrates. With alkanes, triplet methylene is known to undergo hydrogen abstraction reactions (97),

\[ ^3\text{CH}_3 + \text{RH} \rightarrow \text{Me} + \text{R} \cdot \]  
\[ ^3\text{CH}_3 + \text{RH} \rightarrow \text{RMe} \]  

and insertion reactions have recently been proposed. The evidence for these was that more of the $\text{C}_n+1$ alkane product was observed in the photolysis of diazomethane and alkane $\text{C}_n$ mixtures than could be accounted for by radical processes or $^1$CH$_3$ insertion. It was noted that the $^3$CH$_3$ insertion process was not quenched by addition of oxygen, whereas all radical processes were. Thus, if the $^3$CH$_3$ insertion reaction does not occur, at least some process occurs which does not involve a conventional long-lived radical intermediate. It is possible that a repulsive triplet state is first formed which may dissociate, corresponding to (97), or spin invert, leading to insertion products. This type of reaction of triplet methylene was not invoked in a discussion of the reactions of methylene with butane since the results did not require it. Furthermore, it has been proposed that the photolysis of diazomethane in the presence of cyclobutene must produce both singlet and triplet methylene if the results are to be explained satisfactorily. Singlet methylene undergoes insertion reactions leading to bicyclo[2,1,0]pentane, 3-methylcyclobutene, and 1-methylcyclobutene. These are all formed with high vibrational energy content and can undergo subsequent unimolecular isomerisations. The principal product involving triplet methylene is vinylcyclopropane. In the presence of hydrogen, methane may arise from either reaction of type (97), involving either singlet or triplet methylene, or of type (98). Reaction (97) would be followed by

\[ \text{Me} + \text{RH} \rightarrow \text{CH}_4 + \text{R} \cdot \]  

where in this case R = H. By photolysis of ketene in wavelength regions which produce mainly singlet methylene (3000 Å) and mainly triplet (3200 Å) it was shown that in both cases methane formation was ca. 10 times slower than ethane formation. The authors proposed that the results

could be explained solely on the basis of reactions (97) and (99), and that
(98) was not necessary. However, this viewpoint is by no means proven,
merely suggested, and it would have been constructive to estimate the
relative proportions of singlet and triplet methylene species formed at the
different wavelengths in an attempt to justify exclusion of (98), which must
be a strong possibility for \(^1\text{CH}_2\) species.

Triplet methylene has been shown to react extraordinarily quickly with
carbon monoxide, the rate being at least twice that of its reaction with
cis-but-2-ene. Different modes of reaction have been proposed for the
reactions of singlet and triplet methylene with ethyl chloride, and ethyl
methyl ether, and the reactions of a substituted methylene, trans-2,3-
dimethylcyclopropylmethylene, in the gas phase have been described.
Novelties in the mercury-photosensitised decomposition of ketene are
described in the section on mercury photosensitisation.

4 Photochemistry of Aldehydes

The structural simplicity of formaldehyde and the extensive knowledge of
its spectroscopy render it of very special interest to the photochemist. A
knowledge of its photochemical behaviour is of great practical value
because of its role in atmospheric pollution, and the same applies to other
aldehydic species considered below. Despite extensive studies, controversy
exists over many aspects of the photochemistry of formaldehyde. Two
distinct primary photodissociative processes have been proposed.

\[
\begin{align*}
\text{CH}_2\text{O} + h\nu & \rightarrow \text{H}^+ + \text{HCO}^- \quad (100) \\
\text{CH}_2\text{O} + h\nu & \rightarrow \text{H}_2 + \text{CO} \quad (101)
\end{align*}
\]

The relative importance of these steps is strongly dependent upon the
excitation wavelength, although different authors are in disagreement as to
the precise dependence. A flash photolysis study of CH\(_2\)O, CD\(_2\)O, and
CHDO and of CH\(_2\)O, CD\(_2\)O mixtures was undertaken to attempt quanti-
tative estimation of the relative extent of processes (100) and (101) as a
function of wavelength and to provide data leading to an estimate of the
bond dissociation energy of the formaldehyde, \(D_{\text{HCO} - \text{H}}\).

From a product analysis, it appears that primary processes (100) and
(101), proceeding through an unidentified excited electronic state, are
followed by reactions:

\[
\begin{align*}
\text{H}^+ + \text{HCO}^- & \rightarrow \text{H}_2\text{CO} \quad (102) \\
\text{H}^+ + \text{H}^+ + \text{M} & \rightarrow \text{H}_2 + \text{M} \quad (103) \\
2\text{HCO}^- & \rightarrow \text{CO} + \text{CH}_2\text{O} \quad (104) \\
2\text{HCO}^- & \rightarrow 2\text{CO} + \text{H}_2 \quad (105)
\end{align*}
\]

Gas-phase Photochemistry

The sum of the quantum yields for processes (100) and (101) was unity over all the wavelengths studied (2800—3650 Å), but for CD₂O and CHDO this sum was somewhat less than unity at the longer wavelengths. The value of \( \Phi_{100}/\Phi_{101} \) varied smoothly from zero to 5-00 when the wavelength of excitation varied from 3650 to 2800 Å. The fact that radicals have been detected (see ref. 60) when formaldehyde was photoysed at 3650 Å leads to speculation that alternative primary process (106) may be important.

\[
\text{CH}_2\text{O}^* + \text{CH}_3\text{O} \rightarrow \cdot\text{CH}_2\text{OH} + \cdot\text{CHO} \quad (106)
\]

However, in this study a careful investigation of the effect of temperature showed that this reaction was not important. The trend of increasing importance of (100) is in direct opposition to that observed earlier by the same group of workers. No satisfactory explanation of this fact can be offered, except to note that the previous calculations may have been in error. From the threshold wavelength at which process (100) appears, the bond dissociation energy may be estimated as 85 kcal mole\(^{-1}\).

Acrolein is worthy of investigation because it is one of the lachrymators in Los Angeles photochemical smog. At 125 °C and 3130 Å excitation, two primary modes of decomposition were noted, arising from two excited states of the molecule.\(^{61}\)

\[
\begin{align*}
\text{A} + h\nu & \rightarrow \text{1}^1\text{A}_n \quad (107) \\
\text{1}^1\text{A}_n & \rightarrow \text{CO} + \text{C}_2\text{H}_4 \quad (108) \\
\text{1}^1\text{A}_n & \rightarrow \text{HCO}^* + \text{C}_2\text{H}_5^* \quad (109) \\
\text{1}^1\text{A}_n & \rightarrow \text{3}^3\text{A}_n \quad (110) \\
\text{1}^1\text{A}_n + \text{A} & \rightarrow \text{1}^1\text{A}_0 + \text{A} \quad (111) \\
\text{1}^1\text{A}_0 & \rightarrow \text{HCO}^* + \text{C}_2\text{H}_5^* \quad (112) \\
\text{1}^1\text{A}_0 & \rightarrow \text{A} \quad (113) \\
\text{3}^3\text{A}_n & \rightarrow \text{CO} + \text{C}_2\text{H}_4 \quad (114) \\
\text{3}^3\text{A}_n & \rightarrow \text{A} \quad (115)
\end{align*}
\]

where A = acrolein, superscripts denote multiplicity, and subscripts vibrational energy level.

Overall decomposition yields are very small, leading to the conclusion that the internal conversion (113) must be very important. If the HCO formed in (112) dissociates to CO and H atoms which are lost by subsequent reaction with acrolein, a consideration of the scheme leads to the expression

\[
\Phi_{\text{CO}} = \frac{1}{k_{108} + k_{109} + k_{110} + k_{111}[\text{A}]} \left( k_{108} + \frac{k_{109} + k_{111}[\text{A}]}{k_{312} + k_{113}} + \frac{k_{110} k_{114}}{k_{114} + k_{115}} \right) \quad (116)
\]

At low pressures of acrolein, \((k_{108} + k_{111}[\text{A}])/(k_{112} + k_{113})\) becomes insignificant and \(\Phi_{\text{CO}}^{-1}\) will be proportional to acrolein pressure. At high pressures,\(^{61}\) J. W. Coomer and J. N. Pitts jun., J. Amer. Chem. Soc., 1969, 91, 547.
the expression becomes

$$\Phi_{CO} = [1 + k_{112}/k_{113}]^{-1}$$  \hspace{1cm} (117)

This predicted behaviour is observed experimentally. From a temperature study,

$$k_{112}/k_{113} = 4.3 \pm 2.0 \exp (-5360 \pm 345)/RT$$  \hspace{1cm} (118)

The small value for overall quantum yields of decomposition of this compound and the fact that its photo-oxidation yields are similarly small mean that the molecule will remain a vexing problem in the pollution of atmospheres.

A similar study on cyclopropane carboxyaldehyde\textsuperscript{62} at 120° and again with 3130 Å radiation shows that the major products can be explained on the basis of reactions (119)—(130).

\[
\begin{align*}
\triangledown{CHO} + h\nu & \rightarrow \triangledown{CHO}^* \hspace{1cm} (119) \\
\triangledown{CHO}^* & \rightarrow \text{MeCH=CH=CHO} \hspace{1cm} (120) \\
\triangledown{CHO}^* & \rightarrow \triangledown{+ HCO} \hspace{1cm} (121) \\
\triangledown{CHO}^* & \rightarrow \triangledown{+ CHO}^* \hspace{1cm} (122) \\
\triangledown{CHO}^* + M & \rightarrow \triangledown{CHO}^* + M \hspace{1cm} (123) \\
\triangledown{CHO}^* & \rightarrow \text{MeCH=CH}_2 + CO \hspace{1cm} (124) \\
\triangledown{CHO}^* & \rightarrow \text{MeCH=CH}_2 + CHO \hspace{1cm} (125) \\
\triangledown{CHO} + \triangledown{.} & \rightarrow \triangledown{H} + \triangledown{CO} \hspace{1cm} (126) \\
\triangledown{CO} . & \rightarrow \triangledown{+ CO} \hspace{1cm} (127) \\
2 \triangledown{.} & \rightarrow \hspace{1cm} (128) \\
\triangledown{.} + R . & \rightarrow \text{products} \hspace{1cm} (129) \\
\triangledown{CO} . + R . & \rightarrow \text{products} \hspace{1cm} (130)
\end{align*}
\]

The states $\triangledown{CHO}^*$, $\triangledown{CHO}^{**}$ and $\triangledown{CHO}^*$ are unspecified, but may correspond to excited singlet, excited triplet, and unreactive ground state respectively. $R.$ represents any free radical in the system. It can be shown that:

$$\Phi_{C} = \frac{k_{120}}{k_{120} + k_{121} + k_{122}} + \left( \frac{k_{125}}{k_{124}} \right) \Phi_{P}$$  \hspace{1cm} (131)

where $\Phi_{C}$ is the quantum yield of crotonaldehyde, and $\Phi_{P}$ is the quantum yield of propylene. This relationship is verified experimentally. Rate constant ratios for the various steps can be evaluated from the data presented.

Gas-phase Photochemistry

Furfural \(^{-} \) irradiated between 2200 and 3130 Å gives carbon monoxide, methylacetylene, cyclopropene, and furan, presumably via reactions (132) and (133). The mass balance expected from these equations was obeyed

\[
\begin{align*}
\text{O} & \xrightarrow{h\nu} \text{O} + \text{CO} \\
\text{CHO} & \xrightarrow{h\nu} \text{C}_3\text{H}_4 + 2\text{CO}
\end{align*}
\]  

well. The decompositions are assumed to occur from the triplet state of furfural which is formed by intersystem crossing from the initially produced singlet state, and an alternative mechanism for (132) involving production of HCO and the furanyl radical can be ruled out on several experimental grounds.

Fluoroaldehydes have sometimes been used as sources of perfluoroalky radicals, \( R_f \). Data have been obtained for the rates of abstraction of aldehydic hydrogen from the parent compounds (\( R_f \text{CHO} \)).

\[
\begin{align*}
\text{R}_f + \text{R}_f \text{CHO} & \longrightarrow \text{R}_f \text{H} + \text{R}_f \text{CO} \\
\text{R}_f \text{CHO} + h\nu & \longrightarrow \text{R}_f \text{H} + \text{CO}
\end{align*}
\]  

It has been pointed out,\(^{44}\) and conceded by the original authors,\(^{45}\) that care must be taken in interpretation of such data since there may be another source of \( R_f \text{H} \) in such systems via reaction (135).

Acetaldehyde excited at 3130 Å produces first the excited singlet state, which after equilibration may internally convert to the ground state or intersystem cross to the triplet. From a study of the variation of rate of production of ethane with pressure,\(^{46}\) it can be shown that the observed linear relationship of \( \Phi_{\text{C}_2\text{H}_6} \) with acetaldehyde pressure [A] can only be derived if the number of second-order reactions preventing formation of methyl radicals is one greater than the number of second-order reactions leading to the production of methyl radicals.

The relevant reactions are

\[
\begin{align*}
^1\text{A} + \text{A} & \longrightarrow 2\text{A} \\
^3\text{A} + \text{A} & \longrightarrow 2\text{A} \\
^1\text{A} + \text{A} & \longrightarrow \text{Me} \cdot + \text{CHO} \cdot \\
^1\text{A} + \text{A} & \longrightarrow ^3\text{A} + \text{A} \\
^3\text{A} + \text{A} & \longrightarrow \text{Me} \cdot + \text{CHO} \cdot
\end{align*}
\]  

Thus, if both (136) and (137) are important, only one of the processes (138)—(140) can be, whereas if either (136) or (137) is unimportant, none of the steps (138), (139), or (140) can be included in the scheme.


Interaction between the triplet state of acetaldehyde and nitric oxide produces intermediates with a finite lifetime which eventually decompose to nitrosoacetaldehyde.

\[ {^3}A + \text{NO} \longrightarrow \ (\text{ANO}) \longrightarrow \text{MeCONO} \]  \hspace{1cm} (141)

Reinvestigation of this system has shown that there is an additional source of the nitrosoacetaldehyde, arising from singlet excited acetaldehyde molecules and NO in the presence of ground-state acetaldehyde molecules.

\[ {^1}A + A + \text{NO} \longrightarrow \text{MeCONO} + \text{other products} \]  \hspace{1cm} (142)

This must be the case at 2537 Å, since the reaction is observed and it is known that little or no triplet state of the aldehyde is formed at this wavelength.

5 Photochemistry of Nitrogen Compounds

Nitric oxide, because of its ground-state doublet character, has long been used as a scavenger for free radicals and other species containing unpaired electrons. For a review of the role of NO in photochemistry, see ref. 68. Nitric oxide shows a new structured absorption band at 3700 Å (ε = 52) when dissolved in carbon tetrachloride or acetonitrile. This has been attributed to the \( ^2\pi \rightarrow ^4\pi \) spin forbidden transition which becomes allowed because of solvent interactions. In the presence of hydrocarbons such as cyclohexane, the excited NO apparently abstracts hydrogen, giving alkyl radicals which react with ground-state NO. Thus in the presence of cyclohexane, the following products are formed in addition to other minor compounds:

\[ \text{NO} \xrightarrow{hv(3500 \text{ Å})} \text{ONO}_2 + \text{NO}_2 + \text{NO}_3 \]  \hspace{1cm} (143)

Nitrogen dioxide decomposes under irradiation at 3660 Å to give nitric oxide and ground-state \(^3\text{P}\) oxygen atoms (144). This reaction is frequently used as a source of O atoms, and has recently been utilised in a study of the addition of O atoms to ethylene:

\[ \text{NO}_2 + hv \longrightarrow \text{NO} + \text{O} \]  \hspace{1cm} (144)

Absorption of ammonia in the first absorption region between 2200 and 1600 Å produces a state which may decompose in two ways via a predissociation.

Gas-phase Photochemistry

\[ \text{NH}_3 + h\nu(2062) \rightarrow \text{NH}_3(^2B_1) + \text{H} \]  \hspace{1cm} (145)

\[ \rightarrow \text{NH}(^1\Delta) + \text{H}_2 \]  \hspace{1cm} (146)

However, at 2062 Å, process (146) has a quantum yield of only 0.005 or less, and thus irradiation at this wavelength provides a virtually clean source of \text{NH}_3 radicals. The reactions of \text{NH}_3 radicals with propane and ethylene have been studied, and flash photolysis has shown that in this system \text{NH} radicals are also produced.\footnote{K. A. Mantie and E. J. Bair, \textit{J. Chem. Phys.}, 1968, 49, 3248.} Since reaction (146) is unimportant in this wavelength region, the \text{NH} radicals must arise \textit{via} a secondary reaction of the primarily produced \text{NH}_3 radicals. Possible reactions are

\[ \text{NH}_3 + \text{H} \rightarrow \text{NH} + \text{H}_2 \]  \hspace{1cm} (147)

\[ 2\text{NH}_3 \rightarrow \text{NH}_3 + \text{NH} \]  \hspace{1cm} (148)

The \text{NH} formed disappears rapidly \textit{via} an insertion reaction into ammonia, producing hydrazine (149).

\[ \text{NH} + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4 \]  \hspace{1cm} (149)

The photolysis of tetrafluorohydrazine in the gas phase at 2537 Å in the presence of allene leads to products which can be accounted for \textit{via} addition of \text{NF}_2 radicals.\footnote{C. L. Bumgardner and K. G. McDaniel, \textit{J. Amer. Chem. Soc.}, 1969, 91, 1032.} Fluorine atoms are produced in the primary decomposition, and these add to the allene to produce a hot 2-fluoropropene radical. This is either collisionally stabilised or loses HF. The radicals thus formed then add \text{NF}_2 to produce the stable final products.

\[ \text{H}_2\text{C} = \text{C} = \text{CH}_2 \]

\[ \text{HF} + \text{HC≡C} \overset{\cdot}{\text{CH}}_2 \leftarrow [\text{H}_2\text{C} = \overset{\cdot}{\text{C} - \text{CH}}_2]^{*} \rightarrow \text{H}_2\text{C} = \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{CH}}_2 \]

\[ \text{NF}_2 \]

\[ \text{HC≡C} - \text{CH}_2\text{NF}_2 \]

\[ \text{H}_2\text{C} = \overset{\cdot}{\text{C} - \text{CH}}_2\text{NF}_2 \]

The photochemistry of aliphatic and (to a lesser extent) aromatic azo-compounds was developed largely because of their usefulness as sources of free radicals. However, there is current interest in the primary processes.
involved in the decomposition of such compounds. Work on azoisopropene in solution and in the gas phase was undertaken to determine the multiplicity of the excited state responsible for the observed decomposition and cis-trans isomerisations.\textsuperscript{74} In the gas phase at low pressures, the quantum yield of decomposition of this compound, $\Phi_{\text{deo}}$, was unity at 366 nm, and no cis-trans isomerisation was observed. Increase of pressure decreased the decomposition yield and increased the yield of isomerisation. At very high pressures the decomposition is only a minor route of energy dissipation, and in iso-octane solution $\Phi_{\text{deo}}$ was only 0.025. There are two possible mechanisms to explain these results.

1. At low pressures both cis- and trans-azoisopropene decompose from their $^1\pi\pi^*$ states (see Figure 1), but collision aids their intersystem crossing to the common $^3\pi\pi^*$ state, from which only relaxation to the cis or trans ground-states may occur.

2. Intersystem crossing from the initially populated $^1\pi\pi^*$ states to the $^3\pi\pi^*$ state is rapid, and decomposition occurs from this state. Collisional vibrational relaxation produces a level of the $^3\pi\pi^*$ state which is incapable of decomposition, and electronic relaxation from this level occurs to the cis or trans ground-states of the molecule (Figure 1).

The radiative lifetime of the $^1\pi\pi^*$ state can be calculated from absorption coefficients to be $1 \times 10^{-8}$ s. Since the fluorescence yield in the gas phase is very low, this state is the primary product of decomposition.


\textbf{Figure 1}  \textit{Energy levels of azoisopropene}
(Reproduced by permission from \textit{J. Amer. Chem. Soc.}, 1969, 91, 1220)
Gas-phase Photochemistry

$<0.5 \times 10^{-5}$, the true lifetime of the upper singlet states must be $0.5 \times 10^{-10}$ s or less. It seems likely therefore that the second mechanism is operative. Sensitisation of trans-azoisopropane by benzophenone ($E_T = 68.5$ kcal) and benzene ($E_T = 84.0$ kcal) in methanol produced very little cis-isomer and no decomposition, presumably because the trans $^3\pi\pi^*$ state is produced by energy transfer which is prevented from crossover to the $^3\pi\pi^*$ or cis $^3\pi\pi^*$ by energy barriers. Naphthalene was a successful sensitisier, but in this case it was almost certain that singlet energy was being transferred.

A similar mechanism has been proposed for the decomposition and cis–trans isomerisation of 1,1'-azoisobutane. It was shown here that the triplet state of this compound lies lower in energy than those of acetone and biacetyl. Thus energy transfer from these ketones may be used to populate the triplet state of the azaalkane. However, when biacetyl is used as the donor ($E_T = 57$ kcal mole$^{-1}$) no decomposition occurs, whereas with the acetone donor ($E_T = 76$ kcal mole$^{-1}$) decomposition is observed. Thus the amount of vibrational energy in the triplet is critical in determining the fate of the molecule. The dissociation of azaalkanes in the long wavelength region may thus be summarised by the reaction sequence (151–158).

\[
\begin{align*}
R_2N_2 + h\nu & \longrightarrow 1(R_2N_2)n \\
1(R_2N_2)n & \longrightarrow 3(R_2N_2)n \\
3(R_2N_2)n & \longrightarrow R_2^+ + RN_2^- \\
& \longrightarrow R_2 + N_2 \\
3(R_2N_2)n + M & \longrightarrow 3(R_2N_2)_0 + M \\
3(R_2N_2)_0 & \longrightarrow (cis-R_2N_2)_m \\
& \longrightarrow (trans-R_2N_2)_n \\
(R_2N_2)_{n,m} + M & \longrightarrow R_2N_2 \\
\end{align*}
\]

(151) (152) (153) (154) (155) (156) (157) (158)

A spectroscopic analysis of the excited states of diazomethane and photodecomposition products has allowed a reinterpretation of previously obtained data. Spectroscopic evidence is presented for formation of the diazomethyl radical and methanal azine, and the isomerisation of diazomethane to diazirine is also discussed.

Decomposition is assumed to occur from the singlet excited state of phenyl-substituted diazomethanes, although evidence for this is scant.

Features of the reactions of radicals produced by the photolysis of 2,2'-azoisobutane, azomethane, and aromatic azides have been discussed. The latter was a flash photolysis study in which triplet-state nitrenes were observed as intermediates. The dissociation energy of the RN$_2$ radical

---

produced in reaction (153) is usually negative, and thus N₂ and an R· radical are spontaneously produced. There is clear evidence however that in the photolysis of 1,1,1-trifluoromethyl azocyclopropane, the RN₂ radical produced is stable to loss of nitrogen.80

The u.v. absorption spectrum of isopropyl nitrite extends from 4000 to 3100 Å in the first band. Absorption into this causes a primary decomposition, presumably from the 1ππ* state, into isopropoxy radicals and nitric oxide (159) with a quantum yield of 0.36 at 3660 Å and 26 °C. There is a minor detachment of HNO or NOH, with a quantum yield of 0.06 (160). The decomposition yields appear to be independent of the amount of vibrational energy in the terminal N=O stretching mode.81 The primary process in the photolysis of nitrosobenzene is a similar split to phenyl radicals and nitric oxide (161).82

\[ \text{Me}_2\text{CHONO} + \text{hv} \rightarrow \text{Me}_2\text{CHO}· + \text{NO} \]  
(159)

\[ \rightarrow \text{MeCOMe} + \text{HNO (or NOH)} \]  
(160)

\[ \text{PhNO} + \text{hv} \rightarrow \text{Ph·} + \text{NO} \]  
(161)

Succinimide vapour undergoes a primary ring opening upon irradiation between 2300 and 2600 Å.83 Subsequent reactions of the diradical formed (162) can account for all of the observed products, and their independence of wavelength, pressure, temperature, and intensity.

\[ \begin{array}{c}
\text{O} \\
\text{H} \\
\text{H}_2\text{C} = \text{CH}_2
\end{array} + \text{hv} \rightarrow \cdot\text{CH}_2 = \text{CH}_2 \cdot \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \]  
(162)

6 Photochemistry of Sulphur Compounds

As in the case of investigations of the photochemistry of nitrogen compounds, workers in the field of sulphur-containing compounds have tended towards interest in secondary reactions of radical species produced photochemically, rather than concern with the nature of the primary photochemical processes.

It has been shown by a number of workers that the photolysis of methane thiol and ethane thiol at 2537 Å results in loss of a hydrogen atom with unit quantum yield.84–86

Gas-phase Photochemistry

\[ \text{RSH} + \text{hv} \rightarrow \text{RS} \cdot + \text{H} \cdot \]  

(163)

The kinetic energy of the hydrogen atom formed is apparently dependent upon the wavelength of excitation used,\(^5\) although this conclusion was not reached in a parallel study.\(^4\) Reactions of the ‘hot’ hydrogen atoms with substrates such as ethylene,\(^4, 8^\) and hydrogen and deuterium,\(^5\) have been studied.

Disulphides undergo primarily an S—S scission on irradiation, yielding thyl radicals.\(^8^7, 8^8\) The excited species responsible for the decomposition may also be collisionally deactivated.\(^8^7\) An alternative mode of decomposition is also observed (166).

\[ \text{RSSR}^* + \text{M} \rightarrow \text{RSSR} + \text{M} \]  

(164)

\[ \rightarrow \text{RS} \cdot + \text{RS} \cdot \]  

(165)

\[ \rightarrow \text{R} \cdot + \cdot \text{SSR} \]  

(166)

\text{Sulphides decompose similarly, e.g. dimethyl sulphide}

\[ \text{MeSMe}^* + \text{M} \rightarrow \text{MeSMe} + \text{M} \]  

(167)

\[ \rightarrow \text{Me} \cdot + \cdot \text{SMe} \]  

(168)

\[ \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{S} \]  

(169)

Reaction (169) is important at temperatures above 250 °C.

Sulphides have been shown to quench the excited triplet state of benzophenone,\(^8^9\) possibly by forming a charge transfer complex, or by H-atom transfer. The photodecomposition of alkyl aryl sulphides has also been considered.\(^9^0\) The direct and mercury photosensitised decomposition of \(\text{H}_2\text{S}\) leads to a primary split into SH radicals and hydrogen atoms\(^9^1, 9^2\)

\[ \text{H}_2\text{S} + \text{hv} \rightarrow \cdot \text{SH} + \cdot \text{H} \]  

(170)

Subsequent reactions of these species include

\[ \cdot \text{H} + \text{H}_2\text{S} \rightarrow \text{H}_3 + \cdot \text{SH} \]  

(171)

\[ 2\text{HS} \cdot \rightarrow \text{H}_2\text{S} + \text{S} \]  

(172)

\[ \text{H} \cdot + \text{HS} \cdot \rightarrow \text{H}_2 + \text{S} \]  

(173)

\[ 2\text{HS} \rightarrow \text{H}_3 + \text{S}_2 \]  

(174)

The kinetics of reactions of ‘hot’ H atoms produced in the photolysis of \(\text{H}_2\text{S}\) at 1849 Å have been studied.\(^9^3\) The quantum yield for hydrogen production in the direct photolysis was a function of pressure, being ca.1.0 at 50 torr \(\text{H}_2\text{S}\) and rising to ca. 1.2 at 200 torr. The yield in the mercury


photosensitised reaction was much lower, ca. 0.4 at 50 torr rising to ca. 0.8 at 200 torr. The species produced in reaction (170) may add to unsaturated compounds, such as propene, and acetylene. In the latter case a polymer is produced which has been identified as poly(ethenethiol), with a repeating unit as shown:

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{SH} \\
\text{H}
\end{array}
\]

This arises from two reactions, addition of SH to acetylene, and subsequent hydrogen abstraction from H₂S by the species thus formed.

\[
\begin{align*}
\cdot \text{SH} + \text{C}_2\text{H}_2 & \rightarrow \text{HS} = \cdot \text{CH} \\
\text{HS} = \cdot \text{CH} + \text{H}_2\text{S} & \rightarrow \text{HS} = \cdot \text{CH} + \text{H}_2 + \cdot \text{HS}
\end{align*}
\]

Sulphur—sulphur bonds also rupture when sulphur monochloride is photolysed (177). Use of flash photolysis enabled the detection of several transients, including the SCI radical, vibrationally excited S₂ molecules, and the metastable \( ^1\Delta_g \) S₂ species. The S₂ transients arise \textit{via} radical—radical reactions of SCI.¹⁴

\[
\text{S}_2\text{Cl}_2 + h\nu \rightarrow 2\text{SCI}.
\]

7 Oxygen Photochemistry

Molecular oxygen has long been used as a scavenger of excited triplet states of molecules; indeed, quenching of reactions by ground-state molecular oxygen is accepted (with some reservations) as a diagnostic test for participation of triplet states. The mechanism of such quenching reactions has been little studied, however, until recently. Some energy transfer studies involving oxygen have been briefly mentioned in Chapter 1, but there is more evidence concerning the excited states of oxygen which may participate in photochemical reactions.

The low-lying electronic energy levels of oxygen are shown in Figure 2. The reactivities of the various states have been discussed. Figure 2 shows that the triplet state of aromatics should be able to populate either the \( ^1\Sigma^+_g \) or \( ^1\Delta_g \) state of oxygen by an energy transfer mechanism

\[
\text{A} + \text{O}_2(\text{\( ^3\Sigma^-_g \)}) \rightarrow \text{A} + \text{O}_2(\text{\( ^1\Delta_g \) or \( ^1\Sigma^+_g \)})
\]

This type of reaction has been observed separately in three independent studies. The emission spectrum of \( ^1\Delta_g \text{O}_2 \) was observed in the

benzene–O₂ photochemical system, whereas that of \( ^1\Sigma^+_g \) was not. However, since O₂(\( ^1\Delta_g \)) will be deactivated rapidly by the aromatic to O₂(\( ^1\Delta_g \)), and the lifetime of the upper state is very much shorter than that of the (\( ^1\Delta_g \)) state, it is possible that O₂(\( ^1\Sigma^+_g \)) is a precursor of the long-lived (\( ^1\Delta_g \))

![Energy levels of benzene, naphthalene, and molecular oxygen](image)

Figure 2  Energy levels of benzene, naphthalene, and molecular oxygen

level. At high oxygen pressures, quenching of singlet benzene by O₂ occurs, and reference to Figure 2 shows that possible reactions involving formation of (\( ^1\Delta_g \))O₂ are:

\[
\begin{align*}
C_6H_6(\text{\( ^1\Delta_g \)}) + O_2(\text{\( ^3\Sigma^-_g \)}) & \rightarrow C_6H_6(\text{\( ^1\Delta_g \)}) + O_2(\text{\( ^1\Delta_g \)} \text{ or \( ^1\Sigma^+_g \)}) \\
C_6H_6(\text{\( ^1\Delta_g \)}) + O_2(\text{\( ^3\Delta_g \)}) & \rightarrow C_6H_6(\text{\( ^3\Delta_g \)}) + O_2(\text{\( ^1\Delta_g \)})
\end{align*}
\]

(179)  (180)

Additional processes not producing excited states of oxygen would be:

\[
\begin{align*}
C_6H_6(\text{\( ^1\Delta_g \)}) + O_2(\text{\( ^3\Delta_g \)}) & \rightarrow C_6H_6(\text{\( ^3\Delta_g \)}) + O_2(\text{\( ^3\Sigma^-_g \)}) \\
C_6H_6(\text{\( ^1\Delta_g \)}) + O_2(\text{\( ^3\Sigma^-_g \)}) & \rightarrow C_6H_6(\text{\( ^3\Delta_g \)}) + O_2(\text{\( ^3\Sigma^-_g \)})
\end{align*}
\]

(181)  (182)

Since no reduction in O₂(\( ^1\Delta_g \)) production is observed with increase in O₂ pressure, reaction (181) can be ruled out. Reaction (180) would lead to a large increase in O₂(\( ^1\Delta_g \)) production since the benzene triplets formed would themselves produce O₂(\( ^1\Delta_g \)) \textit{via} (178). It seems likely, therefore, that (179) or (182) are the most likely routes for singlet quenching, and that the expected small rise in concentration of O₂(\( ^1\Delta_g \)) is not observed because of a counterbalancing deactivation step (183).
Naphthalene $^{97,98}$ and substituted naphthalene $^{98}$ donors also produce $\text{O}_2(\Delta_g)$, detected by e.p.r. measurements. Preliminary measurements indicated that the quantum yield of $\text{O}_2(\Delta_g)$ formation in these systems was very high (ca. 0.5). The observations above provide a mechanism for the population of the excited states of oxygen which are important in mechanisms of photochemical air pollution. $^{99}$ Direct excitation of oxygen would not be important because of low transition probabilities, although it has been shown that the transitions can be observed if sufficiently high pressure of oxygen is used. $^{100}$ Thus irradiation at 2000 lb/sq. in. pressure of $\text{O}_2$ dissolved in 1,1,2-trichloro-1,1,2-trifluoroethane by a helium–neon laser produces $\text{O}_2(\Delta_g)$ which oxidises 9,10-dimethylanthracene to the peroxide. Singlet oxygen intermediates in many sensitised photo-oxidations have been proposed, $^{101}$ and the experiments described above provide confirmatory evidence that the mechanism is correct.

8 Halogens, Hydrogen Halides, and Alkyl Halides

Ground-state iodine molecules, $\text{I}_2(\Sigma_g^+)$ when excited to the $B(3\pi_{0u}^+)$ state are known to dissociate to give ground-state and excited-state iodine atoms, $\text{I}(5^2P_1)$ and $\text{I}(5^2P_3)$ respectively. Since the excited iodine atoms relax quickly to the ground state, evidence for their formation is primarily of a chemical nature. However, absorption lines due to this atom have now been observed when mixtures of $\text{I}_2$ and $\text{CO}_2$ were flashed. $^{102}$ The mechanism of the dissociation has been hitherto assumed to be a collisional predissociation or continuum dissociation depending on the region of absorption. It has now been demonstrated that excitation with the mercury 5461 Å line which is below the 5000 Å continuum threshold produces high concentrations of ground-state iodine atoms, independent of the iodine pressure between 0.3 and 0.01 torr. $^{103}$ Clearly, neither continuum dissociation nor collisional predissociation can account for these results, and it is therefore proposed that direct predissociation must also be an important mechanism in the decomposition of $\text{I}_2(B(3\pi_{0u}^+))$. Excitation of IBr in the continuous region of absorption higher than 3000 Å causes decomposition to give a ground-state iodine atom and excited bromine atom. $^{104}$

$$\text{IBr}(X^1\Sigma_g^+) + h\nu \rightarrow \text{I}(5^2P_1) + \text{Br}(4^2P_g)$$

The excited bromine atoms are rapidly removed by reaction with the parent compound, or by spin–orbit relaxation to their ground state.


Gas-phase Photochemistry

\[ \text{Br}(4^2P_4) + \text{IBr}(X^1\Sigma^+) \rightarrow \text{Br}_2(X^1\Sigma^+)^+ + I(5^2P_4) \]  

(185)

The ground state atoms may react in a manner entirely analogous to reaction (185). Thus Br atoms were not detected spectroscopically. Similar results were obtained in the photolysis of ICl at wavelengths greater than 2000 Å, since the excited chlorine atoms produced disappeared by reaction with the parent molecule.

\[ \text{Cl}(3^2P_4) + \text{ICl}(X^1\Sigma^+) \rightarrow \text{Cl}_2(X^1\Sigma^+)^+ + I(5^2P_4) \]  

(186)

Thus the reaction of an excited halogen with homonuclear or interhalogen compounds leads predominantly to a reaction of this sort. By analogy, excitation of BrCl\((X^1\Sigma^+)\) to the BrCl\((3\pi_0^+\rangle)\) state should produce ground-state Br and excited Cl atoms, although these have not been detected.

Excited iodine atoms, I\((5^2P_4)\) will react with methyl iodide to produce iodine molecules and methyl radicals, or be collisionally relaxed to the ground state.

\[ \text{I}(5^2P_4) + \text{MeI} \rightarrow \text{I}_2 + \text{Me} \cdot \]  

(187)

\[ \text{I}(5^2P_4) + \text{MeI} \rightarrow \text{I}(5^2P_4) + \text{MeI} \]  

(188)

The rate constant for the first reaction has been measured by time-resolved mass spectrometric measurements on the formation of \(\text{I}_2\), and a value of \(k_{187} = 1.23 \times 10^{-14} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}\) obtained.\(^{108}\) By monitoring the decay of excited iodine atoms from their absorption,

\[ \text{I}(5^2P_4) \xrightarrow{\text{hv}} \text{I}(65^5P_5) \]  

(189)

a value of \(k_{187} + k_{188}\) was obtained of \(1.7 \times 10^{-13} \text{ cm}^2 \text{ mole}^{-1}\) at the same temperature, 300 K. Thus \(k_{187}/k_{188} = ca. 10^{-2} at 300 K.\) 'Hot'-atom effects in the photolysis of HI in the gas phase have been discussed,\(^{107, 108}\) and flash spectroscopic investigations of aqueous solutions of Br\(_2\) and I\(_2\) have been described.\(^{109}\)

Light from a pulsed ruby laser has been used to induce dissociation in bromine molecules.\(^{110}\) Since the wavelength of light used, 6940 Å, is insufficient in energy to excite the bromine molecule to the continuum, bound levels are initially produced. The additional energy required for dissociation is produced by collision of the excited molecules with ground-state Br\(_2\) molecules. The dissociation was monitored by reaction of the Br atoms produced with fluoro-olefins. Direct bimolecular addition of excited Br\(_2\) to the olefins was found to be negligible. Only ca. 1% of the excited Br\(_2\) molecules dissociate, the remainder relaxing electronically at a rate estimated to be somewhat faster than the gas kinetic collision rate.

---


Thermal effects in the recombination of bromine atoms following the flash photolysis of bromine molecules have been pointed out, and the need for care in interpreting such data established.\textsuperscript{111}

The reaction of bromine molecules and hydrogen molecules both thermally and photochemically to produce HBr is one of the classical textbook examples of a self-inhibited chain reaction. However, the original photochemical experiments were carried out using extremely crude techniques in that sunlight was the light source used. A recent investigation\textsuperscript{118} has shown that at room temperature, the rate of formation of HBr is proportional to the intensity of light absorbed, and not its square root. Furthermore, the temperature dependence indicates that the reaction requires zero activation energy, and that rates of formation are a factor of some 200 greater than those calculated on the basis of a Br atom chain mechanism. Three mechanisms consistent with these observations are possible.

\begin{align*}
(A) & \quad 2\text{Br} + \text{H}_2 \quad \longrightarrow \quad 2\text{HBr} \\
(B) & \quad \text{Br} + \text{H}_2 + \text{M} \quad \longleftrightarrow \quad \text{BrH}_3 + \text{M} \\
& \quad \text{BrH}_3 + \text{Br} \quad \longrightarrow \quad 2\text{HBr} \\
(C) & \quad 2\text{Br} + \text{M} \quad \longrightarrow \quad \text{Br}^* + \text{M} \\
& \quad \text{Br}^*_2 + \text{H}_2 \quad \longrightarrow \quad 2\text{HBr}
\end{align*}

(190) \quad (191) \quad (192) \quad (193) \quad (194)

The excited electronic state postulated in (C) could be either the $^3\pi_{1u}$ or $^3\pi_{\alpha +}$, both of which have been observed in Br atom recombination. If (C) is the mechanism responsible, the conclusions should be open to experimental verification by populating non-dissociative levels of the Br$_2$ excited molecules as in ref. 110, and observing the rate of HBr formation. Chain reactions initiated by halogen atoms produced photochemically from molecular halogens,\textsuperscript{118-117} hydrogen halides,\textsuperscript{118} and halogen-substituted alkanes\textsuperscript{119,120} have been extensively investigated.

### 9 Mercury-photosensitised Reactions

In this section discussion is limited to processes initiated by the excited ($6^3P_1$) mercury atom, and the corresponding excited triplet zinc and cadmium atoms. Processes arising from the mercury ($6^3P_1$) state produced

by absorption of 1849 Å radiation are discussed in the section dealing with vacuum u.v. photochemistry. Mercury photosensitisation continues to be used as a means of generating excited molecules, but attention has also been focused on the nature of the primary processes involved. By use of a flash photolysis method, the kinetics of the combination of ground-state mercury atoms with chlorine atoms have been studied.\textsuperscript{121} The chlorine atoms were generated by the Hg(6^3P_1) sensitised photolysis of CF₃Cl, which yields only mercury atoms and chlorine atoms (196).

\[
\text{Hg}(6^1S_0) + h\nu \quad \rightarrow \quad \text{Hg}(6^3P_1) \quad (195)
\]

\[
\text{CF}_3\text{Cl} + \text{Hg}(6^3P_1) \quad \rightarrow \quad \text{CF}_3^\cdot + \text{Cl}^\cdot + \text{Hg}(6^1S_0) \quad (196)
\]

Transient absorption spectra were obtained in the regions 2450—2550 Å and 2710—2820 Å. The first band is identified with the \( D^2\pi_4 \leftarrow X^2\Sigma \) transition of the radical HgCl, while the second is more tentatively assigned to the \( C^2\pi_4 \leftarrow X^2\Sigma \) transition in the same radical. Both bands showed identical time dependence; in kinetic analyses, the intensity at 2790 Å was used as a measure of HgCl concentration.

The decay of the HgCl spectrum may be accounted for by the following additional reactions,

\[
\text{Hg} + \text{Cl} \quad \overset{M}{\rightarrow} \quad \text{HgCl} \quad (197)
\]

\[
\text{HgCl} + \text{HgCl} \quad \overset{M}{\rightarrow} \quad \text{Hg}_2\text{Cl}_2 \quad (198)
\]

\[
\cdot\text{CF}_3 + \cdot\text{CF}_3 \quad \overset{M}{\rightarrow} \quad \text{C}_2\text{F}_6 \quad (199)
\]

The fact that at zero time delay the concentration of HgCl is zero precludes the possibility of the alternative primary process (200).

\[
\text{Hg}(6^3P_1) + \text{CF}_3\text{Cl} \quad \rightarrow \quad \text{HgCl} + \cdot\text{CF}_3 \quad (200)
\]

HgCl may also disappear \textit{via} a disproportionation reaction (201);

\[
\text{HgCl} + \text{HgCl} \quad \rightarrow \quad \text{HgCl}_2 + \text{Hg} \quad (201)
\]

although this does not affect the observed kinetics of HgCl formation, and combination has been shown to be the major route for HgCl disappearance. Discounting (201), an estimate of the extinction coefficient of HgCl at 2790 Å can be obtained from which values of \( k_{196} \) are calculated. These are 3·0 ± 1·8 and 1·9 ± 1·3 \( \times 10^{11} \) mole\(^{-1}\) s\(^{-1}\) for 720 torr CF₃Cl, and 10 torr CF₃Cl plus 710 torr again respectively. The corresponding values of \( k_{197} \) are 3 and 0·9 \( \times 10^{10} \) 1 mole\(^{-1}\) s\(^{-1}\). The large errors are due to the accumulation of experimental errors involved in the evaluation, but the authors state that they are probably correct to within a factor of three. The values obtained are high compared with the gas kinetic collision rate constants of \( k_{198} = 6·3 \times 10^{10} \) 1 mole\(^{-1}\) s\(^{-1}\) (\( \sigma \) assumed 5 Å) and \( k_{197} = 6·2 \times 10^{10} \) 1 mole\(^{-1}\) s\(^{-1}\) (\( \sigma \) assumed = 3 and 2 Å). These high values suggest that the mechanism may involve the formation of a radical–molecule complex.

\[
\text{HgCl} + \text{CF}_3\text{Cl} \quad \xrightarrow{\text{M}} \quad [\text{CF}_3\text{Cl} \cdot \text{HgCl}]^* \\
\text{Hg}_2\text{Cl}_2 + \text{CF}_3\text{Cl} \quad \xleftrightarrow{\text{HgCl}} \quad [\text{CF}_3\text{Cl} \cdot \text{HgCl}] \\
\begin{aligned}
\text{Cl} + \text{CF}_3\text{Cl} & \quad \xrightarrow{\text{M}} \quad [\text{CF}_3\text{Cl} \cdot \text{Cl}]^* \\
\text{HgCl} + \text{CF}_3\text{Cl} & \quad \xrightarrow{\text{HR}} \quad [\text{CF}_3\text{Cl} \cdot \text{Cl}] 
\end{aligned}
\] (202)

From the lack of temperature effect in these experiments, it can be estimated that the activation energy involved in such reactions would not be less than \(-1.2\) kcal/mole\(^{-1}\).

The primary reaction of mercury (6\(^3\)P\(_1\)) with oxygen has been the subject of a new study,\(^{123}\) in which a monoisotopic lamp containing 96\% of the \(^{202}\text{Hg}\) isotope was used. From a study of the isotopic distribution of mercury in the products, a reaction mechanism has been proposed. Spectroscopic measurements enabled the concentration of mercury atoms to be monitored continuously, and it was shown that in a static system under continuous illumination, there was a short induction period before mercury atoms were consumed. If the exciting light was shut off after the induction period, mercury atoms continued to be consumed in a dark reaction. However, addition of 1,3-butadiene quenched the dark reaction completely, although under continuous irradiation mercury atoms were consumed as before. Experiments in a flow system showed that solid mercury compounds formed on the walls of the vessel were highly enriched in \(^{202}\text{Hg}\).

The results clearly show that an accumulation of oxidised species is necessary to cause the rapid disappearance of the mercury atoms, and that 1,3-butadiene reacts very quickly with the intermediate. Three possible intermediates have been considered:

\((a)\) an atom of mercury in a lower excited state;

\[
\text{Hg}(6^3\text{P}_1) + \text{O}_2 \quad \xrightarrow{} \quad \text{Hg}(6^3\text{P}_0) + \text{O}_2^* 
\] (204)

\((b)\) an excited mercuric oxide species;

\[
\begin{aligned}
\text{Hg}(6^3\text{P}_1) + \text{O}_2 & \quad \xrightarrow{} \quad \text{HgO}^* + \text{O} \\
\text{HgO}^* & \quad \xrightarrow{} \quad \text{Hg}(6^1\text{S}_0) + \text{O} 
\end{aligned}
\] (205)

\((c)\) a complex between the excited mercury atom and molecular oxygen.

\[
\begin{aligned}
\text{Hg}(6^3\text{P}_1) + \text{O}_2 & \quad \xrightarrow{} \quad \text{HgO}_2^* \\
\text{HgO}_2^* & \quad \xrightarrow{} \quad \text{Hg}(6^1\text{S}_0) + \text{O}_2 
\end{aligned}
\] (207)

Possibility \((a)\) is discounted because it has been shown that oxygen does not form the metastable \((6^3\text{P}_0)\) state of mercury on collision, and \((b)\) may be discounted on energetic grounds. It seems likely, therefore, that \((c)\) is the

mechanism of intermediate formation. The following complete reaction scheme is therefore proposed by the authors to explain the oxidation of mercury.

\[
\begin{align*}
\text{Hg}(6\text{P}_1) + \text{O}_2 &\rightarrow \text{HgO}_2 \\
\sigma = 20 \text{ Å}^2 &\quad \quad \text{Hg}(6\text{P}_1) + \text{O}_2 \\
\downarrow &\quad \text{Hg}(6\text{P}_1) + \text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{Hg}(6\text{S}_0) + \text{O}_2 &\rightarrow \text{HgO}_2 \\
\sigma = 0.25 \text{ Å}^2 &\quad \quad \text{HgO}_2 + \text{C}_4\text{H}_6 \\
\downarrow &\quad \text{Hg}(6\text{S}_0) + \text{C}_4\text{H}_6
\end{align*}
\]

\[
\begin{align*}
\text{Hg}(6\text{S}_0) + \text{C}_4\text{H}_6 &\rightarrow \text{Hg}(6\text{S}_0) + \text{C}_4\text{H}_6
\end{align*}
\]

(209)

It is not at all clear from this scheme what is the nature of the dark reaction which is largely responsible for the disappearance of mercury atoms from the system. It clearly involves the HgO\(_2^*\) species, but the authors do not discuss this reaction, nor is there a satisfactory explanation of the fact that the oxides recovered from such experiments contain largely the \(^{202}\text{Hg}\) isotope. Obviously the HgO\(_2^*\) species contains exclusively the \(^{202}\text{Hg}\) isotope, except at very high pressure where, due to Lorentz broadening, there will be some absorption by the \(^{200}\text{Hg}\) isotope also, but it is difficult to envisage the fate of the excited complex which leads exclusively to a mercury oxide containing only the \(^{202}\text{Hg}\) isotope, since process (210) followed by (211) or (212) will both lead to one molecule of natural mercury for every atom of \(^{202}\text{Hg}\) formed.

\[
\begin{align*}
\text{HgO}_2^* &\rightarrow \text{HgO} + \text{O} \\
\text{O} + \text{Hg} &\rightarrow \text{HgO} \\
\text{HgO}_2 + \text{Hg} &\rightarrow \text{HgO} + \text{HgO}
\end{align*}
\]

(210) (211) (212)

It is generally assumed that quenching of an excited triplet \(\text{Hg}(6\text{P}_1)\) mercury atom by a singlet ground-state molecule will necessarily produce a triplet excited state of the quencher if the mercury atom returns to the ground state, because of the Wigner spin conservation law. This assumption is made in a study of the primary processes in the mercury-photosensitised decomposition of ketene.\(^{128}\) However, severe doubt has been cast on the validity of the assumption by two independent investigations of the stereo-

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specificity of methylene reactions produced by mercury photosensitisation.\(^{124,125}\) It has been shown that addition of triplet methylene to but-2-ene produces the same equilibrium ratio of 1,2-dimethylcyclopropane independent of whether the cis- or trans-olefin is used. Attainment of equilibrium requires that rotation about the single bond in the diradical (213) is faster than ring closure (214), with the implication that in gaseous

\[
\begin{align*}
^{3}\text{CH}_2 + \text{MeCH} &= \text{CHMe} & \rightarrow & \text{MeCH}^{+} \text{CHMe} \\
\text{MeCH}^{+} \text{CHMe} & \rightarrow & \text{Me} \overset{\text{CH}}{\text{Me}} & \text{cis} \text{ and } \text{trans}
\end{align*}
\] (213) (214)

systems where the equilibrium ratio of trans : cis of 2.9 is not found, species other than \(^{3}\text{CH}_2\) are also present. In the Hg (\(^{(6)P_1}\)) photosensitisation of ketene, it has been shown that a non-equilibrium ratio of trans- to cis-dimethylcyclopropanes is formed.\(^{124}\) The discrepancy is attributed to the formation of some singlet methylene in the initial process, which adds stereospecifically to the butene, and is also insensitive to the addition of oxygen. Results show that \(13 \pm 2\%\) of the methylene produced by this method may be in the singlet state. Direct absorption by the ketene could account for this, but it has been estimated that under these conditions only \(2\%\) should arise this way.\(^{128}\) It therefore appears that ca. 10\% of the singlet methylene arises via a reaction which violates the spin conservation rule. This is confirmed by experiments in which competitive quenching of triplet mercury atoms by keten and neopentane produces methylene and neopentyl radicals (215), (216).

\[
\begin{align*}
\text{Hg}(^{(6)P_1}) + \text{CH}_2\text{CO} & \rightarrow & ^{3}\text{CH}_2 + \text{CO} + \text{Hg}(^{1}S_0) \\
\text{Hg}(^{(6)P_1}) + \text{CMe}_4 & \rightarrow & \cdot \text{CH}_3\text{C}(\text{CH}_3)_2 + \text{H} + \text{Hg}(^{1}S_0)
\end{align*}
\] (215) (216)

In the absence of insertion reactions, the fate of the methylene radicals is hydrogen abstraction (217), or reaction with keten to give ethylene (218).

\[
\begin{align*}
^{3}\text{CH}_2 + \text{CMe}_4 & \rightarrow & \cdot \text{Me} + \cdot \text{CH}_2\text{CMe}_3 \\
^{3}\text{CH}_2 + \text{CH}_2\text{CO} & \rightarrow & \text{C}_2\text{H}_4 + \text{CO}
\end{align*}
\] (217) (218)

The radicals so formed disappear by the following reactions:

\[
\begin{align*}
\cdot \text{Me} + \cdot \text{CH}_2\text{CMe}_3 & \rightarrow & \text{MeCH}_2\text{CMe}_3 \\
2\cdot \text{Me} & \rightarrow & \text{C}_2\text{H}_4 \\
2 \cdot \text{CH}_2\text{CMe}_3 & \rightarrow & \text{dimer}
\end{align*}
\] (219) (220) (221)

From collision theory, it would be expected that

\[
k_{218}/(k_{220} k_{221})^4 = 2
\] (222)


From this expression, the yield of dimethylbutane arising via direct insertion may be calculated. Analysis shows that only about half of the dimethylbutane arises from reaction (25), which implies that either $^3\text{CH}_2$ inserts readily or that singlet methylene is also present in the system. Since other studies indicate that $^3\text{CH}_2$ does not readily insert, it must be supposed again that the mercury-photosensitised photolysis of keten can lead to the production of singlet methylene. It may be noted that an interesting novel reaction (223) of triplet methylene was discovered during the course of this investigation.  

\[ ^2\text{CH}_2 + \text{CMe}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{Me}_3\text{C}^- \quad (223) \]

Quenching cross-sections for reactions of mercury (6$^3$P$_1$) atoms and gases can be determined by 'physical' and 'chemical' methods, and in general the results obtained by these different techniques are not consistent. The chemical method involves competitive quenching of mercury atoms by nitrous oxide and the gas under investigation, e.g. in the case of a hydrocarbon RH:

\[ \text{Hg}(6^3P_1) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} + \text{Hg}(6^1S_0) \quad (224) \]
\[ \text{Hg}(6^3P_1) + \text{RH} \rightarrow \text{R}^- + \text{H}^- + \text{Hg}(6^1S_0) \quad (225) \]

These would be followed by

\[ \text{O} + \text{RH} \rightarrow \text{products} \quad (226) \]
\[ \text{H}^- + \text{RH} \rightarrow \text{products} \quad (227) \]

It can be shown that the reciprocal rate of nitrogen production is given by an expression of the type

\[ 1/R_{N_2} = \alpha(1 + \beta[\text{RH}]/[\text{N}_2\text{O}]) \quad (228) \]

where $\beta$ is related to the quenching cross-sections for the two processes by

\[ \frac{\sigma_{\text{RH}}}{\sigma_{\text{N}_2\text{O}}} = \beta \left( \frac{1 + M_{\text{Hg}}/M_{\text{N}_2\text{O}}}{1 + M_{\text{Hg}}/M_{\text{RH}}} \right) \quad (229) \]

Although it has been claimed that the expression (229) holds good over a wide variation in experimental parameters, including light intensity, there is evidence to show that this is not the case in two systems, viz. n-butane and propylene. With these quenching gases, plots of reciprocal nitrogen yield against ratio of hydrocarbon and nitrous oxide pressures yielded straight lines, the slopes of which changed by a factor of 4·7 as the incident light intensity was changed by a factor of 10$^3$. Since there is nothing in expression (229) to indicate that $\beta$ should be dependent upon incident intensity, it seems that the scheme may well be incomplete, and thus values for cross-sections determined by this method must be treated with some caution. Values of $\sigma^2$ for propylene show a spread of values from 11·1 to 40·8 Å$^2$, depending upon $I_o$, the intensity of light absorbed. This dependence

upon $I_a$ may well account for the discrepancies in literature values for $\sigma_{\text{Hg-H}}$, which vary between 29.8 and 46 Å².

Mercury photosensitisation continues to be used as a means of generating excited species and free radicals$^{128-130}$ as well as a method of studying some unusual compounds.$^{131, 132}$ Two primary decomposition processes have been observed in the sensitised decomposition of alkyl mercaptans, one involving $S$–$H$ bond rupture, the other arising from $C$–$S$ split.$^{131}$

$$\text{Hg}(6^3P_1) + \text{RSH} \longrightarrow \text{RS} + \text{H} + \text{Hg}(6^1S_0) \quad (230)$$

$$\text{Hg}(6^3P_1) + \text{RSH} \longrightarrow \text{R} + \text{SH} + \text{Hg}(6^1S_0) \quad (231)$$

In a re-examination of the mercury photosensitisation of cyclopropane,$^{130}$ recent results from several laboratories have been rationalised by the proposal that the initial step is the formation of a vibrationally excited triplet trimethylene species (232).

$$\text{Hg}(6^3P_1) + \Delta \longrightarrow \text{Hg}(6^1S_0) + [\wedge.]^{**} \quad (232)$$

All products, including the major polymer reaction product may then be explained by subsequent reactions of the trimethylene.

No chemical quenching of $\text{Hg}(6^3P_1)$ atoms has been observed by $\text{CF}_4$, $\text{CF}_3\text{H}$, $\text{CF}_2\text{H}_2$,$^{128}$ whereas $\text{CH}_3\text{F}$ gives rise to a variety of fluorinated and non-fluorinated products. The quenching efficiency of octafluorobut-2-ene relative to cis-but-2-ene is small, only 0.15 ± 0.01.$^{133}$ Taking the efficiency of cis-but-2-ene relative to $\text{N}_2\text{O}$ as 2.78,$^{136}$ this gives an efficiency for octafluorobut-2-ene relative to $\text{N}_2\text{O}$ of 0.42, which is somewhat smaller than comparable figures for the relative quenching efficiencies of perfluorocyclobutene and perfluorobuta-1,3-diene of 0.71 and 1.38 respectively.$^{132}$ Mercury photosensitisation of either of these last compounds yields the other, via a common intermediate which reverts competitively to 1,3-$\text{C}_4\text{F}_6$ (86%) and cyclo-$\text{C}_4\text{F}_6$ (14%).

The importance of intensity measurements in mercury-photosensitised reactions has already been mentioned.$^{127}$ Other evidence of the necessity of studying intensity effects is given in a brief report of the decomposition of acetaldehyde.$^{134}$ In the direct photolysis at 3130 Å, the rate of formation of ethane was found to be proportional to the intensity of light absorbed. However, with mercury photosensitisation at 2537 Å, there is no simple dependence upon $I_a$. The results can be explained if it is assumed that at high light intensities a biphotonic process is important, in which an excited acetaldehyde molecule interacts with an excited mercury atom.

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\[ \text{Hg}(6^3P_1) + \text{MeCHO} \rightarrow \text{Hg}(6^1S_0) + \text{MeCHO}^* \quad (233) \]
\[ \text{Hg}(6^3P_1) + \text{MeCHO}^* \rightarrow \text{MeCHO}^{**} + \text{Hg}(6^1S_0) \quad (234) \]

There is no evidence for a doubly excited mercury atom in this system. If it is assumed that the doubly excited acetaldehyde molecule also yields ethane, the observed dependence upon intensity may be explained.

High intensities may also yield results incompatible with those obtained at lower levels of light input through the increased importance of radical–radical reactions under these conditions. Thus it has been demonstrated that in the sensitised decomposition of dimethyl ether,\textsuperscript{135} a probable primary process is the formation of an excited dimethyl ether molecule (235).

\[ \text{Hg}(6^3P_1) + \text{MeOMe} \rightarrow (\text{MeOMe})^* + \text{Hg}(6^1S_0) \quad (235) \]

However, excited ether molecules may also be formed via a radical–atom recombination (236).

\[ \text{H}^* + \cdot \text{CH}_2\text{OMe} \rightarrow (\text{MeOMe})^* \quad (236) \]

Since reaction (236) may be very important at high light intensities, a proper account of such reactions may be taken in any interpretation of results.

Mercury has long been used as an efficient energy transfer agent in the gas phase, although other atoms have excited states which lie at convenient energy differences from their ground states. Thus zinc and cadmium both have \( ^3P_1 \) states which are reached by absorption of 3076 and 3261 Å radiation respectively. The main obstacle to their use is the low vapour pressure of these metals at ambient temperatures, and the consequent use of high temperatures to produce a concentration of atoms sufficient to provide significant absorption. This increases the danger of complicating thermal reactions in many systems. Nevertheless, both metals have been used to photosensitise the reactions of several compounds recently.\textsuperscript{134–140}

A comparison is possible between the results of the zinc\textsuperscript{136} and cadmium\textsuperscript{137} photosensitised reactions of cis, trans, and geminal \([\text{H}_2\text{]}\)ethylenes at 325\(^\circ\). In the case of the more energetic zinc photosensitisation, cis→trans isomerisation is the most important reaction, with isomerisation to the geminal dideuterioethylene a very slow process by comparison. The quantum yield of cis→trans isomerisation was pressure dependent, and reached >20 at a pressure of 40 torr, indicating a chain reaction. In contrast, cis→trans isomerisation and intramolecular hydrogen scrambling were the only processes observed in the cadmium photosensitisation,\textsuperscript{137} with a total quantum yield of unity. Trace amounts of acetylene (\( \Phi \sim 10^{-9} \)) were also found; the yields decreased with increasing pressure.

The results are explained by the following reaction sequence:

\[
\begin{align*}
\text{Cd}(^3P_1) + E & \longrightarrow E^* + \text{Cd} \quad (237) \\
E^* & \longrightarrow E_c + E_t \\
E^* & \longrightarrow E^{**} \\
E^{**} & \longrightarrow E^*_g \\
E^* & \longrightarrow E_c + E_t + E_g \\
E^{**} & \longrightarrow E^+ \\
E^+ & \longrightarrow E_c + E_t + E_g \\
E^+ & \longrightarrow C_2H_2 + H_2 \\
\end{align*}
\]

where \( E_c = \text{cis-[}^3\text{H}_2\text{]} \text{ethylene} \), \( E_t = \text{trans-[}^3\text{H}_2\text{]} \text{ethylene} \), \( E_g \) = geminal \([^3\text{H}_2]\)ethylene, \( E^* \) = triplet ethylene, \( E^{**} \) = triplet ethylidyne, \( E^*_g \) = triplet ethylene with scrambling of deuterium atoms, and \( E^+ \) = vibrationally excited ground-state ethylene.

If reaction (242) is assumed to be unimportant, and the probabilities of formation of \textit{cis}, \textit{trans}, and geminal \([^3\text{H}_2]\)ethylene from \( E^*_g \) are equal, it can be shown that:

\[
\frac{1}{\Phi_g} = 3(1 + k_{235}/k_{236}). 
\]  
(245)

Note that \( k_{236} \) is not a true rate constant, since the step is pressure dependent; but extrapolation to zero pressure yields an intercept of 3.7 rather than the 3 predicted by equation (245). Thus the probability of formation of geminal \([^3\text{H}_2]\)ethylene is rather less than \( \frac{1}{3} \).

But-2-ene has also been studied as a quencher of \(^{136}\text{Cd}\) and \(^{138}\text{Zn}\) triplet atoms. In the former case, a dark \textit{cis–trans} isomerisation reaction was observed which was quenched by the addition of small amounts of acetylene. Thus the excited cadmium atoms react with acetylene to produce species which catalyse the \textit{cis–trans} isomerisation of the butene. The nature of this reaction has been the subject of an investigation at slightly lower temperatures (270°).\(^{138}\) The main stable products from the reaction are benzene and vinylacetylene. A mechanism is proposed in which successive quenching of excited monomeric and dimeric acetylene species yields the observed products (246)–(255).

\[
\begin{align*}
\text{Cd}(^3P_1) + A & \longrightarrow \text{CdA}^* \\
\text{CdA}^* & \longrightarrow \text{Cd} + A_1^* \\
\text{CdA}^* + A & \longrightarrow \text{Cd} + 2A \\
A + A_1^* & \longrightarrow A_2^* \\
& \longrightarrow 2A \\
A_3^* + A & \longrightarrow A_3^* \\
A_3^* & \longrightarrow 3A \\
& \longrightarrow C_4H_4 + A \\
\end{align*}
\]
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\[ \text{C}_6\text{H}_6 \quad (254) \]

\[ \text{A}_3^* + \text{A} \quad \rightarrow \quad \text{C}_6\text{H}_6 + \text{A} \quad (255) \]

A steady-state treatment gives the following expression:

\[ \left( \Phi_{\text{C}_6\text{H}_6}/\Phi_{\text{C}_4\text{H}_4} \right) = (k_{254}/k_{252}) + (k_{255}/k_{253})[\text{A}] \quad (256) \]

Although plots of \( \Phi_{\text{C}_6\text{H}_6}/\Phi_{\text{C}_4\text{H}_4} \) against acetylene pressure yield reasonably straight lines, the authors appear to ignore the possibility that \( \text{A}_3^* \) can react directly to give products. Presumably it is the excited species outlined above which are responsible for the sensitisation of but-2-ene isomerisation.\(^\text{138}\) The quenching efficiencies of 16 hydrocarbons relative to \( \text{cis}-\text{but}-2\)-ene for \( \text{Cd}(^2\text{P}_1) \) atoms have been tabulated.\(^\text{140}\) All olefins studied had almost the same efficiency as the but-2-ene, but saturated hydrocarbons were extremely inefficient quenchers. Competition between \( \text{cis}-\text{but}-2\)-ene and benzene\(^\text{138}\) for the quenching of \( \text{Cd}(^2\text{P}_1) \) atoms at 590 K leads to the conclusion that energy is transferred from the metal atom to the benzene, populating the lowest triplet state. This in turn may transfer triplet energy to the olefin, causing \( \text{cis} \)-\( \text{trans} \) isomerisation (see section 2 on aromatics, this Chapter).

Mercury-photosensitised reactions of large organic molecules, such as nor-camphor\(^\text{141}\) and hexa-1,5-diene\(^\text{142}\) (see Part III ch. 3) include eliminations, and in the photosensitisation of hydrazine,\(^\text{143}\) transients such as \( \text{N}_2\text{H}_3 \), \( \text{N}_2\text{H}_4 \), \( \text{NH}_2 \), and \( \text{NH} \) have been detected by mass spectrometry. Two primary decomposition processes were established.

\[ \text{Hg}(^2\text{P}_1) + \text{N}_2\text{H}_4 \quad \rightarrow \quad \cdot\text{NH}_3 + \cdot\text{NH}_2 + \text{Hg}(^6\text{S}_0) \quad (257) \]

\[ \text{Hg}(^2\text{P}_1) + \text{N}_2\text{H}_4 \quad \rightarrow \quad \cdot\text{N}_2\text{H}_3 + \cdot\text{H} + \text{Hg}(^6\text{S}_0) \quad (258) \]

10 Vacuum-ultraviolet Photochemistry

Absorption of radiation in the wavelength region shorter than 2000 Å can produce excited states of molecules, or if the energy of the photon is sufficient may ionise the molecule. Considerable interest in the latter process has developed, and the dramatic increase in volume of work published in the area may be due in part to the rising interest in photoelectron spectroscopy. Vacuum-u.v. photochemistry provides a useful link between the chemistry of molecules absorbing low-energy photons in the u.v. and visible regions, and the kind of process observed when molecules are subjected to high energy radiation.

Because air absorbs radiation of wavelengths shorter than \( \text{ca.} \ 2000 \) Å, special techniques must be used.\(^\text{144}\) The sources of radiation used in such experiments are generally low-pressure resonance lines of noble gases. The wavelength and energy of some commonly used lamps are shown in


Table 4, together with those of singlet excited mercury atoms, radiation from which lies just in the vacuum-u.v. region.

Table 4  Resonance lines of Hg(6^1P_1) and noble gases

<table>
<thead>
<tr>
<th>Vapour</th>
<th>Wavelength (Å)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(6^1P_1)</td>
<td>1849</td>
<td>6.7</td>
</tr>
<tr>
<td>Xenon</td>
<td>1470</td>
<td>8.4</td>
</tr>
<tr>
<td>Krypton</td>
<td>1236</td>
<td>10.0</td>
</tr>
<tr>
<td>Argon</td>
<td>1048—1067</td>
<td>11.81—11.60</td>
</tr>
<tr>
<td>Helium</td>
<td>584</td>
<td>21.21</td>
</tr>
</tbody>
</table>

The interaction of radiation in this wavelength region with diatomic and triatomic molecules is mainly of spectroscopic interest. Several groups of workers have studied the photoionisation and photodissociation of the H₂ molecule. Data obtained support the idea that vibration–rotation interaction must be considered in calculations of Franck–Condon factors for small molecules. The appearance potentials for different ionic states produced in the dissociative photoionisation of oxygen have been measured mass-spectrometrically.

Visible emission is produced from CO excited at 1470 Å directly and in the presence of xenon. In the direct absorption case, the emission can be attributed to fluorescence from the d²∆ r=γ level initially excited to the a²π state (see Figure 3), whereas in the cases of xenon sensitisation, emission is observed from various vibrational levels of d²Δ, e¹Σ, and a¹³Σ states. Evidence is presented that there is a precursor to the emitting CO molecule which is presumably a collision complex of the excited Xe atom (³P₁) and CO. The complex has a lifetime of 2 × 10⁻⁶ s, and the reaction appears to occur on every collision.

Franck–Condon factors for the photoionisation of carbon dioxide have been considered. The photolysis of this molecule at 1470 and 1236 Å between 25 and 100 °C shows CO:O₂ ratios decreasing with increasing pressure of CO₂, levelling off at ca. 5, a value which is then independent of both temperature and pressure. At least at the longer wavelength, the primary processes are:

\[
\text{CO}_2 + h\nu \rightarrow \text{CO}_2(^1\Delta_r) \quad (259)
\]

\[
\text{CO}_2(^1\Delta_r) \rightarrow \text{CO}(^1\Sigma) + O(^1D) \quad (260)
\]

It is proposed that in addition to reactions of O(^1D) usually considered, the following reaction may be important on the walls.


CO₂ may be adsorbed on to the OH radicals produced in reaction (261).

Electronic transitions of SO₂ in the vacuum-u.v. region¹⁵⁰ and the primary processes occurring in the photolysis of this compound at 1849 Å have been investigated.¹⁵¹ Oxides of nitrogen have also attracted attention. The photolysis of NO at 1470 Å¹⁵² produces emission from a number of upper states of NO to the A²Σ, B²Π, C²Π, and D²Σ states.¹⁵³ Oxygen excited at the same wavelength produces emission only from the atmospheric bands. The emitting species, O₆(³Σ⁺), is presumably formed via quenching of O(¹D) atoms formed upon absorption.¹⁵³

\[
\begin{align*}
O₆ + hν & \rightarrow O(³P) + O(¹D) \quad (262) \\
O(¹D) + O₂ & \rightarrow O₂(²Σ₆⁺) + O(³P) \quad (263)
\end{align*}
\]

The rate of reaction of O(¹D) with a variety of gases was found to be the same, viz. \(4 \times 10^{-11}\) ml molecule\(^{-1}\) s\(^{-1}\).¹⁵³

The absorption coefficients for photoionisation transitions in N₂O have been determined.¹⁵⁴ At 1470 Å, several primary dissociative processes are possible.¹⁵⁵

---

\[ \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2(\text{X}^1\Sigma) + \text{O}(^{3}P) \] (264)

\[ \rightarrow \text{N}_2(\text{X}^1\Sigma) + \text{O}(^{1}D) \] (265)

\[ \rightarrow \text{N}_2(\text{X}^1\Sigma) + \text{O}(^{1}S) \] (266)

\[ \rightarrow \text{N}_2(\text{A}^3\Sigma) + \text{O}(^{3}P) \] (267)

\[ \rightarrow \text{NO}(^{2}\pi) + \text{N}(^{4}S) \] (268)

\[ \rightarrow \text{NO}(^{2}\pi) + \text{N}(^{2}D) \] (269)

The total quantum yield of atoms formed was unity. \( \text{O}(^{1}S) \) was produced with a quantum yield of 0.5, and the measured quantum yield of \( \text{O}(^{1}D) \) was 0.55, although this may include atoms which are quenched from the \( \text{O}(^{1}S) \) state. The \( \text{N}_2(\text{A}^3\Sigma) \) state had a quantum yield of formation of 0.08, and thus the \( \text{O}(^{3}P) \) concentration must also be 0.08, if reaction (264) is discounted on spin conservation considerations. \( \text{N}(^{2}D) \) is produced which reacts inefficiently with \( \text{N}_2\text{O} \) (270).

\[ \text{N}(^{2}D) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO}(^{2}\pi) \] (270)

Photolysis of mixtures of hydrazine and hydrazine \(^{15}\text{N} \) at 1470 Å results in the formation of isotopic nitrogens which are only 13% randomised. The initial step in the process is the molecular elimination of hydrogen (271),

\[ \text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_2 + \text{H}_2 \] (271)

or the formation of excited \( \text{N}_2\text{H}_3 \) and a hydrogen atom,

\[ \text{N}_2\text{H}_4 + h\nu \rightarrow \cdot \text{N}_2\text{H}_3^* + \cdot \text{H} \] (272)

followed by decomposition of the \( \text{N}_2\text{H}_3 \) radical.

\[ \cdot \text{N}_2\text{H}_3^* \rightarrow \text{N}_2\text{H}_2 + \text{H} \cdot \] (273)

\( \text{N}_2\text{H}_2 \) formed by either step will then dissociate to nitrogen and hydrogen:

\[ \text{N}_2\text{H}_2 \rightarrow \text{N}_2 + \text{H}_2 \] (274)

\( \text{N}_2\text{H}_2 \) may also be formed by radical–radical processes

\[ 2\cdot \text{N}_2\text{H}_3 \rightarrow \text{N}_2\text{H}_3 + \text{N}_2\text{H}_4 \] (275)

\[ \cdot \text{N}_2\text{H}_3 + \cdot \text{NH}_2 \rightarrow \text{N}_2\text{H}_2 + \text{NH}_3 \] (276)

By using \(^{14}\text{NO} \) to quench out radical processes, and only \(^{15}\text{N}\)hydrazine, the relative importance of the molecular elimination step could be determined.

\[ \cdot \text{N}_2\text{H}_3 + \text{NO} \rightarrow \text{N}_2\text{O} + \text{NH}_3 \] (277)

\[ ^{15}\text{NH}_2 \cdot + ^{14}\text{NO} \rightarrow ^{28}\text{N}_2 + \text{H}_2\text{O} \] (278)

The \( \text{N}_2 \) formed in (278) has a different isotopic distribution from that formed in (274). In the presence of \(^{14}\text{NO} \), the limiting value of \( ^{28}\text{N}_2/^{30}\text{N}_2 \) was found to be close to two, suggesting that (271) represents the major mode of breakdown of the hydrazine, since (272) followed by (273) would lead to a limiting value for this ratio of unity. The randomised nitrogen observed arises from combination of radicals, as follows:
Gas-phase Photochemistry

\[ ^{30}\text{N}_2\text{H}_3^\cdot + ^{28}\text{N}_2\text{H}_3^\cdot \rightarrow ^{28}\text{N}_2 + ^{15}\text{NH}_3 + ^{14}\text{NH}_3 \]  
\[ (279) \]

\[ ^{14}\text{NH}_2^\cdot + ^{15}\text{NH}_2^\cdot \rightarrow ^{28}\text{N}_2 + 2\text{H}_2 \]  
\[ (280) \]

The ratio of disproportionation (275, 276) to combination (279, 280) was found to be ca. 5. In the presence of \(^{14}\)NO, photolysis of hydrazine \(^{15}\)N produces a significant amount of \(^{28}\)N\(_2\). This is assumed to arise from the initial breakdown (272), followed by processes (281—283).

\[ \text{H} + ^{14}\text{NO} + \text{M} \rightarrow \text{H}^{14}\text{NO} + \text{M} \]  
\[ (281) \]

\[ \text{H}^{14}\text{NO} + 2^{14}\text{NO} \rightarrow ^{28}\text{N}_2 + \text{H} + ^{14}\text{NO}_3 \]  
\[ (282) \]

or

\[ \text{H}^{14}\text{NO} + 2^{14}\text{NO} \rightarrow ^{28}\text{N}_2 + \text{H}^{14}\text{NO}_3 \]  
\[ (283) \]

Emission from a number of nitrogen-containing species excited in the vacuum-u.v. region has been observed.\textsuperscript{156—158} The method of detection of fluorescence from CN(\(^2\Sigma^+\)) from various cyanogen compounds has been used to measure the bond dissociation energies in these compounds.\textsuperscript{158}

Vacuum-u.v. Photolysis of Alkanes.—A mass spectrometric study of the photoionisation of methane has revealed that near the threshold for CH\(_3^+\) production an ion pair process,

\[ \text{CH}_4 + h\nu \rightarrow \text{CH}_3^+ + \text{H}^- \]  
\[ (284) \]

occurs in addition to the usual photodissociative process.\textsuperscript{159}

\[ \text{CH}_4 + h\nu \rightarrow \text{CH}_3^+ + \text{H}^- + e^- \]  
\[ (285) \]

The difference in energies between the two processes agrees well with the electron affinity of the hydrogen atom (0.754 ev). It has been proposed that rotational energy may contribute significantly to the breaking of the C—H bond in the CH\(_4\) molecule.\textsuperscript{159}

The products arising from methane photolysis at 584 Å\textsuperscript{160, 161} differ significantly from those observed at longer wavelengths.\textsuperscript{162} The source of 584 Å radiation also emits the 1216 Å hydrogen Lyman \(\alpha\) line which is difficult to remove owing to diffusion of hydrogen from hot elements within the lamps. However, the use of an aluminium foil filter (200—400 nm in thickness) to isolate the 584 Å line has been reported.\textsuperscript{160, 161}

The initial process upon absorption is the ionisation of the methane molecule.

\[ \text{CH}_4 + h\nu \rightarrow [\text{CH}_4^+]^0 + e^- \]  
\[ (286) \]

There is evidence that the quantum yield for this process is 0.95.\textsuperscript{161} It should be noted that the electrons released in process (286) have only a maximum of 8.5 ev energy, and therefore do not cause collisional electronic excitation of the methane.

\textsuperscript{159} W. A. Chupka, \textit{J. Chem. Phys.}, 1968, 48, 2337.
The methane parent ions may dissociate (287, 288) or react with neutral methane molecules (289), as follows:\textsuperscript{160,161}

\[
\begin{align*}
[\text{CH}_4^+]^* & \longrightarrow \text{CH}_4^+ + \text{H}^- \quad (287) \\
[\text{CH}_4^+]^* & \longrightarrow \text{CH}_2^+ + \text{H}_2 \quad (288) \\
\text{CH}_4^+ + \text{CH}_4 & \longrightarrow \text{CH}_5^+ + \cdot \text{CH}_3 \quad (289)
\end{align*}
\]

In the presence of 5\% added \textsuperscript{12}H\textsubscript{10}isobutane and NO as a free radical scavenger, reactions (290—293) occur:\textsuperscript{161}

\[
\begin{align*}
\text{CH}_3^+ + \text{CH}_4 & \longrightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \quad (290) \\
\text{C}_2\text{H}_5^+ + \cdot \text{C}_4\text{D}_{10} & \longrightarrow \text{C}_2\text{H}_5\text{D} + \text{C}_4\text{D}_9^+ \quad (291) \\
\text{CH}_6^+ + \cdot \text{C}_4\text{D}_{10} & \longrightarrow \text{CH}_4 + \text{C}_2\text{D}_{10}\text{H}^+ \\
& \longrightarrow \text{CH}_4 + \text{C}_2\text{H}_5\text{H} + \text{C}_3\text{D}_7^+ \quad (292) \\
\text{C}_4\text{D}_7^+ + \cdot \text{C}_4\text{D}_{10} & \longrightarrow \text{C}_2\text{D}_8^+ + \text{C}_4\text{D}_9^+ \quad (293)
\end{align*}
\]

Thus an estimate of the amount of CD\textsubscript{3}H and C\textsubscript{2}H\textsubscript{5}D formed in the system give a value of 0.85 for the ratio CH\textsubscript{4}+:CH\textsubscript{3}+ which is close to the literature values (see ref. 161). Different CH\textsubscript{4}+:CH\textsubscript{3}+ ratios could be measured by sensitising the photolysis of methane with rare gases. By use of a rare gas: methane ratio of 10, and a total pressure of gas of 15 torr, methane ions are formed mainly by charge transfer.

\[
\begin{align*}
\text{A} + h\nu & \longrightarrow \text{A}^+ + e^- \quad (294) \\
\text{A}^+ + \text{CH}_4 & \longrightarrow [\text{CH}_4^+]^* + \text{A} \quad (295)
\end{align*}
\]

The CH\textsubscript{4}+:CH\textsubscript{3}+ ratios for Kr\textsuperscript{+} (14.00—14.66 ev) and Ar\textsuperscript{+} (15.76—15.93 ev) were 1.25 and <0.07 respectively. Results indicated that reaction (294) was very efficient. In the absence of added gases, reactions (286) to (290) are followed by:

\[
\begin{align*}
\text{CH}_2^+ + \text{CH}_4 & \longrightarrow \text{C}_2\text{H}_4^+ + \text{H}_2 \quad (296) \\
& \longrightarrow \text{C}_2\text{H}_3^+ + \text{H}_2 + \cdot \text{H} \quad (297)
\end{align*}
\]

In addition to the ions already mentioned, small amounts of CH\textsuperscript{+} and C\textsuperscript{+} may also be present, and also neutral fragments such as CH and C. These will also be reactive.

\[
\begin{align*}
\text{CH}^+ + \text{CH}_4 & \longrightarrow \text{C}_2\text{H}_2^+ + \text{H}_2 + \cdot \text{H} \quad (298) \\
\text{C}^+ + \text{CH}_4 & \longrightarrow ? \quad (299) \\
\text{CH} + \text{CH}_4 & \longrightarrow \text{C}_2\text{H}_4 + \cdot \text{H} \quad (300) \\
\text{C} + \text{CH}_4 & \longrightarrow ? \quad (301)
\end{align*}
\]

A study of the stable products arising from further reactions\textsuperscript{160} reveals that the major products are hydrogen (\(\Phi = 0.45\)), ethylene (\(\Phi = 0.07\)), and a polymeric material (\(\Phi = 0.30\)), as well as several hydrocarbons up to C\textsubscript{7}. If it is assumed that reaction (300) is the sole source of ethylene, and the quantum yield of ionisation of methane at 584 Å is taken as 0.95,\textsuperscript{161} it may
then be assumed that CH is the only neutral fragment formed, and thus reaction (301) is unnecessary. The precursors of the polymeric material observed may be CH$_3^+$, CH$^+$, or C$^+$.

Photolysis of methane in the longer wavelength region at 1236 Å does not give rise to ion formation.$^{142}$ Previously results have shown that hydrogen, the major product, is formed chiefly by the molecular elimination process.

$$\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H}_2$$  \hspace{1cm} (302)

with the remainder of the hydrogen being formed in either of the steps (303) or (304).

$$\text{CH}_4 + h\nu \rightarrow \cdot \text{CH}_3 + \text{H}.$$ \hspace{1cm} (303)

$$\text{CH}_4 + h\nu \rightarrow \text{CH}$$. + $\text{H}_2 + \text{H}.$ \hspace{1cm} (304)

An accurate estimation of the relative importance of such processes has been made using a split-cell technique.$^{145}$ in which CH$_4$ and CD$_4$ were photolyzed simultaneously at 1236 Å. This method of determination of relative quantum yields using the split cell merits special mention. Ethylene and $^4$H$_4$ethylene were used as a standard, since in photolysis at 1236 Å hydrogen results only from the primary process. Calling the two halves of the cell, cell I and cell II respectively, with C$_3$H$_4$ in cell I and C$_3$D$_4$ in cell II, the H$_2$ produced in I is

$$I_{H_2} = \Phi_{H_2} I_\text{SL}$$ \hspace{1cm} (305)

where $\Phi_{H_2}$ = quantum yield of H$_2$ from C$_3$H$_4$, and $I_\text{SL}$ is the light absorbed in cell I. If the pressure is high, $I_\text{SL} = I_\text{OL}$.

Similarly

$$I_{D_2} = \Phi_{D_2} I_\text{OL}.$$ \hspace{1cm} (306)

The measured H$_2$:D$_2$ ratio is therefore:

$$[\text{H}_2 : \text{D}_2]_\text{I,II} = \frac{\Phi_{H_2} I_\text{OL}}{\Phi_{D_2} I_\text{OL}}$$ \hspace{1cm} (307)

when the cells are reversed the following ratio is obtained:

$$[\text{H}_2 : \text{D}_2]_\text{II, I} = \frac{\Phi_{H_2} I_\text{OL}}{\Phi_{D_2} I_\text{OL}}$$ \hspace{1cm} (308)

Thus

$$I_\text{OL}/I_\text{OL} = [(\text{H}_2/\text{D}_2)_\text{I,II}]/[(\text{H}_2/\text{D}_2)_\text{II, I}]$$ \hspace{1cm} (309)

assuming the $\Phi$'s are independent of intensity. The elegance of this method is that the relationship is valid, even if the light intensity varies during a run, or the light intensity is different for the II, I case from the I, II case. In experiments using C$_3$H$_4$ and C$_3$D$_4$ as scavengers for D and H atoms respectively, mixtures of CH$_4$ and C$_3$D$_4$ and CD$_4$ and C$_2$H$_4$ were photolyzed first in cell I then in cell II. Results indicate that

$$\Phi_{H_4}(\text{M})/\Phi_{D_4}(\text{M}) = 1.02 \pm 0.02 \quad (\text{M} = \text{molecular})$$

i.e. the quantum yields of formation of hydrogen and deuterium by molecular processes are the same. In the absence of scavengers the ratio of
quantum yields is 1.18. Using a CO₂ actinometer, it has been shown that Φ_H₂(M) = 0.58, and Φ_H₂(atomic) = 0.21. Similarly Φ_D₂(M) = 0.57 and Φ_D₂(atomic) = 0.09.

The results indicate that a significant fraction of the atoms produced disappear via association reactions such as:

\[ M + H \cdot + \cdot CH₃ \rightarrow CH₄ + M \]  

(310)

Also, since the measured total quantum yield for H₂ and H formation is greater than unity, fragmentation of CH₂ or \( \cdot CH₃ \) formed in the primary process is suggested.

\[ \cdot CH₃ \rightarrow \cdot H + CH₂ \]  

(311)

\[ CH₂ \rightarrow \cdot H + \cdot CH \]  

(312)

The combined yield of D₂ + D is much lower, suggesting that fragmentation of \( \cdot CD₃ \) and CD₂ is much less important than in the protium species.

Acetylene photolyzed at 1470 Å yields ethylene and diacetylene as the main products. If methane is added, ethane and propylene are also formed.⁶³ These arise via radicals formed by collision of the excited acetylene molecule with methane. The following competition exists:

\[ C₂H₄⁺ + C₂H₂ \rightarrow C₄H₂ + 2H⁺ \]  

(313)

\[ C₂H₄⁺ + CH₄ \rightarrow C₂H₂ + \cdot CH₃ + H⁺ \]  

or \[ \cdot C₂H₃ + \cdot CH₃ \]  

(314)

Using deuterated species the relative importance of reactions (313) and (314) can be determined, and the ratio of rate constants is estimated to be

\[ k_{321}/k_{322} \approx 10^8 \]

The processes subsequent to absorption of 1470 Å resonance radiation are summarised by equations (315)—(318).⁶⁴

\[ Xe(^3S₀) + h\nu(1470 Å) \rightarrow Xe(^3P₁) \]  

(315)

\[ Xe(^3P₁) \rightarrow Xe(^3S₀) + h\nu \]  

(316)

\[ Xe(^3P₁) + nXe \rightarrow Xe₂⁺ + (n-1)Xe \]  

(317)

\[ Xe₂⁺ \rightarrow 2Xe + \text{continuum} \]  

(318)

Step (317) probably includes formation of the xenon metastable atom Xe(^3P₂). Addition of methane to the system causes breakdown of the added alkane. It seems likely that collision of Xe(^3P₁) atoms with methane leads to the molecular split to CH₂ and H₂, whereas quenching of the metastable Xe(^3P₂) atoms tends to favour C—H cleavage. A transient species is proposed which behaves as a freely diffusing H atom: this is presumably XeH.

\[ Xe⁺ + CH₄ \rightarrow XeH + \cdot CH₃ \]  

(319)

---


The photolysis of a number of hydrocarbons at wavelengths produced by the rare gas resonance lamps has been described. The interest here has been to compare the mode of decomposition of molecules excited below their ionisation limits (at the longer wavelengths) with the mode when excited just above the ionisation limit where a so-called 'superexcited' molecule is formed. In all cases the hydrocarbon species were irradiated in the presence of O₂ and NO as radical scavengers, and a technique used to determine the importance of molecular processes in which the deuterated analogues of the hydrocarbons were irradiated in the presence of H₂S. In this case, D atoms and fully deuterated alkyl radicals are scavenged by the H₂S to form HD and RₓD respectively, whereas molecular products arising from unimolecular elimination processes are seen as fully deuterated molecules.

\[ \cdot R_D + H_2S \rightarrow R_DH + HS^- \]  

(320)

This technique gives rise to higher quantum yields of D atom production than in the study previously mentioned, since here all D atoms are scavenged by the H₂S, and none are lost via reactions such as (310).

At 1470 and 1236 Å, cyclopropane is excited below the ionisation limit (ionisation energy = 10·06 ev). Use of the techniques described above shows that the major primary mode of decomposition of the neutral excited cyclopropane molecule can be written as,

\[ \text{cyclo-C}_3\text{H}_6 + h\nu \rightarrow \cdot \text{CH}_2\text{CH}_2\text{CH}_2^- \]  

(321)

The highly excited trimethylene diradical decomposes in two ways.

\[ \cdot \text{CH}_2\text{CH}_2\text{CH}_2^- \rightarrow \text{C}_3\text{H}_4 + \text{CH}_3 \]  

(322)

\[ \cdot \text{CH}_2\text{CH}_2\text{CH}_2^- \rightarrow \text{C}_3\text{H}_4 + 2\text{H}^- \]  

(323)

There is also evidence of the rearrangement of \( \cdot \text{CH}_2\text{CH}_2\text{CH}_2^- \) to an excited propylene molecule, which fragments at low pressures. The primary molecular elimination process

\[ \text{cyclo-C}_3\text{H}_6 + h\nu \rightarrow \text{C}_3\text{H}_4 + \text{H}_2 \]  

(324)

is shown to be of negligible importance. At 1236 Å, the quantum yield of decomposition of the excited cyclopropane molecules is unity, within experimental error.

Below 1048 Å, \( \text{C}_3\text{H}_6^+ \) ions are formed which, although they have as much as 1·5 ev internal energy, do not fragment. The quantum yield of photoionisation (\( \eta \)) was determined as 0·405, based on the figure for NO of 0·71. The yield for \( \text{C}_5\text{D}_6 \) was somewhat higher, \( \text{viz.} 0·415 \). The \( \text{C}_3\text{H}_6^+ \) ion may react by four different routes with cyclopropane

\[ \text{C}_5\text{H}_6^+ + \text{C}_3\text{H}_6 \rightarrow \text{C}_5\text{H}_7^+ + \text{C}_3\text{H}_5^- \]  

(325)

\[ \rightarrow \text{C}_5\text{H}_6^+ + \cdot \text{CH}_3 \]  

(326)

Evidence is presented that ca. 30% of the C₃H₆⁺ ions undergo reaction (328). Photoionisation of cyclopropane–NO mixtures leads to the conclusion that charge-transfer processes (329) and (330) are important at 1040—1067 Å.

\[
\begin{align*}
\text{C}_3\text{H}_6 + \text{NO} & \longrightarrow \text{C}_3\text{H}_6 + \text{NO}^+ + e^- \quad (329) \\
(\text{NO}^+)^* + \text{C}_3\text{H}_6 & \longrightarrow \text{C}_3\text{H}_6^+ + \text{NO} \quad (330)
\end{align*}
\]

Such reactions produce propylene eventually, through an unknown mechanism [(NO⁺)* is a vibrationally excited NO⁺ ion].

A similar study on isobutane and deuterated isobutanes has shown that the neutral excited isobutane molecule decomposes in the following ways:

\[
\begin{align*}
\text{i-C}_4\text{H}_{10}^* & \longrightarrow \text{CH}_4 + \text{C}_3\text{H}_6 \quad (331) \\
& \longrightarrow \text{C}_3\text{H}_8 + \text{CH}_2 \quad (332) \\
& \longrightarrow \cdot \text{CH}_3 + s - \text{C}_3\text{H}_7 \cdot \quad (333) \\
& \longrightarrow \text{H}_2 + \text{i-C}_4\text{H}_8 \quad (334)
\end{align*}
\]

Most of the propyl radicals decompose further

\[
\begin{align*}
\cdot \text{C}_3\text{H}_7 & \longrightarrow \cdot \text{H} + \text{C}_3\text{H}_6 \quad (335) \\
& \longrightarrow \cdot \text{CH}_3 + \text{C}_4\text{H}_4 \quad (336)
\end{align*}
\]

Increase in photon energy increases C—C cleavage reactions.

At the shortest wavelength ionisation is a possibility, either directly or via a ‘superexcited’ molecule.

\[
\begin{align*}
\text{i-C}_4\text{H}_{10} + h\nu & \longrightarrow [\text{i-C}_4\text{H}_{10}^+]^* + e^- \quad (337) \\
\text{i-C}_4\text{H}_{10} + h\nu & \longrightarrow \text{i-C}_4\text{H}_{10}^* \quad (338) \\
\text{i-C}_4\text{H}_{10}^* & \longrightarrow [\text{i-C}_4\text{H}_{10}^+]^* + e^- \quad (339) \\
\text{i-C}_4\text{H}_{10}^* & \longrightarrow \text{neutral fragments} \quad (340)
\end{align*}
\]

The ions formed in (337) or (339) have sufficient energy to fragment.

\[
\begin{align*}
[\text{i-C}_4\text{H}_{10}^+]^* & \longrightarrow \cdot \text{CH}_3 + \text{C}_3\text{H}_7^+ \quad (341) \\
& \longrightarrow \text{CH}_4 + \text{C}_3\text{H}_6^+ \quad (342)
\end{align*}
\]

These ions can then react with the parent compound.

\[
\begin{align*}
\text{C}_3\text{H}_7^+ + \text{i-C}_4\text{H}_{10} & \longrightarrow \text{C}_5\text{H}_8 + \text{C}_4\text{H}_8^+ \quad (343) \\
\text{C}_3\text{H}_6^+ + \text{i-C}_4\text{H}_{10} & \longrightarrow \text{C}_5\text{H}_8 + \text{C}_4\text{H}_8^+ \quad (344) \\
& \longrightarrow \cdot \text{C}_3\text{H}_7 + \text{C}_4\text{H}_8^+ \quad (345)
\end{align*}
\]

From the effects of O₃ and NO, it is evident that the polymer which is formed on the window at the shortest wavelengths arises from free-radical reactions, in contrast with the ionic mechanism proposed in the photolysis
of methane. Evidence is presented that reaction (345) is 1.5 times more rapid than (344).

At 1849 Å in the presence of mercury, cyclobutane (c-C₄H₈) decomposes to give radicals (346) or an excited singlet state of the alkane (347).

$$\text{Hg}^0 + \text{c-C}_4\text{H}_8 \rightarrow \text{Hg}^0 + \text{c-C}_4\text{H}_7 + \text{H}$$  \hspace{1cm} (346)

$$\text{Hg}^0 + \text{c-C}_4\text{H}_8 \rightarrow \text{Hg}^0 + \text{c-C}_4\text{H}_8^*$$  \hspace{1cm} (347)

The excited molecule formed in reaction (347) may decompose to two molecules of ethylene, or split in other ways.

$$\text{c-C}_4\text{H}_8^* \rightarrow 2\text{C}_2\text{H}_4$$  \hspace{1cm} (348)

$$\text{c-C}_4\text{H}_8^* \rightarrow \text{H} + \text{c-C}_4\text{H}_7^*$$  \hspace{1cm} (349)

$$\rightarrow \text{H}_2 + \text{c-C}_4\text{H}_6 \text{ or C}_4\text{H}_6$$  \hspace{1cm} (350)

$$\rightarrow \text{CH}_3 + \text{C}_3\text{H}_6$$  \hspace{1cm} (351)

The pressure dependence of the yields of products arising from reaction (348) is different from those arising from reactions (349)—(351), and thus different excited states are probably involved. Since (349)—(351) are quenched by increasing pressure, the precursor may well be a highly vibrationally excited state of the alkane, whereas the precursor in (348) is probably the electronically excited singlet state.

Cyclohexane (ionisation potential = 9.88 eV) can form ions and superexcited molecules at the two shortest wavelengths, but forms only neutral excited species at 1470 Å. The primary mode of decomposition at 1470 Å is molecular elimination of hydrogen, giving rise to an internally excited C₆H₁₀ species, which can either dissociate or be stabilised by collision.

$$\text{c-C}_6\text{H}_{12}^* \rightarrow \text{C}_6\text{H}_{10}^+ + \text{H}_2$$  \hspace{1cm} (352)

$$\text{C}_6\text{H}_{10}^+ \rightarrow 1,3-\text{C}_4\text{H}_6 + \text{C}_2\text{H}_4$$  \hspace{1cm} (353)

$$\rightarrow \text{C}_6\text{H}_{10} + \text{M}$$  \hspace{1cm} (354)

The product of reaction (354) is largely cyclohexene. The process (353) is readily quenched by increase of pressure, but at higher photon energies little pressure effect is seen.

At 1236 and 1048—1067 Å, ions or superexcited molecules may be formed. The ions formed at 1236 Å do not have sufficient energy to fragment, unlike those formed at the shortest wavelength. However, at pressures above 1 torr fragmentation is negligible. The photoionisation quantum yields (η) at 1236 Å are very small compared with those at shorter wavelengths (Table 5).

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Ionisation yields of cyclohexane and [²H₁₄] cyclohexane (data from Table 1, P. Ausloos, R. E. Rebbert, and S. C. Lias, <em>J. Phys. Chem.</em>, 1968, 72, 3904)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>η₁₂₃₆</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.045</td>
</tr>
<tr>
<td>Perdeuteriocyclohexane</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The importance of reaction (354) in the liquid phase photolysis of cyclohexane at 1236 and 1470 Å is shown by the high quantum yields of cyclohexene.\(^\text{167}\) However, it was shown in this study that addition of benzene or cyclohexene drastically reduces the quantum yield of products, and energy transfer from the excited cyclohexane species to the benzene or olefin was proposed to account for this, implying that the lifetime of the excited cyclohexane is relatively long (0·3 ns). But a study of the effect of benzene and nitrous oxide on the quantum yield of hydrogen formation in the gas phase photolysis of cyclohexane at 1470 Å has revealed that energy transfer definitely does not occur, at least up to pressures of 70 torr.\(^\text{168}\) From these results, an upper limit for the lifetime of the excited cyclohexane molecule of \(\tau<0.2\) ns can be derived. This does not differ significantly from the 0·3 ns derived from the liquid-state study, where the assumption was made that the quenching process was diffusion controlled.

**Olefins and Aromatics.**—Ethylene can be used as a chemical actinometer in the vacuum-u.v. region, and a recent reinvestigation of the photolysis at 1849 Å of this compound\(^\text{169}\) has provided a value for the quantum yield of hydrogen which is different from previous literature values. The value obtained, 0·62, based on the use of nitrous oxide as an actinometer, is substantially lower than the previously accepted value. It can be shown that provided the rate of formation of a product \((R)\) is related simply to the amount of light absorbed in the system, \(I_a, i.e.

\[
R = I_a, \Phi
\]

(355)

where \(\Phi = \) quantum yield, then from the Beer–Lambert law,

\[
-\log (1 - R/R_0) = ecl
\]

(356)

where \(R_0 = \) rate for total absorption, \(e = \) molar extinction coefficient, \(c = \) concentration of reactant, \(l = \) absorbing path-length. Thus a plot of the left-hand side \(vs.\ c\) can provide a value for \(e\). The value obtained for the molar extinction coefficient for \(\text{N}_2\text{O}\) is 30·9 ± 2·1 mole\(^{-1}\) cm\(^{-1}\) which agrees well with previously obtained values. However, the value for \(\text{C}_2\text{H}_4\) is 35 ± 3·1 mole\(^{-1}\), which is very much lower than other reported values. This may well be due to the fact that the ethylene spectrum is highly structured in this region, and line-width of the source may have a drastic effect.

Buta-1,3-diene has been photolysed at 1470 and 1236 Å and the products compared with the photolysis at 2200—2600 Å.\(^\text{170}\) Quantum yields have not been determined in this study, and thus all product yields are reported relative to the yield of acetylene, which is one of the major products; these show little pressure or wavelength dependence in the vacuum-u.v. region. In the near-u.v. region buta-1,2-diene and but-2-yne are also formed.

At 1236 Å, the energy of the quantum is sufficiently high to permit ionisation of the buta-1,3-diene, since the ionisation potential of this


compound is 9.07 ± 0.02 ev. However, the product distribution obtained with light of this wavelength did not differ appreciably from that at 1470 Å, suggesting that possible reactions of the parent ion with butadiene molecules do not occur in this system. Fragmentation of the parent ion is not possible at this wavelength, since the appearance potentials of C₆H₆⁺ and C₆H₅⁺ ions, for instance, lie at much higher energies.

Two novel compounds, cis- and trans-hexa-1,3-dien-5-yne have been observed in the vacuum-u.v. photolysis of benzene in the vapour phase.¹⁷²,¹⁷³

\[
\text{[Diagram]} \quad \text{hv} \quad 1849 \text{Å} \quad \text{(357)} \quad \text{[Chemical structure]} \quad + \quad \text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}≡\text{CH} \quad \text{cis and trans}
\]

These are formed in addition to the major product fulvene, and small quantities of reduced and alkylated benzenes, biphenyl, dihydrobiphenyls, polymer, and fragmentation products.

Using 1849 Å radiation and various pressures of benzene in an atmosphere of nitrogen, it was shown that the ratio of trans- to cis-hexadienyne increases from 0.1 to unity as the duration of the photolysis is increased.¹⁷² However, the ratio of the total yield of hexadienyynes to fulvene varies only slightly with irradiation time, which indicates that the trans-dienyne may arise from a secondary photolysis of the cis-compound (as one would expect a priori). It was shown that photolysis of cis-hexa-1,3-dien-5-yne under these conditions did yield the trans-compound, in addition to some polymer. However, a similar study using an oxygen discharge lamp has shown that the ratio of cis- to trans-photoisomers is unity over a wide variety of conditions, even at small conversions.¹⁷³ In addition, the fulvene:diyne ratio was found to be pressure dependent, with the dienynes predominating at pressures below 10 torr. At any given pressure, the ratio of total dienyne yield to fulvene yield was independent of irradiation time, in agreement with the work at 1849 Å. It seems likely therefore that the fulvene and dienyne are primary photolysis products, although the possibility exists that the dienyne arises from secondary photolysis of fulvene, since this process has been shown to occur.¹⁷² However, if this were the case, a photostationary state would have to be set up in an extremely short time (<30 s) in order to explain the results.

At a total pressure of 10 torr, the yields of dienynes and fulvene are comparable. Addition of an inert gas (nitrogen) decreased the dienyne yield steadily, whereas the fulvene yield passed through a maximum at

80 torr. At 200 torr, the relative yields of fulvene and dienyne are in substantial agreement with those observed in an atmosphere of nitrogen. It is speculated that the precursors of fulvenes and other C₆ products may be a highly vibrationally excited ground-state benzene formed by internal conversion from the initially populated higher excited singlet state, since there is a reported similarity between the products of the photolysis and those of pyrolysis. However, there are many facts yet unexplained concerning the mechanism, and the publication of further experimental results will be awaited with interest.

Other compounds have been studied. The formation of non-isomeric products in the vacuum-u.v. irradiation of o-xylene appears to proceed via a free radical dissociation.¹⁷³ CH₅Br photolysed at 1849 Å has been used as a source of high-energy methyl radicals.¹⁷⁴ Methanol has an absorption continuum in the 1850 Å region, attributed to the first Rydberg transition. However, the dissociation quantum yield at this wavelength increases with increasing pressure of added gas. The implication is that there is a collision-induced predissociation.¹⁷⁵ The efficiency of different gases in promoting the predissociation correlates well with their polarisability, except for Kr and Xe in which spin–orbit coupling is an additional dissociative channel. The photoionisation of the lower aliphatic alcohols has also been studied mass spectrometrically.¹⁷⁶ The formation of hydrogen in the 1849 Å photolysis of diborane appears to occur primarily via free radical dissociation (358) rather than a direct molecular elimination.¹⁷⁷

\[ \text{B}_2\text{H}_6 + h\nu \rightarrow \cdot\text{B}_2\text{H}_5 + \text{H} \]  
(358)

Methylsilane when photolysed at 1470 and 1236 Å fragments in many of the possible ways to give molecular and atomic hydrogen, among other products.¹⁷⁸ Dichlorosilane and difluorosilane can be used as sources of SiCl₃ and SiF₃ radicals respectively when irradiated in the vacuum-u.v. region at liquid nitrogen temperatures.¹⁷⁹

11 Recent Advances in Flash Photolysis Techniques

It is astonishing that in the short time since the conception of flash photolysis, the technique has developed to the high degree of sophistication which is at present available. Flash spectroscopy nowadays provides a standard technique for the identification and estimation of transients in the submicrosecond region, and in the preceding chapters reference has been made to many such studies. Some of the applications of this technique have been

referred to in the Nobel addresses of its creators, Professors G. Porter and R. G. W. Norrish. The practical details of conventional flash-photolysis systems have been reviewed, and several developments, such as systems for studying fast reactions using a Z-pin in argon, a short duration flash photolysis lamp, and systems utilising flash photolysis in conjunction with time-resolved mass spectrometry, and electron spin resonance spectrometry have been described. However, it is undoubtedly the recent use of lasers in photochemistry which is the most significant and exciting advance in this field. Previously transients could be observed only when their lifetimes were longer than the duration of the photolysis flash, generally in the microsecond region. This meant that excited singlet states of molecules, with lifetimes in the nanosecond region, could not be observed by conventional techniques. However, using Q-switched ruby lasers, nanosecond pulses of high intensity are now available, and several studies of absorption by excited singlet states of molecules have been undertaken. The first studies were carried out simultaneously by Porter and co-workers and Novak and Windsor. The apparatus used by Porter is elegant. A ruby laser with a vanadyl phthalocyanine Q-switch delivers a pulse which is frequency doubled by an ammonium dihydrogen phosphate crystal. The beam is filtered to remove red light and scattered light, and then passes into a beam splitter, which divides it into two parts. The first part acts as the photolysis flash, while the second passes into an optical delay system, which can give delays up to 100 ns. This pulse is reflected to the beam splitter and thence into a cell containing a fluorescent solution (1,1,4,4-tetraphenylbuta-1,3-diene) which emits a pulse lasting 18 ns and with a continuous spectrum from 400 to 600 nm. This pulse passes through the irradiation cell and into the slit of a spectrograph. A single laser pulse is thus adequate for photolysis and spectrographic recording of absorption spectra. Using this technique, singlet absorption spectra were obtained for phenanthrene, triphenylene, 1,2-benzanthracene, 3,4-benzpyrene, 1,2,3,4-dibenzanthracene, coronene, and pyrene. The assignation of absorption bands to singlet states is on the basis of two observations: (i) The lifetimes are identical to fluorescence lifetimes, and (ii) the decay rate is equal to the rate of growth of triplet states simultaneously recorded.

Novak and Windsor recorded time-resolved spectra using an image converter tube with a laser spark as source. They recorded singlet absorption spectra of coronene, 1,2-benzanthracene, and 1,2,3,4-dibenzanthracene in agreement with Porter’s data. Conventional flash spectroscopy provides data on singlet–singlet absorption in pyrene in agreement with these of Porter.\textsuperscript{190} A double frequency-doubled neodymium laser has been used to record the singlet absorption spectrum of naphthalene.\textsuperscript{191} The techniques are as yet in their infancy, and prospects eagerly foreseen include measurement of absorption and relaxation of molecules excited in the gas phase at shorter wavelengths, and use of picosecond pulses.

D. P.


Part II

INORGANIC PHOTOCHEMISTRY
1 Photolysis of Water and Hydrogen Peroxide

Since water is almost invariably used as solvent in the study of the photochemistry of inorganic materials, its photodecomposition and that of the related hydrogen peroxide will be considered first. Liquid water (and ice) do not absorb in the near-u.v., but the vacuum-u.v. absorption spectrum is known. Liquid water has been photolyzed with light of wavelengths 1236, 1470, and 1849 Å (for details of lamps and energies see section on vacuum-u.v. photochemistry, Part I, Chapter 2). The primary process occurring is dissociation of the water into hydrogen atoms and hydroxyl radicals (1).

\[ \text{H}_2\text{O} + h\nu \rightarrow (\text{H}_2\text{O})^* \rightarrow \text{H}^+ + \cdot\text{OH} \]  \hspace{1cm} (1)

Addition of formate ion to the water acts as a scavenger for the species produced in process (1)

\[ \text{HCOO}^- + \cdot\text{OH} \rightarrow \cdot\text{COO}^- + \text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{HCOO}^- + \cdot\text{H} \rightarrow \cdot\text{COO}^- + \text{H}_2 \]  \hspace{1cm} (3)

\[ \cdot\text{COO}^- + \cdot\text{COO}^- \rightarrow (\text{COO}^-)_2 \]  \hspace{1cm} (4)

The oxalate produced in (4) was analysed by permanganate titration. Possible complicating reactions are reaction of the formate ion with a solvated electron, (5);

\[ \text{HCOO}^- + e_{\text{aq}}^- \rightarrow \cdot\text{COO}^- + \text{H}_2 + \text{OH}_{\text{aq}}^- \]  \hspace{1cm} (5)

or direct reaction of the excited state of water with the formate ion, (6);

\[ (\text{H}_2\text{O})^* + \text{HCOO}^- \rightarrow \cdot\text{COO}^- + \cdot\text{OH} + \text{H}_2 \]  \hspace{1cm} (6)

and absorption of radiation by the formate ion followed by decomposition, (7);

\[ \text{HCOO}^- + h\nu \rightarrow (\text{HCOO}^-)^* \rightarrow \cdot\text{COO}^- + \cdot\text{H} \]  \hspace{1cm} (7)

However, (5) is a very slow reaction and is thus unimportant; and the concentration of formate is very low, so reaction (7) may also be discounted. Since the OH radical produced in (6) will react with formate to produce \( \cdot\text{COO}^- \) as in equation (2), the net result of (6) followed by (2) is the same.

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as (1), (2), and (3), i.e. one molecule of oxalate is formed for each quantum absorbed. The yields of oxalate are pH-dependent, although they were constant above pH 4. Based on this scheme, the quantum yield of dissociation of water to H and OH at 1235 Å was 1·03 ± 0·02, and at 1470 Å 0·72 ± 0·02. Previously obtained values for this quantum yield at 1849 Å have shown a wide variation, depending upon the actinometer used. This new work has shown that if the literature values are corrected to a single actinometer standard, such as hydrogen formation from 5m-ethanol (Φ = 0·5), or disappearance of N₂O (Φ = 1·0), good agreement is obtained between the results of various groups of workers. The average value based on the first actinometer is Φ_{H,OH} = 0·37, and on the second, Φ_{H,OH} = 0·295. Since it is not known which actinometer gives the correct quantum yield, an average value of Φ_{H,OH} = 0·335 can be quoted for water photolysis at 1849 Å.

At the shorter wavelengths, there is evidence of formation of the hydrated electron. Addition of carbon dioxide to the system scavenges this species and causes an increase in oxalate production: equation (8).

\[
\text{CO}_2 + e_{\text{aq}}^- \longrightarrow \cdot\text{COO}^- + n\text{H}_2\text{O} \quad (8)
\]

Increase in oxalate production is not unambiguous evidence that reaction (8) occurs since oxalate could be formed via reactions (9) and (10) followed by (2):

\[
\text{CO}_2 + (\text{H}_2\text{O})^* \longrightarrow \cdot\text{COOH} + \cdot\text{OH} \quad (9)
\]

\[
\text{CO}_2\text{aq} + \text{hv} \quad \longrightarrow \quad (\text{CO}_2\text{aq})^* \longrightarrow \cdot\text{COOH} + \cdot\text{OH} \quad (10)
\]

However it is felt that the increase in oxalate yield observed when CO₂ is added to the system is probably due to reaction (8). The hydrated electron possibly originates from photolysis of the formate ion (11); and photodestruction of water is possible if the solvation energy of the electron is 2–2·5 ev.

\[
\text{HCOO}_{\text{aq}}^- + \text{hv} \longrightarrow \quad (\text{HCOO}_{\text{aq}}^-)^* \longrightarrow \quad e_{\text{aq}}^- + \cdot\text{COOH} \quad (11)
\]

At 1470 Å, there is insufficient energy in a single quantum to produce the hydrated electron, and thus any production of this species must be a double quantum process, (12) or (13)

\[
(\text{H}_2\text{O})^* + (\text{H}_2\text{O})^* \longrightarrow \quad (\text{H}_2\text{O})^{**} + \text{H}_2\text{O} \quad (12)
\]

\[
(\text{H}_2\text{O})^* + \text{hv} \longrightarrow \quad (\text{H}_2\text{O})^{**} \quad (13)
\]

\[
(\text{H}_2\text{O})^{**} \longrightarrow \quad e^- + \text{H}_2\text{O}^+ \quad (14)
\]

\[
e^- + \text{H}_2\text{O} \longrightarrow \quad e_{\text{aq}}^- \quad (15)
\]

In the vapour phase at 1236 Å³ the OH radicals produced in reaction (1) are in an excited electronic state, OH (A ³Σ⁺), and emission from this to the ground state, OH (X ²Π), may be observed (16).

\[
\text{OH}(A ³Σ⁺) \longrightarrow \quad \text{OH}(X ²Π) + \text{hv} \quad (16)
\]

---

Processes which compete with this emission are quenching by water molecules and added gases, M.

\[
\begin{align*}
\text{OH}(^3\Sigma^+) + \text{H}_2\text{O} & \rightarrow \text{OH}(^2\pi) + \text{H}_2\text{O} \\
\text{OH}(^3\Sigma^+) + \text{M} & \rightarrow \text{OH}(^2\pi) + \text{M}
\end{align*}
\]

The quenching parameters for gases such as CO, N\textsubscript{2}, D\textsubscript{2}, H\textsubscript{2}, and He were obtained from a study of the fluorescence, and it was found that cross-sections for water and carbon monoxide were very large, those for nitrogen, deuterium, and hydrogen an order of magnitude less, and that for helium very small. Complex formation of the type shown in (19) has been considered to explain the high quenching cross-sections.

\[
\text{OH}(^3\Sigma^+) + \text{CO} \rightarrow \text{CO} + \text{OH} \rightarrow \text{OH}(^2\pi) + \text{CO}
\]

From a detailed study of the fluorescence spectrum, rotational relaxation of the excited OH species could be measured. It was found that added gases relaxed the molecule rotationally within a few collisions.

The photolysis of hydrogen peroxide vapour at 1236 and 1470 Å leads to the conclusion that, in addition to the primary process producing two ground state OH radicals (20), some excited OH radicals are also formed, since emission is observed from them:

\[
\begin{align*}
\text{H}_2\text{O}_2 + h\nu & \rightarrow 2\text{OH}(^2\pi) \\
\text{H}_2\text{O}_2 + h\nu & \rightarrow 2\text{OH}(^3\Sigma^+)
\end{align*}
\]

At 1236 Å, there is evidence of hydrogen atom formation which may occur via either of the primary processes (22) or (23).

\[
\begin{align*}
\text{H}_2\text{O}_2 + h\nu & \rightarrow \text{H}^\cdot + \text{HO}_2^\cdot \\
\text{H}_2\text{O}_2 + h\nu & \rightarrow 2\text{H}^\cdot + \text{O}_3
\end{align*}
\]

There was no evidence for the primary production of excited singlet oxygen atoms as in the hypothetical equation (24).

\[
\text{H}_2\text{O}_2 + h\nu \rightarrow \text{H}_2\text{O} + \text{O} \quad (^1S \text{ or } ^1D)
\]

When photolysed at 1470 or 2537 Å, no hydrogen was formed, and it was supposed that (20) was the only primary step occurring at 2537 Å; but both (20) and (21) are of importance at 1470 Å.

The quantum yield of O\textsubscript{2}-formation at 1236 Å was high, (φ = 4—10) compared with the hydrogen yield (φ = 0.5), suggesting a chain mechanism for the formation of O\textsubscript{2} but not for H\textsubscript{2}. An energy chain mechanism is proposed [equations (25), (26)] in which OH\textsuperscript{*} represents a vibrationally excited OH radical.

\[
\begin{align*}
\text{H}^\cdot + \text{H}_2\text{O}_2 & \rightarrow \cdot\text{OH}^\ast + \text{H}_2\text{O} \\
\cdot\text{OH}^\ast + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_3 + \text{H}^\cdot
\end{align*}
\]

\footnote{L. J. Stief and V. J. de Carlo, \textit{J. Chem. Phys.}, 1969, \textbf{50}, 1234.}
The high quantum yield of CO₂ observed when CO is added to the system supports this mechanism, since reaction between CO and OH* regenerates the hydrogen atom chain carrier: equation (27).

\[
\text{CO} + \cdot\text{OH}^* \longrightarrow \text{CO}_2 + \cdot\text{H}^* \quad (27)
\]

With an oxygen discharge lamp as source (wavelengths 1600—2000 Å), the flash photolysis of hydrogen peroxide in basic aqueous oxygenated solution produced the O₅⁻ ion.⁶ The decay of this species was first order under all conditions, and obeyed the equation:

\[
-d[O_5^-]/dt = k_{\text{obs}}[O_5^-] \quad (28)
\]

The observed pseudo first-order rate constant, \(k_{\text{obs}}\), was found to be dependent upon \(H_2O_2\) and \(O_2\) concentrations, and obeyed the empirical equation:

\[
k_{\text{obs}} = \frac{a[H_2O_2]}{b[O_2] + c[H_2O_2]} \quad (29)
\]

An expression of this type may be obtained if the following represents the scheme by which \(O_5^-\) is formed and decays.

**Formation**

\[
\begin{align*}
\text{HO}_5^- & \longrightarrow \cdot\text{OH} + \cdot\text{O}^- \\
\cdot\text{OH} + \text{OH}^- & \longrightarrow \cdot\text{O}^- + \text{H}_2\text{O} \\
\cdot\text{O}^- + \text{O}_2 & \longrightarrow \cdot\text{O}_5^- \quad (31)
\end{align*}
\]

**Decay**

\[
\begin{align*}
\cdot\text{O}_5^- & \longrightarrow \text{O}_2 + \cdot\text{O}^- \\
\cdot\text{O}^- + \text{HO}_5^- & \longrightarrow \text{OH}^- + \cdot\text{O}_2^- \quad (34)
\end{align*}
\]

Then

\[
\frac{d[O_5^-]}{dt} = \frac{k_{\text{33}}k_{\text{34}}[H_2O_2]}{k_{\text{33}}[O_2] + k_{\text{34}}[H_2O_2]} \quad (35)
\]

Equation (35) has the same form as (29).

In the absence of hydrogen peroxide, the decay of the \(O_5^-\) radical-ion species is more complex, having two parts, one first order with respect to \([O_5^-]\), the other second order. A scheme may be written to explain this, although assumptions are necessary.

The photochemical decomposition of water in the presence of chloride ions has been studied by derivative polarography.⁶

### 2 Photolysis of Aqueous Anions

The photochemistry of the ferrioxalate ion is well characterised since the substance is widely used as a chemical actinometer. Recently the photochemistry of the oxalate ion in the presence of iron(III) and zinc(II) has been reinvestigated.⁷ The photolysis of many negative ions in solution results in

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the formation of the hydrated electron. Thus in the vacuum-u.v. flash photolysis of the phosphate anions, \( \text{H}_2\text{PO}_4^- \), \( \text{HPO}_4^{2-} \), and \( \text{P}_2\text{O}_7^{4-} \) in aqueous solution, the main act is the detachment of an electron:\(^{10}\) equation (36).

\[
\text{M}_{\text{aq}}^{n^-} + h\nu \rightarrow \text{M}_{\text{aq}}^{(n-1)^-} + e_{\text{aq}}^-
\]

(36)

The absorption spectrum of the hydrated electron was determined in solutions of \( \text{HPO}_4^{2-} \) and \( \text{P}_2\text{O}_7^{4-} \) ions, as were the transient absorption spectra of various phosphate radical anions: these decayed by second-order processes. In solutions containing \( \text{O}_2 \), a transient was produced which was assigned to the \( \text{O}_2^- \) radical-ion.

Sulphite ions decompose on photolysis to yield the hydrated electron.\(^{10}\)

\[
\text{SO}_3^{2-}_{\text{aq}} + h\nu \rightarrow \text{SO}_3^- + 2e_{\text{aq}}^-
\]

(37)

A short-lived species with first-order decay was formed, apparently by addition of the hydrated electron to sulphite ions; this was thought to be the \( \text{HSO}_3^- \) species. \( \text{SO}_3^- \) decayed by a second-order reaction. Thiocyanate ions decomposed in two ways upon irradiation: equations (38), (39).

\[
\text{CNS}_{\text{aq}}^- + h\nu \rightarrow \cdot\text{CNS} + e_{\text{aq}}^-
\]

(38)

\[
\text{CNS}^- + h\nu \rightarrow \text{CN}^- + \text{S}
\]

(39)

In this system, the absorption spectrum of the (CNS)\(^-\) transient was observed. This species decayed by a first-order process in air-free solutions and by a second-order process in the presence of oxygen. Thiosulphate ions also decompose in two ways upon irradiation: equations (40), (41).

\[
\text{S}_2\text{O}_3^{2-}_{\text{aq}} + h\nu \rightarrow \cdot\text{S}_2\text{O}_3^- + e_{\text{aq}}^-
\]

(40)

\[
\text{S}_2\text{O}_3^{2-}_{\text{aq}} + h\nu \rightarrow \text{S}_2\text{O}_2^- + \cdot\text{OH} + \text{OH}^-
\]

(41)

The OH radicals produced react with \( \text{S}_2\text{O}_2^- \) to form \( \text{S}_2\text{O}_3^- \) radical-ions. These again decay by a first-order process in the absence of oxygen, and by a second-order reaction in oxygenated solutions. The type of second-order reaction may be as follows.

\[
e_{\text{aq}}^- + \text{O}_2 \rightarrow \cdot\text{O}_2^-
\]

(42)

\[
(\text{CNS})_3^- + \cdot\text{O}_2^- \rightarrow \text{products}
\]

(43)

\[
\text{S}_2\text{O}_3^- + \cdot\text{O}_2^- \rightarrow \text{products}
\]

(44)

Organic anions may also produce the solvated electron upon irradiation.\(^{11}\) Thus naphthalene (N) in ethereal solutions reacts with sodium metal to produce naphthalenide ions.

\[
\text{N} + \text{Na} \rightarrow \cdot\text{N}^- + \text{Na}^+
\]

(45)

\[
\cdot\text{N}^- + \text{Na} \rightarrow \text{N}^2^- + \text{Na}^+
\]

(46)

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\(^{9}\) G. Czapskii and M. Ottolenghi, \textit{Israel J. Chem.}, 1968, 6, 75.


\(^{11}\) S. Pardham and L. Fischer, \textit{Arkiv Kemi}, 1968, 29, 577.
Irradiation of such solutions causes the detachment of an electron:

\[ \text{N}_3^- + h\nu \rightarrow \cdot \text{N}^- + e^- \]  
\[ \cdot \text{N}^- + h\nu \rightarrow \text{N} + e^- \]  

(47)  
(48)

Aged solutions show a different spectrum owing to other reactions:

\[ \cdot \text{N}^- + \text{HA} \rightarrow \text{NH} \cdot + \text{A}^- \]  
\[ \text{NH} \cdot + \cdot \text{N}^- \rightarrow \text{NH}^- + \text{N} \]  

(49)  
(50)

The proton donor is water adsorbed on the walls of the vessel.

If deaerated solutions of sodium azide are flash photolysed with a flash energy of 1000 J at 4 μsec duration, a transient absorption is observed in the 4500—7000 Å region which again corresponds to the solvated electron.\(^{12}\) A second transient which absorbs in the 2500—3000 Å region was attributed to the N\(_3\) species.

\[ \text{N}_3^- + h\nu \rightarrow \cdot \text{N}_3 + e_{aq} \]  

(51)

Deaerated potassium nitrate under the same conditions gives no transient in the 4000—7000 Å region; thus the primary act in this case is not the photodetachment of an electron. In aerated solutions an absorption band is produced in the 2500—3600 Å region which in alkali solution persists for 10 min: this is attributed to the pernitrite ion, \(\text{O}=\text{N}^-\text{O}^-\text{O}^-\). Steady-state photolysis of nitrate in aqueous solution causes evolution of gaseous oxygen and nitrite formation, and at higher pH values, pernitrite formation.\(^{13}\)

Nitrite salts of the post-transition series exhibit a long-lived luminescence centred at 5500 Å in both frozen glassy solutions and in the crystalline state.\(^{14}\) This probably originates in a triplet state of the system, and is attributed to molecular \(T_1 \rightarrow S_0\) phosphorescence. The spin-orbit interaction produced by the heavy cation is responsible for the emission, and this is also responsible for the \(S_0 \rightarrow T_1\) absorptivity which gives the heavy-metal nitrites their yellow-orange colours. Sodium salicylate is sometimes used in conjunction with photomultiplier and photo tubes in measurement of light intensities, since the quantum yield of its luminescence is independent of the wavelength of the exciting light. The shape of the emission curve of this compound has been examined in the light of pseudoharmonic oscillator theory recently, but the influence of temperature was not entirely explained by such considerations.\(^{15}\)

### 3 Photolysis of Transition-metal Complexes in Solution

The photosensitivity of co-ordination compounds is being increasingly investigated in a quantitative manner. An excellent and authoritative review of this field has recently been published, comprising a comprehensive report of work performed on transition-metal complexes up to and

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including 1967. A Japanese review has more recently appeared. Because of the comprehensiveness of these reviews, no attempt will be made to cover the ground again. Instead, a brief indication will be given of additional papers which have appeared during 1968 and the early part of 1969. These should be consulted in conjunction with ref. 16. In addition, the use of transition-metal complexes in organic photochemistry will be briefly considered.

**Chromium Compounds.**—The luminescence of CrIII complexes has been studied, and a preliminary investigation of the partial photoresolution of some oxalato-complexes of CrIII room temperature has appeared. Aspects of the photochemistry of aqueous hexacyanochromate(III) and thiocyanatopentaminechromium(III) have been reported, and also the photochemical solvolysis of hexathiocyanatocromate(III) in acetonitrile-water mixtures.

**Europium.**—Attention has been focused mainly upon the luminescence of europium complexes. Thus αα'-bipyridyl complexes of europium(III) chloride fluoresce, and an analysis of their fluorescence spectra has been performed. The luminescence of αα'-bipyridyl complexes, and other eight-fold co-ordination compounds, has been studied. Complementary studies on the luminescence from other co-ordination compounds have been reported, and the effects of deuterium substitution and the symmetry of the environment have been considered.

**Cobalt.**—The photochemical reactions of pentammine cobalt(II) complexes have been reported, where the anion is NO₂, Cl, N₃, and others.

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Uranium.—The roles of temperature,\textsuperscript{38} impurities,\textsuperscript{39} and deuterium substitution \textsuperscript{40} in the ligand upon emission from uranyl salts have been discussed, and also the effect of photochemical processes.\textsuperscript{41} The polarisation of the emission has been studied \textsuperscript{42, 43} and classifications of the electronic\textsuperscript{44} and vibrational states have been proposed.\textsuperscript{45}

Miscellaneous.—Novel dehydrohexamethyl Dewar-benzene complexes of platinum(II) \textsuperscript{46} and other platinum(II)\textsuperscript{47} and platinum (IV) complexes \textsuperscript{48} have been studied, and a similar palladium complex has been prepared.\textsuperscript{49} Spectroscopic studies on ruthenium compounds,\textsuperscript{50–53} and photochemical investigations on iron carbonyls\textsuperscript{54–56} and other iron compounds \textsuperscript{57} have been performed, and the photolysis of dioxalatocopper(II) ions in solution has been considered.\textsuperscript{58} Antimony compounds \textsuperscript{59, 60} and cerium compounds have also been investigated.\textsuperscript{61–65} A study has been made of the uranyl-uranous system in aldehydes.\textsuperscript{66}

Energy Transfer.—The fluorescence of rare-earth chelates involves triplet energy transfer from an excited ligand to the metal ion.\textsuperscript{67, 68} The fluorescence of unchelated rare-earth ions can be sensitised by triplet donors in solution,

\textsuperscript{40} D. D. Pant and H. B. Tripathi, \textit{Indian J. Pure Appl. Phys.}, 1969, 7, 140.
\textsuperscript{43} E. Lucata, \textit{Compt. rend.}, 1968, 267, A, 1146.
\textsuperscript{64} N. S. Poluevok and A. I. Kirilov, \textit{Optics and Spectroscopy}, 1967, 23, 413.
\textsuperscript{66} R. M. Haas, \textit{Diss. Abs.}, 1968, 28, B, 4527.
presumably as a consequence of bimolecular transfer of the triplet donor energy to the solvated metal ion. The use of lanthanide ions as sensitive probes in organic photochemistry for triplet states has been developed,

70 but it has been pointed out that some ketonic triplet states are inefficient donors in this process.

4 Photolysis of Non-aqueous Systems

There are a few studies of the photochemistry of inorganic materials in the vapour phase, but these are of course very limited since most inorganic substances are of low vapour pressure. Nevertheless, the photoionisation of a number of metal atom vapours and their halogen compounds, as well as molecular sulphur species, has been investigated at high temperatures.71 The photoionisation of XeF₂ has also been demonstrated, and ionisation potentials measured.72

The flash photolysis of chromyl chloride vapour produces two transient species which were identified as the CrO₂Cl radical and the CrO₂ molecule.73 It was proposed that the CrO₂Cl arose from photoexcited CrO₂Cl radicals. The decay of the species was independent, and the final products were Cl₂ and amorphous CrO₂. The following scheme accounts for the observed phenomena.

Excitation: \[ \text{CrO}_2\text{Cl}_2 + h\nu \rightarrow \text{CrO}_2\text{Cl}_2^* \] (52)

Deactivation: \[ \cdot\text{CrO}_2\text{Cl} \rightarrow \cdot\text{CrO}_2\text{Cl}^* \] (53)

\[ \text{CrO}_2\text{Cl}_2^* \rightarrow \text{CrO}_2\text{Cl}_2 \] (54)

\[ \cdot\text{CrO}_2\text{Cl}^* \rightarrow \cdot\text{CrO}_2\text{Cl} \] (55)

\[ \text{CrO}_2\text{Cl}_2 \rightarrow \cdot\text{CrO}_2\text{Cl} + \text{Cl} \cdot \] (56)

\[ \text{CrO}_2\text{Cl} \rightarrow \text{CrO}_2 + \text{Cl} \cdot \] (57)

Decomposition: \[ \text{CrO}_2\text{Cl}_2 \rightarrow \cdot\text{CrO}_2\text{Cl} + \text{Cl} \cdot \] (58)

\[ \cdot\text{CrO}_2\text{Cl}^* \rightarrow \text{CrO}_2 + \text{Cl} \cdot \] (59)

\[ \cdot\text{CrO}_2\text{Cl} \rightarrow \text{CrO}_2 + \text{Cl} \cdot \] (60)

Termination: \[ 2\cdot\text{CrO}_2\text{Cl} \rightarrow (\text{CrO}_2\text{Cl})_2 \] (61)

\[ \cdot\text{CrO}_2\text{Cl} + \text{Cl} \cdot \rightarrow \text{CrO}_2\text{Cl}_2 \] (62)

\[ \text{Cl} \cdot + \text{Cl} \cdot \rightarrow \text{Cl}_2 \] (63)

\[ \text{CrO}_2\text{Cl}_2 + \text{Cl} \cdot \rightarrow \cdot\text{CrO}_2\text{Cl} + \text{Cl}_2 \] (64)

\[ \text{CrO}_2\text{Cl}_n + (\text{CrO}_2\text{Cl})_m \rightarrow (\text{CrO}_2\text{Cl})_{n+m} \] (65)

The gas-phase photochemical decomposition of lead halides from automobile exhausts has been studied in connection with current concern over the danger to public health which may arise from pollution of the environment by residues from lead-based 'anti-knock' agents. Photochemical free radical reactions in non-aqueous solutions of PbCl₄ have been investigated.

Photodecomposition in the solid state of various metal azides (NaN₃, KN₃, BaN₆, AgN₃, and PbN₆) results in the evolution of nitrogen gas and, in the case of NaN₃, BaN₆, and AgN₃, nitride production. No nitrides were formed from KN₃ or PbN₆ photolysis. The nitrides formed were themselves decomposed with light of a long wavelength. It was noted that the rate of decomposition of the azide was accelerated as the percentage decomposition increased. This acceleration was attributed to the photodecomposition of the nitride, and photoionisation of metal atoms if light of sufficient energy was present.

\[
\begin{align*}
N_3^- & \xrightarrow{hv} N_3^* \quad (66) \\
N_3^- + S & \rightarrow N_3eS \quad (67) \\
N_3^* + N_2eS & \rightarrow 3N_2 + \theta e\theta + S^- \quad (68) \\
Na^+ + \theta e\theta & \rightarrow Na + 2\theta \quad (69) \\
S^- + Na^+ & \rightarrow Na + S' \quad (70)
\end{align*}
\]

where \( S \) is a trap, \( N_3^* \) an exciton, \( \theta \) an anion vacancy and \( S' \) another trap. In \( \theta e\theta \) an electron is occupying one of two vacancies. Continuous repetition of the above processes leads to the formation of a metal nucleus. The second acceleration process than comes into operation:

\[
\begin{align*}
Na_n & \rightarrow Na_n^+ + e \quad (71) \\
N_3^* + Na_n & \rightarrow Na_n + N_3 \quad (72) \\
N_3^* + N_3 & \rightarrow 3N_2 + 2\theta + e \quad (73) \\
Na_n + 2e + 2Na^+ & \rightarrow Na_{(n+2)} \quad (74)
\end{align*}
\]

The photodecomposition of trimethylsilyl azide in solid argon has also been studied. Other solid-state photolysis systems investigated include triethyltin(iv) oxide, and the use of oxide semiconductors as photocatalysis agents.

It is the luminescent rather than the photochemical properties of inorganic solids which attract attention since these materials are widely used as phosphors in industry. The subject is too large to be included in

this review in detail; however references will be given to work on particular types of phosphor. Zinc sulphide phosphors activated by copper and bismuth have been further investigated, and absorption and fluorescence in SnS and SnO have been considered with evidence presented for matrix-induced intersystem crossing. Luminescence in MgO, and by Bi has been reported, and the types of luminescent centre in MnF, KCl and KBr, and silver, and thallium-doped sodium chloride have been described. Many phosphors based on rare earth systems have been discussed, and investigations have been reported on the fluorescence of compounds with the fresnoite (Ba,TiSi, O) and the Ln Mn4+Me6+O8 structures. Bi-activated phosphors have also been studied in the same laboratory. Considerable interest in phosphors has developed from the observed capacity of such systems to act as lasers. There is a need for lasers of new wavelengths, especially in the u.v. region; these might perhaps be obtained by frequency doubling new lasers based on the systems above, the output of which is generally in the visible region.

D. P.

97 A. V. Dolgopolova and B. S. Skorobagatov, Optics and Spectroscopy, 1968, 24, 102.
Part III

ORGANIC ASPECTS OF PHOTOCHEMISTRY
Photolysis of Carbonyl Compounds

Several review articles have appeared during the past year which have some relevance to the subject matter of this chapter. Some of the chemistry of cyclic ketones is reported by Yates\(^1\) in a transcript of a lecture given at Enschede, and a shorter article by Swenton\(^2\) is also of general interest. A broad spectrum review has been published.\(^3\)

This chapter is intended to cover aspects of photochemistry related to the simpler ketones both acyclic and cyclic. Most of the material refers to liquid-phase reactions, and emphasises chemical aspects. Photophysical aspects are considered in Part I. For the sake of continuity, fairly broad sections have been employed. It will be seen, however, that the photochemistry described in this section is rather scrappy, apart from a few notable exceptions, and it is unfortunate that such scrappiness seems to pervade many areas at this time.

1 H-Abstraction Reactions (Cyclobutanol Formation—Norrish Type II Reactions)

In the photolysis of alkyl ketones with γ-hydrogens, one of the routes open to the reaction after initial hydrogen abstraction by the excited ketone is ring-closure to form cyclobutanols. Thus in the photolysis\(^4\) of β-alkoxy-acetophenones (1) both acetophenone, the product of Norrish type II elimination, and cyclobutanols (2), are formed in a number of solvents. Cyclobutanol formation has been shown to be less favourable in more polar solvents, and it is suggested\(^4\) that this effect is due to H-bonding in the diradical.

\[ \text{PhCOCH}_2\text{CHR}^1\text{OR}^2 \]

(a) \( \text{R}^1 = \text{R}^2 = \text{H} \)
(b) \( \text{R}^1 = \text{R}^2 = \text{Me} \)
(c) \( \text{R}^1 = \text{H}, \text{R}^2 = \text{Me} \)

(1)

\[ \text{HO} \quad \text{R}^1 \quad \text{O} \quad \text{R}^2 \]

(2)

---

\(^1\) P. Yates, Pure Appl. Chem., 1968, 16, 93.
\(^3\) G. Adam, Z. Chem., 1968, 8, 441.
Cyclobutanol formation has also been reported from the photolysis of steroids and triterpenes where the stereochemical environment of the carbonyl groups ensures proximity of the two radical centres. Two examples of these are reported in the oleanene series. 16-Oxo-oleanene (3) undergoes photolysis\(^5\) in methanol to yield cyclobutanol (4) by initial

\[
CH_2OAc
\]

\[
H
\]

\[
OR
\]

\[
AcO
\]

\[
(3) \text{ R = H or Ac}
\]

H-abstraction from ring \(e\), and 11-oxoolean-12-ene (5, \(R^1 = \text{Ac}, R^2 = \text{Me}\)) can also be made to photocyclise\(^6\) by \(\pi \rightarrow \pi^*\) excitation to produce compound (6, \(R^1 = \text{Ac}, R^2 = \text{Me}\)) in low yield through H-abstraction from the proximate 10\(\beta\)-methyl group. Similarly 18\(\alpha\)- and 18\(\beta\)-glycyrrhetic acids (5, \(R^1 = \text{H}, R^2 = \text{CO}_2\text{Me}\)) gave\(^7\) two isomeric cyclobutanols (6a and 6b)

\[
R^1O
\]

\[
(5)
\]

\[
R^2
\]

\[
(6a)
\]

\[
(6b)
\]

depending on the wavelength used: with photolysis at \(\lambda > 300\) nm (\(\pi \rightarrow \pi^*\)) the hydroxy-cyclobutanol (6a) predominates, whereas with \(\lambda\) 280 nm (\(\pi \rightarrow \pi^*\)) the hydroxy-cyclobutanol (6b) is the major product.

Cyclobutanol (7) is formed\(^8\) without loss of the initial stereochemistry by the photolysis of methylisopulegone (8) through Pyrex (\(\lambda > 300\) nm) in cyclohexane solution.

An investigation into the synthetic utility of double-bond migration in photolysis of \(\alpha,\beta\)-unsaturated esters (9) has been reported.\(^9\) Photolysis of the esters, which show an absorption maximum at 210 nm, was achieved using the 253.7 nm line. No isomerisation was effected by irradiation

---


above 300 nm. The mechanism of the reaction is proposed as $\gamma$-hydrogen abstraction via diradical (10) to yield, after $H$-transfer, the isomerised ester (11). The process is twice as fast in methanol as in hexane, a fact which appears to exemplify the stabilising influence of protic solvents on the intermediate diradical (10).

A similar study by Jorgenson reports an abnormally large deuterium solvent isotope effect. Thus in methanol the $\alpha,\beta$-unsaturated ester (9, $R^1 = R^2 = R^4 = Me$, $R^3 = Et$) gives the corresponding unsaturated ester (11, $R^1 = R^2 = R^4 = Me$, $R^3 = Et$) whereas in [hydroxy-$^2$H]methanol both the tetrasubstituted olefin (11, $R^1 = R^3 = R^4 = Me$, $R^2 = Et$) and the terminal olefin (12) are formed in equal amounts with a 90% incorporation of deuterium. The observation that (12) is formed faster than (11, $R^1 = R^a = R^4 = Me$, $R^3 = Et$) in MeOD is in agreement with the proposal that deconjugation reactions occur stereospecifically from the different geometric states (9, $R^1 = R^a = R^4 = Me$, $R^3 = Et$) and (13) of the starting materials. It is noteworthy that the irradiation of the ester (14) in non-hydroxylic solvents gives only the cyclopropane (15).

The photodecomposition by a Norrish type II process of 2-ethoxyethyl phenylacetate to give phenylacetic acid and ethyl vinyl ether could be

\[ R^1 \quad R^2 \quad R^3 \quad R^4 \\
(a) \quad Me \quad Me \quad Et \quad H \\
(b) \quad Me \quad H \quad Me \quad H \\
(c) \quad H \quad H \quad Me \quad H \\
(d) \quad n-C_8H_{13} \quad H \quad H \quad H \\

quenched by 1,3-pentadiene. This result was thought to show the intermediary of a triplet excited state;\(^\text{11}\) but the evidence is not unambiguous in the light of the known examples of singlet quenching by conjugated dienes. A Stern–Volmer plot of $\Phi_0/\Phi$ against quencher is linear with a slope of 80 l mole$^{-1}$. The quantum efficiency for ester disappearance was measured as 0·12, and this efficiency is claimed\(^\text{11}\) to be due to intramolecular energy transfer. Mechanistic studies on the photolysis of alkyl phenyl ketones have been reported.\(^\text{15–16}\) The results obtained from the photolysis of a series of such ketones are in accord with the accepted diradical intermediates resulting from H-abstraction. However the quantum yield for the Norrish type II process decreases as the $\gamma$-hydrogen environment changes from primary to secondary to tertiary. These results are interpreted to show steric interference in the cleavage reaction.\(^\text{14}\) The introduction of groups $\gamma$-to the carbonyl (16) which stabilise the diradical brings about\(^\text{14}\) an increase

$$\text{PhCOCH}_2\text{R}$$

$$R = \text{OMe, CH}_2\text{CH}_2\text{Ph, CH}_2\text{CH}_2\text{CO}_2\text{Me}$$

(16)

in $\Phi$. Pitts et al.\(^\text{15}\) studied similar systems and report values of $\Phi$ which are in reasonable agreement with those of Wagner and Kemppainen.\(^\text{14}\) Pitts and co-workers\(^\text{12}\) claim that while $k_\text{r}$, the rate of hydrogen abstraction, increases when the environment of the $\gamma$-hydrogen changes from primary to tertiary, there is no simple rationale for the decrease in $\Phi$; although Wagner and Kemppainen’s proposal of steric interference appears a reasonable interpretation. Coupled with the above observations is the unravelling of the nature of the excited state responsible for the Norrish type II elimination reactions. It was originally accepted that the excited state was a triplet with some little contribution from the singlet state and this idea has further support from the above observations. The influence of ring-substituents on the excited states of acetophenone\(^\text{16}\) and on the quantum yield of the type II process is reported.\(^\text{15}\) Yang and Dusenbury\(^\text{16}\) have found that methylated acetophenones with a low lying $\pi \rightarrow \pi^*$ state are less reactive than acetophenone. There is also considerable vibronic coupling of the $\pi \rightarrow \pi^*$ with the $n \rightarrow \pi^*$ triplet. The amount of coupling appears to determine the reactivity of the particular ketone under study. From the data for the four ketones investigated (Table 1) it appears that ketones with a low $n \rightarrow \pi^*$ triplet are more reactive but have faster non-radiative decay processes.


Photolysis of Carbonyl Compounds

Table 1  Influence of ring substituents on acetophenone excited states

<table>
<thead>
<tr>
<th>Ketone</th>
<th>$n-\pi^*$ Emission</th>
<th>Absorpt</th>
<th>$\pi-\pi^*$ Emission</th>
<th>Absorpt</th>
<th>$10^7 I$ (sec)</th>
<th>$10^{-4} k_r \times 2 M$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Trifluoromethylacetophenone</td>
<td>397</td>
<td>384</td>
<td>384</td>
<td></td>
<td>1.31</td>
<td>552</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>386</td>
<td>372</td>
<td>373</td>
<td></td>
<td>4.07</td>
<td>86.6</td>
</tr>
<tr>
<td>p-Methylacetophenone</td>
<td>368</td>
<td>392</td>
<td>386</td>
<td></td>
<td>42.3</td>
<td>7.88</td>
</tr>
<tr>
<td>3,4-Dimethylacetophenone</td>
<td>367</td>
<td>399</td>
<td>392</td>
<td></td>
<td>41.0</td>
<td>1.68</td>
</tr>
</tbody>
</table>

meta-Substitution has the greatest effect in the suppression of the type II process: (see Table 2). Thus while the $p$-MeO-substituent reduces $\Phi$ by a factor of 3 there is a thirty-fold decrease with a $m$-MeO-substituent. These results cannot be fully interpreted as yet: the lowest triplet state of the ketones appears to be $\pi \rightarrow \pi^*$, but as far as reactivity is concerned there must be some mixing of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states in agreement with the interpretations of Yang and Dusenbery and Pitts et al. who have also examined the reaction using $\gamma$-irradiation.

On the other hand Barltrop and Coyle claim that Norrish type II elimination and cyclobutanol formation, which accompanies elimination, result from an $n \rightarrow \pi^*$ state in the ketones studied by them. These authors studied the effect of solvent polarity, and in one case ($p$-methoxybutyrophenone) found the lowest triplet state to be $\pi \rightarrow \pi^*$ in acetonitrile and $n \rightarrow \pi^*$ in cyclohexane. Obviously it is important to bear in mind that just as absorption maxima undergo solvent shifts so may there be solvent-dependent complete changes of lowest triplet states or mixing of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states. The increase in the solvent polarity ($C_6H_6 < MeCN < MeOH$) increased the quantum yield of the type II process and this is interpreted as evidence for the diradical intermediate (17). Studies on the effect of temperature on $\Phi$ give values for an apparent activation energy (thus for PhCOPr, $E_a = 5.8$; PhCOBu, $E_a = 0$; PhCO-isopentyl, $E_a = -2.1$ kcal/mole) which is interpreted as a measure of the ability of the diradical to return to the ground state.


† There are many rather loose references in the current photochemical literature to the effects of solvent 'polarity'. Solvent effects can result from various causes, including differences in dielectric constants, hydrogen-bonding, and other solvating properties, and viscosities. These are often inadequately distinguished.
The introduction of hetero-atoms into the side-chain of phenyl ketone derivatives, as already mentioned, also influences the type II process. Turro and Lewis in the above-mentioned investigation into the type II photoelimination of \( \beta \)-alkoxyacetophenones (18) to give cyclobutanols and acetophenone found that \( \Phi \) decreases from unity in benzene to only 0.45 in acetonitrile or t-butanol, whereas Barltrop and Coyle observed the converse of this for butyrophenone. However, an explanation for this apparent contradiction is found in the spectra of the molecules; in more polar solvents the \( \pi \rightarrow \pi^* \) state contributes to the reaction processes and type II reactions are not favoured from such a state. Such an interaction between \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) is observed in the emission spectrum and is compatible with observations by other workers. Padwa et al. have studied the involvement of a nitrogen atom in the alkyl chain of alkyl aryl ketones and report evidence for electron transfer. They photolyzed the ketone (19) in ethanol to obtain a \( p \)-substituted acetophenone and an imine (20). The triplet energies of (19a) and (b) were measured by phosphorescence studies giving values of 73 kcal/mole for (19a) \( (n \rightarrow \pi^*) \) and 61 kcal/mole for (19b) \( (\pi \rightarrow \pi^*) \). Attempted quenching with cyclohexadiene and piperylene gave negative results which were explained by the rate of fission exceeding the rate of diffusion-controlled quenching. An electron-transfer mechanism was proposed (Scheme 1). The Norrish type

\[
\begin{align*}
(19) & \xrightarrow{\text{hv}} \text{PhCOCH}_2\text{CHR}^3\text{OR}^3 \\
& \text{R}^1 = \text{R}^2 = \text{H} \\
& \text{R}^1 = \text{R}^2 = \text{Me} \text{ or } \text{R}^1 = \text{H}, \text{R}^2 = \text{Me} \\
(18) & \quad \quad \text{PhCOCH}_2\text{CHR}^3\text{OR}^3 \\
(19) & \quad \quad \text{PhCOCH}_2\text{CHR}^3\text{OR}^3 \\
& \text{R} = \text{H} \\
& \text{R} = \text{Ph}
\end{align*}
\]

Scheme 1

Photolysis of Carbonyl Compounds

II elimination has also been applied\textsuperscript{19} to the synthesis of isoxazoles (21) by the photolysis of dihydroisoxazole derivatives (22).

Suitably substituted benzophenone derivatives are also capable of exhibiting H-transfer to the excited carbonyl group—the initial step of the

\[
\text{PhCH} = \text{NCH}_2\text{Ph} \quad (20)
\]

Norrish type II reaction. 2-Methylbenzophenone undergoes this reaction\textsuperscript{20} to give the labile photo-enol (23) in dioxan solution. Evidence for the existence of the enol was obtained by trapping with maleic anhydride to give the adduct (24), identified by i.r. and n.m.r. spectra. Fumaric and

\[
\text{Ph} \quad \text{OH} \\
(23)
\]

maleic acid [products (25) and (26) respectively obtained by esterification] gave similar Diels–Alder adducts. Analogous results are reported\textsuperscript{21} from the photolysis of 2,6-dimethylbenzophenone in the presence of diethyl acetylenedicarboxylate to yield the adduct (27) of the photo-enol.

\[
\text{Ph} \quad \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} \\
(25)
\]

\[
\text{Ph} \quad \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} \\
(26)
\]

\[
\text{Me} \quad \text{Ph} \quad \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} \\
(27)
\]

Hydroxyalkyl benzophenones behave slightly differently. In the example reported by O’Connell\textsuperscript{22} the photolysis of 2,4-di-t-butyl-6-hydroxybenzophenone (28, \(R = H\)) is extremely inefficient (\(\Phi = 2.0 \times 10^{-3}\)) although the emission spectrum shows that the lowest triplet and singlet excited states have an \(n \rightarrow \pi^*\) configuration and efficient intersystem crossing might have been expected. However, the \(pK_a\) is very low (–4 to –5), so deprotonation may compete with intersystem crossing. Methylation of the OH (28, \(R = \text{Me}\)) and photolysis in isopropanol gives alcohol (29) efficiently (\(\Phi = 0.5\)). The photolytic rearrangements of \(o\)-phthalaldehyde in sunlight are closely analogous to the above H-abstractions from alkyl substi-

The two products isolated are the dimer (30) in the erythro-form, and phthalide (31). These products are presumed to arise from either the ketene (32a) or the carbene (32b), and in the presence of maleic anhydride the ketene can be trapped as the ketoanhydride (33). The yield of phthalide is greatly enhanced by carrying out the photolysis in HCl-acetic acid mixtures.

Irradiation of the trans-aziridine (34a) in moist pentane is reported to give four products: an oxazole (35, 38%), an enamine (36, 41%, $\Phi = 0.018$), benzaldehyde (4%), and a benzaldehyde imine (37, 6%). Labelling experiments using aziridine (34b) gave the enamine (36) ($\Phi = 0.006$) which

(a) $R^1 = H, R^2 = Bu^t$
(b) $R^1 = D, R^2 = Bu^t$
(c) $R^1 = Ph, Ph^1 = H, R^2 = Bu^t$
(d) $R^1 = H, R^2 = C_6H_{11}$
(e) $R^1 = Ph, Ph^1 = H, R^2 = C_6H_{11}$

(34)

was isolated with 98% loss of deuterium. Thus the reaction was envisaged as shown in Scheme 2 with an uncommon 1,5-H migration as an essential step. The reaction could not be quenched by known triplet quenchers, a result which implied either a singlet, or a triplet state whose rate of reaction exceeded the diffusion controlled rate. Irradiation of the cis-aziridine (34c) gave only the oxazole (35) and the imine (33). Closely analogous work has been reported\textsuperscript{25} involving the photolysis of cis-aziridines (34d and e).

\[(34a) \xrightarrow{hv} Ph\overset{\text{O}^*}{\text{N}}\overset{\text{H}}{\text{N}}\overset{\text{Bu}^t}{\text{Ph}} \rightarrow Ph\overset{\text{N}}{\text{N}}\overset{\text{Bu}^t}{\text{Ph}} \rightarrow Ph\overset{\text{H}}{\text{N}}\overset{\text{Bu}^t}{\text{Ph}} \rightarrow (36)\]

Scheme 2

\[
\begin{align*}
(38a) & \quad \text{Ar} & \quad \text{Bu}^t & \quad \text{Ph} \\
(38b) & \quad \text{Ar} & \quad \text{Bu}^t & \quad \text{Ph} \\
(a) & \quad R^1 = \text{Ph}, R^2 = \text{H} \\
(b) & \quad R^1 = \text{H}, R^2 = \text{Ph} \\
(c) & \quad \text{Ar} = \text{Ph}, R^1 = R^2 = \text{H} \\
(39)
\end{align*}
\]

The preferred pathway for the formation of the isomeric pyrroles (38a) and (38b) from the photolysis of azetidine (39a) in ethanol\textsuperscript{25,26} is shown in Scheme 3 which involves the transient formation of an azabicyclo[2,1,0]-

\[
\begin{align*}
(39a) & \quad \text{Ar} \\
(38a) & \quad \text{Ar} & \quad \text{N} & \quad \text{Bu}^t & \quad \text{Ph} \\
(38b) & \quad \text{Ar} & \quad \text{OH} & \quad \text{Bu}^t & \quad \text{Ph} \\
(40)
\end{align*}
\]

\[
\begin{align*}
(38b) & \quad \text{Ar} & \quad \text{OH} & \quad \text{Bu}^t & \quad \text{Ph} \\
(38a) & \quad \text{Ar} & \quad \text{OH} & \quad \text{Bu}^t & \quad \text{Ph} \\
(40)
\end{align*}
\]

\[
\text{Scheme 3}
\]

\textsuperscript{25} L. R. Hamilton, Diss. Abs., 1967, 28, B, 2341.
pentane (40). Pyrrole (38a) predominates over pyrrole (38b) in the ratio of 2:1 since formation of diradical (i) is preferred over the other possibility (j). However pyrrole (38b) can be obtained from the photolysis of the cis-azetidine (39b) where attack at the benzylic position is conformationally forbidden. Experiments with deuterium labelling point towards reversibility of the H-transfer step. The symmetrical azetidine (39c) undergoes photolysis in ethanol to give one pyrrole (38, Ph = H, Ar = Ph) in 20% yield.

The carbon analogues of azetidines provide somewhat different results. The photolysis of cyclobutylphenyl ketone (41, R = H) in benzene solution gave four products, including a reduced ketone (42, 8%) and a pinacol (43, 10%) [which is the only product from the photolysis of (41) in isopropanol]. The other products were the result of transannular hydrogen abstraction and are the ring-opened product (44, 24%) and the bicyclo[1,1,1]pentanol (45, 38%), the structure of which has been verified by X-ray crystallography. The photolytic reaction to form (44) and (45) has been shown by quenching studies to be a triplet process; the excited state is $n \rightarrow \pi^*$ in nature ($E_T = 74.3$ kcal/mole). The proposed route for the formation of (44) and (45) is shown in Scheme 3a.

In comparison cyclopentylphenyl ketone gave various products depending on the time of irradiation. After 4 hr., the products were as shown in Scheme 4. With increasing time the ketone (i) disappears and independent photolysis of this gives rise to acetophenone, butadiene, the cyclobutanol, and the cyclohexenol. Padwa and Eastman claim that irradiation of cyclohexylphenyl ketone for 20 hours gives only a trace of acetophenone arising from an unusual double Norrish type II process. However, Stocker and Kern re-examined this reaction, and after irradiation in isopropanol for 96 hr. pinacols of acetophenone (51%) and unchanged starting material (15%) were isolated. In benzene solution acetophenone (23%), determined

---

Photolysis of Carbonyl Compounds

Scheme 3a

$$\Phi_{\text{disappearance}} = 0.4$$

Scheme 4

by n.m.r., was detected after photolysis for the same length of time. It is difficult to rationalise the difference between these two observations.

The use of the Norrish type II reaction for the removal of methoxy substituents in pyranosiduloses has been reported.\textsuperscript{31} In t-butanol solution, ketone (46) undergoes a photolytic reaction to give formaldehyde and the demethoxylated ketone (47) in 40\% yield. In the photolysis of the 3-sidulone (48) two products, a mono-demethoxylated product (49, 10\%), and a

di-demethoxylated compound (50, 90%), were reported. While the mono-demethoxyltion is readily accounted for by a straightforward Norrish type II process, the di-demethoxyltion appears to involve a radical recombination followed by collapse of the hydroxyoxetan shown in Scheme 5.

![Scheme 5](image)

The mechanistic speculation concerning removal of one methoxy-group is perfectly valid in the light of current knowledge, but it is remarkable that there is no evidence for the oxetan formation in this demethoxyltion reaction which seems essential for the high yield of di-demethoxylated material in the second example.

In the photochemistry of simple alkanones, attempts have been reported to establish the difference between the contribution of singlet and triplet states to the overall fragmentation process. Both groups of workers have shown that the triplet quantum yield is enhanced in hydroxylic solvents, a fact which suggests that there is some stabilisation of the triplet diradical (51) by solvation. Wagner has shown in a study involving pentan-2-one and hexan-2-one that in hexane solution 30% of the elimination, represented in Scheme 6, arises from the singlet state.† This state shows a selectivity for hydrogen abstraction with secondary hydrogens preferred to primary in the ratio of 12 : 1. The triplet state reaction is even more selective, the abstraction of secondary hydrogens being preferred to primary hydrogen abstraction in the ratio of 17 : 1.

The introduction of fluorine atoms into a simple alkanone alters the amount of singlet state elimination. Thus in the photolysis of pentafluorocan-2-one (52), four products (53—56) are obtained. Products (53)

---


† In the gas phase, photolysis of pentan-2-one shows that 35% of the elimination reaction occurs from the S¹ state with 316 nm light while with 265-4 nm light 82% elimination occurs from the singlet state. The triplet state plays a much bigger part in solution, and in quenching experiments 85% of the reaction could be suppressed after low conversions (3-6%).
Photolysis of Carbonyl Compounds

and (54) appear in equal amounts since they arise from the Norrish type II reaction. Quenching studies show that 93% of the reaction occurs from the triplet state. The difference between these results and those reported earlier could be due to enhanced intersystem crossing (heavy atom effect).

2 Norrish Type I Reactions

Norrish type I cleavage of organic molecules is now a well documented reaction. During the past year several reports have been devoted solely to this study. The reaction now known as the 'seco-acid process' is typical, and is exemplified by the reported photolysis in aqueous dioxan of oxosteroid (57). The reaction involves cleavage of the cyclohexanone ring to give the more stable diradical† which after H-abstraction gives rise to the ketene (58). Subsequent attack by nucleophiles (H₂O, Bu₄OH, or MeOH).

† In the photochemical ring-opening reactions of cyclohexanones the direction in which the ring cleaves adjacent to the carbonyl group is influenced by α-substituents. This influence is due to the stabilising effect substituents can exert on the resulting diradical and the normal differences in stability, tertiary > secondary > primary, are observed.

---

gave the products (59). As is typical of the reaction the stereochemical integrity of the atom originally bonded to the carbonyl group is lost. Similar results are obtained \(^{37}\) from the photochemical ring opening of ring A of friedelien (60) in ethanol. Various products are obtained from this reaction, the major one being the ester (61a). Minor amounts of other products are also isolated, namely isofriedelien (62) the product of recombination of diradical intermediate (63), friedelanol, and a hydrocarbon mixture resulting from photochemical decarbonylation. The seco-acid (61b) is the major product from photolysis in acetic acid–water mixtures.

A novel example of this reaction is the use of an intramolecular nucleophile as a trap for the keten intermediate. The photolysis of 3-β-acetoxy-5α-hydroxycholestan-6-one (64) in ethanol or benzene is reported \(^{38}\) to give the lactone (65) completely stereospecifically. The 5–β isomer of (64) gives the opposite stereochemistry shown in lactone (66). The complete specificity of the reaction is remarkable since usually the generation of the radical centres in this cleavage reaction allows attack by the rehybridised C-atom either on the top or underside of the molecule. The fact in this case that H-abstraction is stereospecific could be due to the retention of configuration by H-bonding of the hydroxy-group with the ketone [represented in (67)] a possibility worthy of further study. Photolysis \(^{38}\) of the non-hydroxylated compound (68) brings about ring-opening analogous to that of compound (64). This is to be expected since bond rupture in this direction gives rise to the more stable diradical.

Octahydro-2-quinoline (69) is also reported \(^{39}\) to photolyse in methanol to give a poor yield (13\%) of the ester (70a). Much better yields (35\%) of products are obtained using amines [e.g. cyclohexylamine and n-butylamine, (70a and c)]. The reaction is envisaged as taking place by N—C


bond rupture to give the enamine keten (71) which is then attacked by external nucleophile to produce the ester or amides.

In the absence of nucleophiles, photolysis of cyclic ketones undergoing Norrish type I cleavage gives rise to different products and there seems little evidence for keten formation under such conditions. Typical of this is the report\(^\text{40}\) of a reinvestigation of the solution photolysis of 2-methylcyclohexanone. Three products are isolated; (72) formed in trace amounts by the less favourable ring-opening route, and (73a) and (73b), the two products from the more stable diradical. An earlier report\(^\text{41}\) suggested that only one isomer of (73) was produced, but this has now been shown to be in error. Possible photoisomerisation of (73a) to (73b) has been excluded by the photolysis of a mixture of (73a) and (73b). No direct conclusion regarding the multiplicity of the reaction was reached, although the authors\(^\text{40}\)


suggested that a triplet state may be involved in liquid-phase reactions. The suggested transition state for formation of the isomeric heptenals (73a, b) is represented in (74).

Mechanistic studies on the photochemical decomposition of γ-lactones (75) in solution have shown that the quantum yield of products is wavelength-dependent, and that the products can arise by either C—C or C—O bond rupture. The overall reactions fall into four classifications: (i) formate formation via (A); (ii) aldehyde formation via (B); (iii) loss of CO_{2}; and (iv) olefin formation. The products formed with the measured values of Φ are shown in Table 3. The effect of wavelength is seen more dramatically by

![Diagram](https://via.placeholder.com/150)

Table 3 Products from the photodecomposition of γ-lactones

<table>
<thead>
<tr>
<th>Lactone</th>
<th>Ester</th>
<th>Dicarbonyl compound</th>
<th>Cyclopropane</th>
</tr>
</thead>
<tbody>
<tr>
<td>(75a) Allyl formate</td>
<td>Succinaldehyde</td>
<td>Cyclopropane</td>
<td>0.013</td>
</tr>
<tr>
<td>Φ (253·7 nm)</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Φ (238 nm)</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(75b) 3-But-2-ethyl formate</td>
<td>2-Me-succinaldehyde</td>
<td>Methylcyclopropane</td>
<td>0.27</td>
</tr>
<tr>
<td>cis and trans</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Φ (253·7 nm)</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Φ (238 nm)</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(75c) 4-(Pent-2-ethyl) formate</td>
<td>Acetonylacetone</td>
<td>Methylcyclopropane</td>
<td>0.004</td>
</tr>
<tr>
<td>Φ (253·7 nm)</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Φ (238 nm)</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

comparison of the formate/aldehyde ratio (R), at the two wavelengths used, for γ-butyrolactone. Thus at 253·7 nm, R = 3.83, while at 238 nm R = 1.91. The α-methyl substituents obviously influence the stability of diradicals of type A. Simonaitis and Pitts attribute the effect either to a decrease in the rate of back reaction or an increase in the disproportionation. Finally, attempts to establish the multiplicity of the reaction by quenching experiments showed that only the decomposition of valerolactone (75c) to 3-but-2-ethyl formate was quenched by pent-2-ene.

Finally, in this section is reported the photolysis of ferrocenyl propiophenone (76) to give numerous compounds, one of which was identified as

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benzoyl ferrocene. The reported work on ferrocene photochemistry is sparse, and appears not to justify an extensive report at this time.

3 Keto-sulphide Photolysis

Several papers have appeared on various aspects of ketone photolysis involving some participation of sulphur atoms, usually in the form of a good leaving group. Elimination of thyl radicals is reported\(^\text{44}\) to account for the formation of \(\alpha\)-naphthol from the photolysis of ketosulphides (77). The stability of the departing radical is of importance and better yields of product are obtained using tolyl (37%) and mesityl (53%) substituents attached to sulphur; conversely benzyl groups give poorer yields (17%). Comparable results are obtained from the photolysis of the acyclic ketone (78a) producing the chalcone (79) in 33% yield. The report that acyclic ketone (78b) did not undergo a similar reaction could be explained on the grounds that the wrong wavelength was being employed for the photolysis; but relevant information was omitted from the paper, and no evidence was put forward for the proposed reaction sequence.\(^\text{44}\)

Tosyl groups are also effective as leaving groups in the photolysis\(^\text{45a}\) of \(\alpha\)-sulphonyloxy-ketones (80). Following \(n \rightarrow \pi^*\) excitation, ketone (80) is converted in benzene solution into enone (81) or in dioxan solution into a 4:1 mixture of enone (81) and cyclohexanone (82). Cationic intermediates are invoked\(^\text{45}\) to explain the formation of enone (81) arising by methyl


migration and deprotonation via intermediate (83). Proof of this was obtained by photolysis of ketone (80) in dioxane–water mixture whence the enone (81) and alcohol (84) were isolated. By separate experiments alcohol (84) was shown to be a product of the initial photolysis. This work is compared with closely similar studies by the same authors.\textsuperscript{46b}

\[
\begin{align*}
\text{(80)} & \quad \text{(81)} & \quad \text{(82)} & \quad \text{(83)} & \quad \text{(84)}
\end{align*}
\]

$\beta$-Ketosulphides (85, $X = \text{CH}_3$) in t-butanol as solvent undergo photoreduction and ring-opening.\textsuperscript{46} The product of the ring-opening reaction is the t-buty1 ester (86) which is produced by a Norrish type I reaction and keten intermediate. Change of solvent to trichlorotrifluoroethane brings about a change in product to give both a ring-contracted (87) and a ring-expanded product (88). Attempts to establish a mechanistic route to the

\[
\begin{align*}
\text{(85)} & \quad \text{(86)} & \quad \text{(87)} & \quad \text{(88)} & \quad \text{(89)} \\
\text{(90)} & \quad \text{(91)} & \quad \text{(92)}
\end{align*}
\]

products via the ylide (89) were futile. The disulphide (85, $X = \text{S}$) is reported to undergo\textsuperscript{46} ring-contraction to 3-thiacyclobutanone by elimination of thioformaldehyde; further proof is awaited. However the spiroketone (90) also gave 3-thiacyclobutanone and a dimer of thiocyclohexanone (91).

Various ketosulphones (92) have also been studied\textsuperscript{47} photochemically in methanol, but only pinacols were isolated.

A photo-Stevens rearrangement may form part of the mechanism of the photochemical rearrangement of keto-stabilised sulphonium ylide (93) to yield indanone as the only volatile product.\textsuperscript{48} Ketocarbene intermediate


(94) was rejected since photolysis of ylide (93) with deuterium atoms at the benzylic position gave a product with deuterium at C-3. The intermediate for the formation of indanone was shown to be ketosulphide (95)

by independent photolysis of this to yield indanone through a Norrish type II elimination. Indanone is also isolated in low yield (7%) from the photolysis of acyclic ylide (93). It seems reasonable that this reaction arises from a carbene intermediate.\textsuperscript{48} Ganter and Moser\textsuperscript{49, 50} have studied the photochemical rearrangement of bicyclic ketosulphide (97a). The molecule shows two discrete absorptions in the u.v., a charge-transfer band at 245 nm and an \( n \rightarrow \pi^* \) band at 305 nm. The products isolated depend to a large extent on which band is excited. Scheme 7 illustrates the structure of the products isolated and Table 4 shows some of the experimental details.

From these results it can be seen that compound (100) is obtained almost exclusively by irradiation in the charge-transfer band in methanol whereas

\[
\text{Scheme 7}
\]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Filter</th>
<th>(97a)</th>
<th>(97b)</th>
<th>(98)</th>
<th>(99)</th>
<th>(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>Quartz</td>
<td>35</td>
<td>0.8</td>
<td>6</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrex</td>
<td>60</td>
<td>2.5</td>
<td>18</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>Quartz</td>
<td>38</td>
<td>9.8</td>
<td>9</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrex</td>
<td>29</td>
<td>23</td>
<td>12.5</td>
<td>10.5</td>
<td></td>
</tr>
</tbody>
</table>

sensitisation by benzene gives compounds (99), (97b), and (100) in almost equal amounts. Irradiation into the \( n \rightarrow \pi^* \) band yields products (98), (97b), and (100). The products (97b), (98), and (99) presumably arise from a Norrish type I photocleavage with keten formation and intermolecular nucleophilic attack in methanol, and intramolecular lactone formation in benzene. The bicyclic ether (100) results from \( S-C \) bond fission followed by ketalisation (Scheme 8); a homolytic mechanism is preferred.

\[
(97a) \quad \text{Scheme 8} \quad (100)
\]

### 4 Photolysis of Bicyclic Ketones

[2,1,1] Systems.—Meinwand and Chapman\(^{51}\) have studied the photocatalytic rearrangement of bicyclo[2,1,1]hexan-2-one (101, \( n = 1 \)). The primary product from the irradiation in pentane is the unsaturated aldehyde (102) resulting from Norrish type I fission. Subsequent photolysis of this gives rise to the tricyclic ether (103) formed by intramolecular Paterno–Büchi addition. Satisfactory proof is given for the structures of the compounds isolated. Change of solvent to ether gives both (102) and (103) and an additional product (104) from the radical addition of ether to the aldehyde function of (102).

\[
(101) \quad \text{(CH}_2\text{)}_n \quad \text{(102)} \quad \text{(103)}
\]

[2,2,1] Systems.—Bicyclo[2,2,1]heptan-2-one (101, \( n = 2 \)) undergoes photolysis\(^{51}\) in a manner exactly analogous to that of bicyclo[2,1,1]hexan-2-one, giving the corresponding unsaturated aldehyde, 3-cyclopent-1-enacet-aldehyde, and the tricyclic ether (105) formed by its subsequent photolysis.

Camphor (106) has received the greatest attention\(^{51–53}\) in this structural

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Photolysis of Carbonyl Compounds

group. The initial product derived photochemically from camphor is the aldehyde (107). Meinwald and Chapman report that this product is photochemically labile and gives rise to the cyclopentadiene (108). Both Agosta and Herron and Takeshita and Fukazawa report the formation of an unsaturated ether (109) derived from the carbene (110). Further evidence for carbene intermediacy is obtained from photolysis of camphor in ethanol, when the ether (111) is isolated.

\[3,1,0\] Systems.—A detailed mechanistic study of the photochemical isomerisation of trans-diphenylbicyclo[3,1,0]hexanone (112) to the cis-isomer (113) and vice versa is reported.\[34,35\] By application of the sensitive isotopic dilution technique, the quantum yields for the processes have been measured\[34\] the reaction scheme and products are recorded in Table 5.

**Table 5** Quantum yields for the photorearrangement of cis- and trans-5,6-diphenylbicyclo[3,1,0]hexanone

<table>
<thead>
<tr>
<th>Ketone ((\Phi_{\text{disappearance}}))</th>
<th>Products ((\Phi_{\text{appearance}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>112 ((\Phi = 0.104))</td>
<td>113 ((\Phi = 0.094))</td>
</tr>
<tr>
<td></td>
<td>3,4-Diphenylcyclohex-2-enone ((\Phi = 0.101))</td>
</tr>
<tr>
<td></td>
<td>4,4-Diphenylcyclohex-2-enone ((\Phi = 0.0007))</td>
</tr>
<tr>
<td>113 ((\Phi = 0.096))</td>
<td>112 ((\Phi = 0.093))</td>
</tr>
<tr>
<td></td>
<td>3,4-Diphenylcyclohex-2-enone ((\Phi = 0.0028))</td>
</tr>
</tbody>
</table>

The triplet nature of the reaction has been demonstrated by photosensitisation with chlorobenzene \((E_T = 82 \text{ kcal/mol})\). However, the use of optically active compounds revealed a divergence in the pathways of the rearrangement. Thus while trans-(112) photolysed cleanly to cis-(113) without loss of

---


configuration at C-5, irradiation of cis-(113) gave the trans-isomer with 28% racemisation. It is thus claimed\(^5^4\) that microscopic reversibility is not followed, implying an efficient crossing of potential energy surfaces. Thus different routes are followed for the cis-trans and the trans-cis isomerisations. Of the two modes of isomerisation available either by cleavage of bond \(i\) (the C-1—C-6 bond) or by cleavage of bond \(j\) (C-1—C-5 bond), the C-1—C-6 bond fission is favoured due to some degree of overlap control exercised by the molecule which makes bond \(i\) in the best position for overlap with the orbitals of the carbonyl group [represented in (114)].

[4,1,0] Systems.—Two reports on the photolysis of caran-4-one isomers have appeared in the past year.\(^5^6,\(^5^7\) (−)-cis-Caran-4-one (115,

\[
\begin{align*}
R^4 &= H, \quad R^1 = Me \\
(115) \\
R^4 &= Me, \quad R^1 = H \\
(116)
\end{align*}
\]

\(R^4 = H, R^1 = Me\) has been shown to undergo a Norrish type I reaction. The ring-opening is unidirectional to give the cyclopropylcarbinyl radical (116) with no evidence\(^6^6\) for isomerisation to the trans-caran-4-one (115, \(R^1 = H, R^2 = Me\)). Cocker et al.\(^5^7\) report preliminarily that the mixture of products from the photolysis in ether contains the cyclopentanone (117a). This compound, assigned trans-geometry by Heckert and Kropp,\(^6^6\) arises from ring-opening of intermediate (116) as shown below. The other mode of ring-opening via intermediate (118) gives a mixture of cis- and trans-cyclobutanones (119). Photolysis\(^6^6\) of the trans-caranone (115, \(R^1 = H, R^2 = Me\)) gives a mixture of the cis- and trans-cyclobutanones

\[
\begin{align*}
(116) &\rightarrow \quad (118) \\
&\downarrow \\
\rightarrow &\quad (119)
\end{align*}
\]


Photolysis of Carbonyl Compounds

(119) and the cis-cyclopentanone (117b). Evidence for the triplet nature of the reaction was obtained by quenching and sensitisation reactions.\(^{56}\)

**[5,2,1] Systems.**—The photochemistry of larger bicyclic ketones has received little attention. Gutsche and Baum\(^{58}\) have examined the photochemistry of bicyclo[5,2,1]decan-10-one (120) and some derivatives. The photo-reactions of the compounds are dependent on the formation of a keten (121) [when \( R = H \) in (120)] arising by Norrish type I cleavage and subsequent transannular hydrogen abstraction. In the presence of nucleophiles the keten can be trapped as ester or amide (122), but in hydrocarbon solvents decarbonylation ensues to produce carbene (123); the isolated products (Scheme 9) can all be explained as arising from this intermediate. It is interesting to speculate on the electronic multiplicity of the carbene produced in the decarbonylation step. The bicyclic hydrocarbons, produced by insertion reactions, presumably arise from a singlet state carbene while the olefin cyclooctene conceivably arises from the triplet. This olefin formation also constitutes another example of 1,2-H-migration occurring during a photochemical reaction. Addition of alkyl substituents (120, \( R = \text{Me} \)) enhances decarbonylation to produce 2,8-dimethylnona-1,8-diene as a major product. That no decarbonylation takes place from the unsubstituted ketone could be attributed to the stability of the radical produced. Evidence for the formation of aldehyde (124) is obtained solely by spectro-

\[ (123) \xrightarrow{} \]

Scheme 9

\[ \text{H} + \text{H} + \text{H} + \text{CHO} \]

scopic techniques since this compound subsequently photolyzes to give a mixture of hydrocarbons.

5 Carbonyl Addition Reactions

Oxetan Formation.—Perhaps one of the better understood photochemical reactions of carbonyl compounds is the addition to olefins to yield oxetans. An extensive review of the subject has appeared covering both mechanistic and synthetic aspects of the process. A review article on energy transfer in the Paterno–Büchi reaction has also been published. The most important aspects of the work published in the past year concerning oxetan formation are those which explore the mechanism of the reaction in an attempt to explain the causes and significance of the process.

Turro and Wriede have examined the addition of acetone to the electron-rich olefin cis-1-methoxybut-1-ene in an attempt to study the reactivities of $S_1$ and $T_1$ acetone in oxetan formation. The analysis of the system was simplified by examining only two of the four isomeric oxetans formed (Scheme 10) since treatment of the reaction mixture with acid removed the two ketals leaving the two isomeric 3-methoxyoxetans (125a, b).

\[
\begin{align*}
\text{Et} & \quad \text{Et} \\
\text{MeO} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\end{align*}
\]

(125a) \quad (125b)

\[
\begin{align*}
\text{OMe} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{Et} & \quad \text{O} \\
\end{align*}
\]

(126a) \quad (126b)

Scheme 10

The use of penta-1,3-diene as quencher gave a limiting ratio of 1:1 for 125a : 125b. In the presence of high quencher concentration this ratio increases to 4:1, and the same value can be obtained by increasing the olefin concentration. Analysis of this information showed that the ratio (125a + 125b) : (126a + 126b) is 1:4 for both singlet and triplet reactions. The rates of reaction of the singlet and the triplet were comparable and this in association with the better stereospecificity of singlet attack implies the same rate-determining step for attack of singlet or triplet on the olefin.

---

Thus it is suggested\(^{61}\) that attack gives rise to two intermediates shown above either as a singlet or a triplet diradical. The preference shown for formation of (125a) is claimed to arise from virtual bonding in the singlet diradical. However, bond closure may be very much faster than rotation and hence the stereospecificity is retained, whereas in the triplet intermediate bond rotation is probably faster than intersystem crossing. The acetals (126a and b) formed arise from the opposite mode of attack of the ketone on olefin and there appears to be only a slight preference (60 : 40) for the mode of attack which gives the better diradical. Such a postulate is also examined by Schroeter\(^{62}\) for the addition of ketones to other alkoxyolefins. The results obtained by this author shows that the cycloaddition cannot be predicted on the basis of the stability of the intermediate biradicals. In this case the reaction is claimed to be predominantly triplet since almost complete quenching can be effected by addition of penta-1,3-diene. Some of the results obtained are shown below in Table 6. The results as published suggest that the 2- and the 3-isomers are obtained pure whereas Turro and Wriede\(^{61}\) obtain cis–trans isomers for each type.

### Table 6

<table>
<thead>
<tr>
<th>Carbonyl compound</th>
<th>Olefin</th>
<th>Oxetan (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-isomer</td>
<td>3-isomer</td>
</tr>
<tr>
<td>Acetone</td>
<td>MeCH═CHOPr&lt;sub&gt;n&lt;/sub&gt;</td>
<td>OR (43)</td>
</tr>
<tr>
<td></td>
<td>Et&lt;sub&gt;4&lt;/sub&gt;C═CHOEt</td>
<td>(85)</td>
</tr>
<tr>
<td></td>
<td>MeCH═C(OEt)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(45)</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>MeCH═CHOPr&lt;sub&gt;n&lt;/sub&gt;</td>
<td>(44)</td>
</tr>
<tr>
<td></td>
<td>MeCH═C(OEt)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(45)</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>MeCH═CHOPr&lt;sub&gt;n&lt;/sub&gt;</td>
<td>(44)</td>
</tr>
<tr>
<td></td>
<td>Me&lt;sub&gt;2&lt;/sub&gt;C═CHOPr&lt;sub&gt;n&lt;/sub&gt;</td>
<td>(70)</td>
</tr>
</tbody>
</table>

The use of aldehydes as the carbonyl component for oxetan formation has not had much attention. Schroeter\(^{62}\), however, reports the addition of propanal to 2-methyl-1-propoxyprop-1-ene to obtain two isomeric oxetans (127a and b), and Shima and Sakurai\(^{63}\) report the addition of the same aldehyde to ethyl vinyl ether to obtain a cis–trans mixture of oxetan (127c) in 10% yield. Yang and Loeschen\(^{64}\) have studied the addition of 9-anthraldehyde to tetramethylethylene, and suggest that an upper triplet


state is the reactive intermediate in oxetan formation by the anthraldehyde.

There is therefore little doubt that with carbonyl compounds and electron-rich olefins the reaction to form oxetans takes place from the triplet state. However with electron-deficient olefins the reaction is reported to take place from the singlet state. Typically acetone and methacrylonitrile produce an oxetan (128) in 42% yield together with dimers (129) of

\[
\text{Et} \quad \text{O} \\
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\text{R}^4 \\
\end{array}
\]

(a) \( \text{R}^1 = \text{R}^2 = \text{Me}, \text{R}^3 = \text{H}, \text{R}^4 = \text{Pr}^\text{n} \text{O} \)
(b) \( \text{R}^1 = \text{R}^4 = \text{Me}, \text{R}^3 = \text{H}, \text{R}^1 = \text{Pr}^\text{n} \text{O} \)
(c) \( \text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}, \text{R}^4 = \text{OEt} \)

(127)

the nitrile. Quenching studies show that dimerisation of the nitrile is suppressed by the quencher implying that this takes place from the triplet while oxetan formation is unaffected. This gives support for the singlet nature of the oxetan formation unless the reaction either (a) takes place at a rate in excess of diffusion control (which is extremely unlikely), or (b) results from excitation of a pre-complex of the two reactants (which is more likely even though no charge-transfer absorption was seen in the u.v. spectrum of the mixture). No explanation was made for the surprising specificity of the reaction which gives the product arising in a formal sense from the less stable hypothetical diradical intermediate. The authors suggest that the stereochemistry of oxetan (128) is consistent with formation in a concerted (singlet) manner via photoexcitation of a weak ground state \( \pi \)-complex of the reactants oriented so as to minimise \( \sigma \)-bond repulsions.

The addition of acetone to dimethyl maleate and dimethyl fumarate has also been examined.\(^{66}\) The reaction analysis was complicated by the ready photoisomerisation of the esters employed, which required extrapolation of the results to time zero. The products formed are shown below: it should be noticed that the maleate forms both \( \text{cis-} \) and \( \text{trans-} \) (130 and 131), and the fumarate only \( \text{trans-} \) (131). Analysis of the kinetic data suggests that the compounds are formed by attack of triplet ester on ground-state ketone. The reaction sequence is suggested\(^{66}\) to provide a further divergence from the generally accepted mechanism for oxetan formation, but such a mechanism has already been suggested\(^{67}\) for the addition of benzophenone to adduct (132a).

A transcript of a lecture given at Caracas, 1967, gives a review of some of the work carried out by Rivas et al.\(^{68}\) on the photoaddition of benzophone

Photolysis of Carbonyl Compounds

\[
\begin{align*}
&\text{O} &\text{H} &\text{CO}_2\text{Me} \\
&\text{H} &\text{CO}_2\text{Me} \\
&\text{(130)} \\
\end{align*}
\]

\[
\begin{align*}
&\text{O} &\text{H} &\text{CO}_2\text{Me} \\
&\text{H} &\text{CO}_2\text{Me} \\
&\text{(131)} \\
\end{align*}
\]

(a) \( R^1 = R^2 = R^3 = R^4 = H \)
(b) \( R^1 = \text{Me}, R^2 = R^3 = R^4 = H \)
(c) \( R^2 = \text{Me}, R^1 = R^3 = R^4 = H \)
(d) \( R^1 = \text{CH}_2\text{OH}, R^2 = R^3 = R^4 = H \)
(e) \( R^1 = R^3 = H, R^2 = R^4 = \text{Me} \)
(f) \( R^1 = R^3 = \text{Me}, R^2 = R^4 = H \)

\[\text{(132)}\]

to various furan derivatives. All follow the route described earlier by other workers and give products which can be predicted on the grounds of the more stable diradical. Compounds (132b–f) are examples of the products.

The use of allenes as the substrate for carbonyl addition is reported by Gotthardt, Steinmetz, and Hammond.\(^9\) For example, acetophenone reacts with tetramethylallene to yield the mono-adduct (133, \( R = \text{Me} \)) and the bis-adduct (134, \( R = \text{Me} \)). The quantum yield for acetophenone disappearance was measured as 0.59 and corresponds to addition of triplet acetophenone to the allene. It is also pointed out that only carbonyl compounds with a lowest \( n-\pi^* \) state add to olefins. The mono-addition is extremely specific and gives only products of the type represented by (133) arising from the diradical intermediate (135). The addition of the second molecule of ketone is less specific, and consideration of the two possibilities for diradical intermediates shows them to be equally likely. Thus with benzophenone and tetramethylallene a mono-adduct (133, \( R = \text{Ph} \)), and two bis-adducts (134, \( R = \text{Ph} \)) and (136) result. Analogous compounds

\[
\begin{align*}
\text{Ph} & & \text{O} & & \text{Me} & & \text{Me} & & \text{Me} \\
\text{R} & & \text{Ph} & & \text{Me} & & \text{Me} & & \text{Me} \\
& & & & & & & & \text{(133)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & & \text{O} & & \text{Me} & & \text{Me} & & \text{Me} \\
\text{R} & & \text{Ph} & & \text{Me} & & \text{Me} & & \text{Me} \\
& & & & & & & & \text{(134)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & & \text{O} & & \text{Me} & & \text{Me} & & \text{Me} \\
\text{R} & & \text{Ph} & & \text{Me} & & \text{Me} & & \text{Me} \\
& & & & & & & & \text{(135)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & & \text{O} & & \text{Me} & & \text{Me} & & \text{Me} \\
\text{R} & & \text{Ph} & & \text{Me} & & \text{Me} & & \text{Me} \\
& & & & & & & & \text{(136)} \\
\end{align*}
\]

The quenching of fluorenone fluorescence by the ketenimine. The suggested mechanistic scheme is shown below (Scheme 11). This takes into account adduct formation by way of a singlet fluorenone \((F^1)\)–ketenimine complex as well as by triplet state \((F^3)\) addition.

\[
\begin{align*}
\text{Fluorenone (F)} & \xrightarrow{h\nu} F^1 \\
F^1 & \xrightarrow{K_t} F + h\nu' \\
F^1 & \xrightarrow{K_{dt}} F \\
F^1 & \xrightarrow{K_{isc}} F^3 \\
F^1 + \text{Ket} & \xrightarrow{K_o} \text{(complex)*} \\
\text{(complex)*} & \xrightarrow{K_{r1}} \text{adduct} \\
\text{(complex)*} & \xrightarrow{K_{d1}} F + \text{Ket} \\
F^1 + Q & \xrightarrow{K_{d1}} F + Q^* \quad \longrightarrow \quad Q \\
F^3 & \xrightarrow{K_{d2}} F \\
F^3 + \text{Ket} & \xrightarrow{K_{r2}} \text{adduct} \\
F^3 + Q & \xrightarrow{K_{d3}} F + Q^* \quad \longrightarrow \quad Q
\end{align*}
\]

Scheme 11

The kinetic analysis of the reaction allows values of \(\Phi\) (singlet) and \(\Phi\) (triplet) to be calculated. The values are found to be ketenimine-concentration-dependent (Table 7). From these results it can be seen that as the ketenimine concentration increases the singlet contribution becomes more important with a three-fold increase in \(\Phi\), and the fluorenone singlet–ketenimine complex proceeds to adduct with a 60% efficiency. Finally at high concentration of ketenimine there is a dramatic decrease in \(\Phi\) for adduct formation which is not explained by this work.

The photochemical intramolecular addition reaction\(^7\) of the norbornene ketone \((143, R = \text{Me})\) is unusual since the product is oxetan

Structure proof was obtained from degradation by reductive ring-opening and oxidation to obtain two acids, one of which was identified as 3-exo-methylnobornane-2-endo-carboxylic acid (145). Several other carbonyl compounds ($R = H, Et, benzyl, Ph, \alpha$-naphthyl) have been examined and cyclised. The exo-isomer of (143) produced no new volatile products on photolysis.

The photoreaction of thiobenzophenone with olefins and dienes has been described. The irradiations were all carried out by the use of the 589-0 nm line of a sodium lamp which is responsible for the $n \rightarrow \pi^*$ excitation of the thioketone. However, no definite assignment regarding the electronic multiplicity is given, the intermediate being assumed to be a triplet. It is also pointed out that both u.v. (366-0 nm) and visible radiation are capable of bringing about the reaction, although better yields are given by the light of longer wavelength. An earlier study had reported that the same excited state was produced by both wavelengths. Of particular interest is the addition to electron-rich olefins whereby thietanes (146) are obtained. Efficient additions are reported to trans- and cis-propenylbenzene, and to $\alpha$-methylystyrene. Addition to trans-propenylbenzene and $\alpha$-methylystyrene only produces one thietane ($R^1 = Ph, R^3 = Me, R^2 = R^4 = H$, and 146, $R^1 = Ph, R^2 = Me, R^3 = R^4 = H$ respectively) while additions to the cis-isomer yields two adducts (146, $R^1 = Ph, R^3 = Me, R^2 = R^4 = H$ and 146, $R^1 = Ph, R^4 = Me, R^3 = R^3 = H$). This isomerisation of the olefin (cis to trans in the ratio of 1:1) is evidence cited by the authors for the triplet nature of the reaction.

Dienes and thiobenzophenone usually yield adducts resulting from 1,4-addition to the diene rather than thietane formation, although cycloocta-1,3-diene is atypical giving an adduct assigned (n.m.r.) structure (147) as the only product. Typical of 1,4-addition to dienes are the reactions with isoprene [two adducts of gross structure, (148a, b)], with cyclopentadiene [adduct (149)], and with 1,4-diphenylbuta-1,3-diene [adduct (148c)]. Contrary to the results of addition to propenylbenzenes

---

(146)

(147)

(a) $R^1 = R^3 = H, R^2 = Me$
(b) $R^1 = R^2 = H, R^3 = Me$
(c) $R^1 = Ph, R^2 = R^3 = H$

(148)

Aryl $= m$ and $p$ anisyl
$m$-Me-phenyl
$p$-Cl-phenyl
$m$ and $p$-CN-phenyl
phenyl

(150)

(which have been previously described as producing thietans), the parent styrene and alkylsubstituted styrenes give bis-adducts (150) on photolysis. It is reported that alkyl substituents have no effect on the addition, and in this respect the addition of thiobenzophenone is very similar to the addition of thyl radicals to olefins. No reasons are given for the differences which lead to bis-adducts or thietans.

6 Reductions, Pinacolisations, etc.

Quenching Effects.—Interest in the mechanistic details of quenching of the photoreduction or pinacolisation of aromatic ketones has continued during the past year. Of particular interest are the studies related to the use of amines and the possibility of electron transfer as an essential step for the photoreduction. Davidson and Lambeth have investigated the effects of physical quenchers on the reduction of benzophenone by amines and alcohols. Values of $k_d/k_r$ ($k_a =$ rate of quenching, $k_r =$ rate of H-abstraction), have been measured, and are recorded in Table 8.

Naphthalene is known to be a good quencher of benzophenone triplets, but if electron transfer is an essential step in the photoreduction, then, the authors claim, inefficiency will be due to a low concentration of ‘free’ excited carbonyl groups. There is, however, the possibility that the electron-transfer process is faster than diffusion-control quenching and this also would account for inefficiency in quenching. This would fit in with the reduced efficiency of the chelate quenchers by a factor of 10 [benzophenone

photooxidation by diphenylmethanol is quenched by iron(III) acetylacetone \( (k_a/k_r = 540) \) and iron(III) dibenzoylmethanate \( (k_a/k_r = 3410) \). The use of diphenylmethanol to reduce benzophenone can also be quenched by amines, and again the results suggest electron transfer with tri-p-tolylamine acting as a better quencher than triphenylamine because the radical cation of the former is more stable. However, an interesting solvent effect is noted in the use of acetonitrile to increase the quenching efficiency of triphenylamine \( (k_a/k_r = 620) \). Davidson and Lambeth conclude that with amines of high ionisation potential the formation of intermediate \( R_2N^+ \overline{O} - \overline{CR}_2 \) is unfavourable.

Cohen and Guttenplan suggest that such an intermediate is possible, at least for the reduction of fluorenone triplets. The overall reduction is shown in equation (1). The postulates are based on a study of fluorenone.

\[
\begin{align*}
& \overset{\text{C=O}}{\text{C}} + \overset{\text{N-CH}}{\text{N}} \rightarrow (\overset{\text{C-\overline{O}}}{\text{C}} \overset{\text{\text{N-CH}}}{\text{N}}) \rightarrow \overset{\text{\text{C-OH}}}{\text{C}} + \overset{\text{\text{N-\text{C}}}'}{\text{N}} \tag{1}
\end{align*}
\]

A two-step mechanism involving electron transfer is also proposed to account for the influence of sulphides on benzophenone photooxidation. From the results shown in Table 9 it can be seen that two effects occur, a quenching effect and a reducing effect. The mechanism is shown in equation (2). With the aliphatic sulphide, back electron transfer to give starting materials is a preferred process whereas in the amine system the rates \( (k_2 \text{ and } k_3) \) are comparable, and efficient photo-reduction takes place.

---

**Table 8** Values for \( k_a/k_r \) for the effect of quenchers on the photooxidation of benzophenone by amines and alcohol

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Amine or alcohol</th>
<th>Quenching species</th>
<th>( k_a/k_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂CO</td>
<td>( N)-Dimethylaniline</td>
<td>Naphthalene</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( N)-Methylidiphenylamine</td>
<td>Naphthalene</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( N)-Dimethylaniline</td>
<td>Iron(III) acetylacetone</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>( N)-Dimethylaniline</td>
<td>Iron(III) dibenzoylmethanate</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>Diphenylmethanol</td>
<td>Triphenylamine</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Diphenylmethanol</td>
<td>Tri-p-tolylamine</td>
<td>525</td>
</tr>
</tbody>
</table>

---

Photolysis of Carbonyl Compounds

\[
\text{Ph}_2\text{CO}^* + \text{RSCH}_2\text{R} \xrightleftharpoons[k_i]{k_s} \text{Ph}_2\text{C}^\ddagger - \ddagger + \text{RSCH}_2\text{R} \\
\text{Ph}_2\text{CO} + \text{RSCH}_2\text{R} \xrightarrow[k_3]{\text{Ph}_2\text{COH} + \text{RSCH}_2\text{R}}
\]

(2)

Table 9  Influence of aliphatic sulphides on the photoreduction of benzo-phenone

<table>
<thead>
<tr>
<th>[Ph₂CO] (m) in benzene</th>
<th>Alcohol or sulphide</th>
<th>Quenching species</th>
<th>Φ</th>
<th>(k_d/k_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.064</td>
<td>iso-Borneol (0.17)</td>
<td>Naphthalene</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>0.062</td>
<td>di-n-Butylsulphide (0.01–0.1)</td>
<td>di-n-Butylsulphide</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>iso-Borneol (0.2 m)</td>
<td>Methyl phenylsulphide</td>
<td>570</td>
<td></td>
</tr>
<tr>
<td>0.067</td>
<td>iso-Borneol (0.21 m)</td>
<td>di-n-Butylsulphide (0.0084 m)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methyl phenylsulphide</td>
<td>7.5</td>
<td></td>
</tr>
</tbody>
</table>

The introduction of electron-donating substituents into the benzene ring of benzo-phenone can radically alter its photoreduction in isopropanol. p-Aminobenzophenone (PABP) is typical: its inefficient photoreductions by isopropanol and 2-butylamine (Φ < 0.001) are reported \(^{80}\) to be due to a low-lying unreactive charge-transfer triplet. However, PABP is reduced by triethylamine (Φ = 0.72–0.57). The quantum yield is highest at low PABP concentration and in dilute solution of amines in hydrocarbons where either light-absorbing transients are minimised or there is more efficient \(S_1\)–\(T_1\) intersystem crossing. PABP also pinacolises efficiently (100%) in di-isopropylamine but gives only 55% pinacol in triethylamine. The results reported \(^{80}\) are in good accord with the electron-transfer concept.

In the above systems, one of the major needs is for an explanation of the observed decrease in quantum yield for the photoreduction of benzo-phenone and its derivatives in isopropanol. The interpretation of the results is of continuing interest, and it is generally thought that highly coloured light-absorbing species (151) are the cause of the inefficiency. Cohen and

(151)

Cohen \(^{81, 82}\) report results arising from the study of change of isopropanol concentration using mixtures diluted with a hydrocarbon solvent. These results, recorded in Table 10, followed the initial observation that a reduction in the overall quantum yield occurred in neat isopropanol; thus at


Table 10  Influence of dilution on the quantum yield of photoreduction of benzophenone in isopropanol–benzene solutions

<table>
<thead>
<tr>
<th>[Isopropanol] (M) in benzene</th>
<th>Φ for benzophenone disappearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat alcohol</td>
<td>1.16</td>
</tr>
<tr>
<td>5.0</td>
<td>1.32</td>
</tr>
<tr>
<td>3.0</td>
<td>1.71</td>
</tr>
<tr>
<td>1.0</td>
<td>1.57</td>
</tr>
<tr>
<td>0.7</td>
<td>1.60</td>
</tr>
<tr>
<td>0.5</td>
<td>1.41</td>
</tr>
<tr>
<td>0.27</td>
<td>1.16</td>
</tr>
<tr>
<td>0.10</td>
<td>0.71</td>
</tr>
<tr>
<td>0.05</td>
<td>0.45</td>
</tr>
</tbody>
</table>

18% reduction Φ = 1.12 whereas at 37% reduction Φ = 0.79 for benzophenone reduction. From the results shown in Table 10 (measured for 9% conversion) the best value of Φ is obtained with a concentration of 3.0—0.7 M Pr4OH. The theoretical limiting value of Φ is 1.9 and this is only obtained in neat alcohol if low light intensities are used. These authors 81, 82 conclude that the effects noticed on dilution are due to the light-absorbing properties of a relatively long-lived transient of the form represented by structure (151). Such isopinacols were originally suggested by Schenck et al. 82a Spectral evidence for these intermediates is reported 83, 84 from a study of benzophenone and substituted benzophenones. Dilute (10-4 M) solutions of benzophenone and some derivatives were irradiated (253.7 nm) until the u.v. spectra showed no further change. The change exhibited by the u.v. spectra was a build-up in a longer wavelength absorption (Table 11). 84 Subsequent irradiation of the long wavelength band by longer wavelength irradiation brings about a gradual disappearance of the new absorption. In explanation of the results Bäckström and Niklasson 84

Table 11  Long-wavelength absorption produced by irradiation of benzophenones in alcohols

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Alcohol</th>
<th>λmax nm</th>
<th>A_μ/c₀ d (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>Pr⁴OH</td>
<td>322</td>
<td>5200</td>
</tr>
<tr>
<td></td>
<td>EtOH</td>
<td>319</td>
<td>4000</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>315</td>
<td>1300</td>
</tr>
<tr>
<td>4,4'-Dimethyl benzophenone</td>
<td>Pr⁴OH</td>
<td>332</td>
<td>4200</td>
</tr>
<tr>
<td></td>
<td>EtOH</td>
<td>318</td>
<td>1900</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>No maxima</td>
<td>700</td>
</tr>
<tr>
<td>4,4'-di-t-Butyl benzophenone</td>
<td>Pr⁴OH</td>
<td>349</td>
<td>3800</td>
</tr>
<tr>
<td></td>
<td>EtOH</td>
<td>345</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>323</td>
<td>600</td>
</tr>
</tbody>
</table>

propose combination of 2-hydroxy-2-propyl radicals and a ketyl radical to give the isopinacol (152). In the case of benzophenone, spectra show the presence of both o- and p-isomers (152). The effect of long-wavelength irradiation is to isomerise the isopinacol to the normal mixed pinacol. A similar independent study of the photochemistry of 4,4-di-t-butylbenzophenone has been reported.\textsuperscript{83} Irradiation in degassed isopropanol gives an absorption at 345 nm which decays slowly with time, in reasonable agreement with the previous work.\textsuperscript{84} The presence of the isopinacol as the light absorbing transient is proposed.

To date, the evidence for isopinacol formation relies heavily on spectroscopic and kinetic studies.\textsuperscript{83, 84} For the synthetic chemist it is always slightly more rewarding to be able to isolate an adduct and prove its structure unambiguously. Such a result has been achieved by Challand\textsuperscript{85} in a study of the photolysis of acetophenone in cyclohexane-ether. In such a system the intermediacy of a phenyl-ketyl radical is beyond question and the usual pinacols (153, as diastereoisomers), as well as products resulting from radical coupling between the phenylbutyl radical and the 1-ethoxy-1-ethyl radical (from solvent ether), are isolated. A third minor product (154) from p-coupling is also isolated giving some further credence to the possibility of p- or o-coupling in alcoholic solvents.

\begin{align*}
\text{(153)} & \quad \text{(154)} & \quad \text{(155)} \\
\end{align*}

From a study\textsuperscript{86, 87} of phenylthienyl and phenylpyridyl ketones it is suggested that for photoreduction there is a relationship between the charge carried by oxygen in the excited state, based on Pariser–Parr calculations, and the chemical reactivity. To exemplify this point 2- and 3-benzoxythiophene undergo photoreduction in isopropanol with quantum yields of 0.17 and 0.25 respectively, compared with the benzophenone value of 1.23. Traynard and Blanchi\textsuperscript{88} have calculated that the 2-isomer should be less reactive than the 3-isomer, and the actual values quoted are 0.14 and 0.30 respectively. Similar conclusions are cited\textsuperscript{87} for benzoxylyridines.

\textsuperscript{87} P. Traynard and J. P. Blanchi, \textit{Compt. rend.}, 1968, 266, C, 1511.
\textsuperscript{88} P. Traynard and J. P. Blanchi, \textit{Compt. rend.}, 1968, 267, C, 1381.
One of the simpler reactions of aromatic ketones is their photo-pinacolisation, which occurs with ease. A study carried out by Matsuura and Kitaura\(^8\) reports the influence of group size and aryl substituent on the \((\pm)\): meso ratio of diastereoisomeric pinacol formation. For alkyl phenyl butanes (156, \(X = H, R = H, Me, Et, Pr^1\)), the \((\pm)\): meso ratio increases slightly as \(R\) increases in bulk. The values for acetophenone and propiophenone are different from those reported\(^8\) by earlier workers.

The influence of aryl substituents on photo-pinacolisation of \(p\)-substituted acetophenones (156, \(R = Me, X = H, Me, Cl, and MeO\)) was also studied,\(^8\) and only in the case of the \(p\)-MeO was there any deviation from a

strict 1:1 ratio of \((\pm)\): meso. No solvent effect was found for acetophenone pinacolisation, in agreement with previous studies. However, the solvent effect was found\(^9\) to be quite large for the pinacolisation of 1-phenylpentan-1,4-dione. The u.v. spectrum of the ketone did not, however, allow identification of the excited state (\(\pi \rightarrow \pi^*\) or \(n \rightarrow \pi^*\)), owing to band overlap. In isopropanol, the \((\pm)\): meso mixture (ratio 7:1) was isolated in 56% yield, in addition to acetalised dimer (157) in 8% yield which could be converted to the \((\pm)\)-compound by treatment with acid. The \((\pm)\)-product is assigned structure (158) and the meso-compound structure (159). Both compounds are formed by pinacolisation of the ketone followed by intramolecular acetalisation. The ratio \((\pm)\): meso changes to 3.5:1 in hexane and 2:1 in benzene. Although the \((\pm)\)-form, viewed as a Newman projection, is the more crowded, its stability may be enhanced in protic solvents. Thus a decrease in stability and a decrease in overall yield in hydrocarbon solvents tends to produce more of the meso-compound (159).

---


Reductions.—Associated with the pinacolisation reaction is the tendency for ketones and ketone derivatives to undergo photo-reduction. The dividing line between the two processes is still obscure, but there is some relationship between the stability of the ketyl radical and the ease with which photo-reduction takes place.

β-Ketophosphonates (160) have been shown to undergo efficient photo-reduction. This reaction occurs only when alkyl ketophosphonates (160, \( R = \text{Me or Et} \)) are used; and with an aryl ketophosphate (160, \( R = \text{Ph} \); \( R^1 = \text{Et} \)), pinacolisation is reported.\(^91\) The reaction takes place from the triplet state and is reasonably efficient (\( \Phi \) for ketone disappearance = 0.66). A study of sensitised ketophosphite (161) photolysis has been reported.\(^92\)

\[
\begin{align*}
\text{RCOCH}_2\text{PO(OR)} &\quad \text{RCOCH}_2\text{OP(OMe)} \\
\text{R} = \text{Me or Ph} &\quad \text{R} = \text{Me or Ph} \\
(160) &\quad (161)
\end{align*}
\]

\[
\begin{align*}
\text{PhCH} &\equiv \text{NR} \\
(164) &\quad \text{PhCH} \equiv \text{NHR} \\
(164a) &\quad \text{PhCH} \equiv \text{NHR}
\end{align*}
\]

\[
\begin{align*}
\text{MeO} &\quad \text{POMe} \\
(161) &\quad \text{MeO} \quad \text{POMe}
\end{align*}
\]

Two pathways are open to the molecule, the more facile being the rearrangement (photo-Arbusov) to produce the phosphinate (162) rather than the phosphinous ester (163). The suggested route to the phosphinate is via the intermediate diradical (1) with phosphorus participation. The quantum yield for the photo-Arbusov reaction has been determined (Table 12).

**Table 12** Quantum yield measurements for the rearrangement of ketophosphite (161)

<table>
<thead>
<tr>
<th>(161)</th>
<th>Solvent</th>
<th>Filter</th>
<th>Irradiating ( \lambda ) (nm)</th>
<th>( \Phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R = \text{Me} )</td>
<td>Acetone</td>
<td>Pyrex</td>
<td>313</td>
<td>0.003</td>
</tr>
<tr>
<td>Acetone</td>
<td>Quartz</td>
<td>253.7</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Acetone + Ph(_2)CO</td>
<td>Pyrex</td>
<td>313</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>( R = \text{Ph} )</td>
<td>Acetone</td>
<td>Quartz</td>
<td>253.7</td>
<td>0.29</td>
</tr>
<tr>
<td>Acetone</td>
<td>Pyrex</td>
<td>313</td>
<td>0.29</td>
<td></td>
</tr>
</tbody>
</table>

Imine Reduction.—Related to ketone reduction and pinacolisation (dimerisation) is the photochemical study of imine reduction. Contrary to earlier reports,\(^93\),\(^94\) that benzaldehyde-\(N\)-alkylimines (164) photodimerised to

---


yield diazocyclobutanes, other workers\textsuperscript{95}–\textsuperscript{97} have shown that the results could be interpreted as the aza-analogue of pinacolisation. Thus imine (164, \(R = C_6H_{11}\)) reacts efficiently in ethanol to yield the dimer (164a, \(R = C_6H_{11}\)) composed of 90\% \textit{meso}- and 5\% (±)-forms. Padwa \textit{et al.}\textsuperscript{95, 96} have studied the mechanism of the reaction and have shown\textsuperscript{96} enhancement by the presence of small quantities of sensitisers (\textit{e.g.} benzaldehyde). However, the triplet imine is not the H-abstraction species since the imine does not exhibit emission or quenching of benzophenone phosphorescence. The suggested reaction (Scheme 12) is shown below. Various ketones have

\[
\begin{align*}
\text{Ph}_2\text{CO}^* + \text{Me}_2\text{CHOH} & \rightarrow \text{Ph}_2\dot{\text{COH}} + \text{Me}_2\ddot{\text{COH}} \\
\text{Ph}_2\dot{\text{COH}} + \text{ArCH}=\text{NR} & \rightarrow \text{Ph}_2\ddot{\text{CO}} + \text{ArCHNHR} \\
\text{Me}_2\dot{\text{COH}} + \text{ArCH}=\text{NR} & \rightarrow \text{Me}_2\ddot{\text{CO}} + \text{ArCHNHR}
\end{align*}
\]

\textbf{Scheme 12}

been shown\textsuperscript{96} to sensitise the reaction although inefficiency is introduced with higher energy triplets due to partial quenching by the imine. On this evidence, and on the evidence that benzonitrile phosphorescence (\(E_T = 77\) kcal/mole) is decreased by increasing imine concentration, the imine triplet energy is in the range 77—85 kcal/mole. No further refinement of this value was made.

Fischer\textsuperscript{98} reported that photoreduction of benzophenoneimine gave benzhydrylamine as the sole product. However, a mechanistic re-examination of this reaction has shown,\textsuperscript{99} that with isopropanol as solvent, ammonia and the azomethine (165) are the products. The mechanism of the reaction

\[
\text{Ph}_2\text{C}=\text{NCHPh}_2
\]

(165)

is assumed to involve an \(n \rightarrow \pi^*\) transition in the imine (\(\lambda_{\text{max}} = 345\) nm, \(\varepsilon = 15\)) followed by H abstraction from the isopropanol solvent. Thus the primary product is benzhydrylamine but this is consumed by reaction with unreacted imine. The photoreduction is less efficient (\(\Phi = 0.03\)) than photoreduction of benzophenone (\(\Phi = 1.31\)) under the same conditions.

Photoreduction of \(N\)-aryI benzophenone imines has been shown\textsuperscript{100} to be a triplet process by quenching studies with piperylene. Unlike the previous case, the \(N\)-acyl benzohydrylamines are stable and can be isolated in quantitative yield.

7 Ketone Fragmentation Reactions

**CO Eliminations.**† The decarboxylation of norbornen-7-ones (166) is one of the more ready photoreactions. Depending on the nature of the substituent groups there are two pathways for subsequent reaction following decarboxylation.\textsuperscript{101} Thus the cyclohexadienes (167b and c) produced can ring-open to yield isomeric linear trienes (168) or eliminate a molecule of acetic acid [from (167d)] to yield 1,2,3,4-tetraphenylbenzene.

\[
\begin{align*}
\text{(166)} \\
\text{(a) } A &= B = \text{CO}_2\text{Me} \\
\text{(b) } A &= B = \text{CH}_2\text{OH} \\
\text{(c) } A &= \text{CN}, B = \text{H} \\
\text{(d) } A &= \text{OAc}, B = \text{H} \\
\text{(167)} \\
\text{(168)} \\
\text{(169)}
\end{align*}
\]

Doubt has been cast\textsuperscript{102} on an earlier report\textsuperscript{103} that photolysis of the norbornen-7-one (166, \(A, B = C\text{–N–C}\)) gives the bicyclo[2,2,0]hexene (169).

Fuchs\textsuperscript{102} has isolated the cyclohexadienes (167, \(A, B = –\text{C–NR–C–}\); \(R = \text{H} \text{ or} \text{Ph}\)) in good yield (80\%) by photolysis at 253-7 nm.

An application of this type of decarboxylation reaction as a two-step synthesis of aromatic compounds is described by Warrener \textit{et al.}\textsuperscript{104} Two photosteps are proposed, (i) decarboxylation to produce a cyclohexadiene, and (ii) aromatisation by photoelimination. Scheme 13 illustrates the approach. Tetraphenyl-o-quinodimethane (170) has been detected following the decarboxylation of 1,1,3,3-tetraphenylindan-2-one.\textsuperscript{106} Initial decarboxylation of the indanone at \(-75^\circ\) brings about formation of the benzocyclobutene derivative (171). This compound is thermally converted at room temperature to the dihydroanthracene (172), the only isolable product in

\textsuperscript{101} B. Fuchs and S. Yankelevich, \textit{Israel J. Chem.}, 1968, 6, 511.
\textsuperscript{102} B. Fuchs, \textit{Israel J. Chem.}, 1968, 6, 517.

† See also chapter 2 for decarboxylation of diketones.
Scheme 13, and by irradiation at $-185^\circ$ to the purple $\sigma$-quinodimethane (170) (which does not give an e.s.r. spectrum, suggesting that the ground state of the quinomethane is a singlet). Photolysis of the dihydroanthracene with 404 nm light at $-185^\circ$ brings about conversion to the $\sigma$-quinodimethane while irradiation of this at 530 nm reconverts the quinomethane to the dihydroanthracene. By irradiation with different wavelengths, photo-stationary states with different proportions of the quinomethane and the dihydroanthracene could be obtained. The interconversions are explained by application of the Woodward–Hoffmann rules. Quinkert et al.\textsuperscript{105} reason that for the cyclisations of the $\sigma$-quinodimethane (170) the molecule cannot be flat and that in order to minimise the steric interactions of the phenyl groups the cyclisations need to be conrotatory. Thus, for the thermal reactions, consideration of the HOMO (highest occupied molecular orbital) shows that the double bonds involved are arranged in a helix (Figure 1a) and that isomerisation of the quinodimethane to the benzocyclobutene is thermally allowed. For the photoinduced reaction the symmetry of the lowest unoccupied molecular orbital (LUMO) (Figure 1b) shows that conrotatory cyclisation to give the dihydroanthracene is an allowed process.

The photolysis of aziridones (173) proceeds by decarbonylation to yield imines.\textsuperscript{106, 107} The nature of the excited state has been shown to be $\pi \rightarrow \pi^\ast$
Photolysis of Carbonyl Compounds

HOMO for \( \alpha \)-quinodimethane:
Bonding between C-6 and C-3 to produce a 4-membered ring by conrotatory cyclisation (thermal process).

LUMO for \( \alpha \)-quinodimethane:
Bonding between C-1 and C-6 to produce a 6-membered ring by conrotatory cyclisation (photo process).

(a) \( \text{HOMO and LUMO diagrams for } \alpha \text{-quinodimethane (170)} \)

since the low intensity maximum at ca. 250 nm shows a hypsochromic shift on changing the solvent from hexane to ethanol. The reaction resembles a Norrish type I reaction and intermediates shown in Scheme 14 are postulated.

\[
\xrightarrow{hv}
\]

(a) \( R^1 = R^2 = \text{Bu}^t \)
(b) \( R^1 = R^2 = \text{adamantyl} \)

(173)

Scheme 14

\( N \)-Hydroxy-2-piperidone is reported\(^{108} \) to decarbonylate to \( N \)-hydroxy-pyrrolidine by photolysis in ethanol.

Gas-phase photolysis of ketones usually gives products arising from decarbonylation by a Norrish type I process. It is therefore not surprising that the perfluoro-derivatives of cyclo-pentanone, \(-\text{hexanone, -heptanone, and -octanone give products of decarbonylation}^{109} \) on irradiation in the \( n \rightarrow \pi^* \) region. No evidence for fluorine migration was found, and the corresponding cyclic fluorocarbon was the major organic product obtained from the cyclopentanone and the cyclohexanone. The large-ring compounds gave rise to additional products (perfluorocyclopentane and tetrafluoroethylene). The results are explained\(^{109} \) on the basis of diradical intermediates.


Decarboxylation.—The interest in possible syntheses of cyclobutadienes has continued during the past year. An approach involving the decarboxylation and decarbonylation of cyclobutenedicarboxylic anhydride (174) has been described. Various products are isolated after photolysis of the anhydride (174, R¹ = R² = Me) in ether through a Vycor filter. The initial process for decomposition appears to be decarboxylation to yield 1,2,3,4-tetramethylbicyclo[2,1,0]pent-2-en-5-one or 2,3,4,5-tetramethylcyclopenta-

dienone as intermediates. Most of the products isolated can be accounted for from these compounds as intermediates. Other products isolated, which could arise from the tetramethylcyclobutadiene, are octamethylcyclo-octatetraene (5.3%), dimers of the cyclobutadiene (anti 2.5%, and syn 0.6%) which are not converted to the cyclo-octatetraene), hexamethylbenzene (0.7%), and the photoisomer of octamethylsemibullvalene (175). These products do not establish beyond doubt the intermediary of the free cyclobutadiene. Subsequent experiments with the same anhydride in an organic glass at −196° gave an intense yellow colouration on irradiation. When the matrix was allowed to melt only two compounds were isolated, (i) the tetramethylcyclopentadienone dimer, and (ii) the Diels–Alder adduct of the cyclobutadiene with the cyclopentadienone (176). Results from the dimethyl anhydride (174, R¹ = H, R² = Me) photolysis are perhaps more convincing. Three isomeric cyclo-octa-
tetraenes, 1,2,5,6-, 1,2,4,7-, and 1,2,4,5-tetramethylcyclo-octatetraenes were

isolated. These derivatives evidently result from the decarboxylation of adducts (177a—c). Such results suggest that the cyclobutadiene exists and cyclo-adds as either form (178a or b), and are less favourably explicable on the basis of a diradical intermediate such as (178c).

The decarboxylation of NO-acylhydroxylamines (179) to give amides (180) by photolysis in benzene solution has been described.\(^\text{112}\) Of two available routes, radical recombination is favoured on the basis of cross-over experiments and photolysis of an optically active NO-acyl-hydroxylamine which gave complete racemisation of the amide product. Krull and Arnold\(^\text{113}\) have studied the gas-phase decarboxylation of \(\gamma\)-lactones and \(\gamma\)- butenolides. The major products are \(\text{CO}_2\) and the corresponding cyclopropane or cyclopropene. This work differs markedly from the solution-phase study of the photoreaction of butyrolactone reported previously (see ref. 42). The difference is presumably due to the lower chance of collisional deactivation of the excited molecules in the gas phase. The other hydrocarbon material isolated from the gas-phase study may arise from secondary photolysis of the vibrationally excited cyclopropane hydrocarbon.

\[ \begin{align*}
\text{PhCONHOCOMe} & \rightarrow \triangle + \text{CO}_2 + \text{CH}_3=\text{CHCH}_3 + \text{HC}=\text{CH} \\
(179) & & (180)
\end{align*} \]

![Scheme 15](image)

**Loss of Molecular Nitrogen.**—Of special interest in photochemical reactions involving loss of nitrogen are the reports\(^\text{114, 115}\) concerned with ring-cleavage of triazinones (181). Photolysis of these in alcohols gives rise\(^\text{114}\) to N-substituted anthranilates by way of the ketenimine intermediate (182a). The nitrogen left in the molecule has been shown\(^\text{115}\) by \({}^{15}\text{N}\) labelling to be that asterisked in structure (181). Such elimination leads to azetidineone (182b) which is in equilibrium with the ketenimine (182a). The nature of the excited state was not determined, but photolysis of (181, \(R = \text{Ph}\)) in acetone gives rise to acridone (183), perhaps by the intermediacy of a triplet state. Also of interest is the evidence\(^\text{116}\) cited for the intermediacy of


benzocyclopropenone in products formed from the photolysis of benzotriazine (181, \( R = \text{NO}_2\text{SC}_6\text{H}_4\text{p-CH}_3 \)) in methanol.

**Photoelimination of Two-carbon Fragments.**—The photochemical ring-opening of azetidones (184) has been investigated by Fischer.\(^{117}\) Two processes compete during the fission, one eliminating an isocyanate (I), the other producing anil (II). These are represented in Scheme 16. The reaction path follows either process I or II, depending on the nature of the substituent. Some of the results are shown in Table 13. The mode of ring

\[
R^1-N=C=O + \overset{R^2}{\underset{R^3}{\rightarrow}} \text{Process I}
\]

\[
\overset{R^1-N}{\underset{R^2}{\rightarrow}} \overset{R^3}{\downarrow} \overset{h\nu}{\rightarrow} \overset{R^1-N}{\underset{R^2}{\rightarrow}} \overset{R^3}{\downarrow}
\]

\[
R^1-N=C + CH_2=CH=O \text{ Process II}
\]

Scheme 16

---

Table 13  Photochemical decomposition of azetidones (184)

<table>
<thead>
<tr>
<th>Azetidone (184)</th>
<th>Solvent</th>
<th>Reaction path</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>R¹ R² R³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a Ph H H</td>
<td>Acetonitrile + aniline</td>
<td>II Ketene 85%</td>
<td></td>
</tr>
<tr>
<td>b Ph Ph H</td>
<td>Acetonitrile + aniline</td>
<td>II Ketene 19% and 0.011</td>
<td></td>
</tr>
<tr>
<td>c Ph Ph Ph</td>
<td>Acetonitrile + aniline</td>
<td>I Isocyanate 64% 0.031</td>
<td></td>
</tr>
<tr>
<td>d Ph CO₂Et CO₂Et</td>
<td>Cyclohexane + aniline</td>
<td>I Isocyanate 51%</td>
<td></td>
</tr>
</tbody>
</table>

opening appears to be dependent on the type of substituent attached to atoms 1 and 4. When groups capable of stabilising free radicals are attached at C-4, process I predominates. One might have expected the transition bringing about the reaction to have been of \( n \to \pi^* \) character, but u.v. data for the azetidones were not reported in this paper. The reaction cannot apparently be photosensitised, azetidone (184b) giving no products on photolysis in acetone; thus a singlet mechanism is implied.

The photolysis of 7-ethoxycarbonylbenzonorcaradiene (185) in cyclohexane does not appear to follow the accepted pathway for such compounds in that only part of the product is accountable by elimination of ethoxycarbonylcarbene (which is trapped by the solvent cyclohexane, and isolated in 10% yield as methyl cyclohexylacetate). Other products, namely methyl 1- and 2-naphthyl acetates (14 and 4%), are formed by cyclopropane bond rupture and H-migration. However, the most unusual product is the bicyclic ester (186), the mechanism of formation of which is still in doubt.

W. M. H.

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Enone Rearrangements and Cycloadditions: Photoreactions of Cyclohexadienones, Tropones, Quinones, etc.

1 Enone Rearrangements

A. α,β-Unsaturated Carbonyl Compounds.—Highly stereoselective photolytic and thermal ring-openings of phenylcyclobutenones (1) via their valence-isomeric keten intermediates (2) in methanol have been described by Baldwin and McDaniel.\(^1\) The products (3) from the reactions were isolated as the methyl esters and spectral analysis of these esters indicated that ring-opening had occurred in such a way as to place the C-4 substituent trans to the phenyl group in the resultant ester. The opposite stereochemistry was obtained in the thermal reactions. The rationale for the photoreaction, and the observed stereochemistry, are difficult to explain. The observed stereochemistry for the photoreaction stems from a rotation of the C-4 atom moving the bulky group in towards C-1, with the smaller H-atom moving out. Several proposals are put forward\(^1\) to explain this, one of which is that the geometry of the ground state of the reactant determines the mode of ring-opening and hence product geometry. However, as far as the cyclobutenone (1a) is concerned, such an argument predicts a ring twisted in the contrary sense to that in the geometry actually determined by X-ray crystallography.\(^1\) Electronic influences are also suggested, but additional studies will be necessary to solve the problem.

For many years the problems of the intermediacy of a keten in photo- or thermal reactions had to be solved by chemical means, namely the addition of a nucleophile to trap the keten. Recently low-temperature studies in i.r.

Enone Rearrangement and Cycloadditions

cells have provided spectroscopic evidence for such intermediates. Typical of this is the work of Chapman et al.\textsuperscript{5,8} One example of this work is pertinent to the above mentioned studies of Baldwin and McDaniel\textsuperscript{1} and involves the spectroscopic observation of the vinyl keten intermediate (\textit{i.r.}\textsubscript{max} at 2145 cm\textsuperscript{-1}) (4) obtained by the photolysis of tetrachlorocyclobutenone at −190°. Chapman et al.\textsuperscript{5,8} have also studied umbellulone (5)

and lumisantonin (6). After irradiation at −190°, neat umbellulone exhibits i.r. absorptions at 2113, 1670, and 1630 cm\textsuperscript{-1} attributable to the keten (7) and the cyclohexadienone (8). The bands attributed to the cyclohexadienone disappear on warming to −90° and the keten bands disappear at −70°: both products give rise to thymol (9). The keten (7a) can be trapped as the ester (7b) by irradiation in a methanol–ether glass at −190°, but direct

irradiation of umbellulone in methanol at room temperature gives only thymol. Thus there are two paths to thymol in the low-temperature experiments. Lumisantonin (6b) shows only absorption for the keten (6a) on irradiation at low temperatures, although the dienone (6b) may also be formed in trace amounts.

The important point of this work, apart from the spectroscopic evidence for keten formation, is that it provides yet another mode of rearrangement of bicyclo[3,1,0]hex-3-en-2-ones.\textsuperscript{4} The difference could be attributed\textsuperscript{8} to substituent effects but this point has still to be investigated. Chapman

et al.\textsuperscript{8} also point out that these results do not exclude keten–carbene mechanisms.\textsuperscript{6}

The photolysis of tetra-substituted bicyclo[3,1,0]hex-3-en-2-ones (10a) in ethanol yields phenols (11).\textsuperscript{6} The excited state is claimed to be \( n \rightarrow \pi^* \) triplet, as in previous reports by the same authors.\textsuperscript{7}

The mechanism is subsequently envisaged as producing a diradical followed, in the best Zimmerman\textsuperscript{8} tradition, by electron demotion to yield the zwitterion (12) which can deprotonate to yield the phenol (11).

\[
\begin{align*}
\text{(a) Aryl} & = p\text{-NMe}_2\text{phenyl} \\
\text{(b) } & = p\text{-anisyl} \\
\text{(c) } & = p\text{-Br-phenyl} \\
\text{(d) } & = p\text{-Cl-phenyl}
\end{align*}
\]

(10)

Monahan\textsuperscript{9} reports a similar photorearrangement of 4,5,6-triphenylbicyclo[3,1,0]hex-3-en-2-one (13) to give two phenols, 2,4,5-triphenylphenol (50\%), and 3,4,5-triphenylphenol (20\%), which can also be accounted for on the basis of zwitterionic intermediates.

(13)

The photorearrangement of 1,5,6-triphenyltricyclo[3,1,0,0\textsuperscript{2,6}]hexan-3-one (14), which can be converted into bicyclohexanone (13) by treatment with base, gives\textsuperscript{9} solely 2,4,5-triphenylphenol. This work is similar to a previous study\textsuperscript{10} on 1,6-diphenyltricyclo[3,1,0,0\textsuperscript{2,6}]hexan-3-one, where the mechanism of the ring-opening was interpreted as shown in Scheme I [applied to tricyclohexanone (14)].

The influence of substitution on the types of reaction which cyclohex-2-en-1-one derivatives can undergo has been reviewed by Dauben, Shaffer, and others.\textsuperscript{10}

\textsuperscript{7} H. Dürr and P. Heitkämper, \textit{Annalen}, 1968, \textit{716}, 212.
Enone Rearrangements and Cycloadditions

(14) \[ \text{Ph} \rightarrow \text{Ph} \]

Scheme 1

and Vietmeyer.\textsuperscript{11} The essential structural feature of the cyclohexenones which undergo the "lumirearrangement" reaction, is 4,4-disubstitution. Thus molecules of structure (15) photorearrange, as exemplified by the conversion of (15a), by photolysis in t-butanol, to bicyclo[3,1,0]hexan-2-one (16). Alkyl migration does not take place in this particular class of re-arrangement. However, investigation\textsuperscript{12-15} on the photolysis (at 366 mm) of

\[
\begin{align*}
\text{(a) } & R^2 = R^3 = \text{Me}, R^1 = R^4 = \text{H} \\
\text{(b) } & R^2 = R^3 = R^1 = \text{Me}, R^4 = \text{H} \\
\text{(c) } & R^2 = \text{Me}, R^3 = R^4 = (\text{CH}_2)_4, R^1 = \text{H}
\end{align*}
\]

(15)

4,4-diphenylcyclohex-2-en-1-one (15, $R^1 = R^4 = \text{H}, R^2 = R^3 = \text{Ph}$) shows that phenyl migration takes place to give three products, viz., trans- and cis-5,6-diphenylbicyclo[3,1,0]hexan-2-one (17a and 17b), and 3,4-diphenylcyclohex-2-en-1-one (18). The previously mentioned technique of reverse

\[
\begin{align*}
\Phi & \cdot 0.043 \\
(17a) & \\
\Phi & \cdot 0.0003 \\
(17b) & \\
\Phi & \cdot 0.0002 \\
(18) &
\end{align*}
\]

\textsuperscript{13} R. L. Morse, \textit{Diss. Abs.}, 1968, 28, B, 4504.
\textsuperscript{14} K. G. Hancock, \textit{Diss. Abs.}, 1968, 29, B, 105.
isotopic dilution was again used employing the starting ketone labelled at C-4. The values of the quantum yield are shown below the appropriate structures. The reaction is remarkably stereoselective, giving the trans-
bicyclic ketone in preference to the cis-ketone in the ratio of 140 : 1. The
mechanistic interpretation given by the authors\textsuperscript{12} suggests two possible
routes, \textit{viz.}, either a stepwise process, which could account for the appearance
of the minor cis-isomer, or a concerted process, represented in (19)

![Diagram](image)

Migration of phenyl group from C(4) to C(3)
involving disrotatory twisting of the C(4)—C(5)
and C(1)—C(2) bonds.

(19)

(this can be classified in Möbius\textsuperscript{16} and Woodward–Hoffmann\textsuperscript{17} nomen-
clature) which produces solely the trans-isomer. Formation of the cyclo-
hexenone presumably also arises like the cis-isomer by hydride transfer from
the 'open-intermediate' (i) (Scheme 2). Triplet intermediates were shown\textsuperscript{13}

![Diagram](image)

\begin{equation}
\begin{align*}
&\text{(i)}
\end{align*}
\end{equation}

\textbf{Scheme 2}

to be formed following \(n \rightarrow \pi^*\) excitation of the starting enone, as with other
4,4-disubstituted cyclohexenones.\textsuperscript{18} The process was sensitised efficiently
by propiophenone, and quenching with naphthalene \((k = 2.5 \times 10^8 \text{ sec}^{-1})\)
gave linear Stern–Volmer plots. The rate of rearrangement of the 4,4-
diphenylcyclohex-2-ene-1-one triplet was estimated to be \(3.8 \times 10^7 \text{ sec}^{-1}\).
Subsequent study\textsuperscript{15} of this reaction has shown that the quantum yield is
independent of wavelength over a 100 nm range, a result which implies
rapid dissipation of excess of vibrational energy to the solvent. This result
also implies that the triplet state is the same regardless of the singlet state
configuration. The problem of solvent viscosity, notably its effect on

\textsuperscript{18} H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, and A. Sembelhack,
quantum yields and quenching, was raised in an earlier publication.\textsuperscript{12} Zimmerman and Elser\textsuperscript{15} have found that $\Phi$ is temperature and solvent dependent, but strikingly independent of solvent viscosity. These results are shown in Table 1 for \textit{trans}-bicyclic ketone (17a) formation. The

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp ($^\circ$C)</th>
<th>Viscosity (mP)</th>
<th>\textit{trans} $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butanol</td>
<td>28</td>
<td>37-4</td>
<td>0-086</td>
</tr>
<tr>
<td></td>
<td>63</td>
<td>9-4</td>
<td>0-231</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>20</td>
<td>3-07</td>
<td>0-029</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>73</td>
<td>6-86</td>
<td>0-180</td>
</tr>
</tbody>
</table>

importance of the temperature dependence was found in a 16-fold increase in the triplet rearrangement rate and only a much smaller increase in rate of triplet decay. Thus an activation energy of 10-5 kcal/mole is required for the rearrangement.

In support of an earlier proposal\textsuperscript{12} that the \textit{trans}-isomer (17a) is formed by a stereospecific concerted route, and the \textit{cis}-isomer (17b) by a nonconcerted process, activation entropies $T\Delta S$ (\textit{trans}) = 2-04 and $T\Delta S$ (\textit{cis}) = −0-19 kcal/mole are reported.\textsuperscript{15} Further investigations devised to differentiate aryl migration aptitudes\textsuperscript{19} are reported involving the photoisomerisation of 4-phenyl-4-\textit{p}-cyanophenylcyclohex-2-en-1-one (20) to produce the three products shown in Scheme 3. Analysis of the results

![Scheme 3](image)

shows that \textit{p}-cyanophenyl migrates more readily than phenyl; the rates are $3-35 \times 10^8$ sec$^{-1}$ and $0-309 \times 10^8$ sec$^{-1}$ respectively. More important from this study is the fact that the reaction is of a triplet nature, as shown by both sensitisation and quenching studies, and that migration of the group from C-4 to C-3 is an odd-electron process not involving electron deficiency, \textit{i.e.} electron demotion to produce a zwitterion.$\dagger$


$\dagger$ \textit{Senior Reporter's Note.} Diradicals, polarised diradicals, and zwitterions can be treated as belonging to a continuum of species only when the electron spins are paired. In the triplet manifold, the molecules can only legitimately be written as diradicals or inductively polarised diradicals since all electrons in the ground-state zwitterions are spin-paired and the involvement of electronically excited zwitterions would normally be ruled out on energy grounds.
The deconjugation of substituted cyclohexen-3-ones has been covered by a review article \(^\text{11}\) on cyclohexenone photochemistry. The geometry of several of these molecules precludes the possibility of intramolecular hydrogen abstraction leading to photoenolisation and subsequent deconjugation. Such is the conclusion stated by Kuwata and Schaffner \(^\text{30}\) in their investigation of \(O\)-acetyl-10\(\alpha\)-testosterone (21). Selective irradiation brought about double-bond isomerisation to 3-oxo-17\(\beta\)-acetoxy-\(\Delta^\text{5}\)-10\(\alpha\)-androstene (22). Thus \(\pi \rightarrow \pi^*\) irradiation in \(\text{Bu}^4\text{OH}\) gave the androstene (22, \(R = \text{H}\)) [or in \(\text{Bu}^4\text{OD}\) androstene (22, \(R = \text{D}\))], while \(n \rightarrow \pi^*\) excitation in benzene gave the same product. The results obtained using \(\text{Bu}^4\text{OH}\) suggest that the reaction arises from a vibrationally excited singlet state or from a triplet \(\pi \rightarrow \pi^*\) state; but it is difficult to make a definite assignment. However, by analogy with other enone deconjugation reactions the hydrogen abstraction process in benzene is thought \(^\text{30}\) to be due to intermolecular interaction of a \(n \rightarrow \pi^*\) triplet. 3\(\beta\)-Acetoxycholest-5-en-7-one (23) undergoes similar isomerisation to 3\(\beta\)-acetoxycholest-4-en-7-one (23a) on irradiation in \(t\)-butanol through a pyrex filter. \(^\text{31}\) An additional product is also isolated by subsequent photorearrangement of 3\(\beta\)-acetoxycholest-4-en-7-one but this will be discussed later. \(^\text{31}\)
A surprising result is the reported\textsuperscript{22} conversion of no-otkatone (24), the principal flavouring constituent of grapefruit, by photolysis in methanol through pyrex to yield (14.5\%) photo-no-otkatone (25). The rearrangement could be quenched by oxygen, inferring a triplet intermediate, presumably of $n \rightarrow \pi^*$. The rearrangement is proposed to take place as shown in Scheme 4. The rearrangement of androstene derivative (26) in a variety of solvents

\[ \text{Scheme 4} \]

and by either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ excitation has been reported in a detailed study\textsuperscript{23} to yield three compounds (27a), (27b), and (28). The bicyclic aldehyde (27a) is described as arising from a formal 1,2-migration of the aldehyde substituent, but the experiments described do not \textit{a priori} rule out a concerted process. The rearrangement to produce the enol (27b), a 1,3-migration, shows a small retarding effect when the deuterium analogue (26, $R = D$) is photolysed.

\[ \text{(26)} \quad \text{(27a)} \quad \text{(27b)} \quad \text{(28)} \]

Saboz \textit{et al.}\textsuperscript{24} report a new partial synthesis of $O$-acetyl-$\beta$-nortestosterone (29) by $\pi \rightarrow \pi^*$ excitation (253.7 nm) of the enone epoxide (30). It was thought that the decarbonylation of aldehyde (31) might account for the formation of the nortestosterone (29), but experiments in dioxan solution did not reveal its existence. The decarbonylation of diketone (32) (isolated as the enol from these reactions) could also be involved, but no experiments


to test this possibility were reported. 24 The diketone (32) could also be obtained from the enone oxide (30) \( n \rightarrow \pi^* \) (>310 nm) excitation, or by triplet sensitisation with acetophenone \( [E_T \text{ of } (30) = 55 \text{ kcal/mole}] \).

\[
\begin{align*}
(30) & \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \\
\text{O} & \quad \text{H} \\
\text{O}
\end{align*}
\]

\[
\begin{align*}
(29) & \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \\
\text{O} & \quad \text{H} \\
\text{O}
\end{align*}
\]

\[
(31) \quad \begin{array}{c}
\text{CHO}
\end{array}
\]

The stabilisation of the diradical intermediate (33) by the hydroxyl substituent facilitates 25 the ring-opening reaction of 5-hydroxyoctalone (34). The products (35a), (35b), and (35c) all result from this process, with product (35c) resulting from the secondary photolysis of (35b).

\[
\begin{align*}
(32) & \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \\
\text{O} & \quad \text{H} \\
\text{O}
\end{align*}
\]

\[
\begin{align*}
(33) & \quad \begin{array}{c}
\text{OHH}
\end{array} \\
\text{O} & \quad \text{H} \\
\text{O}
\end{align*}
\]

\[
(34) \quad \text{OH}
\]

\[
(35a) \quad \text{OH}
\]

\[
(35b) \quad \text{O}
\]

\[
(35c) \quad \text{O}
\]

The photolysis of O-ethoxycarbonyldimedone (36, \( R^1 = H, R^2 = \text{CO}_2\text{Et} \)) yields dimedone (36, \( R^1 = R^2 = H \)) and the product of recombination, 2-ethoxycarbonyl dimedone (36, \( R^1 = \text{CO}_2\text{Et}, R^2 = H \)), in low yield. 26

In larger cyclic enone systems, the stability of the \textit{trans}-isomer is enhanced by decrease of ring-strain. The results reported in a recent publication 27 confirm the earlier studies of Eaton and Lin 28 of the singlet state \textit{cis-trans} isomerisation of \textit{cis}-cyclo-oct-2-enone on photolysis. The basis of the assignment of the singlet nature of the reaction was an experiment with piperylene as quencher; however, the value of the triplet energy \( (E_T = 50 \text{ kcal/mole}) \) quoted for piperylene is in error 29 and it is conceivable that exothermal energy transfer was not possible. Addition of alcohols to the

28 D. I. Schuster and N. P. Kong Lau, \textit{Chemical Society Annual Meeting, Nottingham, April 1969}; Abstract 5.34 gives a value of \( E_T = 57-60 \text{ kcal/mole for piperylene}. \)
trans-enone (37) has been shown\(^{27}\) to be a ground-state reaction with no detectable contribution from a hypothetical dipolar intermediate (37a).

The potential use of the photocyclisation of cyclodeca-2,7-dien-1-one derivatives (38) for the synthesis of bourbonene and copaeene skeletons is described by Heathcock and Badger.\(^{30}\) The photolysis of the enone (38, R = Me) through a Corex filter gave as two readily identifiable products the copaeene (39a) and the bourbonene (39b): the yields were 22 and 32% respectively. These results have suggested caution in the application of Srinivasan’s\(^{31}\) ‘Rule of Five.’\(^{30}\)

One of the simpler examples\(^{32}\) in the photochemistry of acyclic \(\alpha,\beta\)-enones which has appeared during the past year is the deconjugation of esters to produce \(\beta,\gamma\)-unsaturated esters, the mechanism of which is a hydrogen abstraction reaction and has been discussed previously (Chapter 1, p. 135). However, a more detailed study by two separate groups\(^{33},^{34}\) of workers has shown the need for trans–cis isomerisation before the deconjugation step. The isomerisation of ethyl crotonate (40, \(R^1 = H, R^2 = Me\)) to ethyl isocrotonate (40; \(R^1 = Me, R^2 = H\)) takes place from an \(n \rightarrow \pi^*\) triplet state, and could be sensitised by benzophenone, acetophenone, and acetone, or quenched by piperylene. However, the conversion of isocrotonate (40; \(R^1 = Me, R^2 = H\))\(^{33}\) and ethyl 3,4,4-trimethylpent-2-enoate\(^{34}\) (40; \(R^1 = Me, R^2 = \text{t-Bu}\)) into the \(\beta,\gamma\)-isomers arose from singlet excitation. An additional product (41) arises from the cis-pentenoate (40; \(R^1 = \text{Bu}^t,\)

---


R² = Me) by H-abstraction and ring-closure. The overall consensus of opinion is that a cyclic intramolecular hydrogen transfer step affords the deconjugated ester as represented by Scheme 5. Similar conclusions were published a few years previously.

\[ \text{Scheme 5} \]

trans–cis Isomerisation has also been observed in the photolysis of \( \beta \)-aryl- and aroyl-acrylic acids, and in the conversion of trans-oxindigo (42a) to the cis-isomer (42b) with a quantum yield of \( \Phi = 0.63 \) for the trans–cis process and \( \Phi = 0.35 \) for the reverse. Irradiation of either trans- or cis-oxindigo gives a stationary state containing 59% of the cis-isomer.

\[ \text{(42a)} \quad \text{(42b)} \]

The photochemistry of 3-benzal-5-phenylazlactone (43a) is reported to be markedly wavelength dependent. Thus on irradiation with 365-0 nm light in isopropanol, the geometrical isomer (43b) of the azlactone was obtained. Similar u.v. irradiation of \( \alpha \)-benzal-\( \gamma \)-butyrolactone (44a) afforded the geometric isomer (44b). Change of the irradiating wavelength to 253-7 nm brought about a hydrogen-abstraction process, the rate of which, with reference to the azlactone, was dependent on the availability of solvent hydrogen. This particular reaction was inhibited by oxygen and by an increase in azlactone concentration. The azlactone inhibition was interpreted as self-quenching, but only of the hydrogen-abstraction reaction, and quantitative measurements gave a linear Stern–Volmer relationship.

\[ \text{References:} \]

The quantum efficiency for hydrogen abstraction was 0.4–1.0, giving a lifetime of ca. $4 \times 10^{-4}$ sec. Such efficiency is only consistent with a triplet excited state, a conclusion confirmed by sensitisation and quenching experiments. A more detailed study\textsuperscript{39} showed that both isomerisations and hydrogen-abstraction are capable of sensitisation. Table 2 shows the effects of various sensitisers on the photoreactions of azlactone (43). While the hydrogen-abstraction varied erratically with triplet energy, isomerisation was efficient with all sensitisers used. It is pointed out\textsuperscript{38} that the hydrogen-abstraction reaction must be related to some factor other than the triplet energy and it was demonstrated that isomerisation is exclusively sensitised when there is matching between the highest filled MO of the sensitiser and the lowest vacant MO of the azlactone. To summarise, the hydrogen-abstraction reaction arises from an $n \rightarrow \pi^*$ triplet and the isomerisation from a $\pi \rightarrow \pi^*$ triplet.\textsuperscript{38} The product isolated from the photoysis of the azlactone (43), by the hydrogen abstraction process was lactone (45) obtained in 17% overall yield. The product isolated from the analogous reaction of lactone (44a) was lactone (46) in an unspecified yield. In the azlactone case, at least, the final product (45) presumably arises by isopropanol addition and rearrangement as shown in Scheme 6, although the intermediate (ii) was not isolated. This is said to be the first study of wavelength dependence in such reactions.\textsuperscript{38, 39}

A similar geometric isomerism is at the base of a coumarin synthesis whereby $\alpha$-hydroxyphenyllactones (47a) or thiolactones (47b) are converted by the influence of light into the coumarin (48). The essential step is conversion into the geometric isomer (47c), followed by nucleophilic attack and ring-opening to afford the 3-substituted coumarins.\textsuperscript{40}

Padwa and Guber\textsuperscript{41} report the ready conversion of enone (49) into 1,4-diphenylbutan-1,4-dione by way of a 1,2-hydrogen migration and rearrangement (Scheme 7) in aqueous dioxan. In cyclohexane, photolysis takes a different route to yield enone (50) as a mixture of cis- and trans-isomers (established by n.m.r.: two Bu\textsuperscript{t} groups, $\tau 9.02$ and $8.71$; two PhCH\textsubscript{2}, $\tau 6.52$ and $6.28$: at $86^\circ$ the rotational barrier is overcome; $\Delta G = -18.5$ kcal/mole).

Enone Rearrangements and Cycloadditions

This product (50) is not the primary product of photolysis and variation of irradiation time allows isolation of the primary photoproduct (51). The conversion of this enone (50) by photolysis involves a 1,3-hydrogen migration which could in principle be concerted (a photochemically allowed $\sigma^* + \pi^*$ process).

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{NHBu}^+ \\
\text{CH}_2\text{Ph} & \quad \text{H} & \quad \text{(50)}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{Ph} \\
\text{CH}_2\text{NHBu}^+ & \quad \text{H} & \quad \text{(51)}
\end{align*}
\]

One of the most interesting results reported in the last year is the photoisomerisation of substituted acyclic acids\(^{42, 43}\) (52) to $\beta$-lactones (53a) or lactams (53b). cis-$\alpha$-Phenylcinnamic acid (52; $R^1 = R^2 = \text{Ph}, R^3 = R^4 = \text{H}, X = \text{O}$) on irradiation in benzene gave both the cis-2,3-diphenyl-3-propiolactone (53a; $R^1 = R^4 = \text{H}, R^2 = R^3 = \text{Ph}$) as the major product plus the trans-isomer (53a; $R^1 = R^3 = \text{Ph}, R^2 = R^4 = \text{H}$) as the minor. The irradiation of the trans-$\alpha$-phenylcinnamic acid (52; $R^1 = R^3 = \text{Ph}, R^2 = R^4 = \text{H}$) yields only the cis-diphenyl-lactone. The synthesis of several $\beta$-lactones is recorded.

\[
\begin{align*}
\text{R}^1 & \quad \text{O} & \quad \text{XR}^4 \\
\text{R}^2 & \quad \text{R}^3 & \quad \text{(52)}
\end{align*}
\]

\[
\begin{align*}
\text{R}^1 & \quad \text{O} & \quad \text{R}^3 \\
\text{R}^2 & \quad \text{(53a)}
\end{align*}
\]

\[
\begin{align*}
\text{R}^1 & \quad \text{O} & \quad \text{NR} \\
\text{R}^3 & \quad \text{(53b)}
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{NH} \\
\text{R} & \quad \text{(54)}
\end{align*}
\]

Subsequent photolysis of the cis-$\beta$-lactone with tetramethylethylen produced trans-diphenyltetramethyleyclobutane, while irradiation of the $\beta$-lactone in ether gave a complex mixture of products from which phenanthrene, a product from cis-stilbene cyclisation, was isolated. N-Phenylamidine (52, $R^4 = R^1 = R^2 = \text{Ph}, R^3 = \text{H}, X = \text{NH}$) and the simple amide (52, $R^1 = R^3 = R^4 = \text{H}, X = \text{NH}$) both give a mixture of cis- and trans-$\beta$-lactams (53b) with the cis-isomer being by far the major product. The $N$-phenyl amide gives an additional product (54), the result of a non-oxidative photocyclisation (see Chapter 4). The mass spectral assignments of the $\beta$-lactam fragmentations confirm the observations of Fischer (ref. 117, Chapter 1) who found that an $N$-phenyl group favoured elimination of benzaldehyde anil following electron bombardment, while the unsubstituted nitrogen favoured phenyl keten elimination. Chapman and Adams\(^{42}\) suggest that the cyclisation of the cinnamic acids takes place from a $\pi \rightarrow \pi^*$ state and belongs to the general class of electrocyclic reactions. Disrotatory ring-closure is favoured from $\psi_{10}$, the lowest unfilled molecular orbital (shown in the Figure), where oxygen—carbon bond formation is


favoured. With the amides, where only N—C bond formation is found, calculations show\textsuperscript{42} that indeed this process should also be favoured from $\psi_{10}$.

![Diagram](image)

\textbf{Figure} $\psi_{10}$ Lowest unfilled molecular orbital

An investigation\textsuperscript{44} into the photochemistry of conjugated aryl acetylenes (55) uncovered an example of an aryl migration followed by cyclisation to afford the major product (56) of the reaction. These results were different from those with esters of alkyl acetylenic acids when only reduction was found to take place.

\[
\text{Ph}_3\text{CC} \equiv \text{CCO}_2\text{Me}
\]

(55)

\[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{CO}_2\text{Me}
\end{array}
\]

(56)

\textbf{B. $\beta,\gamma$-Ketones.}—Williams and Ziffer report more fully their observations\textsuperscript{45, 46} on the photochemistry of $\beta,\gamma$-unsaturated ketones (57a) and (57b) to yield cyclopropanes (58a) and (58b) respectively. The reaction could formally be explained as a Norrish Type I photocleavage to give the allylic diradical, although the intermediate does not show hydrogen abstraction reactions which might be expected from a stable diradical.\textsuperscript{46} The formation of only one cyclopropane (58b) from the photolysis of the enone (57b)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

(57a)

\[
\begin{array}{c}
\text{OR} \\
\text{OR}
\end{array}
\]

(57b)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

(58a)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

(58b)


points towards a concerted process; a similar suggestion had been made previously, but could not be verified. A ring-contraction, similar in the essential steps to the previous example but without cyclopropane formation, has been described in the photolysis of \( \text{A-homo-cholest-[4a(5)]-en-3-one} \) (59). The products (60a) and (60b) are again the results of \( \alpha \)-cleavage followed by rebonding as represented in Scheme 8.

\[
\begin{align*}
\text{(59)} & \quad \rightarrow \quad \text{O} \\
& \quad \rightarrow \\
\text{(60a)} & \quad 53\% \\
\text{(60b)} & \quad 7\%
\end{align*}
\]

\[\text{Scheme 8}\]

Simpler examples of the above reactions are the subject of a paper by Paquette, Eizember, and Cox. Irradiation (\( n \rightarrow \pi^* \) excitation) of two cycloheptenones (61, \( R^1 = R^2 = \text{H} \) and \( R^1 = R^2 = \text{CH}_2 \)) gave the ring-contracted products (62a and 62b) respectively without any competing hydrogen-abstraction reaction or cyclopropane ring-opening. The reaction could not be quenched by piperylene, and was therefore either a singlet reaction or a triplet process exceeding diffusion control. The photoreaction of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (63) to methylcar-4-en-2-one (64) without any decarbonylation could be sensitised by benzophenone or acetone, but could not be quenched. The authors suggest that decarbonylation, the singlet process, is hindered by the secondary isotope effects of the four methyl substituents. Reference is made to earlier work of Schuster et al. where it was stated that the unsubstituted cycloheptadienone,

from a triplet state, was converted into a twisted cis-trans-3,5-cycloheptadienone followed by cyclisation into bicyclo[3,2,0]hepta-6-en-3-one. However, with the tetramethyl-substituted example, 'intracyclic' interactions would preclude this reorganisation and force the molecule into the carenone skeleton.

The photochemical ring-opening of 3-methylcar-4-en-2-one (64) has been observed to proceed via the keten intermediate (65a). The observation of this in the i.r. could be made at liquid nitrogen temperature or in ether at room temperature. Subsequent reaction of the keten with methanol gave rise to the expected ester (65b).

Baldwin and Krueger have shown the reaction to be remarkably stereoselective by the photolysis of deuterium-labelled molecules (asterisked methyl in 64) whereby the label appears in the ester at a specific site (asterisked in 65a and b). The photolysis of the epimeric labelled material gives labels appearing on the other methyl group. The claim that the mode of ring-opening is determined by the geometric shape of the molecule in the ground state and not by the nature of the substituents seems to be reasonably well substantiated. Thus the process can be viewed as a concerted 2+2+2+2 reaction proceeding suprafacially on each unit.

The photolysis of 3β-acetoxycholest-4-en-7-one (66; R = Ac, R¹ = H) has been previously reported (p. 184) to produce a β,γ-ketone (67). However, together with this product a rearranged ketone (68), is isolated shown to be derived from the β,γ-ketone. Incorporation of deuterium at C-6 of the starting material (66, R¹ = D, R = OAc) produces a rearrangement product with deuterium solely in the exocyclic methylene. (Table 3 shows the % deuterium at Hα and Hβ, as determined by n.m.r.)

<table>
<thead>
<tr>
<th>Compound (66)</th>
<th>Hα</th>
<th>Hβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = OAc, R¹ = 70% D</td>
<td>22</td>
<td>46</td>
</tr>
<tr>
<td>R = H, R¹ = 90% D</td>
<td>31</td>
<td>59</td>
</tr>
</tbody>
</table>

Enone Rearrangements and Cycloadditions

Additionally it has been shown by the photolysis of 4β-deuterio-3β-acetoxycholest-5-en-7-one (66) in [hydroxy-\(^{2}H\)\(_{1}\)]-butanol, from which labelled product was obtained, that the identity of the 6\(\alpha\) and 6\(\beta\) hydrogens is retained by orbital overlap (i) despite the reversibility of the reaction to the \(\gamma,\gamma\)-ketone (67) (Scheme 9).

![Scheme 9](image)

In a closely related study Paquette and Meehan\(^{52}\) have shown, from a study of simpler ketones (69), that the reactions to produce the bicyclic ketones (70) are completely reversible; in the cases studied, the photoequilibrium lies more toward the starting ketone (69).

![Diagram](image)

(69) \(R = \text{Me}, n = 1\)  
\(R = \text{H}, n = 1\)  
\(R = \text{H}, n = 0\)

(70) \(R = \text{Me}, n = 1; 13:0:1\)  
\(R = \text{H}, n = 1; 4:2:1\)  
\(R = \text{H}, n = 0; 7:3:1\)

C. \(\gamma,\delta\)-Ketones.—The ability of cyclopropyl groups to conjugate with ethylenic double bonds and carbonyl groups has been of interest for a number of years. In this connection, it has been shown that cis-bicyclo[5,1,0]octenone (71a, \(R = O\)) rearranges in methanol via a singlet excited state to the bicyclo[3,3,0]octenone (72a, \(R = O\)).\(^{53}\) The conjugated ketone (73a, \(R = O\)) undergoes a similar rearrangement via a singlet excited state to the bicyclic product (74a, \(R = O\)).


The hydrocarbons (71b and 73b) undergo reactions analogous to those of the above ketonic compounds. Thus, (71b, R = CH₃) is converted to the hydrocarbon (72b, R = CH₃) by direct irradiation (a singlet process), whereas the conjugated diene (73b, R = CH₃) was converted to hydrocarbon (74b, R = CH₃) by triplet sensitisation. This particular example is highly stereospecific, and raises again the interesting question whether triplet intermediates can react in a concerted manner, *i.e.* whether bond formation can be concerted to some degree with spin inversion. The Reporters foresee that substantially concerted processes involving triplet species will be increasingly recognised in the future. For convenience Scheme 10 shows product formation *via* a diradical intermediate.

![Scheme 10](#)

2 Addition and Cycloaddition Reactions of Enones

Hückel MO calculations on the influence of methyl groups on electron distribution in acrolein, cyclohexenone, and their derivatives have been reported, and an attempt has been made to correlate the calculations with experimental facts. In most cases photocycloaddition to olefins appears to have electrophilic character whereas cyclohexenone rearrangements should have radical character (see p. 183).

Typical of the synthetic value of photocycloaddition reactions is the addition of a variety of acetylenes and allenes to the C-16—C-17 double bond of 3β-hydroxypregna-5,16-dien-20-one acetate to furnish good yields of cyclobutenes and methylenecyclobutanes.

Dimethyl acetylenedicarboxylate is reported to photoadd efficiently to dihydropyran, producing the cis-cyclobutene adduct (75), but exceptionally inefficiently to furan. The adduct from furan is claimed on the basis of

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Enone Rearrangements and Cycloadditions

n.m.r. to have the exo:exo structure (76) as the result of 1:2 addition. The additional product from this reaction, is a 1:1 adduct and could well arise from a thermal process. The photoaddition of acetylenedicarboxylic acid and cyclohexa-1,4-diene produces an unusual product (77) which differs from the thermal product and might arise by a concerted addition, since 8 π-electrons are involved.

A. Cyclopentenone Cycloadditions.—During the past year de Mayo and his coworkers have reported a synthetic and mechanistic study of the scope of the photoaddition of olefins to cyclopentenone to form cyclobutanes. The quantum yield for the reaction has been shown to be independent of wavelength and solvent, apart from an inexplicable deviation in the case of benzene. The product distribution (Table 4) also does not vary with wavelength.

Table 4 Mixtures of cyclobutane adducts formed from cyclopentane and various olefins

| Olefin                | No. of products | Product ratio
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-But-2-ene</td>
<td>4</td>
<td>1.0 : 2.71 : 2.57 : 0.14</td>
</tr>
<tr>
<td>trans-But-2-ene</td>
<td>4</td>
<td>1.0 : 1.18 : 2.50 : 0.07</td>
</tr>
<tr>
<td>trans-Dichloroethylene</td>
<td>3</td>
<td>1.0 : 1.0 : 3.5</td>
</tr>
<tr>
<td>cis-Dichloroethylene</td>
<td>3</td>
<td>1.0 : 0.19 : 0.36</td>
</tr>
<tr>
<td>cis-Hex-3-ene</td>
<td>5</td>
<td>1.0 : 3.57^a : 0.05</td>
</tr>
<tr>
<td>trans-Hex-3-ene</td>
<td>5</td>
<td>1.0 : 2.32^a : 0.06</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>4</td>
<td>1.0 : 6.1^b : 1.5</td>
</tr>
<tr>
<td>Cyclo-octene</td>
<td>4</td>
<td>1.0 : 0.69 : 1.14 : 0.22</td>
</tr>
</tbody>
</table>

^ Determined by g.l.c.  ^ Composed of three isomers.  ^ Composed of two isomers.

The reaction has been shown to be a triplet process and this may account for the lack of stereospecificity (but see above). From the use of a variety of sensitisers, the conclusion is reached that cycloaddition with cyclopentenone takes place from an upper triplet state (E_T ca. 74 kcal/mole), and other reactions, such as reduction, take place from a lower state (E_T ca. 61 kcal/mole).

The lack of specificity is also exemplified in the cycloaddition of cyclopentenone to cycloheptene when four adducts (78a–d) in the ratio of 4:0:22:6:7:1:0 are isolated.

\[
\begin{align*}
\text{(a)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\text{(b)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\text{(c)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\text{(d)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

(78)

The synthesis of β-bourbonene (79) has also been achieved utilising the addition of cyclopentenone to 1-methyl-3-isopropylcyclopent-1-ene. Two isomers (80a and 80b) are isolated from the basic photoaddition. The correct isomer (80a) for the synthesis was shown to be structurally accurate by X-ray crystallography of the crystalline thiosemicarbazone. Conversion of ketone (80a) to β-bourbonene (79) was achieved by reaction with methylene triphenylphosphorane.

\[
\begin{align*}
\text{(79)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\text{(80a)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\text{(80b)} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

As shown in the above cycloaddition reaction there is always the problem of head-to-head and head-to-tail additions. Attempts have been made to propose a mechanism utilising the polar nature of the double bonds which could predict readily which isomer would predominate. It has been shown from a study of the cycloaddition of 2-methyl-3-acetoxydocalcophenone and the ethylene acetal of cyclohexenone that other effects are operative. While in many examples the polar theory does predict the direction of addition the overall dipole of the molecules, i.e. the dipole of the excited state enone.

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and the acetal olefin, could also contribute to the direction of addition. Two adducts (81a) and (81b) are isolated from the reaction and either can predominate depending on the solvent: in iso-octane, adduct (81a) is obtained in 98% yield, whereas in more polar solvents, e.g. methanol, adduct (81b) is isolated in 55% yield. From these results it seems to be possible, with careful choice of solvent, to control the direction of addition. It is stated that in this example the directing effects are greater than other previously studied systems. A paper has been published giving details of the synthetic applications of cyclopentenone cycloadditions.

B. Cyclohexenone Cycloadditions.—Cycloadditions of several olefins to 3-substituted cyclohexenones (82, R = Me, OAc, Ph) have been reported. The reactions could be sensitised by xanthone and quantum yields for product formation were determined as 0.54, 0.38, and 0.45 for the three cyclohexenones studied. No major deviations from Corey's π-complex hypothesis were found. Examples of the additions studied are shown in Scheme 11.

\[
\begin{align*}
\text{Scheme 11}
\end{align*}
\]
Chapman et al.\textsuperscript{69} have found evidence for competing additions to C=C and C=O in cyclohexenones (a duality often encountered in quinone photochemistry). Thus 4,4-dimethylcyclohexenone in tetramethylethylene gives two major products, a ketone (83) as the \textit{trans}-isomer only, and an oxetan (84). Subsequent photolysis of the ketone (83) in tetramethylethylene gave the two new products (85a and 85b) as the result of a Norrish type I cleavage followed by oxetan formation with the aldehyde (86).

\begin{center}
\begin{tikzpicture}
\node (83) at (0,0) {\includegraphics[width=0.5\textwidth]{83}};
\node (84) at (2.5,0) {\includegraphics[width=0.5\textwidth]{84}};
\node (86) at (5,0) {\includegraphics[width=0.5\textwidth]{86}};
\end{tikzpicture}
\end{center}

(83) (84) (86)

Direct irradiation of carbostyril (87) was originally reported\textsuperscript{70} to produce the \textit{anti} head-to-head dimer. During the past year further studies of cycloaddition reactions of carbostyril and olefins have been published.\textsuperscript{71, 72} The reaction is reasonably stereospecific, a feature explicable on the basis of Corey’s hypothesis\textsuperscript{64} whereby a $\pi$-complex is built up, following $n \rightarrow \pi^*$ excitation, and transforms into a product derived from the more stabilised diradical\textsuperscript{71, 72} [[iii] in Scheme 12].

Only \textit{cis}-fused products are isolated,\textsuperscript{71} the lack of \textit{trans}-isomers being attributed to strain (not usually a key factor in photochemistry). Several examples of the additions which can be achieved in good yields by direct irradiation,\textsuperscript{71} or in poorer yields \textit{via} benzophenone or acetone sensitisation,\textsuperscript{78} are given in Table 5. The dimer of the carbostyril is always a by-product.

Closely related to these observations is the reported\textsuperscript{73} photoaddition ($\lambda > 300$) nm of diphenylacetylene to $N$-methyl-5,6,7,8-tetrahydro-2-quinolone (88) giving the 1:1 adduct (89), presumably \textit{via} the diene (90). A highly insoluble dimer (91) of the quinolone and a second 1:1 adduct (92, 1\%)\textsuperscript{76}.

\textsuperscript{69} O. Buchardt, \textit{Acta Chem. Scand.}, 1964, 18, 1389.
Table 5  Cyclobutane adducts formed from carbostyril (87) and olefins

<table>
<thead>
<tr>
<th>Carbostyril</th>
<th>Olefin</th>
<th>% Adduct (No. of isomers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(87) R' = R^2 = H</td>
<td>Tetramethylethylene</td>
<td>90 (1)</td>
</tr>
<tr>
<td>(ref. 71)</td>
<td>Isobutylene</td>
<td>57 (1)</td>
</tr>
<tr>
<td></td>
<td>Methyl vinyl ether</td>
<td>36 (2)</td>
</tr>
<tr>
<td></td>
<td>Cyclopentene</td>
<td>59 (1)</td>
</tr>
<tr>
<td>(87) R' = Me</td>
<td>N-Methylmaleimide</td>
<td>40 (1)</td>
</tr>
<tr>
<td>R_2 = CF_3</td>
<td>Maleic anhydride</td>
<td>10 (1)</td>
</tr>
<tr>
<td>(ref. 72)</td>
<td>Cyclopentene</td>
<td>53 (1)</td>
</tr>
<tr>
<td></td>
<td>Ethyl acrylate</td>
<td>70 (1)</td>
</tr>
</tbody>
</table>

Scheme 12
were also formed. Subsequent investigation of the photoysis (253–7 nm) of the quadricyclane (89) in benzene solution (sensitisation possible?) brought about its conversion to adduct (92). This conversion could not be effected by 360 nm light.

C. Cyclodecenone Reactions.—An earlier report of the photoisomerisation of cis,cis-cyclodec-3,8-diene-1,6-dione (93a) suggested that the products are the cis,trans isomer (93b), and cis,syn,cis-tricyclo[5,3,0,0\textsuperscript{2,6}]decan-4,9-dione (94). However, Scheffer and Lunge dispute that latter assignment and propose that the cis,trans isomer (93b) is formed first, and subsequently transforms into the photoisomer (95). The cis,anti,cis geometry of (95) was proved by Clemmensen reduction to the known cis,anti,cis-tricyclo[5,3,0,0\textsuperscript{2,6}]decane.

3 Dimerisation of Enones

A reinvestigation of the solid-state dimerisation of benzalacetone, originally reported to give a head-to-head dimer, has shown that the dimerisation is in fact similar to that of other \(\alpha,\beta\)-unsaturated carbonyl compounds and yields the \(\alpha\)-truxilllic type, a head-to-tail dimer (96).

The photodimerisation of 1-acetylcyclopentene and 1-acetyl-2-methylcyclopentene, following \(n \rightarrow \pi^*\) excitation by direct irradiation, is reported.

A. Cyclopentenones.—Cyclopentenone is known to give two dimers, the head-to-tail (97a) and the head-to-head (97b). The ratio of these depends on the solvent employed. Two reports show that there is a reasonable

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linear relationship between the logarithm of the dimer ratio and the
dielectric constant (a term derived from the Kirkwood–Onsager equation)
for a variety of solvents. Table 6 shows the change in dimer ratio for
various solvents.

Table 6 Influence of solvent on dimerisation of cyclopentenone

<table>
<thead>
<tr>
<th>Dimer ratio (97a) : (97b)</th>
<th>Solvent (dielectric constant)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.16</td>
<td>t-Butanol (2.20)</td>
<td>1 M</td>
</tr>
<tr>
<td>2.70</td>
<td>Benzene (2.28)</td>
<td>2 M</td>
</tr>
<tr>
<td>2.03</td>
<td>Ethyl acetate (6.02)</td>
<td>1 M</td>
</tr>
<tr>
<td>1.44</td>
<td>Methanol (32.63)</td>
<td>1 M</td>
</tr>
</tbody>
</table>

A mechanistic study of the dimerisation has produced evidence for a
reversible step in the cycloaddition process.\textsuperscript{88} In acetonitrile, the dimer
ratio (97a:97b) did not vary when the concentration of ketone was
changed from 0.1 to 3.0M. The usual mechanism (equation 1) for photo-
dimerisation assumes irreversible addition.

\begin{align*}
\text{Cyclopentenone } S_0 & \longrightarrow \text{ Cyclopentenone } S_1 \\
\text{Cyclopentenone } S_1 & \longrightarrow \text{ Cyclopentenone } T_1 \\
\text{Cyclopentenone } T_1 & \longrightarrow \text{ Cyclopentenone } S_0 \\
\text{Cyclopentenone } T_1 + \text{ Cyclopentenone } S_0 & \longrightarrow \text{ dimers }
\end{align*}

(1)

However, values for the quantum yield of ketone disappearance (Table 7)
indicate that this process is inefficient compared to the quantum efficiency

Table 7 Quantum yield values for disappearance of cyclopentenone during
dimerisation

<table>
<thead>
<tr>
<th>Cyclopentenone (M\textsuperscript{-1})</th>
<th>$\Phi_{\text{dis}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.34</td>
</tr>
<tr>
<td>0.50</td>
<td>0.32</td>
</tr>
<tr>
<td>0.375</td>
<td>0.31</td>
</tr>
<tr>
<td>0.25</td>
<td>0.29</td>
</tr>
</tbody>
</table>

for intersystem crossing which is unity. To account for this, dimerisation in
two steps is required, the overall efficiency being 36%. Equations (1) have
to be modified as follows (equations 2): Similar conclusions have been

\begin{align*}
\text{Cyclopentenone } S_0 & \longrightarrow \text{ Cyclopentenone } S_1 & \longrightarrow \text{ Cyclopentenone } T_1 \\
\text{Cyclopentenone } T_1 & \longrightarrow \text{ Cyclopentenone } S_0 \\
\text{Cyclopentenone } T_1 + \text{ Cyclopentenone } S_0 & \longrightarrow (\text{Cyclopentenone})_2^* \\
(\text{Cyclopentenone})_2^* & \longrightarrow 2 \text{ Cyclopentenone } S_0 \\
(\text{Cyclopentenone})_2^* & \longrightarrow \text{ Dimers }
\end{align*}

(2)

reached by de Mayo et al. from a kinetic study of cycloadditions of olefins to cyclopentenone; the absence of evidence for cis–trans isomerisation in the olefins suggested an intermediate complex rather than a diradical.

Bellamy's report of the dimerisation of 4,4-dimethylcyclopentenone in sunlight to give dimers (97a and b, \( R = \text{Me} \)) is largely of synthetic interest.

### B. Cyclohexenones

The dimerisation of coumarins and furo-coumarins has been reported. Coumarin (98) has been shown to photodimerise giving a head-to-head syn-dimer (99a) and a head-to-head anti-dimer (99b) in solution. A recent publication has shown that the dimer ratio is dependent on the dielectric constant of the solvent: the change in dielectric constant was achieved by addition of sodium perchlorate. Table 8 shows the marked enhancement for the formation of the syn-isomer (99a). The smaller enhancement for the anti-isomer (99b) has been attributed to the effect of heavy-atom perturbation on the rate of intersystem crossing.

The photodimerisation of 2,3-dihydro-2,6-dimethylpyrone gives only cis,anti,cis products in close analogy to cyclohexenone dimerisation. Three isomers (100 a—c) are obtained from the dimerisation in a corresponding ratio of 9:15:1.

### Table 8 Effect of dielectric constant on the photo-dimerisation of coumarin

<table>
<thead>
<tr>
<th>Perchlorate conc. (M)</th>
<th>syn</th>
<th>anti</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.01</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>0.03</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>0.05</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.10</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>1.0</td>
<td>3.8</td>
<td>1.7</td>
</tr>
<tr>
<td>2.0</td>
<td>6.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The figures quoted are relative to the conversion to dimers in pure acetonitrile.

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C. Dimerisation of Thymines etc.—An extremely useful review on the photochemistry of nucleic acid derivatives has been published. Wagner and Buecheck have studied the photodimerisation of thymine (101a) and uracil (101b) in acetonitrile solution, and have found important kinetic differences between their singlet and triplet states. In the reasonably dilute solution (10^{-8}–10^{-4}M) studied by these authors, dimerisation occurs mainly from the triplet state. From quenching studies it can be shown that only 30% of thymine triplets and 10% of uracil triplets dimerise. The major inefficiency in the dimerisation can be explained if the original adduct of triplet-state base with ground-state base is able to decay back to ground-state molecules. Much the same argument was used to explain the inefficiency in cyclopentenonone dimerisations (p. 203). The complex could be a triplet excimer or ground-state σ-diradical.

A theoretical paper suggests a possible mechanism for the triplet dimerisation of pyrimidine bases involving a benzophenone–pyrimidine triplet adduct (102). Such a proposal appears less compelling than those contained in the above kinetic examination.

The photodimerisation of dimethylthymine in ice gives only two dimers, but a recent study of the dimerisation in water reports four dimers. The overall quantum yield has been measured as \( \Phi = 5.0 \times 10^{-2} \) with chemical yields of the four dimers as 38%, 36%, 19%, and 7%. The dimerisation of a 0.1M-solution of dimethylthymine in acetonitrile has been shown to be predominantly a singlet process with only 12% dimerisation taking place from the triplet state. The structures of the dimers have been assigned as

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syn head-to-head (103a), syn head-to-tail (103b), anti head-to-tail (103c), and anti head-to-head (103d). The syn head-to-tail (103b) is the structure proposed for the previously unassigned second ice dimer. A subsequent study has shown that the dimer yields are dependent to a certain extent on the solvent employed (Table 9). Experiments with quenchers and sensitisers showed that both singlet and triplet states are operative, but the nature of the solvent appears to control the contribution of each. The work of Lisewski and Wierzchowski is complementary to these investigations, and shows that the dimerisation of dimethylthymine in aqueous solution is temperature dependent. The results lead the authors to the conclusion that dimerisation from the singlet state arises from singlet excimers which are formed from Van der Waals' complexes. The product distribution strongly supports this involvement of stacked complexes.

### Table 9  Effect of solvent on the photo-dimerisation of dimethylthymine

<table>
<thead>
<tr>
<th>Solvent</th>
<th>syn h–h (103a)</th>
<th>syn h–t (103b)</th>
<th>anti h–t (103c)</th>
<th>anti h–h (103d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>17</td>
<td>59</td>
<td>21</td>
<td>3</td>
</tr>
<tr>
<td>Dioxan</td>
<td>12</td>
<td>61</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>39</td>
<td>37</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>Methanol</td>
<td>37</td>
<td>42</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>49</td>
<td>36</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>53</td>
<td>33</td>
<td>10</td>
<td>4</td>
</tr>
</tbody>
</table>

4 Photochemistry of Dienones

**A. Cross-conjugated Cyclohexadienones.**—A new contestant has entered the lists. Tezuka claims that the mechanisms of the complex photoreactions of cross-conjugated cyclohexadienones are not satisfactorily described

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Enone Rearrangements and Cycloadditions

by the proposals of Taylor,\textsuperscript{97} Chapman,\textsuperscript{98} or Zimmerman.\textsuperscript{99} On the basis of MO calculations, he suggests that $\pi \rightarrow \pi^*$ excitation can give either positive or negative character to the $\beta$-carbon atom of the system. The resulting dualistic nature of the intermediate species is said to be able to accommodate the various reactions which are encountered.

The mechanistic examination of cyclohexadienone rearrangements has continued throughout the past year. Swenton \textit{et al.}\textsuperscript{100} have shown that in the gas phase, the 4,4-disubstituted cyclohexadienone (104a) gives the bicyclic ketone (105a) as the initial product ($\Phi = 0.40$ at 366-0 nm) which is

![Chemical structures](image)

readily converted to the cyclohexa-2,4-dienone (106). In cyclohexane solution the same two ketones are obtained but in aqueous dioxan two phenols are isolated as well as the bicyclic ketone (105a). The gas-phase reactions are interpreted\textsuperscript{100} as diradical processes (intermediates 106a), whereas in aqueous solvents the stabilisation of polar intermediates is more probable. The phenols formed by methyl migration probably result from such intermediates.

In solution the dipolar intermediates appear to be important, and the rearrangement of spirocyclohexadienone (107) to the two isomeric bicyclic ketones (108a) and (108b) in solvent dependent.\textsuperscript{101} In more polar solvents the reaction is more stereoselective (Table 10), a finding explained\textsuperscript{101} by preferential solvation of the diastereoismeric intermediates which lead to the products.

\textsuperscript{98} O. L. Chapman, \textit{Adv. Photochem.}, 1963, 1, 323.
Table 10  *Solvent dependency in the photolysis of spirodienone (109)*

<table>
<thead>
<tr>
<th>Solvent</th>
<th>108a : 108b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.50</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>2.04</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.09</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.91</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.79</td>
</tr>
</tbody>
</table>

A solvent dependency is also encountered in the photolysis of the spirodienone (109) where, in methanol, irradiation gives the 'lumi' or bicyclic ketone (110). In ether, under the same irradiation conditions, this bicyclic ketone (110) or the starting spirodienone (109) rearranges to the linearly conjugated dienone (111). The most acceptable mechanism for this conversion is ring-opening of the lumiketone to a keten-diene (112) which recylclises to the conjugated dienone (111). A similar mechanism was proposed for the conversion of 6,6-dimethylbicyclo[3,1,0]hex-3-en-2-one (105) to 6,6-dimethylcyclohexa-2,4-dienone (106).

The intermediacy of polar species has been used to explain the products isolated from the photolysis of 4-trichloromethyl-4-methylcyclohexa-

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2,5-dienone (104b). The reaction exhibits a certain degree of solvent dependency; in good hydrogen-donating solvents a high yield of p-cresol, the product of fragmentation, is obtained. In benzene, however, the lumiketone (105b) could be obtained stereospecifically with optimum yield from 253-7 nm, irradiation. With a pyrex filter (λ > 300 nm), the main product (50%) was a bicyclo[3,2,0]heptenone (113a or b). Photolysis in methanol gave further products which appeared to result from carbonium ion trapping, viz. a cyclopentenone (114) and (possibly) a bicyclo[3,1,0]hexanone (115). The mechanistic interpretation of the reaction follows relatively familiar pathways. Any ambiguity regarding the nature of the reactive excited state has been removed, at least in this instance, by the production of oxetans 103 (116) following irradiation of the dienone (104b) in the presence of olefins. This finding confirms that n,π* and not a π,π* state, is operational; the triplet nature of the intermediates has been shown by quenching, sensitisation, and emission studies. 105 The mechanistic interpretation 105 of the reaction, based on the results shown above, is represented in Scheme 13. Matsuura and Ogura 108 have reported the photochemistry of 2,4,6-tri-t-butyl-4-hydroxycyclohexa-2,5-dienone (117a, R = H) in various solvents. The results obtained are similar, as might be expected, to those obtained by the same authors 107 from photolysis of the corresponding methyl ether (117b, R = Me). The compounds obtained from the photolysis can all be accounted for on the basis of formation of the bicyclohexenone (118) and subsequent photolysis to yield the dienone (119), or thermal ring-opening of the hydroxycyclopropane to give two isomeric cyclopentenones (120a and 120b) (Scheme 14). Subsequent photolysis of these cyclopentenones produces the isomeric bicyclo[2,1,0]pentanones (121a and 121b). Similar observations have been recorded previously, 108 although there are slight variations in the reported n.m.r. spectra.

B. Santonin-type Rearrangements—Reports have appeared on the photolysis of α-santonin and 6-epi-α-santonin in solution, 109 and of santonin (122) in the crystal. 110 The solid-phase photolysis reports evidence for the existence of a cyclopentadienone isomer (123) of santonin which spontaneously dimerises (124).

Further examples of santonin-type rearrangements are reported 111 in the photolysis of cyclohexadienone (125) in dioxan to yield the lumiketone (126) or in acetic acid to yield the ring-expanded product (127). The products from the photolysis of 6–5 fused cross-conjugated ketones such as (128) are analogous to those obtained from 6–6 fused systems. Thus

Scheme 13
Enone Rearrangements and Cycloadditions

(a) $R = H$
(b) $R = \text{Me}$

(117)

$\xrightarrow{h\nu}$

(118)

$\xrightarrow{\Delta}$

(120a)

(120b)

$\xrightarrow{h\nu}$

(121a)

(121b)

(119)

Scheme 14

(122)

(123)

(124)
cyclohexadienone (128) gives the lumiketone (129), and the linearly conjugated ketone (130) on irradiation \(^{112}\) in dioxan.

\[ \text{(125)} \quad \text{(126)} \quad \text{(127)} \quad \text{(128)} \quad \text{(129)} \quad \text{(130)} \]

C. Other Dienone Rearrangements.—It is noteworthy that some of the problems surrounding the photochemistry of spiro[2,5]octa-4,7-dien-6-ones (131a and 131b) have now been unravelled.\(^{113}\) Thus irradiation of isomers (131a) or (131b) with 350 nm light brings about cis-trans isomerisation via opening of the cyclopropane ring. Change of wavelength to 253.7 nm converts either isomer to a mixture of quinone methides (132a) and (132b). The cis-isomer (131a) gives quinone methide (132a) by preferential methyl migration, whereas the trans-isomer (131b) gives quinone methide (132b) by hydrogen migration. These results are represented in Scheme 15: consideration of the relative values for the quantum yields (\(\Phi_1 - \Phi_3 = 25, 19, 6, 9, 0, 90, 73, 0, 0\)) shows that while cis–trans isomerisation takes place readily the quinone methides are formed by reasonably specific processes with little cross-over from the intermediates.

In protic solvents cyclohepta-2,6-dienone is reported\(^{114}\) to add solvent at the expense of dimerisation. The initial product isolated is 6-methoxy-cyclohept-2-enone, which perhaps arises from cis–trans isomerisation followed by thermal addition of methanol to the reactive trans double bond. Prolonged irradiation yields a cis–trans mixture of 3,6-dimethoxycycloheptenone. In acetic acid solution, a 1:1 mixture of endo- and exo-2-acetoxybicyclo[3,2,0]heptan-3-one (133a and 133b respectively) arises from transannular conrotatory cyclisation of a protonated excited state (as with cross-conjugated cyclohexadienones). Similar products are obtained from the photolysis of cyclohepta-2,6-dienone in acidic alcohol solution.

A ground-state intermediate, the cis,trans-cyclo-octadienone (134) or valence isomers of it, is claimed\(^{115,116}\) to account for all the products isolated from the photolysis of cis,cis-cyclo-octa-2,7-dienone in a variety of solvents. Experimental evidence for this is reported from low-temperature

Scheme 15
photolysis. Typical products isolated from the reaction are exo- and endo-2-acetoxy-cis-bicyclo[3,3,0]octan-3-one, and a Diels–Alder adduct (135) isolated from a reaction with furan.

D. Linearly Conjugated Dienones.—The low-temperature i.r. study of the photolysis of 6-methyl-6-dichloromethylcyclohexa-2,4-diene (136a) has shown the intermediacy of a keten (137a). Baldwin and McDaniel, from a study of three cyclohexadienones (136b–d), have shown that the ring-opening reaction to the keten (137), followed by nucleophilic attack, shows a remarkable specificity. An explanation for this specificity is being sought. A keten intermediate is also observed (by its i.r. spectrum) during the photolysis of 2-pyrene in methanol. Addition of methanol to this intermediate allows for the isolation of methyl trans-4-formyl-3-butoanoate. Photolysis of 2-pyrene in ether leads to bicyclo[2,2,0]pyran-2-one which on subsequent photolysis in methanol yields methyl cis- and trans-4-formyl-3-butoanoate.

Evidence has been presented that in the ring-opening of cyclohexa-2,4-dienones the only photoreaction is keten formation, all other subsequent reactions are said to result from thermal processes. It was originally proposed that the type of reaction which the keten underwent was solely dependent on the pattern of substitution. Subsequent studies have

shown that most of the cyclohexadienones (138) studied can be made to undergo rearrangement to bicyclo[3,1,0]hexenones (139) by selective \( \pi \rightarrow \pi^* \) singlet excitation, and that the intermediacy of the keten was unnecessary, a point which has been demonstrated independently.\textsuperscript{121} Indeed it has been shown that \( n \rightarrow \pi^* \) excitation gives rise to the keten (140) which can then react with nucleophiles to yield, \textit{e.g.}, esters. The fact that previous studies\textsuperscript{119} had pointed to effects of the pattern of substituents on the direction of reaction (\( \rightarrow \) ester or bicyclic ketone) has also been resolved, and choice of a suitable solvent or the use of a silica substrate to bring about overlap of the \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) absorptions can ensure ready conversions to the bicyclic ketones.\textsuperscript{120} 2,4,6-Triphenyl-6-acetoxycyclohexa-2,4-dienone furnishes an analogous bicyclic ketone (141).\textsuperscript{122} Thermolysis of this ketone regenerates the original cyclohexadienone.

In contrast to the above specific photoreactions, 2,4,6-trialkyl-6-acetoxycyclohexa-2,4-dienones (142a) are reported to give a mixture of products.\textsuperscript{123} However, the initial major product is a bicyclo[3,1,0]hexenone (143a) which is proposed to arise by acetoxyl migration accompanied by rearrangement.

\[
\begin{align*}
\text{(141)} & \\
\text{(a) } R = \text{Bu}^t & \lambda_{\text{max}} = 309 \text{ (4200)} \\
\text{(b) } R = \text{Me} & \lambda_{\text{max}} = 315 \text{ (3400)} \\
\text{(142)} & \\
\text{(143)} & \\
\text{(144)} & 
\end{align*}
\]

The di-\text{t}-butylmethyl analogue (142b) gives a minor initial product, the bicyclohexenone (144), analogous to the products obtained by Hart \textit{et al.}\textsuperscript{120} and Perst and Dimroth.\textsuperscript{128} No explanation is given for the difference in reaction path, \textit{i.e.}, acetoxyl migration or rearrangement. The u.v. spectra of the starting materials are remarkably different, and bearing in mind the postulates of Hart \textit{et al.},\textsuperscript{120} the difference in reaction pathways could be due to a difference in the nature of the excited state.

The larger ring dienones (145) photoisomerise by disrotatory cyclisation to 2,3-dihydro-1,2-diazepine ketones (146).\textsuperscript{124} In a reinvestigation of the

photochemistry of 2,4,6-cyclo-octatrienone, the presence of a keten has been demonstrated.\textsuperscript{125} Such an intermediate, originally proposed by Büchi and Burgess,\textsuperscript{126} accounts for the mixture of methyl octatrienoates isolated after irradiation in methanol. In hydrocarbon solvents the intermediate which gives rise to bicyclo[4,2,0]octa-4,6-dien-2-one (147) has been shown to be a \textit{trans},\textit{cis},\textit{cis}-isomer (148) of the starting ketone, and this can be trapped as a Diels–Alder adduct with furan.\textsuperscript{125}

\begin{align*}
\text{(145)} & \quad \text{(146)} \\
\text{(147)} & \quad \text{(148)}
\end{align*}

\section*{5 Tropones}

The gas-phase decarboxylation of tropone to benzene and carbon monoxide has been shown\textsuperscript{127} to be quenched by oxygen and carbon dioxide. A study\textsuperscript{128} of the photorearrangement of tri-\textit{O}-methyl purpurogallin (149) (labelled at asterisk) has shown that methyl 1,2,3-trimethoxynaphthalene-8-carboxylate (label in carboxyl carbon) is formed \textit{via} an oxabicyclobutane intermediate. Water has been shown\textsuperscript{129} to be essential for the transformation, and in an independent examination\textsuperscript{128} it has been shown that a decrease in the amount of water in the system promotes the formation of a new product, 1,2,3-trimethoxy-8-hydroxynaphthalene. In hydrocarbon solvents, a bicyclic ketone (150) is formed,\textsuperscript{129} and may arise as shown in Scheme 16.

A further examination of the photochemistry of 2-phenoxy-4,5-benzotropones has been described.\textsuperscript{130} 2-Methyl-4,5-benzotropane is reported\textsuperscript{131} to yield two products in low yield, a dimer (152) and a dehydrogenated compound (153).

The exclusive head-to-head dimerisation of the tropone is presumed to be due to steric interference of the methyl groups. On the other hand, 2-chlorotropane yields two dimers, a \((6+6)\pi\) dimer (154), and a \((2+4)\pi\) dimer (155), on irradiation in benzene.\textsuperscript{132} Differences between tropone and


\textsuperscript{128} T. J. Murphy, \textit{Diss. Abs.}, 1968, \textit{28}, B, 3652.


Enone Rearrangements and Cycloadditions

Scheme 16

2-chlorotropone dimerisations are explained on the grounds of enhanced intersystem crossing efficiency by heavy-atom perturbation. Subsequent photolysis of the $(4+2)\pi$ dimer (155) yields the dihydroindene derivative (156) a reaction sequence which has been previously reported.\textsuperscript{133}

6 Quinones

A. \textit{p}-Benzoquinones.—The cyclisation of alkylamino-substituted \textit{p}-benzoquinones (157a) and \textit{p}-benzoquinone imines (157b) has been described.\textsuperscript{134, 135} Both processes formally involve excitation of the quinone followed by


intramolecular hydrogen abstraction to yield a diradical intermediate (158) which cyclises to produce a benzoxazoline (159 from 157a) or benzimidazole (160 from 157b). In general, if there is a choice, hydrogen abstraction takes place preferentially at a tertiary amine. The scope of the reaction has been thoroughly investigated. With the closely related (2-N-substituted anilino)-1,4-naphthaquinones (161), the formation of benzo[c]phenoxazozone derivatives (161a) is reported.\textsuperscript{138} The products are formed in methanol or aqueous tetrahydrofuran by attack on the phenyl substituent rather than by hydrogen abstraction. In the photolysis of alkyl-substituted \( p \)-benzoquinones, a novel side-chain rearrangement has been discovered.\textsuperscript{137} An \( n \rightarrow \pi^* \) transition was involved but no investigation of the multiplicity of the reaction was carried out. With an unbranched side-chain the products isolated were either the corresponding quinols or products resulting from solvent (alcohols) incorporation. The side-chain rearrangement encountered in branched-chain substituted quinones gives evidence for carbonion ion intermediates as a result of photoexcitation. For example, isobutyl and t-butyl-\( p \)-benzoquinone (162a and b) afford the same ether (163a) as well as 2,2-dimethyl-5-hydroxycoumaran (163b) from the t-butyl isomer. To account for this rearrangement, a mechanism involving hydrogen-abstraction, cyclopropane formation, electron demotion, and ring-opening to give the more stabilised carbonion ion adequately accounts for the products (Scheme 17). Such a mechanism obviates the need for hydrogen transfer suggested by Giles and Cameron\textsuperscript{134} for aminooquinone rearrangements, and indeed the new mechanism is also applicable to the rearrangements described by these authors.\textsuperscript{134, 135}

The photocycloaddition of a few acetylenes to methoxy-\(p\)-benzoquinone and 2-methoxynaphthaquinone has been described, and is essentially a fuller account of a previous report. The products formed are 1-methoxy-bicyclo[4,2,0]octa-3,7-diene-2,5-diones (164). The unsymmetrical acetylene, phenylmethylacetylene, yields only one orientational isomer (164c), similarly, phenylacetylene gives only adduct (164d). Anet and Mullis have shown that photolysis of adduct (164d) converts it into an isomerised product (165), by a Norrish type I cleavage and rebonding, and an oxetan

\[ \text{(164)} \]

(a) \( R^1 = R^3 = \text{Ph} \)
(b) \( R^1 = R^3 = \text{Me} \)
(c) \( R^1 = \text{Ph}, R^3 = \text{Me} \)
(d) \( R^1 = \text{Ph}, R^3 = \text{H} \)

---

(166) by Norrish type II hydrogen-abstraction (Scheme 18). These authors\textsuperscript{140} have extended the reaction and shown that the addition of vinyl acetate to 2-methoxy naphtha-1,4-quinone gives only the extraordinary spiro-compound (167).

![Scheme 18](Image)

The addition of the acetylene is almost certainly a two-step process, and the orientational specificity shown by the addition of phenylacetylene and phenylmethylacetylene could be due to the stability of the diradical intermediate. Such a postulate has been used by Barltrip and Giles\textsuperscript{141} to explain the orientational specificity of the addition of olefins and acetylenes to certain enediones (168). The reaction has been shown to involve an electrophilic $\pi \rightarrow \pi^*$ triplet state since there is no evidence for hydrogen-abstraction reactions from isopropanol. Phosphorescence studies have given a value of 57.8 kcal/mole for the triplet energy of the enediones. Some of the results of the addition are shown below (169) and it should be noticed that even although a diradical ring-closure is involved no evidence was obtained for the more strained trans-fusion of the new ring.\textsuperscript{141}

In contrast to the $\pi \rightarrow \pi^*$ triplet proposed by Barltrip and Giles,\textsuperscript{141} slimmer evidence for the involvement of an $n \rightarrow \pi^*$ triplet state has been obtained\textsuperscript{143} in an investigation of the cycloaddition of cyclohexene to 3-carene-2,5-dione (170), which gives the oxetan (171, 10\%). Cycloadditions of various other acetylenes and olefins to this dione gave cyclobutane adducts (172). Again the orientational specificity can be explained on the basis of the more stabilised diradical, or by postulation of an intermediate polar complex.

A reinvestigation of the photochemical dimerisation of vitamin K\textsubscript{3} (2-methylnaphtha-1,4-quinone) has been reported.\textsuperscript{143} Contrary to the initial report, four dimers were isolated, a head-to-head \textit{syn}, a head-to-tail \textit{syn}, a head-to-head \textit{anti}, and a head-to-tail \textit{anti}. In addition to these, a dehydrogenated dimer (173) and an unidentified oxetan dimer were reported.\textsuperscript{144}


Enone Rearrangements and Cycloadditions

Naphtha-1,4-quinone has also been reported\textsuperscript{145} to react photochemically with p-dioxan to yield 2-dioxanyl-naphtha-1,4-quinone. 9,10-Anthraquinone has been shown\textsuperscript{146} to form oxetans (174), with those olefins or dienes which cannot quench the anthraquinone triplet state ($E_T = 62.5$ kcal/mole).

\begin{align*}
\text{(168)} & \quad R^1 = R^2 = \text{Me} \\
& \quad R^1 = R^2 = \text{H} \\
& \quad R^1 = \text{Me}, R^2 = \text{H} \\
& \quad R^1 = \text{Ph}, R^2 = \text{H} \\
& \quad R^1 = \text{MeO}, R^2 = \text{H}
\end{align*}

Thus products are obtained from cyclo-octene (a mono- and a bis-oxetan adduct), and the substantially unconjugated cyclo-octa-1,3-diene ($E_T = 70-72$ kcal/mole), but not from butadiene ($E_T = 60$ kcal/mole). Diphenyl-acetylene yields the quinone methide (175) and not the oxetene, although this is presumably an intermediate.\textsuperscript{146}

\begin{align*}
\text{(170)} \\
\text{(171)} \\
\text{(172)} \\
\text{(173)} \\
\text{(174)} \\
\text{(175)}
\end{align*}

B. 1,2-Quinones.—A further investigation of the mechanism of photo-addition of olefins to phenanthrenequinone has been reported.\textsuperscript{147} Photocycloaddition of the quinone to either cis- or trans-but-2-ene gave a mixture of the cis and trans dioxen adducts (176a and 176b) in a ratio of 57:43. A similar study with trans-oct-4-ene gave a similar mixture, and no cis-octene could be detected in the recovered olefin. This experiment rules out any reversion from intermediate (177), and suggests that the initial $n \rightarrow \pi^*$ singlet state of the quinone rapidly crosses to the triplet state; evidently, the triplet diradical produced (177) is sufficiently long lived to equilibrate almost completely before bond closure. Farid and Scholz\textsuperscript{148} have reported the isolation of other products from olefin additions to phenanthrenequinone. Using but-2-ene the cis- and trans-dioxene adducts (176a and b) were isolated as well as three less expected products, \textit{viz.} an oxetan (178) and two hydroxyketones (179a and b) arising from hydrogen-abstraction reactions. Similar products are reported from 2-methylpropene, 2-methylbutene, and tetramethylethylene. Quantum yield and quenching studies have shown that both processes proceed from a triplet excited state.

In specific cases (\textit{i.e.} the use of di-t-butylethylene, $\alpha$-chlorostilbene, and $NN$-diphenylimidazolinone\textsuperscript{149,150}) dioxoles (180) have been isolated from the photoreactions of phenanthrenequinone with olefins. It has been

\begin{itemize}
  \item (178)
  \item (179a)
  \item (179b)
  \item (180)
\end{itemize}

shown that these adducts arise from secondary photolysis of the intermediate oxetans. Phenanthrenequinone and tetrachlorobenzo-1,2-quinone form monophenyl ethers, e.g. (181), on photolysis in benzene solutions. These reactions exemplify a hitherto-unknown mode of photofunctioning benzene, and are further unusual in that the benzene ring is preserved in the products. Tetrachloro-1,2-benzoquinone undergoes photofunctioning trans-stilbene to give mostly the trans-dioxene (182a, 88%) with smaller amounts of the cis-dioxene (182b, 12%). The retention of much of the stereospecificity (the thermal reaction is completely specific) is explained on the basis of a zwitterionic intermediate (182c) or a correspondingly polarised triplet diradical. Tetrachloro-1,2-benzoquinone and cis-stilbene gave a 1:5 mixture of adducts (182a and b) on photolysis in acetone or acetonitrile.

\[
\begin{align*}
(181) & \quad \begin{array}{cc}
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{O} & \text{Ph} \\
\text{Ph} & \text{OH}
\end{array} \\
(182a) & \quad \begin{array}{cc}
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{O} & \text{H} \\
\text{H} & \text{Ph}
\end{array} \\
(182b) & \quad \begin{array}{cc}
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{O} & \text{H} \\
\text{H} & \text{Ph}
\end{array} \\
(182c) & \quad \begin{array}{cc}
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{O} & \text{Ph} \\
\text{Ph}
\end{array}
\end{align*}
\]

Pyracycloquinone (183) is reported to yield diester (184) via diketene (185) on photolysis in methanol, whereas in 1,2-dimethoxyethane (unpurified) the anhydride (186) was formed presumably the latter system was not water-free.

\[
\begin{align*}
(183) & \quad \begin{array}{cc}
\text{O} & \text{O}
\end{array} \\
(184) & \quad \begin{array}{cc}
\text{MeO}_2\text{C} & \text{CO}_2\text{Me}
\end{array} \\
(185) & \quad \begin{array}{cc}
\text{O} & \text{O}
\end{array} \\
(186) & \quad \begin{array}{cc}
\text{O} & \text{O}
\end{array}
\end{align*}
\]

7 1,2-Diketones

Quenching experiments have shown that α-ketodecanoic acid undergoes a Norrish type II elimination from the triplet state. Unlike Norrish type II

reactions in aliphatic ketones, this reaction is completely quenchable. The intersystem crossing rate \((k_{ie})\) is much greater than for aliphatic ketones and it is suggested that this is due to enhanced spin–orbit coupling. The quantum yield for the formation of pyruvic acid and hept-1-ene, the products of the reaction, has been determined as 0.2. Surprisingly, the 2-oxo-amides (187) have been shown\(^{157}\) to form oxazolopiperidines (188) in moderate yields and only poor yields of the expected cyclobutanols (189).

\[
\begin{align*}
(187) \text{ R} &= \text{Me or Ph} \\
(188) \text{ R} &= \text{Me or Ph} \\
(189) \text{ R} &= \text{Me or Ph}
\end{align*}
\]

No explanation for the observed reactions was given; one might infer that a degree of conformational rigidity in the excited state prevents hydrogen-abstraction by oxygen. The photochemistry of benzil\(^{158}\) and biacetyl\(^{159}\) in cyclohexane solution has been described. The products isolated arise mainly from the acetyl or benzoyl radical although acetoin and benzoin have also been detected.

Camphorquinone (190) \((E_T = 51.6 \text{ kcal/mole})\) has been photoreduced in isopropanol \((\Phi = 0.057)\) to yield the isomeric hydroxyketones (191a and b).

\[
\begin{align*}
(190) \\
(191a) \\
(191b)
\end{align*}
\]

In methanol \((\Phi = 0.18)\) the same products were formed together with two dihydroxyketones (192a and b)\(^{160,161}\). The reaction takes place from the triplet state and can be photosensitisised by \(m\)-methoxyacetophenone \((E_T = 72.4 \text{ kcal/mole})\). Attempted sensitisation of the reduction by benzophenone gave values for the quantum yield much higher than by direct irradiation. This phenomenon is explained by two mechanisms, \textit{viz.}, the normal energy transfer (physical sensitisation) and proton transfer (chemical sensitisation)\(^ {162}\). The intermediate which undergoes reduction has been demonstrated to be a symmetrical radical (193) by e.s.r. spectroscopy.

A complete report of the results of the photolysis of benzocyclobuten-1,2-dione has been published\(^ {163}\). The original proposal for the intermediacy

of a diketen and/or carbene (194) has been substantiated. Thus photolysis of the dione in ethanol yielded the ether (195), presumably via carbene insertion into the solvent, and in the presence of acetylenes or olefins, spirocyclopropenes or propanes (196) respectively were obtained. On the other hand, the diketene intermediate was trapped as dihydroxynaphthalene derivative (197) by photolysis in the presence of maleic anhydride.

The photochemical extrusion of 2 moles of carbon monoxide from bicyclo[2,2,2]octadiene-diones (198) has been reported by two groups of workers.\textsuperscript{152, 164} The elimination occurs very readily, even in the solid phase,\textsuperscript{152} the driving force being aromatisation of the residue (i.e. formation of anthracene, naphthalene, or benzene). Mass spectral evidence suggested\textsuperscript{164} that the elimination might produce the elusive dimer of carbon monoxide; but attempts to trap this were unsuccessful.

W. M. H.

3
Photochemistry of Olefins, Acetylenes, and Related Compounds

Several reviews have been published during the past year. Reviews have covered the photochemistry of allylic compounds\(^1\) and olefins\(^2\) in solution. Articles have also appeared dealing with excited states in solution,\(^3\) electronic energy transfer in solution,\(^4\) and the triplet state.\(^5\) This chapter is largely concerned with the photochemical behaviour of the ethylenic bond in liquid phases, but work on acetylenes, nitriles, etc. is also covered.

1 Dimerisation and Cycloadditions

The cyclodimerisation of cis-but-2-ene by radiation from a cadmium or zinc lamp has been reported.\(^6\) Acrylonitrile can be dimerised by direct or sensitised irradiation to give only head-to-head dimers as a cis–trans mixture.\(^7\) Surprisingly the cyclodimerisation of aromatic enamines (1) has been shown to require the presence of oxygen.\(^8\) Even in the presence of sensitisers, other than anthraquinone and \(p\)-chloranil, there is no dimerisation if oxygen is rigorously excluded. The evidence cited points not towards the need for singlet oxygen but towards a cation radical–superoxide complex. A possible mechanism is shown in Scheme 1.

\[ R^1 \]
\[ R^2 = H, R^3 = CH = CH_3 \]
\[ R^1 = H, R^2 = CH = CHMe \]
\[ R^3 = Et, R^1 = CH = CH_2 \]

(1)

\[ \text{Me} \]
\[ \text{Me} \]

(2)

trans-1,2-Diethyl-1,2-dimethylcyclobutane (2) is reported as the major product from the sensitised dimerisation of 2-methylbut-1-ene-3-yne.\textsuperscript{9} Vinylacetylene yielded a similar product but cis-methoxybut-1-ene-3-yne only isomerised to the trans-isomer under similar sensitisation conditions (ketones with $E_T \geq 59$ kcal/mole).

The study of ‘mixed’ cycloadditions has been described.\textsuperscript{10, 11} Under sensitisation conditions isoprene and $\alpha$-acetoxyacrylonitrile give rise to six 1:1 adducts as well as the known dimers of isoprene. With high-energy triplet sensitisers, the cyclobutane products (3a—d) predominate, whereas lower energy sensitisers appear to favour the formation of cyclohexenes (3e and f): (Table 1).\textsuperscript{10} The ‘mixed’ cycloaddition reaction relies on energy transfer from the sensitiser to the diene for its success and the preponderance of the cyclohexene adducts must result from selective energy transfer to the s-cis-isoprene. The addition of cyclopentadiene to the same nitrile gave four products of cross-cycloaddition (4a—d).\textsuperscript{11} Analysis of the products

Table 1  *Influence of sensitiser triplet energy on cycloaddition of isoprene with α-acetoxyacrylonitrile*

<table>
<thead>
<tr>
<th>Sensitiser</th>
<th>$E_T$</th>
<th>(3a)</th>
<th>(3b)</th>
<th>(3c + 3d)</th>
<th>(3e + 3f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>73.6</td>
<td>8.1</td>
<td>8.4</td>
<td>10.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Benzil</td>
<td>53.7</td>
<td>7.6</td>
<td>5.6</td>
<td>19.0</td>
<td>16.8</td>
</tr>
</tbody>
</table>

and degradative work shows that the sensitised dimerisation results from the more stable radical (5). The intermolecular cycloaddition of heptafulvalene (6) is reported to yield the remarkable cage compound (7).\(^{12,13}\) A kinetic study of the photodimerisation of indene suggests that there is an energy-wasting step.\(^{14}\) The two possibilities considered were either of the


Photochemistry of Olefins, Acetylenes, and Related Compounds

processes represented in equations (1) and (2). However, proposal (1) was rejected on the basis of an experiment with a mixture of indene, sensitiser, and trans-stilbene where no lack of efficiency was detected for the stilbene

\[
sens^3 + \text{indene} \rightarrow \text{sens} + \text{indene} + \text{heat} \quad (1)
\]

\[
\text{indene}^3 + \text{indene} \rightarrow 2 \text{indene} + \text{heat} \quad (2)
\]

isomerisation. Thus by elimination triplet indene–indene collision [equation (2)] was considered to be the wasteful step. A triplet excimer is likely as an intermediate, rather than a diradical.† These results are to be compared with those reported by de Mayo et al.¹⁵ for inefficiencies in the cycloaddition reactions of cyclopentenone. Metzner and Hartmann¹⁶ and McCullough and Huang¹⁷ report cycloaddition reactions of indene. The additions of chloroethylenes to indene can best be carried out by sensitisation with benzophenone.¹⁶ Only poor yields are reported for the addition of ethylene to indene and it is to be presumed that the enhanced yields of product with the chloroethylenes is due to heavy-atom perturbation which facilitates intersystem crossing in the indene excited state. The products isolated from the reaction are cyclobutanes: cis-dichloroethylene gave four isomers, (8a—d). Indene and acrylonitrile gave three products (9a and b, 10). Although there is no proof in this paper¹⁷ for the assumption of singlet intermediates these are likely a priori because of the low rate of intersystem

![Diagram](8)

\[
a, \ R^1 = R^3 = Cl; \ R^2 = R^4 = H \quad 4.1\
\[
b, \ R^2 = R^4 = Cl; \ R^1 = R^3 = H \quad 53.4\
\[
c, \ R^1 = R^4 = Cl; \ R^2 = R^3 = H \quad 12.9\
\[
d, \ R^2 = R^3 = Cl; \ R^1 = R^4 = H \quad 29.6\
\]

![Diagram](9)

![Diagram](10)


† Calculations show, at least in the benzene case, that triplet excimers are likely to be dissociative (see Part I, Chapter 1).
crossing in indene.¹⁷ Sensitisation of the reaction using acetophenone leads to two isomeric products (11a and b) consistent with a two-step process.

![Chemical structures](image)

Sensitisation studies have shown that vinylene carbonate (12) has a triplet energy of ca. 74 kcal/mole.¹⁸ Sensitised reactions of this addend with various simple olefins give both the cis,syn,cis and the cis,anti,cis dimers (13a and b) as well as good yields of the mixed cycloadducts of type (14). The substituted nitrogen analogue of vinylene carbonate, 1,3-diphenyl-Δ⁴-2-imidazolone (15) is reported to photodimerise on sensitisation with acetone to yield the cis-anti-cis dimer (16).¹⁹ Irradiation of the imidazolone in the presence of benzophenone in benzene solution gave the oxetan (17), and with dimethylmaleic anhydride the adduct (18) was isolated.

![Chemical structures](image)

2,3-Dihydroxypropyran is reported to undergo cycloaddition reactions with diphenylacetylene to yield one adduct (19).²⁰ The reaction could be

---

sensitised by triphenylene ($E_T = 66.6$ kcal/mole); therefore it is proposed that triplet tolal is involved. In contrast the addition of $cis$- or $trans$-stilbene to the dihydropyran to yield two isomers (20a and b) as well as stilbene dimers has been classed as a singlet process, but on rather thin grounds. Support for a revised structure for cannabinocyclo (21) has been obtained following its synthesis from cannabichromene (22) by intramolecular cycloaddition. A report of the results from the photolysis of 2,3-diphenylcycloprop-2-enyl derivatives has appeared. $NN$-Alkylene-dimaleimides (23) have been shown to cyclise by a singlet process. The yield of product (24) was almost quantitative. The cyclisation of $o$-bisiodo-ethynylbenzene to tetraiodonaphthalene has been reported.

A review covering some recent chemistry of the ($2\pi + 2\pi$) intramolecular cycloaddition has been published. Typical of this process is the cyclisation of monohomobarrelele (25a) to the pentacyclic isomer (26a) by direct irradiation. Dimethyl bicyclo[2,2,2]octadiene-2,3-dicarboxylate

---

(27a) is reported to undergo the same type of addition to yield adduct (28a).\textsuperscript{27} Liu \textsuperscript{28} has reported similar cycloadditions. Compounds (25b, 29) could be cyclised to the tetracyclic isomers (26b and 30). The reactions could not be sensitised, but direct irradiation (253-7 nm) gave up to 85\% conversion. Of particular interest is the discrepancy between the photolysis of the substituted bicyclo-octadienes (25a and b) and that of the unsubstituted compound (25c): the latter isomerised to tricyclo[3,3,1,0\textsuperscript{3,8}]trona-3,7-diene (31).\textsuperscript{29} Annellated oxanorbornadiene (32) could also be made to photocyclise\textsuperscript{30} to the tetracyclic compound (33), thermolysis of which brings about ring-opening to the oxepine (34). Prinzbach \textsuperscript{31} has developed this oxepine synthesis further to prepare a benzene oxide (35) by initial photocyclisation.

\textsuperscript{29} J. Daub and P. V. R. Schleyer, \textit{Angew. Chem. Internat. Edn.}, 1968, 7, 468.
of the oxanorbornadiene (36) to the quadricyclane (37) followed by thermolytic ring-opening to give the benzene oxide in 36% yield. Benzene oxides are also of current interest as possible intermediates in the biochemical oxidation of aromatic rings.

The above examples have all been of the $2\pi + 2\pi$ type. Extensions of the process to the photocyclisation of $2\sigma + 2\pi$ systems have been reported. Prinzbach and Eberbach\(^8\) have described the ready cyclisation of spirocyclopropyltricyclo[3,2,1,0\(^4\),4]octene (38) in both the exo- and endo-configurations (38a or b). Generally it has been found that the exo-isomers (38a) cyclise more readily to the pentacyclic derivatives (39) than do the

endo-isomers (38b). In fact the tri-ester (38b i) does not undergo cyclisation, but only reduction to the dihydro-compound (40). The tricarboxylic-acid (38b ii) photocyclises in water to yield the quadricyclane and a lactone (41), and it is suggested that a carbonium ion arising from protonation of the double bond is involved. The proposed mechanism for lactone formation is shown in Scheme 2.

![Scheme 2](image)

Extensions of this work continue to appear. Thus the polycyclic compound (43) has been reported\textsuperscript{33} to photocyclise to the 5-methylenetetracyclo[4,3,0,0\textsuperscript{4,7}]non-8-ene (44) at \(-20^\circ\) in acetonitrile solution, and the oxiran compound (45) gives the tetracyclic oxide (46) as well as products of reduction without oxiran ring-opening.\textsuperscript{34}


\textsuperscript{34} H. Prinzbach and M. Klaus, Angew. Chem. Internat. Edn., 1969, 8, 276.
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(a) \( R^1 = H, \ R = R^2 = \text{CO}_2\text{Me} \)
(b) \( R = R^1 = \text{CO}_2\text{Me}, \ R^2 = H \)
(c) \( R^1 = R^2 = H, \ R = \text{CO}_2\text{Me} \)
(d) \( R = R^1 = R^2 = \text{CO}_2\text{Me} \)

(43)

(45)

(46)

(a) \( X = \text{CH}_2, \ Y = \text{O} \)
(b) \( X = \text{CO}, \ Y = \text{NMe} \)

(47)

(a) \( X = \text{CH}_2, \ Y = \text{O} \)
(b) \( X = \text{CO}, \ Y = \text{NMe} \)

(48)

(a) \( X = \text{CH}_2, \ Y = \text{O} \)
(b) \( X = \text{CO}, \ Y = \text{NMe} \)

(49)

(50)
The development of the chemistry and photochemistry of the propellanes has been reviewed.\textsuperscript{35} An example of the type of study to which this fruitful area has led is contained in a report \textsuperscript{36} of the photolysis of an oxapropellane (47a). From this photolysis was isolated a 'fluxional' diene (48a) which on standing at room temperature was quantitatively converted into a tetaene (49a). The photolysis of the imide (47b) gave a slightly more stable diene (48b, \( t_1 = 3 \) hr. at 60°) which also underwent the thermal electrocyclic conversion (a Cope rearrangement) into a tetaene (49b). The initial conversion of the propellane into the diene is an example of a photochemically allowed \( 4\pi + 4\pi \) addition. Masamune \textit{et al.}\textsuperscript{37} have reported the intermediacy of the parent tetracyclo[4,4,0,0\textsuperscript{2,10,14}]deca-3,8,9-diene (48c) in the photolysis of three C\textsubscript{10}H\textsubscript{19} isomers (50) at -110°. On warming the photosylate a thermal conversion of the intermediate (48c) to bicyclo\[4,2,2\]deca-2,4,7,9-tetaene (49c) took place.

2 Rearrangement Reactions

A. \textit{cis–trans} Isomerisation.—The irradiation of \textit{cis}-6,7,8-trideoxy-1,2;3,4-di-O-isopropylidene-7-C-nitro-\( \alpha \)-D-galacto-oct-6-enose in acetone solution has been reported to yield, in a plethora of compounds, the \textit{trans}-isomer (51) in 30% yield.\textsuperscript{38}

\begin{center}
\begin{tikzpicture}
\begin{scope}[scale=0.5]
\node (m) at (0,0) {\textit{H}};
\node (a1) at (1,1) {\textit{O}};
\node (a2) at (1,-1) {\textit{O}};
\node (a3) at (-1,1) {\textit{NO}_2};
\node (a4) at (-1,-1) {\textit{O}};
\node (a5) at (-2,0) {\textit{O}};
\node (a6) at (2,0) {\textit{O}};
\draw (a1) -- (a2) -- (a3) -- (a4) -- (a5) -- (a6);
\end{scope}
\end{tikzpicture}
\end{center}

(51)

Saltiel\textsuperscript{39} has shown in the \textit{cis–trans} isomerisation of stilbene that there is no loss in efficiency in the sensitised isomerisation of perdeuterio-stilbene compared with stilbene (Table 2). From this it is concluded that the triplet decay rate is not affected by the deuteration. However, perdeuteriation increases the lifetime of stilbene triplets by 30%, to judge from measurements based on azulene as an energy acceptor. These results also showed that the rate of decay from the twisted triplet state is sensitive to temperature and viscosity changes.

The slight increase in the \textit{cis–trans} photostationary ratios observed at higher temperatures was originally attributed to the case with which the

Table 2  Comparison of photostationary state composition of sensitised isomerisation of stilbene and perdeuterio-stilbene

<table>
<thead>
<tr>
<th>Sensitiser</th>
<th>Concentration (M)</th>
<th>C\textsubscript{\text{cis-H\textsubscript{12}}} (%)</th>
<th>C\textsubscript{\text{cis-D\textsubscript{12}}} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>0.05</td>
<td>58.1</td>
<td>58.3</td>
</tr>
<tr>
<td>9,10-Anthraquinone</td>
<td>0.01</td>
<td>60.0</td>
<td>57.2</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.02</td>
<td>74.2</td>
<td>75.9</td>
</tr>
<tr>
<td>Benzin</td>
<td>0.05</td>
<td>92.4</td>
<td>93.4</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.05</td>
<td>84.6</td>
<td>86.3</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.02</td>
<td>91.5</td>
<td>91.9</td>
</tr>
</tbody>
</table>

twisted triplet state could decay to the cis-singlet.⁴⁰ Saltiel claims ⁹⁰ that for direct irradiation the isomerisation involves rotation about the central S\textsubscript{1} bond to give a common twisted singlet state (Figure). There is therefore

\[
\begin{array}{c}
T = \text{trans} \\
P = \text{cis} \\
P' = \text{twisted state} \\
S = \text{singlet} \\
tl = \text{triplet}
\end{array}
\]

Figure  Potential energy diagram for lowest electronic excited states of stilbene
(Based on Figure in ref. 39)

a small activation energy of 2 kcal/mole, which accounts for the temperature effects for the rotation of the trans-singlet to the singlet twisted state. These results are in accord with the singlet state mechanism now accepted for the direct isomerisation of stilbene. It is also suggested that the similarities in the cis-trans decay ratios from stilbene excited states in the direct and sensitised isomerisations arise from crossing of reaction paths. This is quite possible since it is not unreasonable to assume geometrical similarity in the triplet and the singlet twisted states, and that crossing can occur en route to the ground state.

Further investigation of the singlet nature of the direct isomerisation of stilbene has continued during the past year. Saltiel et al.⁴¹ have studied

models for a *trans*-excited state. The molecule chosen was the indeno-inden (52). Results from this study show that the quantum yield of fluorescence is 0.94 and is independent of temperature, in contrast to the observations on *trans*-stilbene; but they are in agreement with a singlet mechanism.

![Chemical Structure](52)

Other models have been examined in which the planarity of the excited state is ensured by the rigidity of the system, *viz*. 1,2,3-triphenylcyclop propane and 1,2-diphenylcyclobutene; singlet–triplet crossing is inefficient. However, the essential difference between these models and *trans*-stilbene is that there can be no twisted (non-planar) state in the models, and in *cis-* or *trans*-stilbene a twisted state may be necessary for intersystem crossing to be efficient.

An investigation and interpretation of the effect of azulene on the direct and sensitised isomerisations of stilbene has also pointed to the lack of intersystem crossing in the direct irradiation experiments. There is no dependency of the slopes of the plots obtained for azulene quenching on the viscosity of the solutions: had triplets been responsible, such a deviation ought to have been discernible. This observation, and the good fit for long-range singlet energy transfer, suggest that the azulene effect is a singlet energy process, represented as follows:

\[ \text{trans-Stilbene}^{1} + \text{Azulene}^{0} \rightarrow \text{Azulene}^{1} + \text{trans-Stilbene}^{0} \]

The influence of *para-* and *meta*-substituents in stilbenes has been shown to be only minimal on the quantum yield of *trans—cis* or *cis—trans* isomerisation. Table 3 shows a representative sample of the published results.

### Table 3 Influence of substituents on photostationary-state composition of stilbene isomerisation

<table>
<thead>
<tr>
<th>Stilbene substituent</th>
<th>( \Phi_{t-c} )</th>
<th>( \Phi_{c-t} )</th>
<th>cis at stationary state (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>para</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.4</td>
<td>0.22</td>
<td>93</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>0.49</td>
<td>0.30</td>
<td>81</td>
</tr>
<tr>
<td>OMe</td>
<td>0.40</td>
<td>0.29</td>
<td>85</td>
</tr>
<tr>
<td>meta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OMe</td>
<td>0.31</td>
<td>0.19</td>
<td>77</td>
</tr>
<tr>
<td>F</td>
<td>0.42</td>
<td>0.40</td>
<td>89</td>
</tr>
<tr>
<td>F</td>
<td>0.39</td>
<td>0.34</td>
<td>91</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.45</td>
<td>0.36</td>
<td>68</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.45</td>
<td>0.41</td>
<td>87</td>
</tr>
</tbody>
</table>

---

An independent study has shown, however, that the quantum yield ($\Phi_t$) for isomerisation of $p$-substituted trans-stilbenes is temperature dependent provided the substituent shows only a limited spin–orbit coupling (Table 4), whereas substituents with a large spin–orbit effect show no temperature dependence on values of $\Phi_t$. These authors explain their observations on the intermediacy of triplet states in the isomerisation process, a conclusion at variance with that reported above for stilbene. The temperature dependence shown for $\Phi_t$ with substituents showing a low spin–orbit effect is explained on the basis of decreased efficiency of intersystem crossing ($S_1-T_2$). However, Saltiel's interpretation based on activation energies required to reach a common twisted singlet state is also a reasonable explanation. As the values of $\Phi_t$ decrease with the drop in temperature there is an increase in the quantum yield of fluorescence. Such a result is equally well explained by either of the two mechanistic explanations. The

Table 4 Temperature dependence of quantum yield for isomerisation of substituted stilbenes

<table>
<thead>
<tr>
<th>Stilbene</th>
<th>$\Phi_t$</th>
<th>Temp. °C</th>
<th>Stilbene</th>
<th>$\Phi_t$</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low spin–orbit coupling</td>
<td></td>
<td></td>
<td>Low spin plus enhanced spin–orbit coupling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.60</td>
<td>25</td>
<td>4-MeO, 4'-NO$_2$</td>
<td>0.60</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>-80</td>
<td>Non-polar solvent</td>
<td>0.55</td>
<td>-100</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enhanced spin–orbit coupling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Br</td>
<td>0.35</td>
<td>25</td>
<td>4-MeO, 4'-NO$_2$</td>
<td>0.10</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>-115</td>
<td></td>
<td>0.06</td>
<td>-25</td>
</tr>
<tr>
<td>4-NO$_2$</td>
<td>0.15</td>
<td>25</td>
<td></td>
<td>0.04</td>
<td>-75</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>-150</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

photoisomerisation of stilbenes with substituents having increased spin–orbit coupling properties (NO$_2$ and Br) shows no temperature dependence in the values of $\Phi_t$ (quantum yield for the isomerisation of the trans-isomer). This change in behaviour could be explained by the involvement of $n\pi^*$ levels of the substituents or by increasing the energy gap between the $S_1$ and $T_2$ states which are almost isoenergetic in other stilbenes. In non-polar solvents stilbenes with both donor and acceptor substituents show no temperature dependence for the values of $\Phi_t$. In polar solvents these stilbenes (with donor and acceptor substituents) show $\Phi_t$ to be again temperature dependent, and it is suggested that this change is due to a change-over in the nature of the excited state ($n\pi^*$ to $\pi\pi^*$) responsible for the isomerisation.

The introduction of other aromatic moieties into the stilbene has also been studied. Reports describing the photochemical isomerisation of

---

\(\beta\)-styrylnaphthalene \(^{45}\) and an inefficiency in the isomerisation of 1,2-bis-(4-pyridyl)ethylene \(^{46}\) have appeared. This inefficiency in the isomerisation of 1,2-bis-(4-pyridyl)ethylene is encountered in the direct irradiation of the ethylene. This ethylene showed very poor intersystem crossing and low fluorescence suggesting a dramatic reduction in the stability of the singlet state compared with stilbene. It is suggested that the inefficiency could be due to the decay of excited trans-singlets to an unstable isomer which decays specifically to the ground state trans-olefin. On the other hand, the sensitised isomerisation of the pyridylethylene is equal in efficiency to that of stilbene.

The cis–trans isomerisations of difurlyl- and dithienyl-ethylenes have been shown to be concentration-dependent with respect to the composition of the photostationary mixture (Table 5).\(^{47}\) This change in the photostationary mixture is related to an excited olefin–ground state olefin interaction at higher concentrations of olefin bringing about collisional quenching (excimer quenching).

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Dithienylethylene trans (%)</th>
<th>Difurylethylene trans (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>9.0</td>
<td>49</td>
</tr>
<tr>
<td>10.0</td>
<td>13</td>
<td>70</td>
</tr>
<tr>
<td>29.9</td>
<td>20</td>
<td>69</td>
</tr>
<tr>
<td>52.0</td>
<td>69</td>
<td>97</td>
</tr>
</tbody>
</table>

**Table 5** Photostationary-state composition for dithienyl- and difurylethylenes

**B. Rearrangements.**—X-Ray crystallographic verification of the structures of two of the four isomeric photocaryophyllenes obtained from the photolysis of caryophyllene or isocaryophyllene has been reported.\(^{48}\)

The photoisomerisation of four octalins (53a—d) in the presence of xylene as sensitisier has been reported.\(^{49}\) The isomerisations of (53a) and (53b) require the reaction to be carried out in the presence of acetic acid; and this observation has prompted the proposal that the reaction proceeds

\[
\text{Me} \\
R^1 \quad R^2
\]

(a) \(R^1 = R^2 = \text{Me}\)
(b) \(R^1 = \text{Me}, R^2 = \text{H}\)
(c) \(R^1 = \text{H}, R^2 = \text{Me}\)
(d) \(R^1 = \text{D}, R^2 = \text{Me}\)

(53)

---


by the intermediacy of carbonium ions. The three cases examined show that protonation of the olefin gives rise to the more stable tertiary carbonium ion (54) which then deprotonates into or out of the ring. Scheme 3 represents the rearrangement of the octalins (53a and b) to produce two isomeric olefins (55) and (56). The minor product (56) of this reaction is, according to this mechanism, formed by deprotonation into the ring. This compound can be subsequently photoisomerised into the major product (55).

\[
\begin{align*}
(53a \text{ or } b) & \rightarrow \begin{array}{c}
\text{Me} \\
\text{R}^1 \quad \text{R}^2
\end{array} \\
& \equiv \\
(54) & \\
\begin{array}{c}
\text{Me} \\
\text{R}^2
\end{array} & \quad \begin{array}{c}
\text{Me} \\
\text{R}^2
\end{array} \\
\begin{array}{c}
\text{Me} \\
\text{R}^2
\end{array} & \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\end{align*}
\]

(a) \( R^3 = \text{Me} \) 60%  
(b) \( R^3 = \text{H} \) 53%  
(55)

(a) \( R^3 = \text{Me} \) 3%  
(b) \( R^3 = \text{H} \) 2%  
(56)

Scheme 3

The reaction is stereospecific giving, in the examples described above, cis-fused decalins as the major products. The isomerisation of octalin (53c) led, without the presence of acid, to an excellent yield of one product, decalin (57), trans-fused, and exocyclic. The stereospecificity of the implied hydride migration was checked by photolysis of the deuterium analogue (53d); this underwent deuteride migration very slowly to furnish the trans-\( \beta \)-deuteriodecalin (57). The stereospecificity of the reaction is explained on the basis of the more stable conformations of the carbonium ions giving rise to the observed products. In the photolysis of (53a) and (53b) the conformations represented above are probably the better arrangements, thus ensuring methide migration in octalin (53a) and hydride migration in octalin (53b) to give cis-fused products. However, in
the photolysis of octalins (53c) and (53d), the better conformation is represented as (58) in Scheme 4, and hydride or deuteride migration then takes place to produce trans-fused products.

![Structures](images)

Scheme 4

Carbonium ion intermediates have also been proposed\(^6\) to account for the rearrangement of 3,4-dichlorodibenzobicyclo[3,2,2]nona-2,6,8-triene (59) to an exo–endo mixture of a triene (60) and the dibenzsemibullvalene (61). The reaction does not take place on direct irradiation but requires the presence of a triplet sensitizer (74–77 kcal/mole). Free-radical mechanistic schemes were considered and rejected by the authors\(^6\) on the grounds that they did not account for the products or possible by-products. Thus it has been suggested that the initial generation of a triplet is followed by rapid decay to a vibrationally excited ground-state which breaks-down to produce a carbonium ion and chloride ion. Rearrangement of this carbonium ion can account for the observed products.

Radical intermediates have been proposed\(^1\) to explain the rearrangement of cyclic enol ethers (62) to cyclopropane aldehydes (63). Dürr\(^2\) has

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reported further studies on the photochemistry of small ring compounds, specifically the ring-opening of bicyclo[3,1,0]hex-3-en-2-ol derivatives (64). The photolysis is by a $\pi \rightarrow \pi^*$ excitation and the reaction could be sensitised by acetophenone; from this fact, the excited state is concluded to be a triplet.† The ring-opening proceeds in part by the generation of the diradical (65), followed by hydrogen transfer, loss of a formyl radical (which requires a second photon), and ring closure to give the cyclopentene products (66). The other products isolated from the reactions were 1,2,3,5-tetrasubstituted benzene derivatives (67) formed by an alternative initial mode of cyclopropane ring-opening and dehydration. Scheme 5 illustrates some of these points.

† Attention is drawn in Part I, Chapter 1 to a possible fallacy in such reasoning.
Although both endo- and exo-derivatives were photolysed, no correlation between the stereochemistry of the starting material and the product could be found. A mass spectral analysis of the above bicyclohexenols has also been published.  

A novel synthesis of pyrroles has been reported by Chapman et al. The process involved the direct photolysis of dihydro-1,2-oxazines (68) in alcoholic solution. The singlet reaction (it could not be quenched by oxygen or naphthalene) was shown to furnish an intermediate by N−O bond fission and hydrogen transfer to afford a γ-aminoketone (69). The presence of the ketone as an intermediate was shown by low-temperature i.r. examination of the photosylate and also by independent synthesis. The reaction to yield the pyrroles (70) was purely a thermal process represented in Scheme 6. The evidence for the thermal step comes from the i.r. study and also from the quantum efficiency of the reaction ($\Phi = 0.76$) since a two-photon reaction would have given a value of $\Phi < 0.5$.

\[
\begin{align*}
R^1 & = R^2 = R^3 = R^4 = H \\
R^1 & = R^4 = Ph, R^2 = R^3 = H \\
R^1 & = R^4 = Me, R^2 = R^3 = H \\
R^2 & = R^4 = H, R^3 = R^3 = Me \\
R^1 & = R^3 = R^3 = H, R^4 = Ph
\end{align*}
\]

Scheme 6

C. Di-π-Methane Rearrangements.—A review on selected topics in olefin photochemistry with a particular leaning towards the novel di-π-methane rearrangements has been published. Elucidation of the mechanistic details of this reaction has been achieved by Zimmerman et al. through a study of the rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethylpenta-1,4-diene (71). The reaction to produce the vinylcyclopropane (72) has been shown to depend mainly on a singlet excited state. Attempts to sensitise the reaction with high-energy sensitisers (benzophenone or chlorobenzene)

showed only a slight enhancement. Although energy transfer certainly took place, the rearrangement from the triplet is highly inefficient. The quantum yield (\( \Phi = 0.0797 \)) of the process has been measured by the extremely sensitive isotopic dilution technique. The reaction is represented in Scheme 7 as a stepwise process, but it is presumably concerted, and is shown in Zimmerman's terms as a Möbius system (1 sign inversion) or in Woodward-Hoffmann nomenclature as a \((2\pi+2\sigma+2\pi)\) photoallowed rearrangement.

![Scheme 7](image)

Closely allied to this type of rearrangement are the rearrangements of benznorbornadiene and benzbarrelene. Ziegler \(^{57}\) reports the rearrangement of 1,4-epoxy-1,4-dihydronaphthalene (73a) to benzo(f)oxepin (74a). The reaction appears to be mainly a singlet process, and cannot be quenched by the addition of dienes. The quantum yield has been measured as 0.1, implying that 90% of the excited molecules decay back to the ground state. The rearrangement proceeds by intramolecular bonding via the intermediacy of a quadricyclane derivative (75), a conclusion justified by the rearrangement of the disubstituted derivative (73b) to give solely the 2,7-disubstituted oxepin (74b). There is a duality of mechanism for the di-\(\pi\)-methane rearrangements; in the above two examples a singlet state mechanism is

operative, whereas in the rearrangement of bicyclo[3,2,1]octadiene (76) either direct or triplet-sensitised processes can lead to the tricyclo[3,2,1,0²,7]octane (77).

![Chemical structures](image)

(a) \( R = H \)  
(b) \( R = CH₂OAc \)  
(a) \( R = H \)  
(b) \( R = CH₂OAc \)  

(73)  
(74)  
(75)  

(76)  
(77)

The photosensitised rearrangement of benzbarrelene (78) gives rise to two products, viz., benzsemibullvalene (79) and benzocyclo-octatetraene (80), whereas direct irradiation gives only the cyclo-octatetraene. By the use of poly-deuteriated starting material with bridge-head protium, the conversion to the semibullvalene (79) has been shown to result not from 'benzo-vinyl' bridging, but from a di-\( \pi \)-methane rearrangement of the two vinyl groups. Scheme 8 shows a rationalisation of the rearrangement to give semibullvalene labelled specifically at the 2,5-positions. From the same experiments it was shown that the cyclo-octatetraene was labelled at both the 4,7 (94\%) and the 3,8 (6\%) positions. Direct irradiation of the benzbarrelene gave the same two labelled cyclo-octatetraenes in the same proportions as in the sensitised experiments, whereas direct irradiation of the benzsemibullvalene gave a cyclo-octatetraene labelled specifically at the 3,8-positions.

The triplet reaction to form the benzsemibullvalene proceeds via vinyl-vinyl bonding and this is explained on the grounds that the vinyl system corresponds electronically to a cis-butadiene, and as the bonding begins it is energetically more favourable by a few kcal/mole than 'benzo-vinyl' bonding. The singlet reaction to produce the cyclo-octatetraenes predominantly proceeds by a 'benzo-vinyl' overlap and is analogous to the oexpin synthesis described previously (p. 245, ref. 57).

Similar observations have been reported by other investigators. Dibenzbarrelenes (81) have also been photolyzed. The results described are contrary to those in a previous report. The direct photolysis of (81a)

---

and (81b) at 253.7 nm gave the symmetrical dibenzocyclo-octatetraenes (82a) and (82b) respectively, with only a trace of the semibullvalene (83). These results imply that intersystem crossing is inefficient in the molecules studied, since it is now generally accepted that a singlet state rearranges to a cyclo-octatetraene and a triplet to a semibullvalene. However, enhancement of the intersystem crossing efficiency is found in the substituted barrelene (81c), and an efficient conversion to the semibullvalene (83c) results. The alcohol (81d) on direct irradiation gives only the cyclo-octatetraene (82d).

(a) $R^1 = R^2 = H$
(b) $R^1 = H, R^2 = Cl$
(c) $R^1 = H, R^1 = CO_2Me$
(d) $R^1 = H, R^1 = Me_2COH$
Tribenzobarrelene (triptycene) (84) has also been studied.\textsuperscript{62, 63} Photo-
rearrangement to the interesting product (85)\textsuperscript{62, 63} takes place by sensitis-
tion with a quantum efficiency of 0.3.\textsuperscript{63} The triplet reaction leads to the
semibullvalene (86) which undergoes stereospecific sigmatropic rearrange-
ment to compound (85).

![Chemical structures](image)

The triplet rearrangement of \textit{anti}-benzobicyc[2,2,2]octadienol (87a) to
furnish two alcohols (88a and 89) also proceeds \textit{via} 'benzo-vinyl' bonding,
and is another example of the di-\textit{n}-methane rearrangement.\textsuperscript{64} A substituent
effect has been observed, and the photolysis of the \textit{syn}-alcohol (87b) gave
only one product (88b) which can only arise from one mode of 'benzo-
vinyl' bonding, and although there is no proof to date for this specificity it
has been suggested that a complex (90) involving the oxygen atom could

![Chemical structures](image)

influence the relative stabilities of the possible intermediates in favour of the
observed pathway.\textsuperscript{64}

It was thought\textsuperscript{65} that the triplet rearrangement of the corresponding
ketones (91) could also proceed \textit{via} a di-\textit{n}-methane rearrangement but

\textsuperscript{63} N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, \textit{J. Amer. Chem. Soc.}, 1969,
\textit{91}, 516.
from analysis of the product (92) it was suggested that formation was by a 1,3-acyl migration (Scheme 9). The singlet reactions of these ketones produce hydrocarbons through elimination of carbon monoxide or ketene.

D. Miscellaneous Rearrangements.—The Woodward–Hoffmann postulates predict that 1,5-hydrogen migrations must be antarafacial if they occur from an excited state. Recently experimental evidence for one such rearrangement has been published. The hydrogen-transfer takes place during the photolysis of tetramethylallene dimer (93) to produce the isomerised product (94). The migration is almost certainly antarafacial owing to the constraint of the puckered cyclobutane ring (not depicted) which places the vinyl methyl groups in an ideal position for the transfer.

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The photolysis of diene (95) brings about what is formally a 1,3-migration. The product isolated from the reaction is a cis–trans-mixture of allylcyclohex-1-enylmalononitriles (96). The isomerisation of the allyl double bond does not arise from sensitised isomerisation, but takes place during the migration; and it is suggested that if the reaction is a concerted 1,3-migration excess of vibrational energy could cause the cis–trans-isomerisation.

Srinivasan has published an interesting paper on the photochemical valence isomerisation of buta-1,3-dienes. A study of trans–trans-, cis-trans- and cis-cis-hexa-2,4-dienes leads to a common photochemical stationary state of $35\cdot7tt : 30\cdot5ct : 33\cdot7cc$, together with cis-3,4-dimethylcyclobutene (97), 1-ethyl-2-methylcyclopropene, and trans- and cis-hexa-1,4-diene. The formation of the cyclobutene follows from a disrotatory cyclisation of trans–trans-hexa-2,4-diene. The cyclopropene is formed from the precursor (98) of a bicyclo[1,1,0]butane. Srinivasan reasons that the formation of bicyclo[1,1,0]butane from a buta-1,3-diene is a two-step process via a diradical, and that hydrogen migration to give the cyclopropene is reasonable.

Dürr and Scheppers describe the synthesis of benzycloheptenes (99), and of bicyclo[6,3,0]undecapentaenes (100). Thus addition of cyclopentadienyldienes to an aromatic substrate produces the labile intermediate norcaradiene (101) and, depending on the substitution pattern of the original cyclopentadiene, benzycloheptenes or the undecapentaenes are obtained.

The conversion of spiro[2,4]hepta-4,6-dienes (102) to fulvenes (103) has been reported. The reaction was found to be rapid up to 34%, when self-quenching of the reaction by product was observed. The reaction was very specific and dependent on the substitution pattern of the cyclopropane ring. Thus only two compounds (102a and b) could be made to isomerise.

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and it is suggested that as the ease of hydrogen-migration is decreased by increased substitution, other non-radiative processes become more efficient than product formation.

The photoisomerisation of phenylated cyclohexa-1,3-dienes to cyclohexatrienes \(^74\) or to bicyclo[3,1,0]hex-2-enes \(^75\) has been described. Gassman and Hymans \(^76\) have applied photochemical bicyclo[1,1,0]butane formation in the steroid series to the synthesis of 5β,7β-cyclocholestanes (104) from dienes (105). A study of benzyl enol-ether rearrangement in the steroid series has been published. \(^77\) Irradiation of 3-benzyloxycholesta-3,5-diene (106) gave three compounds as shown in Scheme 10. The stereochemistry of the products was of interest since products (107) and (108) both had α-benzyl groups. The specificity of the reaction is surprising since the reaction probably arises by homolysis of the PhCH\(_2\)-O bond; but the 4β and 6β isomers would be less stable and epimerisation might have taken place during chromatographic work-up.

Similar conformational preferences have been shown as a result of the photolysis of the trichloromethyl enol acetates (109a and b) where the

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\(^{75}\) J. H. Smith, Diss. Abs., 1968, 28, B, 4033.


recombination of the trichloromethyl radical with the mesomeric radical (110) gave the more stable equatorial isomers (111a and 111b respectively).\textsuperscript{78}

\begin{align*}
\text{CCl}_3\text{COO} & \quad \text{CCl}_3\text{COO} \\
(109a) & \quad (109b)
\end{align*}

\begin{align*}
\text{O} & \quad \text{O} \\
(110) & \\
\text{CCl}_3 & \quad \text{CCl}_3 \\
(111a) & \quad (111b)
\end{align*}

Benzene-sensitised photolysis of cyclonona-1,2-diene in the gas-phase has been shown to produce tricyclo[4,3,0]nonane (112).\textsuperscript{79} It has been suggested that the product is formed via a carbene (113), followed by transannular insertion. Calculations have indicated\textsuperscript{80} that a vibrationally excited ground-state allene-cyclopropylidene rearrangement is symmetry allowed and that the triplet process is symmetry forbidden; these considerations have obvious relevance to the above formation of tricyclononane (112).

A more extensive study of the photochemistry of cis–cis-cyclo-octa-1,3-diene has been published.\textsuperscript{81} The original observations made by Liu\textsuperscript{82} have been shown to be incomplete. Direct irradiation of the cyclo-octadiene gave two photoproducts, viz. the cis–trans-isomer (114) and bicyclo[4,2,0]-oct-7-ene (115). Irradiation for longer time gave appreciable quantities of cis–cis-cyclo-octa-1,4-diene, the product of a suprafacial 1,3-sigmatropic hydrogen-migration. The formation of bicyclo[4,2,0]oct-7-ene is of interest

\begin{align*}
(112) & \quad (113) & (114) & (115)
\end{align*}


since thermolysis of the cis—trans-cyclo-octadiene is known to produce this product readily. Thus on the basis of the Woodward–Hoffmann rules, photocyclisation of the cis—trans isomer (114) would give a trans-bicyclo-octene. There is no evidence in this paper to suggest that the bicyclic olefin is formed thermally, but the possible involvement of an excited ground state of the cis—trans diene is suggested.81

The photolysis of cyclo-octa-1,4-diene has been reported not to proceed by the di-π-methane route.83, 84 Instead, a straightforward intramolecular cycloaddition reaction yields83 cis—syn—cis-tricyclo[3,3,0,04.5]octane (116a), which can be thermally isomerised to the cis—anti—cis isomer (116b).

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
(116a)

\[ \text{H} \quad \text{H} \]
(116b)

Quadricyclane (117) and norbornadiene have been reported85 as quenchers of aromatic hydrocarbon fluorescence. Quadricyclane is the more efficient, and the product from the quenching reaction is norbornadiene produced from a singlet excited state. Day and Wright report a study of the quenching of the fluorescence of 2,3-diazabicyclo[2,2,2]oct-2-ene (118) by conjugated dienes.86 Little difference is exhibited by cis- or trans-dienes but increased substitution, particularly at the termini of the diene system, has a marked influence. This sensitivity to the substitution pattern could be related to the singlet excitation energies of the dienes studied.

3 Polyene Rearrangements

A full report of results of the direct irradiation of allo-octimene (2,6-dimethylocta-2,4,6-triene) has been published.87 Calculations on the photochemical cyclisation of 3-methylenhepta-1,5-diene to 2-methylene-6-methylbicyclo[2,1,1]hexane have shown88 that the reaction should be concerted, and are in agreement with the Woodward–Hoffmann postulates.

A further study of the singlet-state photochemistry of methylenecyclohexadienes (119) has shown that isomerisation of compound (119a) to the bicyclo[3,1,0]hexene (120a) takes place without methyl migration. This was verified by experiments with deuterium-labelled compound (119b) to furnish labelled bicyclohexene (120b). A ‘bond-crossing’ mechanism is favoured but no check on whether the process is concerted or not has been made. It is conceivable that the reaction is an example of a \( \sigma^a_6 + \pi^a_6 \) concerted isomerisation.

![Chemical structures](image)

The unsensitised irradiation of 1,3,4,5,6-pentamethyl-2-methylenebicyclo[3,1,0]hex-3-ene (120c) has been reported to yield 1-methylene-2,3,4,5,6-pentamethylcyclohexa-2,4-diene (121). The all-*cis*-oxacyclocnonatetraene (122) is proposed as the common transient intermediate in the photolysis of cyclo-octatetraene oxide (123). Conrotatory cyclisation gives rise, by 2,7-bonding, to the dihydrofuran (124), and by 2,8-bonding to the oxetene (125). Disrotatory cyclisation and 2,5-bonding produce the cyclobutene (126). All these processes are photochemically allowed. The only unexplained product is cycloheptatriene, a compound formally derived from cyclo-octatetraene oxide by the loss of carbon monoxide.

The benzene-photosensitised isomerisation of 1,2,6-cyclononatriene in the gas phase gave only 1,5-divinylcyclopentene as the initial product (a)

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Cope reaction). This was presumably derived from a vibrationally excited ground state since it is also produced by thermolysis of the nonatriene.\textsuperscript{92}

Interest in the photochemistry of the fluctuating molecules 2-methoxyazabullvalene (127) and 2-methoxybenzazabullvalene (128) will have been awakened by the publications of Paquette et al.\textsuperscript{93, 94} The simple azabullvalene (127) gave five products (129a—e) on irradiation in methanol or tetrahydrofuran. Intersystem crossing efficiency has been shown to be poor and the results can be explained on the basis of symmetry-allowed reactions. Products (129b—d) all arise from compound (129a) which itself is formally derived from the azabullvalene by a 1,3-cyclopropyl bond migration.\textsuperscript{93} A retro-reaction corresponding to this process is observed in the sensitised photolysis of the iminoether (130), which furnishes, by a \((2\sigma+2\pi)\)-cycloaddition, an excellent yield of benzazabullvalene (128), and a poorer yield of the isoazabullvalene (131).\textsuperscript{94}

Givens has observed a 1,7-hydrogen migration in the formation of 1,7-isomer (132) from the singlet photolysis of 7,7-ditropyl (133). A second 1,7-hydrogen-migration resulted from further photolysis to yield 1,1-ditropyl (134). Although triplet energy could be transferred from benzophenone to the ditropyl, the triplet state was found to be totally unreactive.

Disparate results have been reported for the photolysis of diazo-compounds in the presence of norbornadiene. Filipescu and DeMember obtained 1-pyrazolines (135) from the photolysis of 9-diazofluorene in the presence of norbornadiene, whereas Dürr et al. isolated spirobicyclooctenes (136) from the photolysis of diazocyclopentadienes with the same olefin. Dürr et al. claim that their product is formed by the ring-opening of the initial adduct (137), whereas Filipescu et al. only isolated the normal cyclopropane adduct (138) by nitrogen elimination by photolysis of the pyrazoline (135). There is no obvious explanation for this difference. Irradiations were carried out under identical conditions, as far as can be assessed from the publications. It is conceivable that the difference lies in the relative amounts of energy absorbed by the two species; and in the case examined by Dürr et al., it is possible that excess of vibrational

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energy could bring about isomerisation of the cyclopropane intermediate (137).

The acetone-photosensitised conversion at $-78^\circ$ of cyclo-octatetraene to semibullvalene (tetracyclo[3,3,0,0$^8$,8]$\text{octa-3,6-diene}$) (139) is specially notable.$^{98}$ Two possible mechanisms for the conversion are 'suggested' one involving the intermediacy of bicyclo[4,2,0]$\text{octa-2,4,7-triene}$ (140) followed by di-$\pi$-methane rearrangement as shown in Scheme 11, and the second via 1,5- and 2,8-bonding. The results of further work on this reaction will be awaited with interest.

An interest in the photochemistry of carbanionic species has been reported recently.$^{99,100}$ In particular the photochemistry of cyclo-octatetraene dianion in the presence of weakly acidic proton donors has been shown to yield cyclo-octatrienes (the 1,3,5 and 1,3,6 isomers) and their photo-products via the protonated mono-anion (141).$^{100}$

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The existence of bond-shift isomers in 1,2-disubstituted cyclo-octatetraenes (142) has been demonstrated by n.m.r. spectroscopy.\textsuperscript{101} The n.m.r. spectrum of methyl 2-methylcyclo-octatetraene carboxylate (142a) shows that the two forms (142a and 143a) are present in the ratio of 17 : 1 at ambient temperatures and after irradiation at $-30$ to $-50^\circ$ the ratio changes to 1 : 1. The transformation of (143a) into (142a) has a rate constant of $1 \times 10^{-3}$ sec$^{-1}$ at $-12^\circ$. Similar observations were reported\textsuperscript{102} for the cyclo-octatetraenyl mandelate (142b).

Yet another weird cyclo-octatetraene ring isomer has been described by White \textit{et al.}\textsuperscript{102, 103} The evidence cited points to the existence of a mono-trans-isomer (144) formed from the irradiation of 1,2,4,7-tetraphenylcyclo-octatetraene (145). The isomer is a crystalline solid which slowly reverts to the original compound ($t_1 = 18$ hr. at 25$^\circ$). The rigidity of the new isomer is used as an explanation for its fluorescence and for the high-field resonance ($\tau 5.31$) for the trans-vinyl hydrogen.

4 Addition Reactions

Photochemical free radical additions of phosphine and phenylphosphine to a hexenofuranose (146) have been described.\textsuperscript{104} The products (Scheme 12) of the addition are sensitive to oxidation and were isolated as the corresponding oxides. The unsensitised irradiation of cyanimidones (147) in the presence of water gives efficient conversion into the ureas (148).\textsuperscript{105} Attempts

\textsuperscript{102} E. W. Friend, \textit{Diss. Abs.}, 1968, 28, B, 4494.
to sensitise the reaction with benzophenone and acetophenone were futile, although it is interesting that acetophenone sensitised the reaction when hydrochloric acid was present. The dependency of the reaction on the presence of acid was interpreted as good evidence for a protonated excited state (149). Cholest-2-ene can be converted to a mixture of alcohols

\[ \overset{+}{N}=C=NH \quad \text{and} \quad \overset{-}{N}=C=NH \]

(149)

(Table 6) by direct irradiation of the steroid in a water–t-butanol–sulphuric acid (1%) mixture.\(^{108}\)

**Table 6**  **Mixture of alcohols form the irradiation of cholest-2-ene in water–acid mixture**

<table>
<thead>
<tr>
<th>Structure</th>
<th>(R^1 = R = H)</th>
<th>(R^2 = R^3 = H)</th>
<th>(2\alpha)</th>
<th>(2\beta)</th>
<th>(3\alpha)</th>
<th>(3\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R^1 = H), (R = OH)</td>
<td>(R^1 = OH), (R^2 = H)</td>
<td>27%</td>
<td>8%</td>
<td>17%</td>
<td>27%</td>
</tr>
</tbody>
</table>

A review describing the recent advances in photosensitised ionic additions to cyclohexenes has been published.\textsuperscript{107} A typical example of this reaction is the unsensitised or benzene-sensitised photochemical addition of methanol to abietic acid (150) or its methyl ester to produce two C\textsubscript{12} epimeric ethers (151a) and (151b).\textsuperscript{108} The protonation of the excited state takes place to produce the tertiary carbonium ion (151c), and subsequent reaction of solvent either above or below the plane of the ring yields the ethers with the a-methoxyl favoured over the \(\beta\)-isomer (9:1). In this example there was no evidence for the formation of products arising from a bicyclobutane intermediate.

Benzene-sensitised reaction of steroid (152) in the presence of methanol produces four products, a diene (153), two ethers (154), and a ketone, the formation of which can be explained on the basis of protonation of the excited state (Scheme 13).\textsuperscript{109} Cholesterol (155) gave similar products on benzene sensitisation, but produced a cyclopropane ether (156a) on direct irradiation, the product of solvolysis of a bicyclobutane formed from the diene (153). The benzene-sensitised photolysis of the alcohol (156b) gave the ether (156a), the product of kinetic-controlled attack on the intermediate cyclopropyl carbonyl carbonium ion (157), together with the cholesteryl ether (155, \(R = \text{Me}\)), the product of thermodynamic control.\textsuperscript{110} This particular photoreaction only occurs with the \(\beta\)-alcohol (156b).

Methanol is also reported\textsuperscript{111} to add efficiently to certain \(\beta\)-aroylacrylic acids (158) to produce the \(\alpha\)-ethers (159).

Bicyclo[1,1,0]butanes are said to be the precursors of the cyclopropyl- and cyclobutyl ethers obtained from the photolysis of linear-conjugated

dienes in methanol. Allyl ethers obtained from the same reactions arise from protonation of the excited state followed by methanolysis. Representative examples of this reaction are given in Table 7. Only two products from the many obtained cannot be explained on the simple basis outlined above. These are 1-methoxyethylcyclopropane and 1-methyl-1-methoxycyclopropane, which are obtained from the photolysis of 2-methylbuta-1,3-diene and 2-methylpenta-1,3-diene respectively. No explanation was

\[
R^1 = \text{Ph}, R^2 = H \\
R^1 = p\text{-tolyl}, R^2 = H \\
R^1 = p\text{-anisyl}, R^2 = H \\
R^1 = p\text{-Br-C}_6\text{H}_4, R^2 = H
\]

(158)

\[
R^1 \text{ CO}_2 R^2 = \text{CO}_2 R^2
\]

(159)

(152)

(153)

(a) \( \alpha\)-MeO
(b) \( \beta\)-MeO

(154)

(a) \( R = \text{Me} \)
(b) \( R = \text{H} \)

(155)

(156)

(157)

Scheme 13

advanced for the formation of these products; but at least in the case of 2-methylpenta-1,3-diene, protonation and isomerisation could produce 2-methylpenta-2,4-diene from which the isolated ether is the expected product. No such isomerisation is possible in the case of isoprene, and some alternative mechanism involving rearrangement must be involved.

Table 7  Photo-products from the addition of methanol to acyclic dienes

<table>
<thead>
<tr>
<th>Diene</th>
<th>Cyclopropyl ether (%)</th>
<th>Cyclobutyl ether (%)</th>
<th>Allyl ether (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R² = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R³ = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R⁴ = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R⁴ = R³ = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R⁴ = R³ = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R³ = R⁴ = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R⁴ = R³ = Me</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5 Alkylations

The use of acetone triplets as radical generators by hydrogen abstraction has been applied to the addition of γ-butyrolactone\textsuperscript{113} and 2-pyrrolidone\textsuperscript{114} to olefins. Extensions of this reaction to carbohydrate chemistry have been described, e.g. the addition of 1,3-dioxolan to the hexenefuranose (160) to produce 2-(5′-deoxy-1′,2′,O-isopropylidene-α-D-xylohexafuranos-6-yl)-1,3-dioxolan (161) has been reported.\textsuperscript{115} The addition of formamide and aniline to crotonic acid derivatives has also been described.\textsuperscript{116}

The photoamination of hept-1-yne by formamide in the presence of benzophenone as sensitiser is reported to yield a dimeric product (162), the formation of which is accounted for by monooaddition followed by amidation of the intermediate (163) and attack on substrate acetylene (Scheme 14).\textsuperscript{117}

\textsuperscript{114} J. Sinreich and D. Elad, \textit{Tetrahedron}, 1968, 24, 4509.
The initial product from the photolysis of ethyl propiolate in cyclohexane by direct irradiation is the trans-ester (163). Subsequent photolysis of this induces isomerisation to the cis-ester (164) followed by isomerisation to yield the $\beta,\gamma$-ester (165). Irradiation of ethyl propiolate in ethanol and isopropanol produced lactones (166) in reasonable yield. The need for a carbonyl function in the molecule was shown to be unnecessary by the photolysis of hexa-1-yne in isopropanol, when a mixture of octenols was obtained. A detailed mechanistic interpretation of the results was not made. However, the only process which requires explanation is the original addition of the substrate to the acetylene, and this is readily accounted for on the basis of $\pi-\pi^*$ excitation and hydrogen-abstraction from the solvent to give the radical (167).

$$\begin{align*}
\text{O} & \quad \text{C} \quad \text{NH}_2 \quad \overset{\text{C}_8\text{H}_7\text{C}=\text{CH}}{\text{C}_3\text{H}_7} \quad \overset{\text{C} = \text{CHCONH}_2}{\longrightarrow} \quad \text{C}_6\text{H}_{11}\text{CH}=\text{CHCONH}_2 \\
\text{C}_6\text{H}_{11}\text{CHCONH}_2 & \quad \overset{\text{C}_8\text{H}_7\text{C}=\text{CH}}{\text{C}_3\text{H}_7} \quad \overset{\text{C} = \text{CHCONH}_2}{\longrightarrow} \\
\text{H}_2\text{NOC} & \quad \overset{\text{CH}=\text{CHC}_8\text{H}_7}{\longrightarrow} \quad \text{C}_6\text{H}_{11}\text{CHCHCONH}_2 \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \quad \text{CO}_2\text{Et} \\
(163) & \quad (164) \quad (165)
\end{align*}$$

(a) $R = \text{H}$, $R' = \text{Me}$ \quad (b) $R = R' = \text{Me}$

$$\begin{align*}
\text{HC}=\text{C}=\text{C} & \quad \overset{\text{OH}}{\text{OH}} \quad \text{HC}=\text{C} \quad \overset{\text{OH}}{\text{HC} \equiv \text{C}} \\
(166) & \quad (167)
\end{align*}$$

6 Fragmentation Reactions

The mercury-sensitised gas-phase decomposition of hexa-1,5-diene to a 1:1 mixture of ethylene and butadiene may be a unimolecular reaction possibly involving the diradical (168). A Stern–Volmer plot of $1/\Phi$ versus ethylene and butadiene gave linear plots, and from this it was concluded that only 9% of the excited molecules follow this reaction path.

It is worth while comparing these results with earlier studies of Srinivasan and Cremer\(^{120}\) where the gas-phase decarbonylation of bicyclo[3,2,0]hept-3-one gave only bicyclo[2,2,0]hexane and butadiene. The difference in these reactions could be due to a difference in electronic multiplicity or to a difference in excess of vibrational energy. Mercury-sensitised photolysis of cyclo-octa-1,5-diene also led to elimination of ethylene.\(^{121}\)

It has been said that the photochemical retro-Diels–Alder reactions exhibited by certain adducts of anthracene (169a and 170) cannot be concerted processes if the laws of conservation of molecular symmetry are obeyed.* Thus a diradical process is suggested\(^{122}\) and confirmed by irradiation of the optically active ester (170b). Examination of the remaining adduct showed that the compound has been racemised by bond rupture, rotation, and rebonding (Scheme 15).

\[
\begin{align*}
\text{(170) (a) aryl} &= \text{Ph} \\
\text{(b) aryl} &= \text{aryl} = \begin{array}{c}
\text{aryl} \\
\text{CO}_2\text{Me}
\end{array}
\end{align*}
\]

\text{Scheme 15}

The photolysis of iodosugar (171) in sodium hydroxide and methanol gave\(^{123}\) the 6-deoxygalactopyranose (172). Photolysis in a solvent with no abstractable hydrogens gave the olefin (173), a result which provides good evidence for the intermediacy of the radical (174) formed by C–I bond rupture. Detosylation of tosylate (175a) into methyl-D-glucopyranoside (175b) by photolysis in methoxide–methanol exemplifies a useful synthetic sequence.\(^{124}\) D-Arabino-\text{-} is reported\(^{125}\) to be formed by the photodegradation of the anilinosugars of the 176.


* Blind extension to aromatic systems of rules based on the symmetry properties of excited aliphatic systems is dangerous even though one may sometimes fortuitously reach a correct conclusion.
The photolysis of ozonides by \( \pi \rightarrow \sigma^* \) excitation gives high yields of hydrocarbons.\(^{126}\) Thus the photolysis of cyclopentene ozonide (177) proceeds by O—O bond cleavage to the diradical (178) (presumably a singlet). Collapse of this by the path shown in Scheme 16 gave rise to high yields of cyclopropane. An ingenious application of this reaction to the formation of tetramethylcyclobutadiene has also been described.\(^{127}\) The essential ozonide is the mono-ozonide of hexamethyl Dewar-benzene (179). The products isolated from the photochemical decomposition of this in pentane were the syn-dimer (180) of the expected singlet cyclobutadiene and a ketone (181) as the major products. Scheme 17 shows possible routes for product formation.

The photolysis of dioxoles has been demonstrated as a novel approach to the generation of carbenes.\(^{128}\) The fluorenedioxole (182) on photolysis in the presence of cis-butene produces a triplet carbene and eventually the cis- and trans-spiro-cyclopropanes (183a and b). In the absence of olefins, the carbene can be trapped by insertion into methanol as 9-methoxyfluorene. Other dioxoles (184) have been shown to react similarly but in poorer yields.


Cyclopropanes have also been isolated from photolysis of the Wittig reagent diphenyldimethylenetriphenylphosphorane in olefins.\textsuperscript{129}

For a number of years Griffin \textit{et al.} have been examining the photochemical breakdown of oxirans to carbenes and carbonyl compounds. Recently a spectroscopic study of the reaction has been published\textsuperscript{130} in which


the decomposition has been shown to be a two-photon process. Initial photon excitation brought about the formation of a highly coloured transient which is stable at 77 K. An ionic intermediate was favoured by Trozzolo et al.,¹³¹ but the present paper suggests that diradical intermediates are to be preferred. Photolysis of this intermediate brings about conversion to the observed products of the reaction. The initial products formed from three oxirans examined are recorded in Table 8.

**Table 8  Products from the irradiation of oxirans in organic glasses**

<table>
<thead>
<tr>
<th>Oxiran</th>
<th>Products</th>
<th>(determined spectroscopically)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, (R^1 = R^4 = H, R^2 = R^3 = Ph)</td>
<td>trans-Stilbene, PhCHO, PhC:</td>
<td></td>
</tr>
<tr>
<td>b, (R^1 = R^2 = R^3 = Ph, R^4 = H)</td>
<td>Triphenylethylene, PhCHO, Ph₂CO, PhCH, Ph₃C:</td>
<td></td>
</tr>
<tr>
<td>c, (R^1 = R^2 = R^3 = R^4 = Ph)</td>
<td>Tetraphenylethylene, Ph₂CO, Ph₃C:</td>
<td></td>
</tr>
</tbody>
</table>

The generation of phenylcyanocarbene (185) is reported¹³² from the photolysis of 1,3,2-dioxaphosphor(v)olan (186). The carbene was trapped as a cyclopropane (187) by insertion into substrate olefins. Oxiran (188), the product of thermolysis of the phospholan, is not considered to be an intermediate in the reaction. However, the photolysis of the fluorene phospholan (189) did not yield a cyclopropane but gave instead a spiroketone (190), perhaps indicating thereby the possibility of a zwitterion or diradical intermediate (191); the former is somewhat preferred. The


possible role of zwitterions or polarised diradicals in the photolysis of oxirans merits further investigation.

Photolysis of the oxadiazoline (192) at $-5^\circ$ gave a good yield of the oxiran (193). Subsequent irradiation of this oxiran in methanol gave the ether (194).\textsuperscript{133}

W. M. H.

Photochemistry of Aromatic Compounds

Ten years ago few reports had appeared concerning aromatic photochemistry. To judge by the number of publications in the past year, more and more workers are now finding the photochemistry of aromatic compounds to contain many fruitful areas of research.

1 Energy Transfer and Isomerisation Reactions

Bryce-Smith¹ has reviewed the isomerisation and addition reactions of the benzene ring known up to 1967, and pointed out that ca. 20 different types of photochemical reaction have been reported; almost all these lead to non-aromatic products. The review discusses mechanistic aspects of both addition and isomerisation processes from the viewpoint of symmetry of the excited states (¹B₂⁺ singlet and ³B₁⁺ triplet) of the benzene molecule, and ends with what may be described as a conducted tour through benzene photochemistry in which a large number of experimental observations are schematically presented within a mechanistic framework (Scheme 1). The proposal that a radical of type (1) (termed 'prefulvene') is a precursor of fulvene²,³ has been supported to some extent by the observation that both fulvene and benzene are formed from the reaction of carbon atoms with cyclopentadiene, from which it is considered that a diradical of type (1) would be formed.⁴ It would of course be interesting to carry out such a thermal reaction in the presence of mono-olefins in order to obtain information concerning the intermediacy of (1) in the 1,3-addition process.⁵

Quenching of the first excited singlet state (¹B₂⁺) of benzene by mono-olefins and di-olefins, and the triplet–triplet energy transfer from (³B₁⁺) benzene to mono-olefins and 1,3-butadiene have been investigated in the vapour phase by Morikawa and Cvetanovic.⁶ The fluorescence of benzene vapour in the presence of the unsaturated compounds was measured in order to determine the rates of collisional deactivation of the singlet state. Most simple mono-olefins were inefficient quenchers, although tri- and

¹ D. Bryce-Smith, Pure Appl. Chem., 1968, 16, 47.
tetramethylethylene showed a significant effect. The rates of fluorescence quenching approximately parallel the corresponding rates of energy transfer from the benzene triplet. It is suggested that the energy transfer to olefins involves a chemical interaction with a triplet benzene molecule. Conjugated dienes were found to be much more efficient quenchers of both singlet (\(1^1B_{2u}\)) and triplet (\(3^3B_{1u}\)) states of benzene whereas, as may be expected, the quenching efficiencies of non-conjugated dienes approximate to those of the mono-olefins.

Energy transfer by benzene has also been investigated in the cadmium-photosensitised isomerisation of but-2-ene in the vapour phase. In the absence of benzene, the quantum yield for isomerisation of the olefin


† In the original publication,\(^1\) the state here termed \(T_1\) was unconventionally termed \(T_0\). The \(T_0\) symbol is in some ways more logical, since \(S_0\) and \(T_0\) then represent the lowest states in the singlet and triplet manifolds respectively, irrespective of their relative energy levels; but the existing usage is probably too firmly entrenched for any reforms of this type to be successful.
approximates to 0.5 for both isomers for which there is no significant difference in the quenching cross-section. Addition of benzene causes the isomerisation quantum yield to be more than half the fraction of \(5^3P_1\) cadmium atoms quenched by but-2-ene. These data are interpreted by a mechanism in which 3-8-ev cadmium \(5^3P_1\) atoms excite the 3-6-ev benzene \(B_{1u}\) level; the triplet benzene then causes the observed isomerisation.

The primary photochemical processes in simple aromatic molecules were further discussed by Noyes and Burton at the Munich Conference in 1967, and a report has now appeared.\(^8\) The importance of vibrational levels formed in the absorption act is stressed since some processes such as isomerisation appear to be competitive with vibrational relaxation even at moderate pressures. It was also pointed out that before definite proposals could be firmly laid down concerning the primary processes in aromatic molecules, more and better data are required. Some of these requirements may be met by results in the current literature.

The characterisation of fulvene, benzenalene, and 'Dewar' benzene by gas chromatography, and their chemical reactions, has allowed workers more easily to investigate processes occurring in the photolysis of benzene at different wavelengths. The vacuum u.v. irradiation of liquid and vapour benzene has been reported.\(^9\) From the band irradiation, 166-200 nm, employed in these studies, at least seven molecular electronic states are accessible by either direct excitation, internal conversion, or intersystem crossing from initial excited states. The major products, fulvene and cis- and trans-hexa-1,3-dien-5-yn, from the benzene vapour reaction are pressure dependent (cf. Part I, Ch. 2). Fulvene is favoured at high, and hexadienyne at the lower pressures. A mechanism involving vibrationally excited ground-state benzene is proposed to account for this pressure dependence. Under similar conditions liquid benzene yields fulvene, benzenalene, and 'Dewar' benzene; formation of the latter compound could arise from benzene excited states with \(B_{1u}\) \(T_1\) and \(S_2\) or \(E_{1u}\) \(S_9\) symmetry, all of which are accessible in this photolysis. Lower vibrational levels of the triplet state have been shown not to yield the 'Dewar' isomer which could, however, still arise from the higher vibrational levels of this state or from upper excited singlet states \(S_2\) and \(S_3\).

Wilzbach and Kaplan, continuing their very precise work on the isomerisation of benzene and its derivatives have also examined the products from benzene vapour irradiation at 184.9 nm and again find fulvene (4-5\%) and cis- and trans-hexadienyne (2\% of each isomer).\(^10\) The trans-isomer was shown to be formed photochemically from the cis-isomer which is produced from benzene at approximately one-quarter the rate of fulvene formation. Irradiation of fulvene at 184.9 nm yields polymer, benzene, and hexadienyne in the ratio 2:1:1. The results indicate that at steady state a substantial

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fraction of the hexadienyne is formed from fulvene. The behaviour of fulvene and hexadienyne irradiated at 253.7 nm in the vapour phase was also investigated. Fulvene yields benzene with the low quantum yield of 0.01; this is in mild contrast to the earlier liquid-phase results in which fulvene was found to be stable.11 cis-Hexadienyne forms not only the trans-isomer at this wavelength but also a 2:1 ratio of benzene and fulvene. Thus irradiation of benzene vapour at 253.7 nm gives a lower steady state of fulvene, and in particular hexadienyne. The irradiation of benzene vapour at 253.7 nm also yields benzvalene which is subsequently decomposed under these conditions with a quantum yield of 0.4 to give a 3:1 ratio of benzene and fulvene.12 In the presence of added benzene, benzvalene was shown to disappear 50 times faster than in its absence, thus indicating very efficient energy transfer from the benzene to the benzvalene. The process was shown to be triplet energy transfer by reactions incorporating but-2-ene into the reaction when the 1,3-intermolecular addition product as well as benzvalene is formed. The yields of these products have an opposite wavelength dependence, a result which was thought to be somewhat opposed to the idea of a common 'prefulvene' intermediate13 for the two reaction processes; but it is not necessarily so.

Photochemical processes of simple benzene derivatives have also received some considerable attention. Unger and co-workers have measured the fluorescence and triplet yields of meta-difluorobenzene and 1,2,4- and 1,3,5-trifluorobenzenes; the latter two compounds show the high quantum yields for triplet formation of 0.4 and 0.64 respectively; and it would seem that the triplet of the 1,2,4-isomer lies below that of cis-but-2-ene.14

The methyl shifts observed with xylenes are assumed to arise from reconversion of a valence-bond isomer of limited stability to a xylene isomer. Most workers seem to favour formation of the intermediate by a singlet mechanism, but the involvement of triplet states and high vibrational levels of the ground state15 have also been considered. This latter proposal may be somewhat supported by the reported thermal isomerisation of the xylenes.16 The process occurs to a small extent together with extensive degradation. The temperature and pressure range for interconversion of the xylenes is very narrow and suggests that vibrational levels involved are not too widely spaced. The predominant isomerisation is a 1,2-shift as in the photochemical process, but since large amounts of benzene and toluene are also produced, it seems that a free-radical pathway might best account for the results. A detailed investigation of the conversion at 253.7 nm of ortho- to meta-xylene in pentane has shown that even when sufficient

trans-but-2-ene to quench all the triplet aromatic is added to the system, the yield of meta-xylene is not affected; and since trans-but-2-ene does not quench the fluorescence of ortho-xylene significantly (cf. also refs. 5, 6) the involvement of triplet states in the isomerisation process is very doubtful. Other work with xenon supports the absence of triplet intermediates in the ortho–meta isomerisation, and the effect of dilution on the system is not consistent with an excimer route. Excimer effects on the triplet state of ortho-xylene have, however, been examined, and triplet lifetimes under various conditions have been estimated. The considerable decrease in these lifetimes with increasing ortho-xylene concentration is consistent with rapid deactivation of the triplet by an excimer route. An estimate of the monomeric triplet lifetime to be greater than 10^{-6} sec is consistent with this work. The evidence presented suggests that excimers may be responsible for the unusually short lifetimes of some aromatic triplet molecules.

The formation of non-isomeric products, toluene, o-ethyltoluene, and 'other isomeric products' from the vapour phase vacuum u.v. irradiation of o-xylene is considered to involve a radical mechanism. Evidence has been obtained that the primary process is (the known) homolytic cleavage of a benzyl carbon hydrogen bond. It is suggested that the hydrogen atom produced adds to the aromatic ring of an o-xylene molecule to yield toluene and a methyl radical; the latter in turn reacts in part by combination with xyllyl radicals produced in the primary process to give ortho-ethyl toluene. The proposed mechanism for expulsion of a methyl radical seems rather odd.

The photolysis of methylated benzene derivatives has also been examined in the solid state. The radicals thus formed are detected by absorption, emission, and excitation spectroscopy. Whereas durene forms only one radical resulting from photo-detachment of a hydrogen from one of the methyl groups, 1,2,3,4- and 1,2,3,5-tetramethyl benzenes show respectively the presence of two and three radicals differing by position of the CH_{2} on the ring. Analogous results were obtained for other methylbenzenes, and the final products of the investigation were reported to be an aldehydic photo-oxidation compound and a substituted triene, neither of specified structure.

Further details have appeared concerning Bergomi and Gazzo's work on the photoisomerisation of hexafluorobenzene to the 'Dewar' isomer, and photoisomerisation reactions of hexakis(trifluoromethyl)- and hexakis(pentafluoroethyl)-benzenes have been reported by Haszeldine et al. The product ratios from the latter two compounds differ significantly.

From the trifluoromethyl derivative, the benzvalene, prismane, and ‘Dewar’ isomers are all formed in up to 82% yield. The proportions of the isomers are time dependent; thus after 50 hr irradiation the benzvalene : prismane : ‘Dewar’ ratio is 43 : 31 : 5 whereas after 100 hr the ratio is 15 : 39 : 28. The variation with time has been shown to be due to interconversions between the isomers. The ‘Dewar’ isomer undergoes ring closure to yield the prismane, as may be expected, whereas the benzvalene derivative is converted to the prismane by re-aromatisation and further photolysis. In contrast to these results hexakis(pentafluoroethyl)benzene gives no benzvalene isomer, only a trace of the ‘Dewar’, but substantial yields of the prismane derivative. I.r. and $^{19}$F n.m.r. data are reported for all these interesting new compounds.

Full details have now appeared on the photoisomerisation of tri-t-butylbenzenes.$^{22}$ The previously unreported 1,2,4-tri-t-butylbenzvalene (2) is formed with a quantum yield of 0·12 as the only initial product from the photolysis of 1,3,5-tri-t-butylbenzene (3) in isohexane at 253.7 nm. The benzvalene (2) is also formed together with 1,2,4-tri-t-butylbenzene (4) and 1,3,5-tri-t-butylbenzene (3) by the photolysis of 1,3,6-tri-t-butylbenzvalene (5). Although not isolated, isomer (2) was found to undergo the expected reactions of re-aromatisation to give compound (3) with a half-life of 17 min at 24·5°, formation of 4-alkoxybicyclo[3,1,0]hexenes with alcohols, and photolysis to give compounds (5), (4), and (3). Scheme 2 summarises the results of the present work: the numbers on the arrows are the quantum yields for the processes.

The intermediacy of a benzvalene derivative and its re-aromatisation has been suggested to account for the 1,2-scrambling observed in the irradiation of 2-, 3-, and 4-trityl anisoles in cyclohexane solution.$^{23}$ The quantum yield for the process is, however, so small that such isomerisations do not interfere to any significant extent with the light-induced addition of D⁺ to anisole, where the quantum yields for ortho-, meta-, and para-isomers are 0·1, 0·06, and 0·00 respectively: contrast conventional electrophilic substitutions.

Reports of photoisomerisation processes of polycyclic aromatic compounds have also appeared, and following the accounts of the light-induced reactions of barrelene (6)$^{24}$ and dibenzbarrelene$^{25}$ to semibullvalene (7)

and the dibenz-derivative, it seems inevitable that the photolysis of triptycene (8) should be examined.\textsuperscript{26} The results are, however, somewhat unexpected since neither the semibullvalene nor the cyclo-octatetraene derivatives are formed. Instead a compound of structure (9) was isolated with a quantum yield of 0.3. The structure was deduced from chemical and spectroscopic evidence, and also by its thermal isomerisation to 8,12\textit{b}-dihydrobenz[a]fluoranthene (10). The formation of this isomer from (8) is suggested to arise by initial production of the intermediate (11) followed by a 1,5-sigmatropic rearrangement.\textsuperscript{27}

Wasserman and Kuhn had earlier shown that irradiation of the \textit{anti-}[2,2]paracyclonaphthane (12) in methyl alcohol produced two

compounds. The assignments of structure (13) and the dibenzoequinene structure (14) to the products have now been substantiated by X-ray crystallography.

2 Addition Reactions
Several accounts have appeared within the past year of the formation of complexes in systems which undergo photochemical reaction.

Perturbations in the near-u.v. absorption spectra of benzene and its simple derivatives are induced by chloroform, and other halogenated protic solutes in hydrocarbon solution below 200 K. Such perturbations are ascribed to hydrogen bonding with the aromatic ring. Two stages of association are distinguished, and assigned to specifically oriented complexes involving one or two molecules of non-aromatic solute. It is further suggested that association modifies the low-temperature photochemistry of benzene and its alkyl derivatives, and substituted polyene adducts from perchloroalkanes are considered to be formed, although the products are not isolated. The evidence for their formation is inferred from the u.v. absorption spectra of the irradiated solution which show bands, for example

\[
\text{C}_6\text{H}_6 + \text{ClCHClCH}_2\text{Cl} \xrightarrow{hv} \text{ClCHClCHCl}_2
\]

with benzene and 1,1′,2,2′-tetrachloroethane, at 296, 310, and 326 nm. Many polyhaloethane and ethylene–aromatic systems have been examined in this way and the u.v. absorptions are suggested to arise from the presence of the octatetraenes.

Maleic anhydride and some N-substituted maleimides are well known to form photoadducts with benzene and its simple derivatives of type (15) which have an exo-configuration of the cyclobutane ring. Solutions of such dienophiles in benzene and carbon tetrachloride have been examined by n.m.r. spectroscopy, and evidence for stereospecific electronic ground-state interaction of the ethylenes with the benzene has been obtained. The large upfield shifts of the ethylenic hydrogen in benzene solution are attributed to a 1:1 exo-stereospecific association of the solute and solvent molecules. In the case of the benzene–maleic anhydride complex, the model which best fits the experimental results is that in which the hydrogens of exo-oriented maleic anhydride are located 2.55 Å above the plane of the benzene ring. The exo-configuration of the complexes deduced here would allow appreciable π orbital overlap, and this conforms with the observation that strong u.v. absorption bands of charge-transfer type are detected in these systems. The role of complexes which undergo charge-transfer excitation in the photochemical addition of dienophiles to benzene and alkylbenzenes has been examined by u.v. spectroscopy. The degree of complexing appears to be determined both by donor strength and steric

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81 See references in Ref. 1.
effects of substituents in the aromatic compound, and is reflected in the relative rates of addition of maleic anhydride to methylbenzenes where, despite the added donor character of the ring, the rate of addition decreases with increase in the number of methyl groups. Tetracyanoethylene and \( p \)-chloranil do not undergo photochemical addition to benzene, yet it would seem that they are completely complexed in benzene solution. The non-addition of these powerful dienophiles is suggested to be either a result of their inability to function as a nucleophile to intercept possible zwitterionic intermediates such as (16), or, the possibility that excitation of the complex

\[
\begin{align*}
&\text{(15)} \\
&X = O, \text{NH, N} - R
\end{align*}
\]

in these cases results preferentially in dissociation. Solid molecular complexes of maleimide and quinol having 1:1 and 2:1 stoichiometry have been isolated, and structures (17) and (18) are proposed. Irradiation of these complexes either solid or in solution gives cyclobutane-1,2-\textit{anti}-3,4-tetracarboxylic acid bis-imide, and none of the adduct of the dienophile and aromatic compound.

\[
\begin{align*}
&\text{(17)} \\
&\text{(18)}
\end{align*}
\]

The photohalogenation of aromatic compounds has been studied by flash techniques, and the transient absorption spectra obtained with bromine and iodine in benzene and toluene are here again attributed to charge-transfer complexes between the halogen atoms and the aromatics.⁸⁶

A photoinduced paramagnetism in the 1,3,5-trinitrobenzene–cyanide ion system has been observed, and evidence has been presented to indicate that the radical species is generated via the 1,3,5-trinitrobenzene–cyanide ion sigma complex [equations (1)—(3)].³⁷ The e.s.r. spectrum was examined in deoxygenated carbon tetrachloride, dichloromethane, ethyl acetate, dioxan, and 1,2-diethoxyethane solutions, and no signal was observed until the system was irradiated.

\[
\begin{align*}
\text{TNB (trinitrobenzene) CN}^- & \xrightarrow{hv} (\text{TNBCN}) \text{ solvated} + e^- \text{ solvated} \quad \text{(paramagnetic species)} \\
(\text{TNBCN}) \text{ solvated} + e^- \text{ solvated} & \longrightarrow \text{TNBCN}^- \\
(\text{TNBCN}) \text{ solvated} + \text{TNBCN}^- & \longrightarrow \text{TNBCN} + (\text{TNBCN})^- \text{ solvated}
\end{align*}
\]

(1) (2) (3)

Following the 1,3-intermolecular addition of non-conjugated olefins to benzene,⁴ an investigation of the intramolecular reaction was expected; this has appeared as the internal photoaddition of 6-phenyl-hex-2-ene.³⁸ The compound undergoes cis–trans isomerism, but the major products of the photolysis are a mixture of isomers resulting from internal 1,3-addition of the olefin to the nucleus. The mixture has, as yet, not been resolved, but compounds of structure (19), (20), (21), and (22) are probable components

![Diagram](image)

as evidenced by n.m.r. spectroscopy. The quantum yield is of the same order as that of the intermolecular addition (ca. 0.25), and both the reaction and the fluorescence of the phenylhexene are quenched by a conjugated diene, indicating singlet intermediates, as proposed for the intermolecular process. An alternative pathway to that involving a 'prefulvene' species is suggested, and involves the intermediate formation of a complex between the excited phenyl group and the olefin moiety. This could yield product or decay to the ground state, thereby giving rise to the very efficient internal fluorescence quenching observed with this system. However, as yet it is not possible to decide between the two mechanisms.

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An internal addition to the benzene ring to yield the oxaquadricyclic compound (23) has been suggested as an intermediate stage in the light-induced rearrangement of 1,4-epoxy-1,4-dihydropnaphthalene (24) to benz(f)oxepin (25). The intermediate is not isolated nor trapped, but in common with many other aromatic photoadditions arises from the singlet state. Triplet sensitisation as expected leads to the formation of a cyclobutane by dimerisation of the starting material.

Kraft and Koltzenburg's complex but rewarding investigations on the addition of conjugated dienes to benzene has been extended by Japanese workers to the addition of 2,3-dimethylbutadiene to benzonitrile; and unlike cases previously examined, here only one compound seems to be formed for which structure (26) is reported, *i.e.* addition of the cisoid conformer.

The work of Sasse on the photoaddition of naphthalene and tolan to yield adduct (27) has been subjected to a spectroscopic study. The quenching of naphthalene fluorescence in solution by tolan is extremely efficient, and increases with decrease in both solvent viscosity and temperature for fluid solvents. Naphthalene has no significant effect on tolan fluorescence. The behaviour of the system is most readily accounted for by exciplex formation. Naphthalene is the initially excited species. The mechanism advanced to account for the quenching of the naphthalene fluorescence suggests that high vibrational levels of the ground state of tolan can lead to the product (27).

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The photoaddition of acrylonitrile to benzene to form the bicyclo[4,2,0]-octadiene system (28) has been investigated for other aromatic hydrocarbons, namely naphthalene and indene. In both cases, unsensitised substitution and addition reactions have been observed; however, using acetophenone as sensitisier, the indene system yields only cyclobutane derivatives of geometry different from that of the unsensitised cyclobutane product, together with the indene photodimer, whereas no detectable products are formed in the naphthalene system. Again, therefore, singlet states would appear to be involved in aromatic addition and substitution reactions, and, not surprisingly, cyclobutanones of different geometry can apparently be formed from states of different multiplicity.

The conversion of aromatic compounds into quinonoid structures on photolysis is invoked to account for the stereospecific cycloaddition of dienophiles to o-methylbenzophenone and the stereospecific dimerisation of o-phthalaldehyde. The intermediate (29) in the latter example can also be trapped with maleic anhydride and may be in equilibrium with the carbene (30) which inserts into the aldehydic C—H of a second molecule of starting material. A second light-induced hydrogen-abstraction step is then required before rearrangement to give the observed product (31).

3 Substitution Reactions

Throughout the past year numerous isolated reports of photosubstitution reactions have appeared. Unfortunately, detailed analyses of the results and accounts of experimental observations have often been sadly lacking. Havinga and Kronenberg have produced a most interesting and readable account of the results in the field of heterolytic aromatic substitution reactions up to 1967. They have pointed out that whereas the direction of many of the reported reactions show a striking correspondence to that predicted from the calculated electron densities in the first excited singlet state.

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state from which reaction occurs (Type A), other examples seem to follow an ortho–para orientation rule similar to that generally observed in ground-state chemistry (Type B). The former reactions have been studied in some detail in contrast to the latter, and with Type B reactions a mechanism involving complexes, or a reaction from vibrationally excited levels of the ground state, and even the participation of triplet excited states, cannot be discounted. Continuing with his work in this field, Havinga has studied the mechanism of the photosolvolyis of m-nitrophenyl phosphate at various hydroxyl concentrations and ionic strengths. The quantum yield is independent of pH and ionic strength in neutral or weakly alkaline solution, a result which suggests that here water is the attacking reagent. At >pH 12, an increase in quantum yield with both hydroxyl ion concentration and ionic strength is observed. The result is interpreted to imply that both hydroxyl ions and water are the attacking nucleophiles. Experiments with 18O-labelled compounds indicate that whereas water attacks phosphorus (O—P splitting), hydroxyl ion attacks at the ring carbon atom (C—O splitting). The corresponding reactions of o- and p-phosphates are slow and seem to be more complex than those of the m-isomer. With 5-chlorophenyl phosphate, there is no indication of hydroxyl ion attack even in 0.1M-sodium hydroxide solution. Thus the water attack is so fast that the hydroxyl ion reaction cannot compete. m-Nitrophenyl sulphate shows similar behaviour to the 5-chloro-compound whereas the 5-bromo- and 5-methyl-phenyl phosphates are comparable in their behaviour with the parent compound. In all cases singlet rather than triplet species are involved.

Photohydrolysis of the side chain of benzotri fluorides in 0.1M-hydrochloric acid and 2N-sodium hydroxide has also been reported. Again the m-isomers of hydroxy- and amino-benzotri fluorides, which are stable to thermal hydrolysis, are particularly susceptible in the light-induced reaction, yielding 70% of the corresponding benzoic acids. The o-hydroxy-isomer is hydrolysed too, but the para- is not, and all three methoxybenzotri fluorides react photochemically to give the acids. Flash studies of the amino- and hydroxy-compounds show that the o- and m-isomers proceed through intermediates, the lifetimes of which increase with decrease of pH. In particular, the intermediate from o-aminobenzotri fluoride at pH 7 has been isolated, and is o-aminobenzoylfluoride.

An account has appeared of the direct amination of aromatic compounds with ammonia in the presence of di-t-butylperoxide using 184-9 nm radiation. Investigation of the reaction at 253-7 nm in the absence of a radical initiator showed that the substituents in nitrobenzene, m-dinitrobenzene, and chlorobenzene were replaced by amino-groups.

Irradiation of benzene and nitric oxide at 350 nm has been reported to yield o-nitrophenol, and 2,4-dinitrophenol, whereas toluene in the same system gives a mixture of nine components in which are identified benzyl nitrate, and α-nitrotoluene, and possibly benzaldehyde and benzyl alcohol. Nitric oxide and cyclohexane on irradiation also give a variety of products (eight in all), the major ones being the nitrate (32) and the nitro-compounds (33) and (34). There is evidence that cyclohexanol, cyclohexanone, and adipic acid are formed in this reaction too. These reactions provide another example of a photochemical method for the functionalisation, albeit non-specifically, of both aromatic and aliphatic hydrocarbons.

Both nuclear and side-chain substitution reactions are observed in the photolysis of the boron tribromide–toluene system which yields, after an aqueous work-up, a mixture of ortho (12.7%), meta (7.5%), and para (54.8%) tolueneboronic acids, and a trace of benzylboronic acid. Ring substitution

\[
\text{Ph–R} + \text{BBr}_3 \rightleftharpoons [\text{C. T. Complex}] \xrightarrow{hv} [\text{C. T. Complex}]^* \\
\]

\[
\begin{align*}
\text{R} & \quad \text{Ph–R} + [\text{BBr}_3]^* \\
& \quad \text{Ph–Br} + \text{HBr} \\
& \quad \text{Ph–R} + [\text{BBr}_3]^* \\
& \quad \text{PhCH}_2\text{BBr}_3 + \text{Br} \\
& \quad \text{Ph–Me} + \text{Br} \\
& \quad \text{Ph–CH}_2\text{+HBr} \\
& \quad \text{BBr}_3 \\
\end{align*}
\]

via charge-transfer excitation of a complex is favoured since additional u.v. absorption maxima have been noted in such systems. Such a mechanism was earlier proposed for the formation of PhBHAl₆ from irradiation of boron tribromide or iodide in benzene where the additional absorptions are at 315 and 435 nm.⁵⁴ The small amount of side-chain boronated products probably arises by a radical process involving a dibromomethyl radical.

Photolysis of 3-(p-bromophenyl)-1-methoxy-1-methyl urea (35) also leads to side-chain and nuclear substitution products.⁵⁶ Hydroxylation of the aromatic nucleus has been reported in two other cases. Poly(ethylene terephthalate) and poly(1,4-cyclohexylene dimethylene terephthalate) exposed in air to u.v. light form mono- and di-hydroxylated products (36) and (37).⁵⁶ The hydroxylation of phenols by photodecomposition of hydrogen peroxide may be used as a preparative procedure.⁵⁷ The o- and p-isomers are the main products, with the ortho predominating. A simple mechanism is proposed (see Scheme 3). In the case of p-substituted phenols only the o-isomer is obtained, except in the cases of p-carboxy- and methoxy-phenols when hydroquinone as well as the catechol derivative is obtained. The best yields of the catechol from p-cresol were obtained at pH 3—8; at pH 1 with light of wavelength 280 nm, in the presence or absence of uranyl sulphate, a mixture of dimers (38), (39), and (40) was obtained.

Replacements of sulphur-containing groups both in and by aromatic groups have been observed. Thus the toluene p-sulphonylhydrazones of camphor and acetone (41) yield p-xylene and a small amount of toluene and ethylbenzene when irradiated in the presence of excess of methyl-lithium

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at 253.7 nm. This is the first example of a light-induced nucleophilic displacement of a dianionic species from an aromatic ring. In the second example, photoexcited arenes have been found to initiate a substitution reaction in which the sulphonyloxy-group of α-sulphonyloxyketones (42) is displaced and the corresponding β-arylketones (43) are formed.

Evidence is presented that the electronically excited arene need not be involved directly in the substitution step; it is more likely that energy transfer to the sulphonyloxyketone gives a reactive species which is capable of aromatic substitution.

Three interesting minor products are formed (as well as the expected pinacol) from the irradiation of acetophenone in ether-cyclohexane. Two of these products are diastereoisomers of the butan-2-ol derivative (44), and one is a p-substitution product arising, it is suggested, by aerial oxidation of the intermediate (45) which in turn is derived by para coupling.

of the phenyl ketyl radical. The intermediate is analogous to (46) and (47) both of which have been reported to be the oxygen-sensitive species in photoreduction of benzophenone in alcohols.\textsuperscript{61}

Irradiation of the aryl ethynyl iodides, 1-iodo-2-phenyl acetylene\textsuperscript{62} and \textit{o}-bis(iodoethylthynyl)benzene\textsuperscript{63} in benzene yields respectively tolan and \textit{o}-bis(phenylethynyl)benzene. From the latter reaction small amounts of a number of substituted naphthalenes are also formed. Both reactions involve radical attack on benzene, and in the first reaction replacement of benzene by thiophen yields two isomeric phenyl-(1-thienyl)acetylenes. All the alkylbenzenes investigated in the reaction were found to be more reactive towards the radical attack than was benzene. This situation is unlike that found with phenyl, cyclohexyl, and cyclohexenyl radicals. The percentage of \textit{ortho} product was found to be considerably higher in both \textit{t}-butylbenzene and cumene than that found from attack by other radicals.

The formation of hydroxyphenyl ethers from the irradiation of benzene solutions of \textit{o}-quinones has been observed for phenanthrene-9,10-quinone\textsuperscript{64} and \textit{o}-chloranil.\textsuperscript{65} These are formally the first examples of photoaddition of quinones to aromatic compounds, although additions involving the methyl groups of xylene have been known for many years.\textsuperscript{66}

A convenient method for the synthesis of chloroazobenzenes has been reported in which azobenzene and acetyl chloride are irradiated to yield NN'-diacetyl-4-chlorohydrazobenzene.\textsuperscript{67} Hydrolysis and oxidation of the

\textsuperscript{61} N. Filipescu and F. L. Minn, \textit{J. Amer. Chem. Soc.}, 1968, 90, 1544.
product gives 4-chloroazobenzene (83%), and the 2-chloro-isomer (12%). Starting with mono-, di-, and tri-chloro-derivatives of azobenzene, it is possible to obtain the di-, tri-, and tetra-chlorinated compounds respectively. Analogous reactions with other acid chlorides show marked variation of ortho:para ratios, and indications are that relative extents of the isomers are associated with the ionisability of the acid chlorides.

In the heterocyclic series, carbazoles have been nitrated with tetraniitromethane to give the 3-nitro-derivatives; in all cases mixing of the reactants gave rise to charge-transfer spectra.\(^{68}\) The thermal reaction with N-alkyl-carbazoles is slow but the photochemical reaction is fairly rapid, and an intermediate of type (48) has been suggested. High yields were only obtained when the concentration of reactants was sufficient to give a concentration of charge-transfer complex in excess of \(2 \times 10^{-2}\)M, otherwise the tetraniitromethane was destroyed by photochemical side reactions. It has been suggested that photoalkylation of aromatic heterocycles could be a general reaction.\(^{69}\) The same school presents results which confirm this suggestion, and in which alkylation takes place at positions other than adjacent to nitrogen.\(^{70}\) Thus quinoline, isoquinoline, and 8-methyl-

\[\text{[Diagram]}\]

---


quinoline in ethanolic hydrochloric acid give 2- and 4-, 1- and 2-, and 4-ethyl derivatives respectively. The general mechanism for imine photoalkylation has been broadened to accommodate alkylations non-adjacent to nitrogen. These results may be compared with the recently reported photoalkylation of such heterocycles by alkylicarboxylic acids.\textsuperscript{71}

Finally a novel light-induced substitution of pyrimidines and condensed pyrimidines has been reported.\textsuperscript{72} This is a new photomethylation reaction, and is effected by irradiation of an acid solution of the bases in methanol. Many bases have been examined in this respect, and yields up to 86\% are reported. The method would seem to have some synthetic value.

\[ \text{e.g.} \quad \begin{array}{c}
\text{NH}_2 \\
\text{Me}
\end{array}
\begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\begin{array}{c}
\text{CN} \\
\text{Me}
\end{array}
\xrightarrow{h\nu, \text{MeOH}}
\begin{array}{c}
\text{NH}_2 \\
\text{Me}
\end{array}
\begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\begin{array}{c}
\text{CN} \\
\text{Me}
\end{array} \]

4 Oxidative Cyclisation Reactions

Literature concerned with the formation of phenanthrene derivatives from stilbenes as a consequence of \textit{trans-cis} isomerism of the olefin has been reviewed in the section concerned with olefin isomerisations. The present section is concerned with the many ring-closure reactions involving aromatic compounds which are either held in a \textit{cis}-olefin configuration, or which do not have an olefinic moiety.

The photolysis of ethanol solutions of 4,5-diphenyloxazoles, -thiazoles, and -imidazoles leads to a convenient synthesis of phenanthro[9,10-\textit{d}]heterocyclic systems.\textsuperscript{73} The reactions are carried out in the presence of the usual oxidant, iodine, and are exposed to the air. There are no side products and the yields are generally good. The dioxan adducts obtained from thermal reactions of \textit{o}-chloranil and either tetracyclone or 2-methyl tricyclone undergo a novel elimination and cyclisation reaction to give a 60\% yield of cyclopentenophenanthrene derivatives.\textsuperscript{74} Here the reaction was run under non-oxidative conditions, but the products may be readily accounted for by the mechanism outlined in Scheme 4. Singlet excited states are possibly involved in the reaction, in line with many other stilbene cyclisations.


\textsuperscript{74} W. M. Horspool, \textit{Chem. Comm.}, 1969, 467.
The overcrowded hydrocarbon (49) is also held in a fixed cis-configuration and undergoes photochemical cyclisation from an excited singlet state to give (50).\textsuperscript{76} A more aromatic state is achieved by a 1,5-intramolecular hydrogen shift through a six-membered transition state to yield (51).

4,4'-Diethoxycarbonylstilbene undergoes rapid photochemical \textit{trans} $\rightarrow$ \textit{cis} isomerism, thereby providing a route for conventional phenanthrene formation from a singlet excited \textit{cis}-state.\textsuperscript{76} A second product from this

reaction is the anthracene derivative (52). It is tentatively proposed that the product is formed from the trans-triplet state following isomerisation of the cis-triplet state.

Stilbene–phenanthrene oxidative cyclisations have been investigated in which positions of cyclisation are blocked.\textsuperscript{27} In such cases removal of the blocking groups has been reported to occur. This may take the course of actual elimination of groups to form, for example, dimethylphenanthrenes (53); or when the blocking substituent is part of a cyclic system, rearrangement within the eliminated part of the cyclic system occurs with no actual

\begin{align*}
(52) \quad R &= \text{CO}_2\text{C}_2\text{H}_5
\end{align*}

\begin{align*}
(53) \quad \text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\hline
\text{Me} & \quad \text{Me}
\end{align*}

\begin{align*}
(54) \quad \text{hv} & \quad \text{hv}
\end{align*}

loss of carbon atoms from the starting molecule, *i.e.* compounds of type (54) are formed.

Phenanthrene-type cyclisations arise from photolysis of all three distyrylbenzenes. The opportunity for formation of isomeric products in each case is fairly high, but the reaction is selective, and the experimental results are in accord with the direction of cyclisation predicted from the free valence, and 1,6-localisation energies. Thus condensed aromatic compounds (55), (56), and (57) are formed from *o*-, *m*-, and *p*-distyrylbenzenes respectively.

![Diagrams of compounds (55), (56), and (57)](image)

Fulgides and fulgimides both show photochromic effects in which the compound with the longer wavelength absorption is considered to have arisen via a cyclisation reaction to yield a more conjugated structure. In the case of the fulgimide (58), the orange-red compound (59) may undergo a 1,5-hydrogen shift to give a quantitative yield of the colourless isomer (60).

![Diagrams of compounds (58), (59), and (60)](image)

Several examples of cyclisation have been published in which new heterocyclic compounds are formed with apparent ease. Photoinduced oxidative cyclisation of diphenylamine and its derivatives to give carbazoles

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has been reported.\textsuperscript{81, 82} Non-oxidative cyclisations, on the other hand, are comparatively rare, but \(N\)-aryl enamines have been shown to undergo such a cyclisation thereby providing a useful two-step synthesis of 2,3-dihydroindoles (61) from ketones and \(N\)-alkylanilines.\textsuperscript{83} The method seems to be suitable for \(N\)-aryl enamines derived from cyclic and acyclic ketones, and the number of carbon atoms in the ring of the indole may be 5, 6, or 7. The cyclisation may be considered as an electrocyclic reaction of a divinyl amine which should occur in a conrotatory manner photochemically to give a \textit{trans}-product (62). However, although the \textit{trans}-product yield is generally higher than that for the \textit{cis}-isomer (63), such a mechanism does not explain the formation of the latter compound.

\[
\begin{array}{c}
\text{R} \quad \text{(CH}_2\text{)}_n \quad \text{Me} \\
\text{(61)} \quad \xrightarrow{\text{hv}} \quad \text{R} \quad \text{(CH}_2\text{)}_n \quad \text{Me} \\
\quad \text{N} \\
\quad \text{(62)} \\
\end{array}
\]

Photolysis of similar sulphur analogues under nitrogen leads to an oxidative cyclisation with the formation of both a ‘normal’ (64) and ‘abnormal’ (65) product, the yield of the ‘normal’ product being increased in the presence of iodine.\textsuperscript{84} The isomeric thioether (66) could not be detected in the photolysis, and only a trace of cyclisation products were obtained from its irradiation. The presence of a phenyl group \(\alpha\) to the sulphur seems to be essential for ‘abnormal’ product formation as many other derivatives have been found to give only the ‘normal’ product. A mechanism to account for the formation of ‘abnormal’ products involves the zwitterionic species (67) and (68). The lack of ‘abnormal’ product for hydrogen or methyl \(\alpha\) to the sulphur could be attributed to the inability of these substituents effectively to stabilise an adjacent partially charged centre.

Photo-oxidative cyclisations have also been reported in the indole series for such derivatives as (69) and (70).\textsuperscript{85}

Incorporation of solvent moieties into products is always a probability in solution photochemistry. This year accounts have appeared describing the incorporation of both carbon and hydroxyl fragments from alcoholic solvents into the reaction products. Two reports deal with the incorporation of C—C moieties; both reactions involve the photolysis of Schiff’s bases in

\begin{itemize}
\item E. Winterfeldt and H. J. Altmann, \textit{Angew. Chem.}, 1968, 80, 486.
\end{itemize}
alcohols and yield benzo[f]quinolines (71) in up to 70% yields. In both cases, the bases were derived from β-naphthylamine; further interesting studies with other Schiff's bases readily spring to mind. In the photocyclisation reaction of 2-(N-substituted anilino)-1,4-naphthoquinone (72) in methanol or water, the elements of hydroxyl from the solvent are incorporated into the product (73). In principle, α-naphthyl phenyl ethers might cyclise to give either compound (74) or (75). Irradiation of the parent compound gives no reaction, but photolysis of the chloro-derivative (76) leads to an eliminative ring closure reaction giving isomer (74) only, in 45% yield.

In the cyclisation reactions of 3-methoxyflavones (77), chromanoo-\(3',2':3,4\)isocoumarins (78) are formed as well as the expected product

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Photochemistry of Aromatic Compounds

(71)

(72)

(73)

MeOH–H⁺

(74)

(75)

(76)

(77)

(78)

(79)
(79). It is suggested that the mechanism for formation of the latter compound involves a further photochemical step together with hydroperoxide formation, as shown on p. 295.

5 Dimerisation Reactions

The photodimerisation of 2-methoxy- and other 2-alkoxy-naphthalenes was reported to yield compounds of structure (80).\textsuperscript{91, 92} In support of this, the photo-oxidative dimerisation of 2-methoxynaphthalene has been said to yield a compound (81) which is conceived as arising from a 4,1'–1,4' dimerisation coupled with oxidative 3–3' bond formation.\textsuperscript{93} There now appears to be some disagreement, however, about the original structure (80) for the dimer, and X-ray crystallographic analysis of the dimeric product is consistent with structure (82).\textsuperscript{94} Further evidence for structure (82) has been obtained by isolation of its Diels–Alder adduct with acetylenedicarboxylic ester. If the original proposed structure (80) is incorrect, as now seems to be the case, it is surprising that two quite different modes of dimerisation should be encountered under oxidative and non-oxidative conditions. However, it appears that further investigations into 2-alkoxy-naphthalene dimerisations which occur in the absence of oxygen at higher concentrations and in other solvents are in progress,\textsuperscript{95} and thus more information may soon be available.

The photodimerisation of anthracene has been known for over 100 years, and yet investigation into this type of process still proves to be an interesting and profitable line of research. Solid-phase dimerisation of anthracene has been reported, and denied. Some workers have suggested that oxygen plays an important part in the solid dimerisation, but it has now been proved by X-ray analysis that solid anthracene will dimerise photochemically when light of wavelength shorter than 300 nm is excluded, and that the presence of oxygen is not important. It was further observed that the dimerisation phenomenon is not wholly a surface effect. It seems somewhat ironic that it requires the talents of an X-ray crystallographer deploying comparatively sophisticated resources to sort out the relatively simple literature ambiguities concerning one of the earliest reported photochemical reactions.

The dimerisation of anthracene derivatives substituted in the meso-position(s) has attracted the attention of several researchers. Substituents in such positions are known to slow down the dimerisation process, and in many cases disubstitution completely inhibits the reaction. Two reasons have been put forward for this state of affairs: firstly that the dimerisation is inhibited sterically (e.g. 9,10-dimethylanthracene does not photodimerise), and secondly that factors linked with the electronic structure of the monomer affect the dimerisation process. This second argument has been invoked in the case of cyano-substituents which have a deactivating influence affecting the free valence of the carbon atoms to which they are attached. It is assumed, however, that the dimerisation is non-polar in character, but in some cases there is evidence which points towards a polar mechanism. The question of whether the ease of the reaction can be related to the amount of energy required to bend the molecules about their meso-axis has been investigated. The distortion energies were computed (by an extended Hückel method), and the interaction between neighbouring molecules ignored. A satisfactory correlation was obtained between the distortion energy and the low tendency for photodimerisation. Other factors connected with the quantum mechanical structure indices or with the steric hindrance between the molecules are also important in the reactivity of the anthracene. The wavefunctions obtained provide satisfactory values for the spectral shift (with reference to anthracene) of the first absorption band of the substituted compounds.

Bouas-Laurent and his co-workers have photodimerised 9-fluoro- (57% yield), 9-chloro- (26% yield), and 9-bromo- (7% yield) anthracene in ether solution, and have suggested that the absence of dimerisation of these compounds in the solid state may result from an unfavourable orientation of the monomers in the crystal. The same team reports the first example of

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a cross dimer which is tetrasubstituted in the meso-positions; the example cited is the addition of 9,10-dimethylantracene to 9,10-dimethoxy-anthracene in ether solution. The thermal stability of this adduct (83) is compared with that of its isomer (84). From a simple approach, it may be thought that the steric and electronic effects of the two adducts are the same, but it is of great interest that adduct (83) was found to decompose thermally three or four times more rapidly than its isomer (84). Clearly minor structural differences are very important in the retro-reaction. The Reporters note that a concerted dissociation of adduct (83), but not of adduct (84), could preserve electronic symmetry about a plane bisecting all the aromatic rings. The preparation and study of adducts of anthracene and its meso-substituted derivatives to yield compounds of structures (85) and (86) have also been reported.

The photochemistry of biphenylene has received little attention in the past although its thermal chemistry has been the subject of many publications. A report appears this year of the photodimerisation of biphenylene in refluxing hexane. Spectral data of the precipitated product are consistent with its formulation as the dimer (87) which bears some relation to that now reported for dimers of 2-alkoxynaphthalenes.

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6 Lateral-nuclear Rearrangements

The photo-Fries reaction is still of considerable interest both from preparative and mechanistic viewpoints, and has been the subject of several publications during the year. The generally accepted mechanism for the reaction is that outlined in Scheme 5 in which the two radicals may re-

combine within a solvent cage to produce rearrangement, or diffuse apart to give phenolic cleavage products. The results of further investigation into the reaction process, however, are not wholly in agreement with this general scheme, and varying accounts of the effect of solvent on the reaction have appeared.

Detailed analysis of the photoreactions of \( p \)-tolyl acetate, benzoate, and hydrocinnamate have been carried out, and evidence has been presented to show that these photo-Fries reactions occur from the singlet state to give the product by a molecular pathway which is independent of external environment, and in which a 1,3-sigmatropic shift is proposed.\(^{103}\) On the other hand, the concomitant formation of \( p \)-cresol is very solvent dependent, the quantum yield increasing with decrease in solvent viscosity. It would appear that the \( p \)-cresol arises from reaction of the \( p \)-methylphenoxy radical. In the case of \([p-Me-^2H_3]\)tolyl acetate, the alcoholic solvent-derived esters which are formed originate at least in part from a keten intermediate (88). These workers now propose that the photo-Fries reaction is a concerted

\[ \begin{align*}
\text{Cage escape} & & \text{R'OH} \\
\text{Cage} & & \rightarrow
\end{align*} \]

\[ \text{CD}_2\text{HCO}_2\text{R'} \]

symmetry-allowed process which differs from the earlier proposed mechanisms in that each fragment of the radical pair retains a symmetry memory; bond formation and cleavage occur synchronously. The reaction is categorised as a simple sigmatropic shift of the ligand on oxygen, and while the rearrangement does not apparently involve true 'free' radical intermediates, the concomitant process leading to phenol certainly does.

The effect of solvents on the course of this reaction has been studied by other workers. Plank has shown that both the ortho : para isomer ratio in the rearranged products of aryl esters (89) and (90) and the formation of phenol are solvent dependent.\(^{104}\) Thus the percentages of the ortho rearrangement product in both cases are 28 and 57 in cyclohexane and t-butanol respectively, and the percentages of the total Fries products are 40 and 84 in the same solvents, the remainder being phenol. Polar solvents therefore favour rearrangement, and non-polar the formation of phenol. The results are interpreted by a mechanism involving two reactive excited states, one of which gives the rearrangement product(s), and the other the phenol. The relative stability of these states is suggested to depend on solvent polarity. This explanation is somewhat similar to that proposed earlier for the solvent effects found in butyrophenone photochemistry.\(^{105}\) The aim of other workers in studying solvent effects has been to make the decarboxylation process (which accompanies the rearrangement reaction) a sufficiently major pathway for it to be useful in synthesis.\(^{106}\) Here again a dramatic effect of solvent on product distribution was observed. Thus while 3,5-di-t-butylphenyl benzoate in ethanol gave 48% rearrangement products, 30% phenol, and no decarboxylation, in 2-methoxyethanol (glyme) the same compound yielded 50% of the decarboxylation product, 41% phenol, and 5% hydroxyketone. The effect of solvent on the phenol : hydroxyketone ratio is in general agreement with that reported by other workers.

The overall reaction, as judged by disappearance of starting material, was also faster in the less-polar solvent. It is specially useful that overcrowded alkylbenzenes such as o-di-t-butylbenzene and t-butylmesitylene may be prepared by such a decarboxylation process.


The effect of substituents on the efficiency of the photo-Fries reaction of $m$- and $p$-substituted phenyl benzoates has been examined.\footnote{P. Slama, D. Bellus, and P. Hrdlovíc, \textit{Coll. Czech. Chem. Comm.}, 1968, 33, 3752.} Electron-donating substituents increase the quantum yield whereas electron acceptors decrease it. For a given substituent, the quantum yield is higher for $m$-derivatives. However, other workers, using the photo-Fries reaction for the preparation of hydroxychalcones from hydroxyphenyl cinnamates, have noted that the $m$-isomer yields only $5\%$ of the desired product, whereas the $o$- and $p$-isomers give rearrangement products in 20 and 16\% yields respectively.\footnote{H. Obora, H. Takahashi, and H. Hirano, \textit{Bull. Chem. Soc. Japan}, 1969, 42, 560.} It is apparent that the nature of the substituent and/or the type of migrating group may be very important. The effect on the reaction of blocking substituents in the 2,4-positions has been reported by both Bradshaw and his co-workers,\footnote{J. S. Bradshaw, E. L. Loveridge, and L. White, \textit{J. Org. Chem.}, 1968, 33, 4127.} and by Hageman.\footnote{H. J. Hageman, \textit{Chem. Comm.}, 1968, 401.} The former researchers found with 2,4-disubstituted phenyl esters that up to six products were formed, which resulted from at least five reaction modes, as follows: (a) photo-Fries rearrangement to give $o$-hydroxyacetophenones, (b) photo-Fries rearrangement in which methoxy-groups are displaced, yielding $o$- and $p$-hydroxyacetophenones, (c) a cleavage reaction leading to phenol, (d) decarboxylation and the formation of methylbenzenes and biphenyls, and (e) phototransposition of ring carbon atoms. On the other hand, where the photorearrangement is completely inhibited by groups which are not readily expelled [e.g. as in (91)] decarboxylation is now the major pathway,

![Diagram](image)

and not only is the yield of decarboxylation dependent upon the nature of the substituent, but also upon the solvent.\footnote{H. Shizuka and I. Tanaka, \textit{Bull. Chem. Soc. Japan}, 1968, 41, 2343; H. Shizuka, \textit{Bull. Chem. Soc. Japan}, 1969, 42, 52; \textit{ibid.}, p. 57.}

The photo-Fries type rearrangement of acetonilide has been studied in detail, and the formation of $o$- and $p$-aminoacetophenones and aniline is concluded to arise from the lowest excited singlet state.\footnote{H. Shizuka and I. Tanaka, \textit{Bull. Chem. Soc. Japan}, 1968, 41, 2343; H. Shizuka, \textit{Bull. Chem. Soc. Japan}, 1969, 42, 52; \textit{ibid.}, p. 57.} In contrast with the other reports of solvent dependence, the yields of the rearrangement products are greatly reduced in polar solvents, and the relative fluorescence intensity is larger than in non-polar solvents. A mechanism for acetonilide
photolysis proposed by Shizuka is based on these studies and is summarised in the Figure. It is reasonably considered that the primary process involves predissociation. 3-Ketoacid amides such as (92), somewhat analogous to acetanilide, do not give the expected rearrangement reaction on photolysis, but undergo an interesting cleavage process to yield isocyanates.\textsuperscript{113}

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{NH} & \quad N=\text{C}=\text{O} \\
\text{Ph-C-CH}_2\text{C}=\text{O} & \quad \text{Ph-C-CH}_2\text{C}=\text{O} \\
& \quad + \text{PhCOMe}
\end{align*}
\]

(92)

The rearrangement of \textit{N}-phenyl carbamates (93) to give \textit{o}- and \textit{p}-amino-benzoates has been reported by two groups.\textsuperscript{113, 114} One group has examined the rearrangement of the \textit{O}-aryl carbamates (94) to give hydroxybenzamides, and points out the formal similarity to the photo-Fries reaction,\textsuperscript{113} while the other workers examined the photoreactions of \textit{N}-phenylthiourcethane (95), and report no tendency for formation of photo-Fries type products.\textsuperscript{114} Instead, aniline and a polymer are formed, and in the presence of oxygen cyclodehydrogenation occurs to give 2-ethoxybenzthiazole (96) as well as ready exchange of the sulphur atom.

2-Alkylamino-4-pyrimidiny1 esters of alkyl and arylsulphonic acids (97) undergo a photorearrangement formally similar to the Fries reaction with the formation of 5-alkylsulphonyl and 5-aryl sulphonyl-2-dialkylamino-4-hydroxypirimidines (98) in yields of up to 60\%.\textsuperscript{115} Typically, small amounts of the parent 2-dialkylamino-4-hydroxy pyrimidine (99) are formed also.

Some 2-amino- and 2-acetyl-derivatives failed to undergo rearrangement, but yielded solvolysis products instead, i.e. arylsulphonic acid salts of the related 2-amino-4-hydroxypyrimidines.

Photoinduced lateral-nuclear migrations of N-phenyl lactams seem to be useful reactions for the synthesis of macrocyclic benzazacycloalkanones (100) and although N-phenylpyrrolidone is converted to N-phenylpyrrole, the reaction proceeds smoothly when in the original lactam ring \( n = 5, 6, \) or 11.\(^2\) There seems to be no tendency for formation of cyclophane-type products (101) even in instances where the carbon chain is sufficiently long to allow this.

The products from irradiation of methanol solutions of aryloxyacetones (102) are 2-methylbenzofurans (103), phenols formed by fission of the O—CH₃ bond, and acetals of type (104). Formation of the benzofurans appears surprising, but by irradiation of p-methoxyphenoxyacetone (105) the intermediate for the cyclisation reaction was isolated, and shown to be the product of ortho rearrangement (106). Under anhydrous conditions a ring closure of (106) occurs to give the normally isolated benzofurans.

Woodward and Hoffmann have suggested that the photo-Claisen reaction to give the para rearrangement product might serve as an example of a [3,5] sigmatropic transformation. There are, however, considerations which tend to conflict with this idea. An eight-membered cyclic transition state would seem to be sterically improbable, and in any case in related rearrangements such as those of phenyl esters, both o- and p-isomers are formed. Also the rearrangement with labelled compounds such as [γ-¹⁴C]allyl-2,6- dimethyl phenyl ether shows that the ethylenic bond may or may not undergo a shift yielding, in the example cited, [4α- and 4γ-¹⁴C]allyl-2,6- dimethyl phenols. The reaction has therefore been investigated in order to ascertain the mechanism. The products with all compounds investigated are o- and p-isomers as well as the parent phenols, and it is thus concluded that the reaction does not proceed via a cyclic intermediate but probably involves a radical or ionic recombination of two fragments. The process is, however, intramolecular since crossed

products in mixed irradiations are not detected. It would seem that the results may best be interpreted as a radical combination in a solvent cage, as is the case with some photo-Fries rearrangements.

7 Furan, Thiophen Rearrangements

Srinivasan has published, in the form of a report of a lecture, further details of his exploratory work on the \( ^2P_1 \) mercury-sensitised reactions of furan.\(^{119} \) The principal reaction is photodecarbonylation \( (\Phi = 0.4) \) to give cyclopropene and methylacetylene as the \( C_3 \) fragments. The minor products of the reaction are the cyclic ethers (107), (108), and (109). The last product suggests that 2-cyclopropenecarboxaldehyde (110) may be the key product of initial rearrangement, and support for this idea can be inferred from kinetic evidence. The work has now been extended to the vapour-phase irradiation of furfural \(^{120} \) and 2- and 3-alkylfurans.\(^{121} \) Direct irradiation of furfural at a number of wavelengths (222.5–313 nm) or by mercury sensitisation, yields furan, methylacetylene, allene, cyclopropene, and carbon monoxide. Two primary processes have been proposed, one of which may lead to furan and carbon monoxide by hydrogen migration, and the other to \( C_3H_4 \) and carbon monoxide. It seems plausible that the latter process proceeds through an excited furan molecule as an intermediate. Evidence is also presented which suggests that much of the observed photochemistry involves low-energy triplets of furfural. 3-Methylfuran undergoes the loss of carbon monoxide with a quantum yield of unity, and the clean production of 1-methyl cyclopropene as the only other product. On the other hand, 2-methylfuran and 2,5-dimethylfuran isomerise to 3-methylfuran and 2,4-dimethylfuran respectively, and again loss of carbon monoxide occurs. The results of decarbonylation processes in furans can be shown to be consistent with the results of the isomerisation process if it is postulated that the same intermediate, cyclopropenecarboxaldehyde (110), is involved in both reactions. van Tamelen and Whitesides have also examined the photolysis of alkylfurans, and have succeeded in isolating the proposed cyclopropenecarboxaldehyde intermediate (111) from 2,5-di-t-butylfuran.\(^{122} \) Irradiation of 2,4-di-t-butylfuran gave the cyclopropenecarboxaldehyde (112) as the only isolable product, and (113) was similarly

formed from the 2,3,5-derivative (114) in low yield. In the latter reaction, the major product has been assigned structure (115), and ketone (113), analogous to aldehyde (110), is suggested as a probable intermediate.

\[
\begin{align*}
&\text{\(\text{hv}\)} \quad \text{(111) 4\%} \\
\text{\(\text{hv}\)} \quad \text{(112) 9\%} \\
\text{\(\text{hv}\)} \quad \text{(113) \sim 5\%} \\
&\text{(115) \sim 95\%}
\end{align*}
\]

The effect of piperylene on the irreversible conversion of 2-phenylthiophen to the 3-isomer has been investigated.\(^{123}\) The diene severely inhibits the rearrangement, and forms a 1:1 adduct with the singlet excited thiophen. This adduct is unstable, and resinified when isolation and purification were attempted. It was further shown that the fluorescence of 2-phenylthiophen is quenched by the diene, and that generation of the triplet thiophen does not lead to the rearrangement. This reaction, like the 1,2-shift in o-xylene,\(^{18}\) therefore seems to occur via a singlet path.

A. G.

5

Photo-oxidation and -reduction Reactions

1 Conversion of C=O to C—OH

The photoreduction of a carbonyl group to an alcohol, with, in many cases, the subsequent formation of a pinacol, has in the past been an active field of research; the year under review has been no exception, and a large proportion of the literature has again been concerned with the reduction of benzophenone to benzpinacol and benzhydril.

\[
\begin{align*}
\text{C}_6\text{D}_5\text{CHO} & + \text{Ph} \text{H--C--OH} \\
\text{C}_6\text{D}_5 & \text{Ph} \\
\text{hv} & \quad \downarrow \\
\text{C}_6\text{D}_5 & \text{Ph} \\
\text{HO--C} & + \text{C--OH} \quad \longrightarrow \quad \text{HO--C--C--OH} \\
\text{C}_6\text{D}_5 & \text{Ph} \\
\end{align*}
\]

Evidence for a solvent cage recombination of semibenzpinacol radicals (1) has been obtained from studying the benzpinacol formation from deca-deuteriobenzophenone in the presence of non-deuteriated benzhydril.\(^1\) A statistical distribution of non-deuteriated, decadeuteriated, and per-deuteriated benzpinacols was formed.

Cohen earlier reported that the photoreduction of benzophenone by isopropyl alcohol proceeds more rapidly using a diluent such as benzene or iso-octane.\(^2\) The system has now been quantitatively examined, and the effects of solvent on transient intermediates and quantum yields of the reaction have been investigated.\(^3\) The conclusions are that the effects of solvents are in part related to properties of a relatively long-lived transient species. Such a species is formed from the light-produced radicals more

rapidly, and grows to a higher concentration at high light intensities when its rate of formation may more greatly exceed its rate of thermal decomposition. The transient absorbs light, and acts as an internal filter, and may also be a triplet quencher. It is present to a large extent in neat and aqueous alcoholic solutions, but it is formed less, or is less persistent, in hydrocarbon media; hence the higher quantum yields using such diluents. This transient is suggested to be a labile radical coupling product which arises either from para–para coupling of two benzophenone ketyl radicals or from para–alpha coupling of benzophenone ketyl and 2-hydroxy-2-propyl radicals. This light-absorbing transient has been discussed for many years but it still eludes isolation. Other systems such as benzophenone-triethylamine-benzene also show media effects attributable to a light-absorbing intermediate. The general characteristics of reduction by amines are consistent with rapid interaction of the triplet state of the ketone with non-bonding electrons of nitrogen, followed partly by transfer of hydrogen and partly by regeneration of ketone and amine.

The irradiation of benzophenone in the presence of enamines leads to the formation of benzpinacol as the major product as expected. However, \( \gamma \)-hydroxyketones (2) are also formed formally by addition of the benzophenone at the \( \beta \)-position of the ketone from which the enamine is derived.\(^4\)

\[
\begin{align*}
\text{O} & \quad + \quad \text{Ph}_2\text{C}=\text{O} \quad \rightarrow \quad \text{Benzpinacol} + \text{Oxetan} \\
\text{Me}-\text{CH}_2\text{C} & \nrightarrow \text{CHMe} \\
\text{(3)}
\end{align*}
\]

While morpholine enamines (3) yield oxetans in addition to the forementioned products, piperidine enamines do not. The change of reaction mode in these two cases where the structures of the reactants only differ far from the reaction site is extraordinary, and difficult to explain. One might suspect that the differences in reaction paths result from differences in the stereochemistry of weak complexes formed between the reactants.

It has been observed that aliphatic sulphides are physical quenchers for excited benzophenone whilst simultaneously acting as weak photoreducing agents.\(^5\) A two-step mechanism involving electron-transfer (Scheme 1) has been suggested to account for the effect of sulphides on the reaction. The first step is very efficient interaction of the excited ketone with the non-bonding electrons of sulphur leading to a complex of the two, and the second step involves reaction of the complex either by completing the

abstraction of hydrogen by the ketone from the thioether (path A) or by formation of ground-state ketone and thioether (path B: quenching).

The effect of other quenchers on the photoreduction of benzophenone by amines and alcohols has been studied by Davidson and Lambeth who find that such reduction by *N,N*-dimethylaniline and *N*-methylpyridylamine is insensitive to added naphthalene. On the other hand, both iron(III)-acetylacetonate and *d*-dibenzoylmethanate quench the reaction involving both amine and alcohol to approximately the same extent. It is known that naphthalene and iron(III) acetylacetonate have similar quenching efficiencies for the benzophenone triplet, and thus it would seem that in the present case the latter species is either not involved or has an abnormally short lifetime. Unfortunately further information on this interesting question does not seem to be available.

The effect of solvent and temperature on the photoreduction of ketones was reported by Suppan at the Munich Conference. The dependence of the quantum yield of reduction on the solvent polarity is interpreted in terms of dipole moments of the excited states, and the temperature effect is suggested to arise from different reactivities of *nπ*, *ππ* and charge-transfer states related to activation energy.

Such charge-transfer states are important in aryl ketone photochemistry, particularly for hydroxy- and amino-benzophenones. A low-lying chemically unreactive charge-transfer triplet state is reported to be responsible for the inefficient reduction of *p*-aminobenzophenone (quantum yield < 0.001) by isopropanol and sec-butylamine. However, reduction is effected by triethylamine at 313 and 360 nm (quantum yields 0.22 to 0.57). The quantum yields are higher at higher light intensity, lower concentration of the ketone, and, as noted for benzophenone reductions generally, in more dilute hydrocarbon solutions of the *p*-aminobenzophenone. In the latter

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case, the increase in quantum yield may arise from more efficient conversion to \( n\pi^* \) triplet ketone. On the other hand, dilution with acetonitrile prevents reduction; this may be quite simply explained since the dipolar aprotic solvent stabilises the unreactive triplet charge-transfer state. Lower quantum yields at higher \( p \)-aminobenzophenone concentrations arise by deactivation of triplet ketone by ground-state ketone with efficiency half that of diffusion-controlled quencher in a process which may convert the \( n\pi^* \) triplet state to a charge-transfer triplet state. The yields of pinacol from reduction of \( p \)-aminobenzophenone by cyclohexane, di-isopropylamine, and triethylamine are 90, 100, and 55\% respectively. The reduction of \( m \)-aminobenzophenone is \( ca. 10 \% \) as efficient as that of the \( p \)-isomer, and the \( o \)-isomer is hardly reduced at all.

Medium effects for the reduction of fluorenone have also been reported. In this case there is no charge-transfer absorption, unlike the case of \( p \)-aminobenzophenone; but fluorenone is reported to have a low-lying \( \pi\pi^* \) triplet and is not reduced by alcohols.\textsuperscript{10} The irradiations of fluorenone were carried out in Pyrex using \( NN \)-dimethylamine as the reducing agent. As in the previous cases, dilution with cyclohexane led to increased reduction, but again no reduction was observed in acetonitrile or even isopropanol in the presence of the amine.\textsuperscript{11} The data are interpreted to imply an inversion of the \( nn^* \) and \( \pi\pi^* \) triplet levels, and the formation of an \( n\pi^* \) state in non-polar media which then reacts efficiently with the tertiary amine via an electron transfer mechanism. The experimental results suggest that the triplet \( nn^* \) state may not be sufficiently energetic to react efficiently with primary and secondary amines and alcohols in hydrocarbon media.

The photoreduction of unsymmetrical aromatic ketones of type \( \text{PhCOR} \) in isopropanol gives a \( (\pm) : \text{meso} \) ratio of diastereoisomeric pinacols which tends to increase as the \( R \) group becomes bulkier.\textsuperscript{12} This ratio has also been determined for several \( p \)-substituted acetophenones, and is approximately unity for hydrogen, chlorine, and methyl substituents, but 1:25 for methoxy. Since the ratio for parent acetophenone is apparently not affected by solvent, (cyclohexane, isopropanol, and benzene–isopropanol mixtures were investigated), it is concluded that steric and electronic factors due to the substituents are responsible for the variations in the \( (\pm) : \text{meso} \) ratio.

The intramolecular hydrogen transfer which occurs in \( o \)-methyl-substituted aryl ketones is well known and the resulting enols (e.g. 4) may be readily trapped by dienophiles.\textsuperscript{13} The case of 2,4-dimethylbenzophenone has been examined in this respect, and a 5–10\% yield of a dimer corresponding to the pinacol was isolated in benzene (which is normally such a


poor hydrogen donor that it is often used as a solvent in trapping experiments.\textsuperscript{14} A series of methylbenzophenones in isopropanol has been investigated and both pinacol and enol trapped with acetylenedicarboxylic ester were isolated. In the case where both benzene and isopropanol were present, only the trapped enol was formed, but in the absence of benzene, the pinacol was produced in 30\% yield.

The photoreduction efficiency of phenyl thienyl ketones and phenyl pyridyl ketones is reported to be in accord with calculations of the charge on the carbonyl oxygen in both classes and all isomers.\textsuperscript{16}

The mechanism for the photoinduced anthrone (5) to anthranol (6) reaction in ether has been elucidated as involving the anthrone ketyl radical (7), detected spectroscopically, and 1-ethoxyethyl radicals.\textsuperscript{16} Anthrapinacol is formed from two of the ketyl radicals, and anthranol and ether from both radicals.

It has been reported that 9-anthraldehyde in the presence of an olefin gives the expected oxetan as the major product at wavelengths shorter than 400 nm.\textsuperscript{17} Although the experimental conditions have not been exactly reproduced (the variant parameters were not stated), other workers have observed that the major products of such irradiations at 366 nm are the pinacol (8) and polymer, and that the anthracene dimer and oxetan are minor products.\textsuperscript{18} At this stage it is not possible to reconcile the two reports, but it would seem that the product ratio is very wavelength-dependent, and in such systems as this where the two reactive states ($\pi\pi^*$ and $\pi\pi^*$) are fairly close, a dependence of product on media could be observed.

Photoreduction of $\beta$- and $\gamma$-ketosulphones (9) and (10) and their derivatives in methanol lead to the formation of the corresponding pinacols by

\textsuperscript{15} P. Traynard and J. P. Blanchi, \textit{Compt. rend.}, 1968, 266, C, 1511; 1968, 267, 1381.
bimolecular reduction of the carbonyl group.\textsuperscript{19} The reaction is relatively insensitive to substitution pattern although lack of reaction in two examples is attributed to steric effects on the neighbouring groups.

In the extension of their work on the photochemistry of organophosphorus compounds, Tomioka \textit{et al.} have examined the photoreduction of $\beta$-ketophosphonates (11) in ether.\textsuperscript{20} Not surprisingly, $\beta$-hydroxyphosphates (12) and pinacols (13) are the products. Triplet intermediates are suggested on the basis of quenching experiments, and the high quantum yields and rates of reaction are considered to be a result of an intramolecular heavy


atom effect and the electronic configuration of the $n\pi^*$ triplet states of these ketones.

The photoreduction of di- and tri-ketones has also been investigated. In 1966 it was reported that camphorquinone in the absence of oxygen had little or no reactivity in photoreduction reactions, but it has now been shown that reduction does occur to give a mixture of compounds (14) and (15). By carrying out the reaction in isopropanol in the cavity of an e.s.r. spectrometer (a technique which more and more photochemists seem to be using), evidence was obtained for the interesting symmetrical radical (16) as an intermediate. The reaction can be sensitised by benzophenone, and thus triplet species are probably involved in the sensitised process at least. The rate of the sensitised reaction increases with decrease in quinone

concentration, a fact attributed to 'chemical sensitisation' in which the benzophenone ketyl radical formed by hydrogen abstraction from the solvent transfers a hydrogen atom to the camphorquinone to yield the intermediate (16). It was also found that camphorquinone in methanol under nitrogen gave the adducts (17) and (18); it had been stated in the earlier report that no reaction occurred with methyl alcohol in oxygen-free atmospheres.

\[
\text{PhCOCH}_2\text{CH}_2\text{COMe} \xrightarrow{h\nu \text{ RH}} \text{PhC(OH)CH}_2\text{CH}_2\text{COMe}
\]

\[
\text{PhC(OH)CH}_2\text{CH}_2\text{COMe}
\]

\[
\text{Isopropanol} \rightarrow \text{H}_2\text{O}
\]

\[
(21)
\]

\[
\begin{align*}
\text{Pr}^1\text{O} & \quad \text{O} \quad \text{C} \quad \text{C} \\
\text{H}_2 & \quad \text{C} \quad \text{O} \quad \text{C} \\
\text{H}_2 & \quad \text{C} \quad \text{O} \quad \text{Pr}^1
\end{align*}
\]

\[
(20)
\]

\[
\text{PhCOCH}_2\text{CH}_2\text{COPh} \xrightarrow{h\nu} \text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph}
\]

\[
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph}
\]

\[
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph}
\]

\[
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph}
\]

\[
(19)
\]

\[
(22)
\]

\[
\begin{align*}
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph} \\
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph}
\end{align*}
\]

\[
\begin{align*}
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph} \\
\text{PhC(OH)CH}_2\text{CH}_2\text{C(OH)Ph}
\end{align*}
\]

(23)

1,4-Diketones have also been found to undergo a light-induced reaction in isopropanol with light of wavelength longer than 280 nm.\(^2^4\) Two products (19) and (20) are formed, but are in fact secondary products from two stereoisomeric pinacols (21). One product (19) is a ketone formed by loss of water from the pinacol, while the other (20) is formed by a further reaction of the pinacol with isopropanol. Photolysis of 1,2-dibenzoylethane in

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isopropanol, on the other hand, leads to a mixture of oligomers (22) and a low yield of a crystalline compound which is supposed to be a dimeric product, possibly formed by dehydration of a cyclo-octanetetrol (23).

\[
\begin{align*}
\text{(24)} & \xrightarrow{H_2O} \text{(26)} & \xrightarrow{hv} & \text{(27)} \\
\text{(26)} & \xrightarrow{hv} & \text{CO}_2\text{H} & \xrightarrow{\delta H} & \text{(31)} \\
\text{(28)} & & \text{CO}_2\text{H} \\
\text{(29)} & \xrightarrow{[O]} & \text{(30)} \\
\end{align*}
\]

It is known that triketoindane (24) undergoes photopinacolisation in isopropanol to give hydridantin (25).\textsuperscript{25} Previously the reaction had been classified as reduction of the carbonyl groups to yield the pinacol, but now evidence has been presented to show that it is to be regarded as a photocleavage of an \(\alpha\)-substituted ketone, a view considered by earlier workers.\textsuperscript{26} The experimental data now reported suggest that the mechanism involves hydration of the triketoindane to ninhydrin (26), and photolysis of this to give hydroxyl and 2-(2-hydroxy-1,3-diketo)indany 1 radicals by cleavage at the \(-\text{C}—\text{OH}\) bond.\textsuperscript{27} Dimerisation of radical (27) then gives the pinacol. The other reaction products (28), (29), and (30) may be explained by a Norrish Type I split of the diol (26) to yield the diradical (31).


2 Reduction of Nitrogen-containing Compounds

The photoreduction of carbonyl compounds is well explored, but much less is known about the corresponding imine reactions. It may be expected by analogy with benzophenone that its imine should give 1,1-, 2,2-tetraphenylethylene diamine (32) as its reduction product. However, Fischer earlier reported that the reaction in isopropanol gave benzhydrylamine (33) in high yield.\(^{28}\) The reaction has now been re-examined, and different

\[
\text{Ph}_2\text{C} = \text{NH} \xrightarrow{h\nu} \text{Ph}_2\text{C} - \text{CPh}_2
\]

\[
\text{Ph}_2\text{C} = \text{NCHPh}_2 + \text{NH}_3 + \text{Me}_2\text{C}=\text{O}
\]

(34)

efficiencies and products reported.\(^{29}\) Thus the irradiation of benzophenone imine in isopropanol is observed to give ammonia, benzhydrylidene benzhydrylamine (34), and acetone. The ammonia and azomethine (34) are most probably formed by condensation of the imine and benzhydrylamine (33) which, although not isolated by any workers since Fischer \(^{28}\) (despite many attempts), is a reasonable intermediate. The reaction is retarded by addition of naphthalene, so the intermediacy of triplet states is suggested. It is interesting to note that the reduction of benzophenone imine with isobutanol to benzhydrylamine (33) is induced by peroxide, and also results in the formation of (34).

The photolysis product of benzaldehyde \(N\)-cyclohexylimine (35) has been reported as \(NN'\)-dicyclohexyl-2,4-diphenyl-1,3-diazetidine (36).\(^{30}\) However, Padwa and co-workers have repeated this reaction and in conjunction with an independent synthesis have assigned the structure of the photolysis product as \(meso-NN'\)-dicyclohexyl-1,2-diphenyl-1,2-diaminoethane (37): \textit{i.e.} reductive dimerisation occurred (cf. pinacol formation) rather than pure dimerisation through the \(\text{C}=\text{N}\) bonds.\(^{31}\) Although the product is somewhat analogous to that from the reduction of aryl ketones, the initial experiments indicate that the reaction is quite different mechanistically in that the excited state of the imine does not appear to be involved as an intermediate. Since water seems to be essential to the reaction, the mechanism proposed


involves partial hydrolysis of the imine followed by photosensitisation with small amounts of benzaldehyde. In support of this view, the imine is found to be readily reduced when irradiated in anhydrous isopropanol in the presence of low concentrations of triplet sensitisers such as benzaldehyde or benzophenone. The photoreduction of the imine is suggested to be brought about by one or more of the intermediates (e.g. Ph₂COH) in the ketone reduction. In the case of the reduction of N-acyldiphenylketimine (38) in isopropanol, the reaction would seem to be less complicated, and

\[
\text{Ph}_2\text{C} = \text{N} - \text{COR} + \text{Me}_2\text{CHOH} \xrightarrow{\text{hv}} \text{Ph}_2\text{CHNHCOR} + \text{Me}_2\text{C} = \text{O}
\]  

(39)

\(\text{N-benzoylbenzhydrylamine (39) is formed (i.e. reduction of C} = \text{N rather than of C} = \text{O) with no mention of the formation of benzophenone or indeed its participation in the reaction.}^{32}\) It is, however, reported that triplet intermediates are involved since the reaction is inhibited by triplet quenchers, and partly so by diphenyl sulphide.

The unusual u.v. absorption at 236 and 245 nm of the photochromic pyredopheninium alkaloids, e.g. (40) was originally suggested to arise from a chromophore consisting of the free electron pair of the nitrogen, the \(\sigma\)-bond arrowed in structure (40), and the \(\pi\)-electron pair of the ethylenic bond.\(^{33}\) The chromophore as described is illustrated by structure (41). By isolation of the product (42) from the photoreduction of dimethoxyphromelophin by sodium borohydride in methanol, the structure proposed for the chromophore has been largely proved.\(^{34}\) Further, experiments with sodium boro-deuteride have shown that one of the hydrogens in the reduction comes from the methanol and one from the borohydride.

Sodium borohydride has also been used in the light-induced reduction of the ethylenic bond in uridine (43) to dihydrouridine (44).\textsuperscript{35} The reduction has been shown to be specific for uridine in nucleic acids and this selective reaction provides a route to dihydrouridine in t-RNA and messenger RNA which is useful in investigations of the physiological role of dihydrouridine.

The photoreduction stops at dihydrouridine, but dark hydrogenolysis continues, and $\gamma$-hydroxypropyl urea is formed. Thymidine differs from uridine in that photoreduction proceeds beyond the dihydrothymidine level and rapid hydrogenolysis with ring-opening occurs. Similar reductions of uracil and 1,3-dimethyluracil have been reported to occur in the absence of sodium borohydride and the presence of isopropanol, aqueous methionone, or ethylenediaminetetra-acetic acid.\textsuperscript{36} It would appear that in this case the hydrogens are probably derived from the water, although this and other aspects are still under investigation.

\textsuperscript{35} B. Witkop, Photochem. and Photobiol., 1968, 7, 813.
Photo-oxidation and -reduction Reactions

The irradiation of aromatic nitro-compounds in solvents containing abstractable hydrogen atoms leads to reduction products, the relative proportions of which depend upon the solvent and exciting wavelength. The overall reaction has been shown to involve a sequence of photochemical and thermal steps, the first of which is hydrogen-abstraction. The state responsible for the abstraction was suggested to be the lowest triplet state, which was of $\pi\pi^*$ type. However, other workers have clearly shown that the lowest triplet is of $n\pi^*$ type and is that which is responsible for hydrogen-abstraction. The overall mechanism for the light-induced reaction of nitro-compounds is outlined in Scheme 2 (compounds isolated are asterisked). The reaction of nitrobenzene has also been examined in the presence of hydrochloric acid: the primary product is reported to be phenylhydroxylamine, and not nitrosobenzene as had been suspected earlier. The final products of the reaction are aniline, $p$-aminophenol, and $p$-chloroaniline. The reaction pathways are thus somewhat complicated, and reports dealing with the light-induced reduction of some of the intermediates indicate the general photolability of the system. Photoreduction of nitroso-benzene in the presence of hydrochloric acid or disodium 2,6-anthraquinone-disulphonate yields azoxybenzene as the primary product, and ultimately

\[ \text{ArNO}_2 \xrightarrow{hv} \text{ArNO}_2 \quad (n\pi^* \text{ triplet}) \]

\[ \text{RH} \]

\[ \text{ArNO}_2 \text{H} \]

\[ \text{RH = Diethylamine, triethylamine, or diethyl ether} \]

\[ \text{ArNO} \xleftarrow{-\text{H}_2\text{O}} \text{ArN(OH)}_2 \]

\[ \text{Base} \quad \text{or Base} \]

\[ \text{ArNOH} \]

\[ \text{ArNOH} \]

\[ \text{RH} \]

\[ \text{O}_2 \]

\[ \text{ArN} = \text{NAr}^* \]

\[ \text{hv} \quad \text{(Sensitized)} \]

\[ \text{ArN} = \text{NAr}^* \]

\[ o\text{-Hydroxyazo-compound}^* \]

\[ \text{ArNH}_2^* \xleftarrow{hv} \text{RH} \]

\[ \text{Scheme 2} \]

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37 J. A. Barltrop and N. J. Bunce, J. Chem. Soc. (C), 1968, 1467.
aniline, o-aminophenol, benzidine, and diphenylene. Direct irradiation of azoxybenzene leads to the formation of 2-hydroxyazobenzene, and cis↔trans isomerisation, whereas the reaction gives only azobenzene when sensitised with compounds having a triplet energy in excess of 62 kcal/mole. The products from the unsensitised process are suggested to arise from an upper singlet state, and those from the sensitised one by a triplet mechanism. Other workers report that the photochemical reduction of azoxybenzene in isopropanol produces 2-hydroxyazobenzene, azobenzene, and hydrazobenzene as intermediates which are further reduced to aniline and o-aminophenol. Again the reaction has been studied in the presence of disodium 2,6-anthraquinonedisulphonate and hydrochloric acid, and an increase in rate was observed. With the disodium compound, it is considered that the semiquinone formed by hydrogen-abstraction from the alcohol is the reducing agent. The photoreduction of hydrazobenzene in hexane under nitrogen has also been studied by the same workers. The products are azobenzene, aniline, and traces of semidines. Since the yield of azobenzene is usually larger than that calculated on the basis of disproportionation of hydrazobenzene, and the yield of aniline is less, it is assumed that the reaction proceeds by oxidation of hydrazobenzene to azobenzene, rather than by disproportionation, and that no N—N bond fission occurs in the formation of azobenzene. It seems that the reports published within the year generally fit into the reaction scheme for photoreduction of aromatic nitrocompounds which is outlined in Scheme 2. However, the situation may be complicated by the observation that aniline undergoes slow photochemical oxidation to azobenzene in the presence of benzophenone. The rate of the sensitised reaction is faster in isopropanol than in benzene, probably due to a specific solvent–solute interaction, e.g. hydrogen bonding in the alcohol.

Although nitrobenzene is effectively reduced in isopropanol, 1-nitronaphthalene is inert under the same conditions. However, both nitrocompounds are reduced to the amines by photolysis of benzene solutions containing tri-n-butylstannane. The ratio of hydrogen-abstraction rate constants for the naphthalene derivatives in tri-n-butyl stannane relative to isopropanol is greater for the ππ* than for the nπ* triplet. This reduction of nitronaphthalene parallels other work with 1-naphthaldehyde.

The reduction of nitro-compounds may be sensitised by pyrrochlorophyll. Comparison of the quantum yield of such photoreduction of substituted nitrobenzenes by hydrazobenzene in ethanol–pyridine solutions with the

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polarographic quarter-wave reduction potential of the nitro-compound leads to the conclusion that an electron can be transferred from triplet-excited pyroc chlorophyll to the nitro-compound without input of additional activation energy. Such transfer is accomplished providing the potential of the nitro-compound is greater than $-0.80\, \text{v}$ in the solvent described. Pyroc chlorophyll also sensitises the reduction of low-potential nitro-compounds in the presence of ascorbic acid by a mechanism involving reduction of the triplet-excited chlorophyll by the acid.

The first instance of combination of the two radicals from the nitro-compound and the hydrogen donor has been reported.\textsuperscript{46} The given example involves the irradiation of dilute ether solutions of dinitro-prehnitene (45), and although the major product (46) is that expected, yellow crystals were also isolated for which the spectroscopic data are consistent with structure (47). The formation of compound (47) is accounted for by Scheme 3.

\begin{center}
\begin{align*}
\text{(45)} & \xrightarrow{h\nu} \text{Ethers} & \text{(46)} + \text{(47)} \\
\text{Ether} & h\nu & -\text{H}_2\text{O} \\
\text{(45)} & \text{N}^+\text{OH} & \text{N}^+\text{OH} \\
\text{CHMe} & \text{OC}_2\text{H}_5 & \text{OC}_2\text{H}_5 \\
\text{MeCHO} & \text{OC}_2\text{H}_5 & \\
\end{align*}
\end{center}

\textbf{Scheme 3}

Irradiation of nitrobenzenes in triethyl phosphite leads to oxygen-transfer, and the formation of triethyl phosphate, and triethyl N-arylphosphorimidate (48) and the corresponding aniline. In cases where the nitrobenzene is substituted with an o-alkyl group, rearranged products (49) containing the pyridine ring are also found. De-oxygenation in the presence of diethylamine is reported to lead to the formation of 2-diethylamino-3H-azepines (50). The reaction is considered to involve the intermediacy of arylnitrenes, as in the case of its thermal analogues.

There is general agreement that the photoreduction of acridine proceeds via its singlet state. The reaction has been investigated by examining the quenching of acridine fluorescence, and chemical reduction of acridine in ethanol by iodide ions. Fluorescence quenching occurs with unit collisional efficiency, and converts the excited singlet to a triplet state. The photoreduction is decreased by an amount corresponding to the fluorescence decrease, an observation which illustrates the intermediacy of the excited singlet state. Essentially the same conclusion has been reached by other workers from a study of the effect of biacetyl on the quantum yield of the reduction of acridine in methyl, ethyl, n-propyl, and isopropyl alcohols, although the results are expressed in somewhat more guarded terms; the singlet excited state is merely considered to be more important than the triplet (nπ*) in the reaction. Further it is reported that there seems to be a

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greater tendency for participation of the triplet state in the presence of alcohols as the number of α-hydrogen atoms on the alcohol increases. In the presence of aliphatic acids, acridine undergoes a novel reductive alkylation accompanied by decarboxylation of the acid. The reaction may be intramolecular, and from δ-(9-acridyld)valeric acid (51) or ε-(9-acridyld)caproic acid (52), the spiro-compounds 9,9-tetramethylene- and 9,9-pentamethylene-acridane [(53) and (54) respectively] are formed. Extension of the reaction to quinoline produces 2- and 4-alkylquinolines and 4-alkyl-1,2,3,4-tetrahydroquinoline. The mechanism for the reaction is discussed in terms of acid-base equilibrium between the carboxylic acid and the photoexcited nitrogen heterocycle.

The photoreduction of phenazine has been studied in both strongly and weakly acidic methanol. In weakly acidic solution, the reaction 'probably involves' protonation of the lowest nπ* singlet followed by electron transfer to produce the semiquinone radical ·PH which then reacts with the solvent to give dihydrophenazine (55). On the other hand, the protonated phenazine triplet was not considered to be reactive in the media examined. In strongly acid solution, protonation of the lowest nπ* singlet state of the phenazinium cation PH⁺ is thought to be the first step; this is

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followed by electron transfer to yield dihydrophenazine (55) $\text{PH}_2$. $\text{PH}_2$ further reacts with the cation $\text{PH}^+$ to produce a dimer which dissociates into two $\text{PH}^-$ radicals. These radicals are subsequently protonated to yield a stable cation radical $\text{PH}_2^{\text{+*}}$ which is green. Similar reduction (i.e. 9,10-hydrogenation) is reported for anthracene derivatives, even those with 

$$
\text{meso-substituents containing a carbonyl group where one might have expected alcohol formation.}$$

The reduction was investigated by flash photolysis and it was found that the trend of substitution effects was the converse of that found by other investigators for the photo-oxidation, in that electron donors decreased the rate of reaction and electron acceptors increased it.

### 3 Oxidation of Aromatic Compounds

Liquid benzene was previously reported to be photo-oxidised to trans,trans-hexa-2,4-dienedioic and a $\text{C}_{12}$ dialdehyde $\text{OCH(CH=CH)_6CHO}$. Intermediates (56) and (57) were thought to be involved. The oxidation of benzene has now been examined in aerated aqueous solutions with

$$
\text{C}_6 \text{H}_6 + \text{O}_2 \xrightarrow{\text{hv}} \text{O}_\text{O} \xrightarrow{\text{H}} \text{OHC(CH=CH)_6CHO}
$$

$253.7 \text{ nm}$ radiation under conditions where the benzene is circulated, and the product extracted from the irradiation zone into $2\text{N-NaOH}$. Percolation of the alkaline extract at pH 11 with ether gave phenol and 'neutral

---

contaminants'; at pH 8 the same procedure yielded a compound for which the tentative structure (58), α-formyl-γ-pyrone, has been assigned. The compound decomposes at its melting point of −25°, but the sodium and barium salts are reported to be stable. Since at ordinary temperatures compound (58) is reported to be stable only in very dilute ether solutions and in aqueous alkali, it is very surprising that it should be formed at all under the acid (pH 5) reaction conditions. The author suggests that the reaction proceeds via an easily oxidisable photoisomer of benzene, since when benzene is irradiated, and oxygen-saturated ice water added in the dark, traces of (58) are found. The isomer considered to be responsible for the reaction is benzvalene, and a mechanistic scheme (Scheme 4) has been proposed in which the formation of mucondialdehyde from benzene could arise from a photoreaction of aldehyde (58), possibly sensitised by benzene.

The photosensitised oxidation of anthracene and naphthalene has been extensively studied by Rigaudy and his co-workers, and a comprehensive report dealing with work up to 1967 in this area has been published.\(^6\) The position of photoperoxide formation in anthracene derivatives is very dependent upon the electronic nature of the substituents. Thus only the 9,10-peroxide (59) is formed when the 1,4-positions are unsubstituted, but substitution in the 1,4-positions with electron-donating groups such as alkoxy results in 1,4-photoperoxide (60) formation, and when the 9,10-substituents are phenyl groups, the 1,4-peroxide is the exclusive product. In other cases where the 9,10-positions bear electron-donor substituents (e.g. 1,4,9,10-tetramethoxy- and 1,4-dimethoxy-9,10-dimethylanthracene) formation of the 9,10-peroxide is favoured. As may be expected, a mixture of 1,4- and 9,10-peroxides is obtained when the donor character of the substituents is more delicately balanced; thus 1,4-dimethyl-9,10-diphenylandanthracene gives a 7:3 ratio of 1,4-:9,10-peroxides, and 1-methoxy-9,10-diphenylanthracene yields a 50:50 mixture of the peroxides. Since these photosensitised reactions involve singlet molecular oxygen, it is not surprising to find that the positions of peroxide formation are in a number

of cases the same as those in Diels–Alder additions; but other factors must be of importance since there are several anomalies (compare e.g. Schemes 5 and 6).

The photoperoxidation of anthracene derivatives has also been achieved by the direct excitation of oxygen at high pressures in inert organic solvents using a helium–neon laser.\(^{57}\) The normal emission of the laser at 632.8 nm

Photo-oxidation and -reduction Reactions

coincides almost exactly with absorption corresponding to the \((\pi\Sigma_g^*)_2 \rightarrow (\pi\Delta_g)_2\) transition of oxygen. The peroxidation of 9,10-dimethylanthracene with oxygen at 2000 lb/sq. in. in 1,1,2-trichloro-1,2,2-trifluoroethane was effected with a quantum yield of 0.13 for the disappearance of the anthracene; and for the reactive 1,3-diphenylisobenzofuran the quantum yield was 0.65. This difficult technique for studying oxidation by singlet states of oxygen at least has the advantage of high selectivity.

The photosensitised oxidation of naphthalene derivatives and the further thermal and photo-reactions of the products have also been studied.\textsuperscript{56, 58, 59} Thus both 1,4-dimethoxy- and 1,4-dimethoxy-5,8-diphenyl-naphthalenes form 1,4-peroxides (61). Further irradiation of the peroxides leads, as with some 1,4-anthracene peroxides (62), to the formation of bis-epoxides which decompose rapidly at room temperature. In the case of the naphthalene derivative, the bis-epoxide (63) may also be formed in the absence of sensitiser by direct irradiation in ether at \(-60^\circ\). Acid-catalysed thermal reactions of the anthracene and naphthalene photoperoxides produce the quinones (64), (65), and (66).\textsuperscript{56, 58} Thus formation of peroxides and the derived quinones from polynuclear aromatic hydrocarbons is a well-established reaction, but within the year an oxidative dimerisation product was also reported from the irradiation of such systems.\textsuperscript{60} Bianthrone (67) as well as anthraquinone was isolated from the irradiation of anthracene in carbon disulphide under oxygen, and it was shown in subsequent

\begin{equation}
\text{OMe} \quad \text{Benzanthrone} \quad \text{O}_2, \quad h\nu
\end{equation}

\[ \rightarrow \]

\begin{equation}
\text{OMe} \quad \text{O} \quad \text{MeO} \quad \text{O}_2H
\end{equation}

\[ \text{(61)} \]

\[ \text{O} \quad \text{MeO} \quad \text{H} \quad \text{H}
\]

\[ \text{(63)} \]

\[ \rightarrow \]

\begin{equation}
\text{MeO} \quad \text{O}_2H
\end{equation}

\[ \text{(64)} \]

\[ \text{H}^+ \quad \text{OMe} \quad \text{H}
\]

\[ \text{(65)} \]

\[ \text{H}^+ \quad \text{OMe} \quad \text{H}
\]

\[ \text{(65)} \]

---


experiments that the peroxide (68) may be the reaction intermediate since its irradiation under these conditions also yielded the former products. Only in carbon disulphide were appreciable amounts of bianthrone formed. In other solvents, benzene and acetone, this product was detected, but only anthraquinone was present after prolonged irradiation. It would therefore seem that carbon disulphide has a considerable influence on the reaction, and it has been suggested that a relatively stable -CS radical produced during the irradiation may play an important part.

The photosensitised oxidation of 9,10-diphenylanthracene using eosin, and of rubrene using methylene blue, has been studied in a system where the sensitisier and oxidisable substrate are separated by oxygen-permeable layers of barium or cadmium stearate as monomolecular films.\[^{61}\] The rate of oxidation was followed by measuring the hydrocarbon fluorescence as a function of stearate thickness. Only for thicknesses up to 500 Å was the sensitised reaction observed, and this depended only on the deactivation process of excited species (singlet oxygen) diffusing through the layer. It

was found also that half of the excited oxygen molecules were deactivated after a diffusion path of 115 Å.

Mechanistic aspects of photoperoxidation of aromatic hydrocarbons have been discussed by Stevens and Algar.62

4 Oxidation of Aliphatic Unsaturated Systems

The typical product of dye-sensitised oxidation of an ethylenic bond is an unsaturated hydroperoxide having the position of unsaturation moved one carbon atom away from the original ethylenic bond; work-up of the products is generally performed under reducing conditions so as to give the corresponding unsaturated alcohols. The process formally resembles the ene-reaction. Participation of singlet-state oxygen is now generally accepted, and a symmetry and spin-allowed concerted cycloaddition of singlet oxygen to olefins containing allylic hydrogens is thought likely to be involved.

Much of the published work in this area is concerned with the sensitised oxidation of natural products such as α- and β-ionone derivatives, and carotenoids. Unusual allenic oxidation products (69) and (70) have been isolated in the dye-sensitised oxidation of such systems, as reported by two groups of workers, one studying the irradiation of 3-methyl-1-(2,6,6-trimethylcyclohexen-1-yl)-1,3-butadiene (71),63 and the others methyl β-ionyldiene acetates (72).64 Both groups isolated the more expected alcohols (73), (74), and (75) after suitable work-up under reducing conditions, together with the products (76) and (77) of Diels–Alder addition of singlet oxygen to the diene system. The formation of the allene systems in compounds (69) and (70) is particularly interesting because of the close relation to those systems of several important carotenoids.

There is no report of such allenic compounds being formed from the Rose Bengal-sensitised oxidation of methyl β-dehydroionyldiene acetates (78).65 Here the products of the reaction are the two Diels–Alder peroxides (79) and (80), and two stereoisomers of a compound (81) in which ethylenic bond migration has occurred. On the other hand, an interesting spiroperoxy lactone (82) is formed from methyl homosuframate (83).66 Specific oxygenation of the tetrasubstituted ethylenic bond in (83) and cyclisation of the peroxide (84) thus formed are believed to account for the formation of such a compound. In addition, the expected diene peroxide (84a) is isolated. The photo-oxidation of β-carotene itself has been examined in benzene and methyl alcohol using Rose Bengal sensitisation.67 The

(71) \[ \text{(i) } h\nu, O_2, \text{Sensitiser} \]
\[ \text{(ii) } \text{NaBH}_4 \]

(69) \[ \text{OH} \]

(73)

(72)

\[ R = \text{CO}_2\text{Me} \]
or \[ \text{CO}_2\text{Me} \]

\[ 10\% \]

(70)

\[ 30\% \]

(75)

(74)

(76)

(77)

(78) \[ h\nu, O_2, \text{Sensitiser} \]

\[ 60\% \]

(79)

\[ 6\% \]

(80)

(83) \[ h\nu, O_2, \text{Sensitiser} \]

\[ 10\% \]

(81)

(84a)

(84)
products of such irradiation are the lactone, dihydrodinidiolide (85), and small amounts of a further unidentified lactone. In the absence of sensitiser, β-carotene yields β-ionone (86) as the major product and lactone (85) as a minor one. It has been shown subsequently that lactone (85) could arise by sensitised oxidation of β-ionone. These and previous results involving sensitised oxidation of carotenoids suggest that C_{11} and C_{13} oxygenated compounds are produced in vivo from such systems by mechanisms analogous to photo-oxygenation.

Photo-oxidation of phylloquinone (87), sensitised by methylene blue, proceeds as expected by attack of singlet oxygen on the quinone to give the 3′-hydroperoxide (88).\textsuperscript{69} This peroxide then undergoes photolytic rearrangement to 6,10,14-trimethylpentadecan-2-one (89). A similar reaction also occurs with the menoquinone (90) where it proves of some use as a side-chain degradation procedure. Such peroxides have also been isolated in the steroid series from compounds containing a βγ-unsaturated ketone moiety (91).\textsuperscript{70} Here again it is proposed from a study of the reaction with 4β-deuteriocholest-5-ene that the reaction is a concerted cycloaddition of the oxygen to the olefin rather than a stepwise ionic addition. A stepwise mechanism (path a) would lead to loss of the deuterium, but path b should retain the deuterium. It was found that 85\% of the deuterium was retained in the product at C-4 hence indicating substantial participation of a concerted oxygen attack. The photo-oxidation of other steroid systems has been examined, but hydroperoxide formation, despite the presence of allylic hydrogens, was not observed. Erythrodiol (92) forms two compounds, an epoxytetrahydrofuran derivative (93) and a simple epoxide (94) of the starting olefin.\textsuperscript{71} On the other hand, Rose Bengal-sensitised oxidation

\[ \text{β-Carotene} \xrightarrow{hv, O_2, \text{Sensitiser}} \text{(85)} \]

\[ \text{(86)} \]


\textsuperscript{70} N. Furutachi, Y. Nakadaira, and K. Nakanishi, \textit{Chem. Comm.}, 1968, 1625.

of 18β-glycyrrhetic polyenes (95) leads to a mixture of a monoketone (96) (60%) and a diketone (97) (20%).\textsuperscript{78} It was shown that the diketone could arise photochemically from the monoketone, and a concerted cyclic attack of oxygen is again postulated to be involved in the formation of (96).

Simple conjugated and non-conjugated polyenes have also been photooxidised in the presence of sensitisers. Allo-ocimene (98), in the presence of hydroquinone to prevent polymer formation, yields the expected hydroperoxide (99),\textsuperscript{73} and both (−)-caryophylene (100) and (−)-isocaryophylene (101) similarly give the 4-allyl hydroperoxides.\textsuperscript{74} The latter account also describes a simple method for the formation of (101) by the irradiation of (100) with a high-pressure mercury lamp in the presence of small amounts of diphenyl disulphide.

The photo-oxidation of phenylpyruric acid derivatives occurs in solvents in which the enol (102) form is the more stable.\textsuperscript{75} In this system (102), there are no allylic hydrogens, but hydroperoxide formation still occurs to provide a precursor for a synthesis of thyroxine (103). The hydroperoxide

(104) is treated with the α-amino acid (105); as yet the mechanism for the formation of thyroxine and the photo-oxidation step have not been elucidated.

Two groups of workers have reported vapour-phase photo-oxidation reactions of olefins in the presence of nitrogen dioxide. The main features of the reaction of ethylene at 336 nm with NO₂ are the addition of oxygen atoms to the olefin to give an energy-rich intermediate, and dissociation of the intermediate into ·CH₃ and ·CHO radicals. This process is followed by rapid interaction of the radicals with NO₂ to give stable products. The photo-oxidation of but-1-ene by NO₂ has been examined at shorter wavelengths. From measured effects of addition of inert and other gases on the product yield, it is concluded that ^1D₂ oxygen atoms participate in the oxidation at 228·8 nm. Ground-state oxygen atoms produced by photodissociation of NO₂ and possibly by quenching of ^1D oxygen by olefin are also important in the process, and are believed to give rise to the main observed addition products, viz. n-butanol and 1,2-epoxybutane. The indications are that reactions of ^1D oxygen with but-1-ene at total pressures below one atmosphere give very little stabilised addition product.


(92) \( R = H, R' = \text{CH}_3\text{OH} \)

\[
\begin{align*}
\text{(93)} & \quad \text{RO} \quad \text{RO} \\
\text{(94)} & \quad \text{CH}_3 \text{CH}_2 \text{O} \\
\text{(95)} & \quad \text{R} \quad \text{R'} = \text{CH}_2\text{OAc} \\
\text{(96)} & \quad \text{RO} \rightarrow \text{O} \\
\text{(97)} & \quad \text{R} \quad \text{R'}
\end{align*}
\]
5 Oxidation of Nitrogen-containing Compounds

The photo-oxidation of enamines has been studied in some detail by Foote and Wei-Ping Lin.\textsuperscript{78} In benzene solution and using zinc tetraphenylporphine as photosensitiser, enamines of type (106) rapidly take up 1 mol of oxygen per mol of enamine to give ketones (107) and formamide derivatives (108). No effect on the reaction is produced by free radical inhibitors. Enamines with less electron-rich ethylenic bonds, such as (109), undergo no photocleavage of this type, but ynamines do exhibit this reaction to yield

\textsuperscript{78} C. S. Foote and J. Wei-Ping Lin, \textit{Tetrahedron Letters}, 1968, 3267.
\[ \text{Me}_2\text{C} = \text{O} \quad (107) \]

\[ \text{Me}_2\text{C} = \text{C} - \text{N}(\text{C}_2\text{H}_5)_2 \quad (108) \]

\[ \text{Me} - \text{C} = \text{C} - \text{N}(\text{C}_2\text{H}_5)_2 \quad (109) \]

\[ \text{Me} - \text{C} = \text{C} - \text{N}(\text{C}_2\text{H}_5)_2 \quad (110) \]

\[ \text{MeO} \quad (111) \]

\[ \text{hv}, \text{O}_2, \text{Sensitiser} \]

\[ \text{hv}, \text{O}_2, \text{Rose Bengal} \]

\[ \text{hv}, \text{O}_2 \quad \text{Sensitiser} \]

\[ \begin{array} {c}
\text{(112)} \\
\text{(113)} \\
\text{(114)}
\end{array} \]

\[ \begin{array} {c}
\text{(115)} \\
\text{MeO} \\
\text{O = C - N} \quad (116)
\end{array} \]
α-diketones (110). By carrying out the reaction at \(-60^\circ, -20^\circ,\) and ambient temperatures in an n.m.r. spectrometer, these workers have been able to demonstrate that an intermediate is formed from the enamine. The intermediate is stable at the lower temperature, but yields the isolated products on warming to room temperature. While no definite structure is proposed for the intermediate, the ethylenic bond of the enamine is retained as C—C, and oxygenation at least on the position \(\beta\) to the nitrogen is inferred. A dimeric species such as (111), with its several configurational and conformational isomers, could account for the complexity of the n.m.r. spectra and their temperature dependence. Other workers examining this photo-oxidation reaction with the steroid (112) have been largely concerned with the use of singlet oxygen as a synthetic tool, but even so they have envisaged that the reaction is simply a 1,2-cycloaddition of singlet oxygen to the enamine, and decomposition of the adduct [analogous to (115)] to give the ketone (113); in this case in quantitative yield.\(^{29}\) A model compound (114) is also examined by these workers with similar results, but no intermediates [e.g. (115)] were detected by t.l.c. or g.l.c. In the light of Foote's observations on the stability of the intermediate of the reaction, its lack of detection by such techniques is not surprising. N-Arylenamines undergo similar photosensitised oxidations.\(^{80}\) Thus enamines (116), (117), and (118) are reported to give ketones (119), (120), and (121) respectively, while a mixture of tautomeric quinoline derivatives (122), and (123), under the same conditions, yielded ketones (120), (124), and (125).

Benzaldehyde anil, in anhydrous alcoholic solvents in the presence of oxygen, undergoes a light-induced sensitised oxidative cleavage of the C≡N bond to yield mainly aniline and benzaldehyde.\(^{81}\) The incorporation of oxygen has been shown not to involve direct attack on the substrate, but proceeds via the formation of water and hydrogen peroxide. Each of these is capable of effecting the photosensitised hydrolysis, but the contribution from the water is minor compared with that from the peroxide. Minor products reported from the reaction are \(NNV'N'\)-tetraphenylethylene-1,2-diamine and 2-phenylquinoline.

The photo-oxidation of nitrogen-containing five-membered ring compounds continues to be an active area of research, particularly with hetero-aromatic systems and purine derivatives. It has been previously shown that \(N\)-unsubstituted pyrroles, and in particular tetraphenylpyrrole, are oxidised in the presence of a dye to such compounds as (126) and (127).\(^{82}\) The reaction has now been investigated with \(N\)-substituted compounds, and the reaction has been found to take a somewhat different course.\(^{83}\) It is suggested that the reaction of compounds (128) and (129) proceeds via the

transannular peroxide (130) which by analogy to ozonide cleavage may yield the carbonyl oxide zwitterion (131) and hence give the observed products (132) and (133). Isolation of (133) from the N-methyl compound (129) appears to be a consequence of the ready hydrolysis of the \( \equiv N - Me \) moiety during work-up. Similar photo-oxidation of tetraphenyl-\( N \)-hydroxy-pyrrole is reported to form the hydroperoxynitrene (134) (m.p. 208—210° dec.) which may revert to starting material, or be converted into compound (135) by treatment with potassium iodide and acetic acid.\(^{84}\)

Light-induced oxidation of the imidazole ring system has been reported by several workers. Imidazole (136) itself in methyl alcohol yields (137),\(^{85}\) and simple alkylated derivatives have been shown to form a number of compounds dependent upon the reaction media and, naturally, upon the

---


Photo-oxidation and -reduction Reactions

\[ \text{Ph, O}_2, \text{MeOH, Sensitiser} \]

\[ \begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*} \]

\[ \xrightarrow{\text{hv}} \]

\[ \begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{C-Ph} & \quad \text{O} \\
\text{Ph} & \quad \text{C-Ph}
\end{align*} \]

\[ \begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{N-C-Ph} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph}
\end{align*} \]

\[ \begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{N} & \quad \text{C-Ph}
\end{align*} \]

(126)

(127)

(128) \( R = \text{Ph} \)

(129) \( R = \text{Me} \)

(130)

(131)

(132)

(133)

(134)

(135)

(136)

(137)
position of substitution (see Scheme 7).\textsuperscript{85} Two groups report the oxidation of 1,2,4,5-tetraphenylimidazole (138) to form (139) in excellent yield.\textsuperscript{85, 87} This mode of ring cleavage has been previously shown for the 2,4,5-triphenylimidazole.\textsuperscript{88} Both groups postulate the same mechanism,

\[
\begin{align*}
\text{N} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\left\uparrow \text{MeOH} \ uparrow \text{hv}, \text{O}_2 \right. \\
\text{MeC} & \quad \text{NH} & + & \text{MeC} & \quad \text{NH} \\
\text{NHMe} & \quad \text{CONHMe} & + & \text{MeC} & \quad \text{NH} \\
& & + & \text{Compounds } \text{C}_7\text{H}_{11}\text{N}_2\text{O}_4 & \text{and } \text{C}_9\text{H}_{19}\text{N}_2\text{O}_4 \\
\text{Scheme 7}
\end{align*}
\]

although in one case\textsuperscript{85} the zwitterionic counterpart (140) of the hydroperoxide is drawn as an intermediate between the transannular peroxide (141) and the dioxo compound (142). \textit{N}-Benzyolhistidine (143)\textsuperscript{89} and its

\textsuperscript{87} A. Ranjon, \textit{Compt. rend.}, 1968, 267, C, 1822.
methyl ester\textsuperscript{85} have been studied in similar fashion in attempts to obtain more data concerning the destruction by singlet oxygen of the histidine residue in enzyme systems. Reaction of both compounds proved to be complex. From the methyl ester, compounds (144) and (145) were isolated, but more than 1 mole of oxygen per mole of substrate was required. Reaction of the acid was carried out at pH 11, and the products were separated into two mixtures of nine components containing no basic residues and of seven components containing basic residues. From the mixture, \(N\)-benzoyl aspartic acid (146), \(N\)-benzoylasparagine (147), and products (148) and (149) were isolated. Spectroscopic data for some of the other products are also presented.

\[
\begin{align*}
\text{CH}_2\text{CHCOOH} & \quad \text{O} \\
\text{NH} & \quad \text{Ph} \\
\text{C}=\text{O} & \\
\text{MeO} & \\
\text{Ph} & \\
(143)
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{Ph} \\
(144)
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{MeO} \\
\text{CO} & \quad \text{Ph} \\
(145)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CHCO}_2\text{H} & \quad \text{H}_2\text{NCOCH}_2\text{CHCO}_2\text{H} \\
\text{HO}_2\text{C} & \quad \text{HN--COPh} \\
\text{HN--COPh} & \\
(146)
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{C}=\text{O} \\
\text{HO}_2\text{C} & \quad \text{N} \quad \text{H} \\
\text{N} \quad \text{H} & \quad \text{O} \\
\text{N} \quad \text{H} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{NH} & \\
\text{Ph} & \\
(148)
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{NH} \\
\text{O} & \quad \text{CO} \\
\text{NH} & \\
(149)
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{N} \\
\text{R} \\
\text{R}' \\
\end{array} & \xrightarrow{h_v, \text{O}_2} & \begin{array}{c}
\text{N} \\
\text{R} \\
\text{R}' \\
\end{array} \\
(150) & \quad & (152)
\end{align*}
\]

The oxidation of 1,5-benzodiazepines (150) to give 3-acylquinoxalines (151) with monopersulphuric acid or peracetic acid is known. In the reaction no 3,6-diaza-4,5-benzotropone (152) is formed, but by photo-oxidation of the 1,5-benzodiazepine system in non-aqueous media the desired oxidation product (152) is formed together with dibenzoyl-o-phenylenediamine.\textsuperscript{80}

There is considerable interest in the photosensitised oxygenation of purine derivatives. This process has significance in connection with the photodynamic degradation of guanine residues in deoxyribonucleic acids. In order to obtain information concerning the degradation, Matsuura and his group have undertaken the oxygenation of various purine derivatives with very profitable results. Thus the N-unsubstituted hydroxypurines, xanthine (153), uric acid (154), and 8-methylxanthine (155) have been irradiated in aqueous alkali and in the presence of Rose Bengal. Xanthine yields allantoin (156) and triuret (157), uric acid leads to the formation of sodium oxonate (158), allantoxoidin (159), and triuret, while 8-methylxanthine gives a complex mixture from which acetamide and sodium oxonate are isolated.\textsuperscript{91} The formation of allantoin may be rationalised by a pathway involving a cyclic peroxide (160) while triuret and sodium oxonate may be accounted for from uric acid, for example, by the pathway outlined in Scheme 8. The isolation of (161) and (162) from such oxidations of uric acid and its derivatives in methanol provides evidence for the formation of zwitterionic peroxide intermediates (163) and (164), as well as peroxides (165) and (166).\textsuperscript{92, 93} The photosensitised oxygenation of hydroxylated 9-phenylpurines has also been subjected to an intensive investigation.\textsuperscript{94} Thus the 9-phenylpurines (167) and (168) yield uric acid derivatives (169) and (170), while 1,3-dimethyl-9-phenyl uric acid (171) and 9-phenyl uric acid itself (172) give the same products (169) and (170) respectively, and 1,3-dimethyl-4-hydroxy-5-methoxy-9-phenyl uric acid (173) is also obtained from (171). Peroxide intermediates similar to those reported earlier are considered for all these reactions. Oxidative degradation procedures are also noted in

\textsuperscript{91} T. Matsuura and I. Saito, \textit{Tetrahedron}, 1968, 24, 6609.
this series. Thus irradiation of 8-methoxy caffeine (174) and related compounds in methanol containing Rose Bengal leads to decarboxylation and the formation of 1-methyl-2,2-dimethoxy-4-methylamino-3-imidazolin-5-one (175) in good yield.\(^{65}\) Guanine (176) also undergoes fragmentation, yielding (177) and (178), and here again a transannular peroxide (179) is considered to be an intermediate.\(^{66}\)

In such lines of research as described above it is not possible to achieve the ultimate objectives in a short time. However, the publication of such exact and pertinent work as Matsuura’s should eventually promote a fuller understanding of comparable reactions in vivo.

### 6 Miscellaneous Oxidation Reactions

Throughout the year several interesting photo-oxidation reactions have been reported which do not readily fit into the above classifications; these reactions are reported in this section.

The vapour-phase photo-oxidation of diethyl ketone over wide temperature (25—200\(^{9}\)) and oxygen partial pressure (0—100 mm) ranges has been studied, and a simple free-radical chain reaction scheme has been proposed to account for the initial major products, acetaldehyde, ethanol, carbon dioxide, and carbon monoxide.\(^{97}\) The formation of methanol in the reaction arises by a secondary process from the acetaldehyde. Ethylene is the only hydrocarbon formed in the reaction and with a low quantum yield. It is considered unlikely that the ethylene is formed by either reactions (A) or (B) since no butane is observed in the photolysis products. The effect of adding inert gases suggests that reaction (C) (i.e. decomposition of ‘hot’ ethylperoxy radicals) is a more likely process.

\[
\begin{align*}
\cdot C_2H_5 + C_2H_5O\cdot & \rightarrow C_2H_4 + C_2H_5OH & (A) \\
\cdot C_2H_5 + C_2H_5OO\cdot & \rightarrow C_2H_5O\cdot + C_2H_4 & (B) \\
C_2H_5OO\cdot & \rightarrow C_2H_4 + HO_2\cdot & (C)
\end{align*}
\]

Up to this year, the only report of photo-oxidation of \(\alpha\)-diketones concerned the oxidation of camphorquinone to camphoric anhydride.\(^{98}\) It is now reported that benzil, acenaphthaquinone, and phenanthrenequinone can be oxidised in benzene or acetonitrile solution in sunlight; the products are benzoic, naphthalene-1,8-dicarboxylic, and biphenyl-2,2'-dicarboxylic anhydrides respectively.\(^{99}\) Similar irradiation of 1,2-diphenylcyclobutendione (180) yields phenanthrene-9,10-dicarboxylic anhydride (181) and the 9,10-dihydro derivative (182), but in contrast with benzocyclobutenione, the dione (180) is photostable under nitrogen. Products (181) and

---


(182) have also been isolated from the irradiation of diphenylmaleic anhydride (183) as might be expected, and it is suggested in the oxidation of α-diketones, that (183) is an intermediate, despite the failure to detect it. The author's remark that cyclisation appears to be 'slightly faster' than photo-oxidation, does not provide a very convincing explanation of the failure to detect a supposed intermediate (183) which is not expected to be markedly unstable under the reaction conditions.

It is known that the photo-oxidation of o-methyl aryl ketones leads to products in which the methyl group is converted into a carboxyl group or a lactone carbonyl group. Thus the oxidation of o-methylbenzophenone yields o-carboxybenzophenone (184) and the corresponding phthalide (185). Since formyl-2-benzophenone is converted into both (184) and (185) by similar photolysis, its intermediacy in the oxidation of the ortho-methyl compounds is suggested. Such intermediate peroxides as (186) are generally too unstable for isolation but from o-methylacetophenone, which forms the lactone (187) on oxidative photolysis in acetic anhydride, it has been possible to isolate the intermediate peroxide (188) by carrying out the reaction in benzene. The photolysis in sunlight of oxygenated benzene solutions of 1-methylanthraquinone has been reported to yield not only the expected 1-carboxylic acid, but also the dilactone (189) and anthraquinone. The mechanism for the formation of the dilactone is well supported by other published data and essentially involves photoenolisation of the quinone, followed by peroxide formation and conversion of the peroxide to the aldehyde. A further step of photoenolisation forms a ketone which rearranges to a lactone or its ketonic tautomer, both of which are capable of undergoing ready oxidation to the isolated dilactone. Experimental evidence for these stages in the process is presented. In pre-oxygenated solution at higher concentrations of the quinone, the oxidative dimer (189) is the major product.

The photo-oxidation of benzoxazinones has been studied, and a surprising specificity of reaction has been observed in that of all the derivatives examined, only N-methyl-2-(p-nitrophenyl)-1,2-dihydro-3,1-benzoxazin-4-one (190) led to formation of an oxidation product (191). One mechanism put forward for the reaction involves the formation of the formyl derivative (192) which, as earlier reported, could undergo photo-oxidation to the acid (191). However, attempts to isolate the formyl derivative (192) from the reaction, or even to synthesise it, failed and a more satisfactory mechanism which also accounts for the specificity of the reaction involves initial nitro-group excitation and cleavage of the C—O, followed by oxidation to yield (191) as shown.

101 A. Eckert, Ber., 1925, 58, 313.
In the auto-oxidation of a methylene group flanked by either oxygen or an aromatic ring, the products are generally sec-hydroperoxides,\textsuperscript{105} and a few examples of ketone formation are known.\textsuperscript{106} The reaction has been investigated for the light-induced oxygenation of dehydrorotenones (193), and conversion of CH$_2$ to C$\equiv$O has been observed only in the presence of sodium borohydride.\textsuperscript{107} The roles of sodium borohydride are probably (i) to convert the hydroperoxide into the hemiacetal from which formation of the ketone would be straightforward, and (ii) to reduce the concentration of free radical initiators which lead to undesirable side reactions.

Mannich bases of types (194), (195), and (196) are reported to undergo photodehydrogenation in tetrahydrofuran, acetonitrile, or methanol to give

\textsuperscript{105} See for example, L. Debiais, M. Niclause, and M. Letort, \textit{Compt. rend.}, 1954, \textbf{239}, 539.


mainly azomethines which are isolated as the enols (197) and (198). In some cases tetra- and penta-substituted pyrroles are also formed. Another example of photoinduced dehydrogenation is found in the irradiation of an acid solution of the 3,4-dihydro-\(\beta\)-carboline (199) to give the aromatic compound (200) in good yield. The process is very acid-dependent, and is a photochemical reaction typical of partially hydrogenated nitrogen heterocyclic compounds.

Following the development of a new solvent system for flavin t.l.c. analysis, two new products have been detected in the anaerobic photolysis of riboflavin.\textsuperscript{110} These products have been tentatively identified as flavins having a five-membered side chain in which one of the hydroxy-groups has been oxidised to a carbonyl group.

The mechanism of the dye (D) sensitised photo-oxidation of 2,4-diaminotoluene (RH\textsubscript{2}) has been elucidated by examining the reaction by flash spectroscopy.\textsuperscript{111} The first chemical reaction is the generation of two free radicals (\textbullet\textit{DH} and \textbullet\textit{RH}) from the triplet dye and hydrogen donor. These radicals may then react in several ways with or without oxygen, as shown below.

\begin{align*}
\textit{With oxygen} & \quad \textit{Without oxygen} \\
\textbullet\textit{DH} + O_2 & \rightarrow \text{D} \quad \textbullet\textit{DH} + \textbullet\textit{RH} \rightarrow \text{D} + \text{RH}_2 \\
\textbullet\textit{RH} + O_2 & \rightarrow \text{R} \quad 2\cdot\text{DH} \rightarrow \text{D} + \text{DH}_2 \\
& \quad 2\cdot\text{RH} \rightarrow \text{RH}_2 + \text{R}
\end{align*}


Photoreactions of Compounds Containing Heteroatoms other than Oxygen

1 N-Oxide Rearrangements

The irradiation of heteroaromatic N-oxides has again this year attracted the attention of several groups of workers, and many examples of the rearrangement of mono- and poly-cyclic compounds have been reported. Typically, such compounds undergo processes of ring expansion and contraction, and loss of oxygen to give the parent compound. Thus 2,6-dicyanopyridine N-oxide has been shown to yield in addition to the parent dicyanopyridine, 5-cyano-2-pyrrolocarbonyl cyanide (1) and an oxazepine which has been tentatively assigned structure (2). The rearrangement is performed in dichloromethane solution with light of wavelength longer than 290 nm. Similarly 2,4,6-triphenylpyridine N-oxide in acetone at wavelengths longer than 300 nm yields a non-separated mixture of 2,4,6-triphenylpyridine and the oxazepine (3), as well as 3-hydroxy-2,4,6-triphenylpyridine (4) and 2-benzoyl-3,5-diphenylpyrrole (5). The mechanism for both reactions involves the initial formation of an oxaziridine ring (6) followed by either rearrangement to an epoxide or ring-cleavage to yield the pyrroles. This is not always the reaction path followed by monocyclic N-oxides, for irradiation of 4-nitropyridine N-oxide leads to reaction by two primary processes with the formation of 4-hydroxypyridine N-oxide nitrate (7) or 4-hydroxylaminopyridine N-oxide (8) depending upon the reaction conditions. In both reactions a common intermediate of unspecified structure is suggested. The intermediate absorbs around 570 and 370 nm and its reaction with unexcited starting material leads to (7) whereas hydrogen abstraction from the solvent yields (8).

Both mono- and di-oxaziridines are reported to be formed from irradiation of the α-dinitrone, hexamethyl-2,3-dihydropyrazine-1,4-dioxide (9). A nitrone oxaziridine, 2,2,3,3,5,6-hexamethyl-1,4-diaza-7-oxabicyclo[4,1,0]hept-4-ene-4-oxide (10) and a mixture of the cis- and trans-forms of the dioxaiziridine (11) are formed. Thermal cycloaddition of the nitroloxaziridine (10) with acrylonitrile yields a 1:1 adduct (12);

this cycloaddition indicates that the inactivity of the original monocyclic α-dinitrone to olefin addition is not due to the ring structure as such, but is rather connected in some way with conjugation of the nitrone functions.

Although in the past there have been many reports concerning N-oxide photolyses, this year sees the first report of the irradiation of a cyclic heteroaromatic compound with an internal azoxy-function, viz. pyridazine N-oxide (13). The photolysis of (13) in the presence of hydrocarbons leads to the oxidation of the substrate and the formation of the pyridazine. Thus benzene is converted to phenol, and toluene to a mixture of cresols. In the latter case no benzyl alcohol was formed, but cyclohexane was converted to cyclohexanol. However, the preference for aromatic oxidation is shown by photolysis of (13) in a mixture of benzene and cyclohexane when twice as much phenol as cyclohexanol was formed. Naphthalene is also converted to naphthol by this process. Among likely mechanisms, it is possible to envisage an initial ejection of atomic oxygen which then undergoes carbene-like insertions into the solvents.

\[ \text{(13)} \]

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The majority of publications within this area of photochemistry are concerned with the reactions of \( N \)-oxides of quinoline derivatives. Buchardt, who has probably published the most valuable accounts, has found that the product distribution from photolysis of quinoline \( N \)-oxides unsubstituted in the 2-position is very solvent dependent.\(^6\) Many derivatives of the system have been examined with fluoro, chloro, bromo, methyl, ethyl, and methoxy substituents. In protic solvents, carbostyrils (14) are formed while in aprotic solvents the carbostyril yield is decreased and production of benz[\( \alpha \)]\( [1,3] \)-oxazepines (15) or their solvolysis products, \( N \)-formyl-2-indolinols (16) and their open-chain tautomers (17), are favoured. The stability of the oxazepine (15) seems to be dependent upon the presence of electron-withdrawing groups in the seven-membered ring.

\[
\begin{align*}
\text{R}^4 & \quad \text{R}^3 & \quad \text{R}^2 & \quad \text{R}^1 \\
\text{O} & | & \downarrow & \\
\text{R}^5 & \quad \text{R}^6 & \quad \text{N} & \quad \text{H} \\
\text{hv} & & & \quad \text{R}^4 & \quad \text{R}^3 & \quad \text{R}^2 & \quad \text{R}^1 \\
& & & \quad \text{O} & \downarrow \\
& & & \text{R}^5 & \quad \text{R}^6 & \quad \text{N} & \quad \text{H} \\
(14) & & & & & & & & & & & & & (15)
\end{align*}
\]

\[
\text{R}^4 & \quad \text{R}^3 & \quad \text{R}^2 & \quad \text{R}^1 \\
\text{R}^5 & \quad \text{R}^6 & \quad \text{N} & \quad \text{OH} \\
\text{hv} & & & \quad \text{R}^4 & \quad \text{R}^3 & \quad \text{R}^2 & \quad \text{R}^1 \\
& & & \quad \text{R}^5 & \quad \text{R}^6 & \quad \text{N} & \quad \text{CHO} \\
(15) & & & (16) & & & (17)
\]

\[
\text{NO}_2 & \quad \text{Cl} \\
\text{N} & \quad \text{O} \\
\text{hv} & & & \quad \text{R}^4 & \quad \text{R}^3 & \quad \text{R}^2 & \quad \text{R}^1 \\
\text{NOCI} & & & \quad \text{R}^4 & \quad \text{R}^3 & \quad \text{R}^2 & \quad \text{R}^1 \\
(18) & & & 5\% & & & (19)
\]

The photolysis of 4-nitroquinoline \( N \)-oxide (18) in the presence of nitrosyl chloride leads in low yield both to the compound formed by substitution of the nitro-group by chlorine and to the photolysis product of this, 4-chlorocarbostyril (19).\(^7\) Since no 4-nitrocarbostyril was detected it would seem more reasonable to postulate substitution followed by rearrangement than rearrangement followed by substitution. A free-radical mechanism is assumed.

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Photoreactions of Compounds with Heteroatoms other than Oxygen

Isoquinoline N-oxides are photolabile and yield both benz[f-1,3]oxazepines (20) and 2a,7a-dihydrobenzofuro[2,3-b]azete derivatives (21). The latter compound is suggested to be formed by a photoclosure of (20). Further it is reported that the back reaction [i.e. (21) to (20)] is thermally induced.

Tetrahydroacridine-N-oxide (22) has earlier been reported to give a good yield of the bridged oxazepine (23); the ketone (24) and the parent tetrahydroacridine are minor products of the reaction. The same workers have now investigated the reaction of acridine N-oxide, and find no analogue of the oxazepine type (25), but a high yield (70–80%) of the ketone (26), as well as small amounts (2–5%) of acridine. It is suggested that the oxazepine (25) is an intermediate in the reaction, but is so photolabile that it is efficiently converted to the ketone (26).

\[
\begin{align*}
\text{N} & \quad \text{R} \\
\text{O} & \\
(20) & \\
\rightarrow & \\
\text{R} & \quad \text{N} \\
\text{O} & \\
\text{hv} & \\
(21) & \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{hv} & \\
(22) & \\
\rightarrow & \\
\text{O} & \quad \text{N} \\
\text{hv} & \\
(23) & \\
+ & \\
\text{O} & \\
(24) & \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{hv} & \\
(25) & \\
\rightarrow & \\
\text{O} & \quad \text{N} \\
(26) & \\
\end{align*}
\]

The light-induced rearrangement of 6-substituted phenanthridine N-oxide (27) to 5-substituted phenanthridin-6(5H)ones (28) has been previously observed. However, as with the case of quinoline N-oxides the reaction is very solvent dependent, and while the (27) to (28) rearrangement occurs almost quantitatively in ethanol, the irradiation of (27) in benzene yields new products. The ketone (28) was still formed (16·7%), but compounds (29), (30), (1%); (31), (10.8%); and (32), (34.8%) were also obtained.

Scheme 1  Photochemical reactions of 6-substituted phenanthridine 5-oxides
Photoreactions of Compounds with Heteroatoms other than Oxygen

The formation of (29) is typical of N-oxide rearrangements and the low yield arises from its hydrolysis to (32), probably on the Florisil column used to separate the products; product (31), the result of a simple de-oxygenation, is also expected. On the other hand, the appearance of the carbazole (30) is not wholly expected. While its formation is formally analogous to the formation of indoles from quinoline N-oxides, compound (30) does not arise from a similar hydrolysis mechanism: in the present case, hydrolysis of (29) leads to (32) which is incapable of closure to the carbazole (30). Compound (30) is thus suggested to be produced by a direct route. The mechanism proposed for these transformations is outlined in Scheme 1.

Rearrangement of 5-membered ring heterocycle N-oxides has also been studied, with no unexpected results. Thus ring expansion occurs on irradiation of 2-phenyl-3H-indol-3-one N-oxide (33) to yield 2-phenyl-4H-3,1-benzoxazin-4-one (34) in a reaction analogous to the formation of

\[
\begin{align*}
(33) & \xrightarrow{\text{hv}} \begin{cases} (35) \rightarrow (34) \\
(36) & \rightarrow \begin{cases} (37) & \rightarrow \begin{cases} (38) & \rightarrow \begin{cases} (39) & \rightarrow \begin{cases} (40) & \rightarrow \end{cases} \end{cases} \end{cases} \end{cases}
\end{align*}
\]
oxazepines from the 6-membered ring compounds.\textsuperscript{13} The intermediacy of the oxaziridines (35) is naturally suggested in this transformation so characteristic of nitrones. The better yields in non-polar solvents have led these workers to suggest that in this case a polar mechanism is not operative. Analogous steroid nitrones have also been investigated. For example, compound (36) gave the expected oxaziridine (37) and the ketone (38), together with olefin (39) formed by elimination and dicarbonyl compound (40) formed by ring-opening.\textsuperscript{14} The oxaziridine (37) is suggested as intermediate in all these processes.

Photolysis of \( N \)-oxide derivatives of quinoxaline,\textsuperscript{15} quinazoline,\textsuperscript{16} and phthalazine\textsuperscript{17} systems have been reported. In the first case, the major product was the benzo[\( d \)][1,3,6]oxadiazepine (41);\textsuperscript{15} and quinazoline-3-oxides yielded benzo[\( f \)][1,3,5]oxadiazepines of type (42).\textsuperscript{16} In the photolysis of the 1-oxide (43) of the quinazoline system, the ring contraction product (44) is isolated, but the oxadiazepine (45) is suggested as the intermediate.\textsuperscript{14} The same workers also investigated the photolysis of a benzodiazepine-4-oxide (46), and isolated both ring contraction (47) and expansion (48) products; both are believed to arise from the common oxaziridine intermediate (49).

An oxaziridine intermediate (50) is also postulated to account for the reaction which results from the irradiation of phthalazine \( N \)-oxides (51) in

acetone.\textsuperscript{17} In the absence of oxygen, nitrogen is evolved from the reaction, and only one product 1,3-diphenylisobenzofuran (52), is initially formed. Continued photolysis yields several compounds of which the phthalazine (53) and 1,2-dibenzoylbenzene (54) have been identified. A tentative mechanism to account for the reaction has been put forward and involves the intermediate diazo-compound (55). The loss of oxygen from (51) to give (53) only occurred to any appreciable extent in the absence of flushing with nitrogen during photolysis, and the process parallels the behaviour of other aromatic amine N-oxides. In order to elucidate further the mechanism involved in such systems, the photolysis of 3,6-diphenylpyrazidine N-oxide (56) has been investigated.\textsuperscript{18} Ring-contraction to 3-benzoyl-5-phenylpyrazole (57) is observed and the intermediacy of a diazo-compound is again suggested. The formation of an intense yellow colour ($\lambda$ 410 nm), and the appearance of an absorption at 2070 cm$^{-1}$ in the i.r. spectrum of the irradiated pyrazidine N-oxide, strongly indicate that an azo-compound is also involved, as shown in Scheme 2. Both absorptions faded in the dark.

The photolysis of exocyclic N-oxides has been the subject of two reports this year. Photolysis of $N$-(2-oxo-3-indolylidine)-aniline N-oxide (58) has been shown to lead to ring expansion, and the formation of 3-phenyl-2,4-(1$H$,3$H$) quinazolinedione (59).\textsuperscript{19} With $\alpha$-$N$-diphenylnitrene (60) in methanol, irradiation again forms the oxaziridine (61), but this latter is unstable, and decomposes in the dark into a multicomponent mixture.\textsuperscript{20} The identified components of the mixture are cis- and trans-2-methoxyazobenzene, cis- and trans-4-methoxyazobenzene, three different methoxyphenylaminoazobenzenes, diphenylformamide, and benzanilide.

\textsuperscript{17} O. Buchardt, \textit{Tetrahedron Letters}, 1968, 1911.
Scheme 2
2 General Rearrangements of Nitrogen-containing Compounds

Numerous publications appear each year concerned with the photochemical rearrangement of various nitrogen-containing compounds. Many of these reports are isolated observations which have no obvious relevance to past literature, and are often concerned with such specialised systems that extension to other compounds is hardly justifiable. Thus the presentation of such researches is inevitably somewhat disjointed particularly when only twelve months of publication are under consideration.

Padwa and his co-workers have studied the effect of irradiation on the aziridine\textsuperscript{21} and azetidine\textsuperscript{22} systems with most interesting results. It has been previously reported that the molecular changes which occur on photolysis of 1-benzyl-2-phenyl-3-benzoyleaziridine are markedly dependent upon the initial stereochemistry,\textsuperscript{23} and this aspect has now been re-examined with an aziridine which has an \textit{N}-substituent bearing no \textit{\alpha}-hydrogen.\textsuperscript{21} Thus the irradiation of 1-t-butyl-2-phenyl-3-benzoyleaziridine has been investigated. The trans-isomer (62) gave two major products, 2,5-diphenyloxazole (63) and (\beta-t-buty lamino)-\textit{trans}-benzalacetophenone (64), and the minor products \textit{N}-t-buty benzalnine (65) and benzaldehyde. Two fundamental mechanisms may be postulated for this process: C–N ring cleavage followed by a 1,2-hydrogen shift, or a prior 1,5-hydrogen shift and subsequent ring-opening. The mechanism was tested by photolysis of the deuterio-compound (66) which gave one of the major products (64) with loss of 98\% of the deuterium, thereby suggesting that a 1,2-shift is not operative. Photolysis of the \textit{cis}-isomer of (62) provides further evidence for the second mechanism since only (63) and (65) are formed, and none of (64).

The photolysis of the analogous four-membered ring system (67) has been reported, and leads to ring expansion with the formation of \textit{N}-substituted pyrroles (68) and (69).\textsuperscript{24} The mechanism of the reaction has been

investigated, and evidence for 1,3-diradical intermediates (70) and (71) has been obtained by carrying out the rearrangement with the appropriate deuterated compounds (72) and (73).\textsuperscript{22}

Ring contraction with the formation of nitrogen-containing side-chains is observed in the photolysis of both 5-phenylpyrazolines\textsuperscript{25} and 5-pyrazolidones.\textsuperscript{26} In the former case, photolysis in benzene of 1-methyl-, and 1,3-dimethyl-5-phenyl-\(\Delta^2\)-pyrazolines (74) and (75) yields cis- (76) and trans- (77) isomers of the cyclopropane system. 5-Phenyl-\(\Delta^2\)-pyrazoline (78), on the other hand, undergoes complete ring cleavage to yield benz- and cinnamald-azines (79) and (80), as well as the mixed aldazine (81). 3-Methyl-1-phenyl-5-pyrazolidone (82) undergoes a novel ring-contraction reaction to form (83) in 70—80% yield, but the 2,3-dimethyl derivative (84) is inert under the same conditions. The reaction would, therefore, seem to involve N—C=O cleavage with a 1,3-hydrogen shift, but in the absence of further details, no mechanistic proposals can usefully be made.

Thiophens, isoxazoles, and certain pyrazoles and imidazoles are known to undergo transposition of ring carbon atoms on photolysis in a manner which is reminiscent of benzene derivatives, and which proceeds at least in one case by a ring contraction-expansion sequence. By contrast, 1\(H\)-1,2,3-

\textsuperscript{26} S. N. Ege, Chem. Comm., 1968, 759.
Triazoles and 1,2,4-oxadiazoles undergo cleavage reactions. A new photocleavage has now been reported for 1,2,5-thiadiazoles, 2H-1,2,3-triazoles, and 1,2,5-oxadiazoles in which two of the ring bonds are broken.\cite{cantrell1968}

Thus compounds (85) and (86) yield elemental sulphur, and benzonitrile and acetonitrile respectively. The dimethyltriazole (87) yields the expected nitrile. Evidence for formation of the diradical (88) in the latter reaction is obtained by isolation of its adduct (89) with cyclopentene. Oddly enough, the diphenyl derivative (90) is reported to be photostable. Diphenyl 1,2,5-oxadiazole (91) yields benzonitrile and phenyl isocyanate on photolysis in ether, and the dimethyl compound (92) forms acetonitrile and tarry products. In the latter case, however, the formation of the N-oxide of acetonitrile (93) may again be assumed since the adduct (94) has been isolated from reactions carried out in the presence of cyclopentene. Other

workers have also examined the photolysis of 3,4-diphenyl-1,2,5-oxadiazole (91), but in benzene solution, and report not only the formation of benzonitrile, but also 3,5-diphenyl-1,2,4-oxadiazole (95) and diphenylfuroxan (96).\textsuperscript{28} The earlier publication did not report the formation of either of the latter two compounds, but here the photolyses were carried out in methanol and ether. The second group of workers, however, report that irradiation of the oxadiazole (91) in methanol yields methyl benzoate, phenacyl alcohol, (95), benzamide, and benzonitrile.\textsuperscript{28} The fact that irradiation of (91) in excess of benzonitrile leads to an increase in the formation of (95) is evidence for the double fragmentation pathway postulated by the former workers. The oxadiazole (95) has been shown to be photolabile, and in aprotic media yields (97), (98), and a trace of (99).\textsuperscript{29} In protic solvents, such as methanol, (98) and (110) are formed.\textsuperscript{30} Formation of (98) implicates an intermediate species such as (101) which yields (98) by intramolecular cyclisation and hydrogen transfer.

The irradiation of 4-hydroxy- and 4-alkoxy-3-pyrazolin-5-one derivatives (102) leads to ring cleavage with the formation of \( \beta \)-diketones (103).\textsuperscript{31}

The phototransposition reaction in the indazole series to give a benzimidazole (104) has been investigated with respect to variations of quantum yield with exciting wavelength, solvent, temperature, and concentration.\textsuperscript{32} It has been assumed from theoretical considerations based on the change in bond orders upon excitation that the reaction occurs from the lowest excited singlet state, and this assumption is compatible with the sensitiser and quencher experiments which have been performed.


Photoreactions of Compounds with Heteroatoms other than Oxygen  

\[ \begin{align*}
\text{N} & \quad \text{N} \\
\text{S} & \quad \text{N} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\begin{array}{c}
\text{hv} \\
\text{RCN} + S
\end{array}
\end{align*} \\
\text{(85) R = Ph} \\
\text{(86) R = Me}
\]

\[ \begin{align*}
\text{N} & \quad \text{N} \\
\text{R'} & \quad \text{R'} \\
\text{N} & \quad \text{N} \\
\end{align*} \\
\text{hv} \rightarrow \text{RCN} + \text{R}^* \begin{array}{c}
\text{C} = \text{N} \quad \text{N} \quad \text{R} \\
\begin{array}{c}
\text{hv}
\end{array}
\end{array}
\]

\text{(87) R' = Me} \\
\text{(90) R' = Ph}

\[ \begin{align*}
\text{N} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph} \\
\text{hv} & \rightarrow \text{PhCN} + \text{PhNCO}
\end{align*} \\
\text{(91)}

\[ \begin{align*}
\text{N} & \quad \text{N} \\
\text{Me} & \quad \text{Me} \\
\text{hv} & \rightarrow \text{MeCN} + \text{Me} \begin{array}{c}
\text{C} = \text{N} \quad \text{O} \\
\begin{array}{c}
\text{hv}
\end{array}
\end{array}
\]

\text{(92)}

\[ \begin{align*}
\text{N} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph} \\
\text{hv} & \rightarrow \text{PhCN} + \text{PhCN} \rightarrow \text{O}
\end{align*} \\
\text{(91)}

\[ \begin{align*}
\text{Ph} & \quad \text{N} \\
\text{N} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{hv} & \rightarrow \text{PhCN} + \text{PhCN} \rightarrow \text{O}
\end{align*} \\
\text{(95)}

\[ \begin{align*}
\text{Ph} & \quad \text{N} \\
\text{N} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{hv} & \rightarrow \text{PhCN} + \text{PhCN} \rightarrow \text{O}
\end{align*} \\
\text{(96)}

Ring expansion leading to a useful synthesis of 1H-1,2-diazepine (105) has been reported to occur on irradiation of pyridinium ethoxyamidate (106).\textsuperscript{33} The photoisomerisation of pyridinium ylides (C\textsubscript{6}H\textsubscript{5}N\textsuperscript{+}N\textsuperscript{-}R) to 1-substituted 1,2-diazepines seems to be a general reaction, and provides a series of new diazepines which in the current work have been characterised by formation of iron tricarbonyl complexes. The obvious intermediate

\textsuperscript{33} J. Streith and J. M. Cassal, \textit{Tetrahedron Letters}, 1968, 4541
(107) is suggested to account for the photolysis results. The photorearrangement of anthranils (e.g. 108) in methanol also leads to ring expansion and the formation of azepines. The suggested mechanism involves N–O bond cleavage followed by ring closure to give what is described as the resonance-stabilised aziridine derivative (109). Probably a more reasonable intermediate for the reaction is the resonance-stabilised aryl nitrene (109a) which could undergo rearrangement to (109b). Rupture of the C–C bond in either (109b) or (109) and addition of solvent to the seven-membered ring ketimine (110) give the observed product. In the case of (109b), addition of methanol may occur directly to give the product.

Photocyclisations analogous to those reported for monocyclic polyene hydrocarbon systems have been observed in the heterocyclic series. Irradiation of dimethyl-1,2-dihydropyridazine-1,2-dicarboxylate (111) in

---

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\[
\begin{align*}
\text{(108)} & \xrightarrow{hv} \text{(109)} \xrightarrow{hv} \text{(109a)} \xrightarrow{hv} \text{(109b)} \\
\text{(110)} & \xrightarrow{\text{MeOH}} \text{(111)} \xrightarrow{hv} \text{(112)} + \text{(113)} \\
\text{(114)} & \xrightarrow{hv} \text{(115)} \\
\text{(116)} & \xrightarrow{hv} \\
\text{(117)} & \xrightarrow{hv} \text{products}
\end{align*}
\]


ether yields, as the major product, the expected bicyclo-compound (112), but the pyrrole derivative (113) is also isolated as a minor product.\textsuperscript{35} The pyrrole is suggested to arise by an initial ring opening of (111) to form (114). A photochemical ring closure reaction of the triene to the aziridine derivative (115), followed by thermal rearrangement, would produce (113); but attempts to detect such intermediates were unsuccessful. Similar photocyclisations have been reported for the seven-membered heterocyclic systems 2,3-dihydro-1,2-diazepine ketones (116) and carbinols (117).\textsuperscript{36} In these examples the rate of reaction is affected by substituents in a manner which for the ketones is roughly the converse of that for the carbinols. Thus the rates of photocyclisation decrease in the order \( R = \text{Me} \approx \text{CH}_2\text{CH}_2\text{CN} > \text{H} > \text{COPh} \approx \text{COMe} \) for the ketone, while the order for the alcohol is \( R = \text{COMe} \approx \text{COPh} > \text{Me} \approx \text{H} \). The photochemical formation of a bicyclo[3,1,0]hexene derivative has been observed in an heterocyclic compound, and constitutes the first example of rearrangement of a 2,3-benzoazoxine (118) to a fused oxaziridine (119); the yield is almost quantitative.\textsuperscript{37} Mechanistic studies of the reaction are in progress, but it would seem that \( \text{C} = \text{O} \) bond rupture must be a first step, followed by attack on the \( \text{C} = \text{N} \) moiety by the resulting fragments. The methoxyazabullvalene (120)\textsuperscript{38} and benzabullvalene\textsuperscript{39} form a series of valence bond tautomers on irradiation.

This year has seen the report of several examples of light-induced intramolecular ring closure reactions involving a nitro-group or an amine. Thus while the triphenylaziridine (121) in alcoholic solvents yields benzacetals, \( N \)-benzylaniline, benzalaniline, and alkyl benzyl ethers, 1-(2,4,6-trinitrophenyl)-2,3-diphenylaziridine (122) undergoes a ring closure to form 1-hydroxy-2-phenyl-4,6-dinitrobenzimidazole (123) in 95% yield.\textsuperscript{40} Benzaldehyde is a by-product of the reaction. A possible sequence to account for the reaction has been put forward and involves formation of an oxadiazepine (124). By similar reaction, 1-(2,4-dinitrophenyl)-2-phenyl-3-benzoylaziridine gives a 96% yield of 1-hydroxy-2-phenyl-6-nitrobenzimidazole. It is known that with \( \alpha \)-nitrobenzyl compounds, photochemical reaction involves attack of the nitro group on the \( \alpha \) carbon atom.\textsuperscript{41} Nitro \( p \)-di-t-butylbenzene (125) is photolabile, as shown, and here the process involves \( \beta \) attack.\textsuperscript{42} The reaction is carried out in the presence of hydroxyl ions; the yield drops in neutral media. Unidentified neutral products were also formed.

\textsuperscript{37} B. Singh, \textit{J. Amer. Chem. Soc.}, 1968, 90, 3893.
\textsuperscript{41} See, for example, J. A. Baril trop and N. J. Bunce, \textit{J. Chem. Soc. (C)}, 1968, 1467.
\textsuperscript{42} D. Döpp, \textit{Chem. Comm.}, 1968, 1284.
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\[ \begin{align*}
&\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
&\text{N} \quad \text{O} \quad \text{Ph} \quad \text{Ph} \\
&\text{(118)} \quad \text{hv} \quad \text{Ph} \quad \text{Ph} \\
&\text{N} \quad \text{O} \\
&\text{(119)}
\end{align*} \]

Diaminated derivatives of 2,5-dimethyl-\(p\)-benzoquinone (126)\(^4\) and the di-imine derivative (127)\(^4\) are converted photochemically into the benzoxazolines (128) and benzimidazoles (129). The example chosen for the latter reaction also necessitates the elimination of benzenesulphinic acid. The reactions would seem to be general and allow the synthesis of such compounds as (130).

A simple photochemical method for the synthesis of \(\beta\)-carbolines from indole derivatives in fairly good yield has been reported.\(^4\) \(\text{L-Tryptophan (131) in glacial acetic acid and in the presence of a sensitiser, such as Rose Bengal or methylene blue, undergoes a process of photocyclohydrogenation involving the amino-group to give 1-methyl-3-carboxy-\(\beta\)-carboline (132). Decarboxylation of (132) or the intermediate (133) yields 1-methyl-\(\beta\)-carboline (134).}\)

2-Hydroxy-\(\beta\)-lactams (135) and (136) and 4-oxazolidinones (137), (138), and (139) have been synthesised from 2-oxoamides (140) and (141) by

Photochemistry

(121) \[ \text{Ph}_3\text{N} \]
(122) \[ \text{Ph}_3\text{N} \]
(123) \[ \text{Ph}_3\text{N} + \text{N}_2 \text{O}_3 \]
(124) \[ \text{Ph}_3\text{N} \]
(125) \[ \text{Ph}_3\text{N} \]
(126) \[ \text{Me}_2\text{N} \]
(127) \[ \text{Me}_2\text{N} \]
(128) \[ \text{Me}_2\text{N} \]
(129) \[ \text{Me}_2\text{N} \]
(130) \[ \text{Me}_2\text{N} \]
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\[
\begin{align*}
\text{(131)} & \xrightarrow{\text{hv}} \text{(133)} \\
\text{(140)} & \xrightarrow{\text{hv}} \text{(132)} & \text{(134)} \\
\text{(137)} & + \text{(138)} & \text{(135)} \\
\text{(141)} & \xleftarrow{\text{hv}} \text{(139)} & \text{(136)}
\end{align*}
\]

photocyclisation involving an evidently easy attack of the carbonyl group on the carbon atom α to the nitrogen.\(^4\)

Chapman first reported the photorearrangement of a nitro-olefin (142) to a keto-oxime (143) in 1966.\(^5\) Since this time several groups have investigated the reaction with more complex systems, and while in many cases the reaction follows the expected course, a different pathway may sometimes be followed. Such is the case with the photolysis of 3-(2-


Here the oxindole (145) and its cis- and trans-isomers are formed. The rearrangement can most easily be rationalised through cleavage of the cyclic intermediates (146) and (147) to the oxindole; an analogous cyclisation of a $\alpha,\beta,\gamma,\delta$-unsaturated ketone to a pyran has been previously observed. The carbohydrate nitro-olefin (148) irradiated at 253.7 nm in acetone gives a complex mixture from which three of the major components have been isolated. These products are the trans-isomer of (148) and cis- and trans-isomers of 6,8-dideoxy-1,2 : 3,4-di-O-isopropylidene-$\alpha$-D-galacto-oct-5-enos-7-ulose (149). Such formation of the

\[
\text{PhCH} = \text{C} \quad \text{Me} \quad \xrightarrow{\text{hv}} \quad \text{Ph} \quad \text{C} \quad \text{C} \quad \text{Me}
\]

\[
(142)
\]

\[
\text{Me}
\]

\[
(143)
\]

\[
\text{Me}
\]

\[
(144)
\]

\[
\text{HO}
\]

\[
(145)
\]

\[
(146)
\]

\[
(147)
\]

\[
\text{Me}
\]

\[
(148)
\]

\[
\text{Me}
\]

\[
(149)
\]

$\alpha,\beta$-unsaturated carbonyl compound (149) is of interest to sugar chemists because of the resemblance to the Nef reaction, a procedure widely used in the synthesis of monosaccharides.

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The irradiation of oximes has been reported to give carboxamides by a photo-Beckmann reaction, together with nitriles: \(^{51}\) \(\text{syn-anti}\) isomerisation also occurs. \(^{53}\) The photo-Beckmann reaction has been investigated in some detail, and it has been shown by \(^{18}\)O-labelled compounds that an intramolecular oxygen-migration is involved, since no exchange was observed with benzaldoxime in the presence of \(p\)-tolualdoxime. \(^{64}\) The highest quantum yield for benzamide production is 0.034 and this drops to 0.002 in the presence of triplet sensitiser; thus a singlet pathway is preferred. Results from low temperature irradiations suggest the intermediacy of an oxaziridine in the rearrangement, and indeed the irradiation of phenylmethylloxaziridine does give the expected amide, thereby supporting an earlier suggestion. \(^{61}\) It is possible that the reaction is induced by abstraction of benzylic hydrogen by small amounts of benzaldehyde produced thermally. The \(\text{syn-anti}\) isomerisation is, however, the major process (quantum yield for \(\alpha\beta = 0.4\) and for \(\beta\alpha = 0.38\) in the case of benzaldoxime), and the authors think that it probably involves the triplet state since it may be sensitised; but see remarks in the Introduction. In a single reported example of an aralkyl ketoxime (\(p\)-anisylmethyl ketoxime), the irradiation products show that both aryl and alkyl migration occurs. \(^{64}\) The intermediacy of an oxaziridine in the photolysis of oximes has been further substantiated by Oine and Mukai with the irradiation of the oxime of 1,1-dimethyl-2-naphthalenone (150). \(^{55}\) An unstable compound is formed in the irradiated solution. On concentration of the solution, this compound decomposes to give the amide (151), the saturated ketone (152), and the unsaturated ketone (153), as well as nitrogen and hydrazine. Evidence for the oxaziridine (154) in this solution was obtained by reconversion into \(\text{syn-}\) and \(\text{anti-}\)oximes through refluxing the acidified benzene solution, and the ability of the irradiated solution to liberate iodine from potassium iodide. In the presence of a Schiff’s base, the irradiated solution formed a diaziridine derivative (155) and the unsaturated ketone (153). These reactions are typical of oxaziridines. Irradiated solutions of other oximes were also shown to liberate iodine from potassium iodide. From the absence of quenching of the reaction by oxygen and piperylene, a singlet mechanism is also favoured by Oine and Mukai for the photo-Beckmann reaction. \(\text{Syn-}\) and \(\text{anti-}\)isomers of semicarbazones have also been prepared by irradiation. \(^{56}\)

Azothemines have a weak \(n\pi^*\) absorption in the 230—250 nm region. Irradiation in this band does not, however, lead to a reaction analogous to the Norrish Type II cleavage of aliphatic ketones. Thus \(N\)-(1,3-dimethyl-

\(^{51}\) J. H. Amin and P. de Mayo, \(\text{Tetrahedron Letters}\), 1963, 1585.

\(^{52}\) G. Just and C. Pace-Asgiat, \(\text{Tetrahedron}\), 1966, 22, 1069.

\(^{53}\) G. Ciamician and P. Silber, \(\text{Ber.}\), 1903, 36, 4268.


butylidene)-butylamine (156) gives compounds (157), (158), and (159).\textsuperscript{57} It was found that reaction of (156) with (158) in the dark gave (157) and (159). The reaction is rationalised by the diradical intermediate (160).

It has recently been reported that the photolysis of enamides in methanol gives vinylogous amides by acyl rearrangement.\textsuperscript{58} The photochemistry of a


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cyclic enamide in methanol, cyclohexylamine, or n-butylamine has now been investigated, and an α-cleavage reaction has been observed. Thus the enamide (161) yields oxocarboxylic acid derivatives via, it is suggested, a keten enamine (162); the final step involves hydrolysis of the enamine. Such behaviour is analogous to that observed in the photochemistry of cycloalkanones. A cleavage reaction is also observed with the somewhat related compound dihydrothymidine which in contrast to dihydrouridine undergoes selective photochemical hydrolysis of the Ciamician–Silber type. The reaction is well known for homocyclic systems, but this is the first reported example with an heterocyclic compound of biological significance. Thus the dihydrothymidine (163) yields (S)-(-)-dihydrothymine, n-propylurea, and N1-deoxyribose-N1-n-propylurea. Dihydrothymine (164) gives 75% n-propylurea and 5% urea. A pathway involving initial C(4)—C(5) bond fission is shown to occur by studying the incorporation of deuterium from deuterium oxide into the urea and carrying out the photolyses in methanol in order to trap the isocyanate (165).

The synthesis of γ- and δ-chloroalkanesulphonamides by the photorearrangement of N-chlorosulphonamides (RCH₂CH₂CH₂CH₂SO₂NClR⁻)

\[ \text{(161)} \xrightarrow{\text{hv}} \text{(162)} \]

(for RH, see text).

\[ \text{(163)} \xrightarrow{\text{hv}} \text{(165)} \]

\[ R^1 = \text{deoxyribose (163)} \]
\[ R^1 = \text{H (164)} \]

---

has been reported, and the reaction has been shown to be fairly general.\textsuperscript{61} The \(N\)-butyl compound yields the \(\gamma\)- and \(\delta\)-chloro derivatives, but the \(N\)-methyl compound (R\(^1\) = Me) yields \(\beta\)-chlorobutane sulphonamide as well as the \(\gamma\)- and \(\delta\)-compounds. In acid solution the rate of formation of the \(\gamma\)-chloro-derivatives increases whereas that of the \(\beta\)-chloro-isomer decreases owing to the relatively higher reactivity of the protonated sulphonamide radical for intramolecular hydrogen abstraction.

Certain ketophosphites undergo a ready intramolecular rearrangement which represents a new pathway for photoexcited ketones.\textsuperscript{62} Thus dimethyl-\(\beta\)-keto ethyl phosphites (166) are converted into dimethyl vinyl phosphates (167). In solvents with readily abstractable hydrogens, intermolecular reactions become important, and lead to such compounds as the phosphonate (168); here only small amounts of the rearranged product are observed. Presumably the phosphonate (168) is formed by a photo-Arbuzov

\[
\begin{align*}
R-COCH_2OP(OMe)_2 & \xrightarrow{\text{hv}} MeO-P-OP(OMe)_2 \quad \text{(166)} \\
R = \text{Me or Ph} \\
\xrightarrow{\text{hv}} & \xrightarrow{\text{hv}} \\
R-C=CH_2OP(OMe)_2 & \quad \text{(169)} \\
MeCCH_2Cl + P(OC_2H_5)_3 & \xrightarrow{\text{hv}} MeC\equiv CH_2 + MeCOCH_2P(OC_2H_5)_2 \quad \text{(168)} \\
\| O & \xrightarrow{\text{hv}} O=P(OC_2H_5)_2 \quad \text{(170)} \\
MeCOCH_2P(OC_2H_5)_3 & \xrightarrow{\text{hv}} + OP(OC_2H_5)_3 + C_2H_5P(OC_2H_5)_2 \quad \text{(171)} \\
& \| O \\
[MeCOCH_2P(OC_2H_5)_3][\text{Cl}^-] & \xrightarrow{\text{hv}} MeCOCH_2P(OC_2H_5)_2 + C_2H_5Cl \quad \text{(172)} \\
& \| O
\end{align*}
\]


rearrangement of the phosphite (169). Both reaction paths are completely quenched by biacetyl, a fact which suggests triplet intermediates. The photochemical reaction of ethereal solutions of chloroacetone with triethyl phosphate also yields a vinyl phosphate (170) in addition to the keto-phosphonate (171). The yield of the latter compound is decreased by radical scavengers whereas that of (170) remains unaffected. The formation of (171) is suggested to arise from the keto quasi-phosphonium salt (172) by a radical mechanism involving initial C—Cl cleavage.

3 Synthesis and Substitution of Nitrogen-containing Compounds

The photo-oximation of saturated hydrocarbons is an extremely important industrial process particularly with cyclohexane, where the product is converted into ε-caprolactam, and subsequently into nylon-type polymers. The process, occasionally referred to as the Tübingen photo-oximation reaction, has reached this satisfactory state of development mainly owing to the efforts of Japanese and German workers. It is fitting, therefore, that Professor Müller of Tübingen has written a review on the topic. The development has come far from Lynn’s original observation in 1919 that small yields of a mixture of various n-heptanone oximes are produced when n-heptane and nitrosyl chloride are exposed to sunlight. In the oximation reaction of today, nitrosyl chloride is replaced by a mixture of nitric oxide and chlorine, with hydrogen chlorine as a catalyst. The interest in the reaction has centred mainly around cyclic alkanes, although reactions with n-alkanes and branched alkanes have been reported. Cyclopropane is inert in the reaction, but other cycloalkanes give the desired product in up to 90% yield. The reaction is subject to steric hindrance; thus whereas cyclohexane yields 90% of the oxime, 1,4-di-t-butyl cyclohexane forms the oxime only in 5% yield. By-products have also been investigated. The reaction has been shown to occur with a variety of bridged ring hydrocarbons (173) as well as phenyl-substituted alkanes (174) and decalins (175). All wavelengths shorter than 600 nm are fruitful of reaction, but the purity of the final product is very wavelength dependent, and removal by suitable filters of the shorter wavelength u.v. radiation results in a purer product (99%), an important industrial consideration, at an acceptable sacrifice in quantum yield. Several workers have investigated the quantum yield of the reaction, but measurement is complicated by the insolubility of the oxime hydrochloride in cyclohexane; the accuracy of early measurements may be in doubt. There does appear to be a small dependence of quantum yield upon wavelength of exciting light, but generally a value of approximately 0.7 is reported. The general reaction scheme for the process is

outlined in Scheme 3. Excess of nitric oxide gives a nitroso-compound whereas excess of chlorine yields the blue 1,1-chloronitroso-compound (176). The best yields of desired product are obtained with a NO : Cl₂ ratio of 2:25 : 1. The conclusion drawn from a full mechanistic study of the reaction is that a free-radical process does not operate under the usual reaction conditions, unlike the case of photochlorination, but that a cage four-centre reaction (177) of an excited nitrosyl chloride molecule is involved. Further to the photo-oxidation reports, Müller and his co-workers have reported the photocyanation of hydrocarbons by CICN, photosulphochlorination with SCl₂, and photophosphonylation by CIPO(OR)₂ to yield products (178), (179), and (180) respectively.

Elad and Sperling report the acetone-initiated selective photochemical alkylation of glycine residues in dipeptides with the formation of residues of leucine, norleucine, and phenylalanine, by reaction of the peptide with isobutene, but-1-ene, and toluene respectively. In glycine dipeptides the α-carbon atoms are in a 1,4-relationship with each other (—NH·CH₂·CO·NH·CHR·CO—) leading to an asymmetric induction process with the chiral centre of the α-carbon of the branched amino-acid residue as an asymmetric agent. The same workers have also investigated such alkylation of glycyl-alanine and glycyl-leucine dipeptide derivatives

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\[ x \text{NO} + y \text{Cl}_2 + z \overset{\text{hv}}{\longrightarrow} \]

\[
\begin{align*}
\text{NO} + \text{HCl} + & \quad \text{CN} \\
& \quad \text{SCl} \\
& \quad \overset{\text{hv}}{\longrightarrow} \quad \overset{\text{hv}}{\longrightarrow} \\
\text{NOCI} + & \quad \overset{\text{hv}}{\longrightarrow} [\cdot \text{NO} + \cdot \text{Cl}] \\
& \quad \overset{\text{hv}}{\longrightarrow} \\
\text{Scheme 3  Reaction scheme for photo-oxidation}
\end{align*}
\]

\[ (178) \quad (179) \quad (180) \]

\[ \text{X-Gly-Gly-OMe} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{X-Nle-Gly-OMe} \]
\[ \text{MeCH}_2\text{CH}=\text{CH}_2 \quad \text{Acetone} \quad \text{X-Gly-Nle-OMe} \]

\[ \text{X-Gly-Gly-OMe} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{X-Phe-Gly-OMe} \]
\[ \text{Toluene} \quad \text{Acetone} \quad \text{X-Gly-Phe-OMe} \]

\[ \text{Me} \quad \overset{\text{but-1-ene}}{\overset{\text{hv}}{\longrightarrow}} \quad \text{Me} \]
\[ \text{CF}_3\text{CONHCHCONHCHCO}_2\text{Me} \quad \text{Acetone} \quad \text{CF}_3\text{CONHCHCONHCHCO}_2\text{Me} \]
\[ \text{Tfa-Gly-L-Ala-OMe} \quad \text{Bu}^n \]
\[ \text{Tfa(C+D)-Nle-L-Ala-OMe} \]
with but-1-ene, and the norleucine residue formed involves two enantiomers in unequal amounts.\textsuperscript{71} The results indicate a 1,4-asymmetric induction effect operating through a free-radical mechanism. Alkylation of 4-methylcinnoline (181) by irradiation in ethers has also been observed; the reaction is formally a 1,4-photoaddition of the ether.\textsuperscript{72}

![Diagram](image)

An interesting synthesis of organic nitrogen compounds has been reported by a group of Italian workers and involves the irradiation of aqueous solutions of ethylene glycol and hydroxylamine.\textsuperscript{73,74} The mixture obtained contains 23 components by paper chromatography, nine of which are the amino-acids lysine, aspartic acid, glutamic acid, histidine, glycine, β-alanine, γ-aminobutyric acid, α-alanine, and tyrosine; ethanolamine and urea are also present. The reaction, however, shows a low quantitative yield, and inorganic oxides and chlorides have been examined as sensitisers. While titanium dioxide and copper(II) chloride showed higher activity for conversion of hydroxylamine, the total yield of the organic nitrogen compounds was not significantly improved. Titanium dioxide did, however, show a high selectivity of photosynthesis of ninhydrin derivatives.

The light-induced amidation of crotonic acid and its esters with formamide gives a 60–70\% yield of 1:1 adducts.\textsuperscript{75} The product distribution differs in the acid and esters and whereas the former gives a 41:28:31 ratio of 2-, 3-, and 4-carboxylbutyric acids (182), (183), and (184), the methyl ester forms

\[
\text{MeCH} = \text{CHCOX} \xrightarrow{\text{hv}} \text{MeCH}_{\text{2}} \text{CHCOX} \quad \text{MeCHCH}_{\text{2}} \text{COX} \\
(X = \text{OH or OMe})
\]

(182) \quad (183) \quad (184)

the corresponding esters in the ratio 8:41:51. It was confirmed that the γ-adduct (184) resulted from addition of formamide to the β,γ-unsaturated acid or ester which had been produced by photoisomerisation of the

\textsuperscript{73} A. Zamorani, P. G. Pifferi, G. Lanyorini, and A. Riva, \textit{Gazzetta}, 1968, 98, 468.
\textsuperscript{74} A. Riva and A. Zamorani, \textit{Gazzetta}, 1968, 98, 822.
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α,β-compounds. An analogous reaction of the acid and ester with aniline gave different yields and distributions according to the conditions, but the acid gave essentially pure β-adduct, and the ester gave mainly the α-adduct. The behaviour of terminal acetylenes has also been examined in such photoamidation reactions; the main products are 2:2 adducts. On the other hand, non-terminal acetylenes form 1:2 photoadducts (186) with formamide. The reaction is carried out in the presence of benzophenone, and is summarised in Scheme 4. It is possible to observe a ‘crossed’ reaction;

\[
\begin{align*}
\text{HCONH}_2 + \text{PhC}=O \xrightarrow{h\nu} \text{RC}=\text{CONH}_2 \xrightarrow{\text{R}=\text{CH}} \text{RC}=\text{CHCONH}_2 \\
\text{RC}=\text{CR}^1 \xrightarrow{\text{RH}} \text{RCH}=\text{CHCONH}_2 \\
\text{RC}=\text{C} \xrightarrow{\text{RH}} \text{RCH}=\text{CONH}_2 \\
\text{RCH}=\text{C} \xrightarrow{\text{RH}} \text{RCH}=\text{C} \xrightarrow{(1) \text{RC}=\text{CH}} \text{H}_2\text{CONC} \xrightarrow{(2) \text{RH}} \text{HC}=\text{CHR} \\
\text{RCH}=\text{C} \xrightarrow{\text{R}^1} \text{RCH}=\text{C} \xrightarrow{\text{RH}} \text{RCH}=\text{CHCONH}_2 \\
\text{RCH}=\text{C} \xrightarrow{\text{R}^1} \text{RCH}=\text{CONH}_2 \\
\text{RCH}=\text{C} \xrightarrow{\text{R}^1} \text{RCH}=\text{CHCONH}_2 \\
\text{RCH}=\text{C} \xrightarrow{\text{R}^1} \text{RCH}=\text{CHCONH}_2 \\
\text{Me(CH}_2)_2\text{CH}=\text{CHCONH}_2 \\
\text{H}_2\text{CONC} \xrightarrow{\text{HC}=\text{CH(CH}_2)_2\text{Me}} \\
\end{align*}
\]

Scheme 4 Reaction of terminal acetylenes with formamide

for example compound (187) is formed from formamide, oct-2-enamide, and pent-1-yne.

Cyanamides, and in particular N-cyanopiperidine, have been shown to undergo photohydration to urea derivatives in the presence of dilute acids by excitation through the \( n \rightarrow \pi^* \) band in the 260 nm region. The reaction

can be sensitised by acetophenone, and the common, but dubious, conclusion is drawn that it is a triplet process. As commented elsewhere in this Report, such a conclusion is really only valid for the sensitised process. The triplet energy of the cyanamide is assessed at 76 kcal/mole. The mechanism suggested for the process is outlined in Scheme 5. This pathway does not deviate in the presence of olefins.

\[
\begin{align*}
H^+ + \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{N} \quad \rightleftharpoons \quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{N} - \text{H} \\
\text{hv} &\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{N} - \text{H} \quad \text{Excited singlet} \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{N} - \text{H} \quad \text{Triplet} \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{NH}_2 \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{NH}_2 \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{NH}_2 \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{NH}_2 \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{NH}_2 \\
&\quad \downarrow &\quad \overset{\cdot}\text{N} &\overset{\cdot}\text{C} = \text{NH}_2 \\
\end{align*}
\]

**Scheme 5**  
*Photohydration of cyanamides*

The formation of aliphatic nitroanions has been detected by e.s.r. spectroscopy in the irradiation of a basic aqueous solution containing an aliphatic compound and nitrite ions. The radicals are formed by replacement of a hydrogen atom of the compound by nitrite ion. Such nitroanions have been produced from formate, acetate, and propionate ions as well as acetone, methanol, butan-2-one, acetamide, ethylamine, and triethylamine. Nitroanions were also observed in the irradiation of basic aqueous or alcohol solutions containing the corresponding nitroalkane.

The photohydration of pyrimidines and the photoaddition of alcohols to purines have attracted the attention of several research groups. Wang and co-workers have examined the effect of substituents on both the photohydration and the photodecarboxylation of pyrimidines. Their intensive researches have shown the importance in photohydration of both steric and electronic effects of the substituents. The rates of hydration of all N(1)-substituted uracils at pH 7 are higher than those of uracil itself, while the rates of N(3)-substituted uracils are lower. A 4 to 10-fold

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rate increase is observed as the N(1)-substituents become more electron-withdrawing. The rate of the reaction is also dependent upon the pH. Thus at pH 2 where protonated quaternary N(1) is favoured, the hydration rates for uracil and 3-methyluracil approach those of N(1)-substituted uracils, and are six and eight times greater than at pH 7. The quaternary N(1) and N(3) mesomeric species (188) and (189) are implicated as intermediates; they evidently react with water to yield either the hydration

\[
\begin{align*}
\text{O} & \xrightarrow{\text{hv}} \text{O}^- \\
\text{N} & \xrightarrow{\text{H}_2\text{O}} \text{O}^- \\
\text{R} & \xrightarrow{\text{H}_2\text{O}} \text{O}^- \\
\text{R} & \xrightarrow{\text{H}_2\text{O}} \text{O}^- \\
\text{N} & \xrightarrow{\text{H}_2\text{O}} \text{O}^- \\
\text{R} & \xrightarrow{\text{H}_2\text{O}} \text{O}^- \\
\end{align*}
\]

product (190) or, from (188), the starting pyrimidine. The rate dependence of this hydration reaction upon pH has been reported by other workers who consider that the effect is best understood in terms of a mechanism which involves protonation of singlet excited uracil molecules.\(^8^1\) The main product-forming reaction is between the excited \(1^*(\text{UH})\) and a neutral water molecule. The transformation of 5-ethyl-deoxyuridine (191) to deoxyuridine (192) induced by 253.7 nm radiation is suggested to occur through hydration of the 5,6-bond and elimination of ethanol.\(^8^2\) Dimers of pyrimidines are

generally formed in all these reactions, but in the 5-ethyldeoxyuridine case the use of wavelengths longer than 265 nm leads to photodimerisation as the principal reaction, and a pronounced effect of oxygen.

Until recently, purines were generally considered to be less reactive photochemically than pyrimidines, and it has been claimed that purine moieties in nucleic acids participate in the physical processes such as absorption, energy transfer, etc., rather than undergo chemical changes.83 But Linschitz and Connolly have reported in two publications that irradiation of deoxygenated solutions of purines leads to an efficient addition of ω-hydroxyalkyl groups to the 6-position of the purine to yield, for example, compound (193).84 The reaction has a quantum yield of ca. 0.2 at 254 nm, and appears to be general as shown by experiments on pyrimidine and several other simple nitrogen heteroaromatic compounds such as pyridine, pyrazine, 1,4,5-triazanaphthalene, benzimidazole, benzoxazole, quinoline, isoquinoline, quinoxaline, and phenazine. The reaction of purines with alcohols has been examined in the case of caffeine, and the results of both γ-ray irradiation and photolysis have been compared.85 The reaction may be induced directly or in the presence of a ketone to yield 8-substituted products in 80% yield. With propan-2-ol, both γ-ray irradiation and photolysis give the dimethylcarbinol (194), but with ethanol the light-induced reaction yields only the alkylation product 8-ethylcaffeine (195), whereas the γ-ray reaction gives both (195) and (196).

\[ \text{(193)} \]
\[ \text{Me} \]
\[ \text{Me} \]
\[ \text{C} \]
\[ \text{OH} \]
\[ \text{HN} \]
\[ \text{HN} \]

\[ \text{Me} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{N} \]
\[ \text{Me} \]

\[ \text{hv} \]
\[ \text{ROH} \]

[Me]

\[ \text{(194) R = Me}_2\text{C} \text{OH} \]

\[ \text{(195) R = C}_2\text{H}_5 \]

\[ \text{(196) R = MeCHOH} \]

The vapour-phase irradiation of borazine and ammonia each at a pressure of 15 mm has proved to be a useful procedure for the preparation of B-monoaminoborazines, and has been extended to a series of deuterium and 15N-labelled species.86

4 Addition Reactions

It is known that olefins are oxidised photochemically in the presence of nitrobenzene to yield products similar to those from an ozonolysis reaction. The process arises by addition of the nitro-group to the olefin. Following photolysis of nitrobenzene and cyclohexene at $-70^\circ$, the intermediate of the reaction has now been isolated and characterised. It is an unstable crystalline 1:1 adduct (197) with a structure analogous to that of a primary ozonide. Confirmation of the structure is obtained by catalytic hydrogenation to give cyclohexane cis-1,2-diol (plus 5% of the trans-isomer), and an equivalent proportion of aniline. At room temperature, the adduct decomposes to give a complex mixture, but at $-80^\circ$ the solid may be crystallised from ethyl acetate. This compound is the first member of a class of cyclic derivatives of trivalent nitrogen compounds containing two N–O bonds. Similar results have been obtained with methylcyclohexene, hex-1-ene, and norbornene as the olefin components.

Sensitised dimerisation reactions have been reported for enamines: cyclobutanes are produced only when oxygen is present in the system. Exceptions to this are dimerisations sensitised by chloranil and anthraquinone where it is implied that the dimerisation proceeds in the absence of oxygen. The yields of the dimers are essentially quantitative, and the process is effected by sensitisers of triplet energy between 33 and 74 kcal/mole. It is interesting to note that the products of such dimerisations have the same structure as those obtained from Fe$^{3+}$ and Ce$^{4+}$ catalysed reactions. The photochemistry of the enamine 1,3-diphenyl Δ(4)-imidazolin-2-one (198) has been reported, and the expected dimerisation, oxetan formation, and addition to olefins and phenanthrenequinone are all encountered.

Irradiation of a benzene solution of 2,5-diphenyl-1,3,4-oxadiazole and indene in the presence of iodine is reported to give a 1:1 adduct (199). In the absence of iodine, however, a 1:2 adduct (minus an oxygen atom) (200) is formed together with resinous material. The stereochemistry of the adduct (200) is uncertain at present.

2-Pyridones are known to both dimerise and undergo valence tautomerism on irradiation. Irradiation of a 2-pyridone in the presence of

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tolan, however, leads not only to formation of the pyridone dimer (201a) but also a 1:1 adduct (201b) of the starting material is produced; this is the first report of a photochemical addition to the 2-pyridone system although thermal additions are known. Further irradiation of the adduct (201b) at 253.7 nm causes isomerisation of the azahomoquadricycylene to a

\[ \text{Ph} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{Ph} \]

(198)

\[ \text{Ph} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{Ph} \]

(199)

\[ \text{Ph} \]
\[ \text{O} \]
\[ \text{Ph} \]

(200)

\[ \text{R} \]
\[ \text{N} \]
\[ \text{O} \]

(201a)

\[ \text{R} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{Ph} \]

(201b)

cyclobutenopyridone. The addition and isomerisation reactions have been found to be fairly general, thereby providing a route to a variety of quadricyclic lactams and fused cyclobutene derivatives.

Photochemical reactions between azoesters and olefins do not yield cyclic compounds; \(\alpha\)-substitution products of the olefin are formed. The results with dideuteriocyclohexene (Scheme 6) indicate that the azoester abstracts a hydrogen atom from the allylic position of the cyclohexene to give the hydrazoester and cyclohexenyl radicals; radical recombination then leads to two isomeric compounds in a 1:1 ratio. The same reaction may be effected thermally (100° for 6 hr.) and molecular orbital calculations indicate that the triplet levels of the ester may be so low as to be attainable in thermal reactions.

### 5 Reactions of Sulphur-containing Compounds

The organic photochemistry of sulphur compounds has been studied less than that of nitrogen compounds. Some interest has in the past been centred around the addition reactions of thioketones to olefins where, at least in the case of thiobenzophenone, new olefins (202) and presumably thioaldehydes (203) are formed by dissociation of the first-formed thiooxetans. In contrast with this work, the photochemical addition of

---

thiobenzophenone to styrene has been found to give 2,2,3,3,5-pentaphenyl-1,4-dithiane (204). The cycloaddition is quite stereospecific, giving a single product in high yield, and in this respect is in complete contrast with the formation of oxetans from ketones where an isomeric mixture of products is generally obtained. Dithianes are the products from olefins substituted with electron-donating groups where there is no restriction for a second addition of the thiolketone. In the case of β-methylstyrene as olefin, a thietan (205) is formed through a triplet \( \pi \pi^* \) process. Here it is suggested that the reaction stops at the 1 : 1 adduct because any further reaction of the 1 : 1 adduct with thiobenzophenone is sterically hindered. Thietans (206)

\[
\begin{align*}
\text{Ph}_2\text{C}=\text{S} & \\
& + \\
\text{R}-\text{CH}=\text{CH}-\text{R}' & \\
\downarrow & \\
\text{RCH}=\text{CPh}_2 & \text{(202)} \\
& + \\
\text{R}'\text{CH}=\text{S} & \text{(203)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{C}=\text{S} & \text{Ph}-\text{CH}=\text{CH}_2 \\
& \xrightarrow{h\nu} \\
\text{Ph}_2\text{C}=\text{S} & \text{Ph}-\text{CH}=\text{CH} \\
& \xrightarrow{h\nu} \\
\text{Ph}_2\text{C}=\text{S} & \xrightarrow{\text{(C.T. Complex)}} \\
& \xrightarrow{h\nu} \\
\end{align*}
\]


are also formed generally where the olefin is substituted with electron-withdrawing groups, but it appears probable in these cases that the reaction proceeds by ππ* charge-transfer (C.T.) excitation in a complex.\textsuperscript{102}

The photolysis of β-ketosulphides has been reported both for compounds which contain the structural unit ArCO\(\text{SR}\)CH\(\text{2}\) (see ref. 86 in Chapter 7), and those in which the carbonyl group and the sulphide are in the same ring. With cyclic bridged compounds of type (207), direct irradiation of methanol or benzene solutions leads to selective α-cleavage between the carbonyl and C\(\text{α}--\text{S}\) bonds.\textsuperscript{102} Ketens are formed by hydrogen transfer, but the compounds isolated depend upon the availability of internal and/or external nucleophiles; typical products from the reaction are compounds (208), (209), (210), and (211). The yields of this reaction are high, and offer an attractive route to new heterocyclic compounds. Irradiation of the non-bridged β-ketosulphide, thiacyclohexa-3-one (212) in t-butanol leads

\begin{align*}
(207) \quad R &= \text{Ac or H} \\
(208) \\
(209) \\
(210) \\
(211) \\
(212) \xrightarrow{h\nu} \left[ \begin{array}{c}
\text{O} \\
\text{S} \\
\hline
\text{CH}_2
\end{array} \right] \xrightarrow{\text{h\nu}} \text{O} + \text{S} \\
(213) \\
(214) \xrightarrow{h\nu} \text{O} + \text{S} \\
(215) \\
(216)
\end{align*}

Scheme 7  Photochromism of aromatic sulphur compounds
to the reduction and addition products, thiacyclohexa-3-ol and t-butyl-5-thiahexanoate.\textsuperscript{104} In polyhalogenated solvents (1,1,2-trichloro-1,2,2-trifluoroethane), however, the reaction of (212) is one of ring contraction and expansion, and the ylid intermediate (213) is suggested to account for the methylene transfer. The contraction–expansion reaction does not occur to any reasonable extent in other thiketones (\textit{e.g.} thiacyclopentan-3-one, thiacyclo-heptan-3-one, 6-methylthiacyclohexan-3-one, 2-methylthiacyclohexan-3-one, and \textit{trans}-thiabicyclo[4,4,0]decan-5-one). In these cases a complex mixture is formed which contains thiophen and dihydrothiophen as the major products. Irradiation of the dithiaketone (214) in acetonitrile yields (215) and (216); this reaction is similar to that reported previously by the same research group with certain dithiaspiroalkanes (ref. 85, Chapter 7).

The oxidation of penicillin by a variety of methods yields a simple sulfoxide which in the case of phenoxyethyl penicillin has the \textit{S} configuration (217). Attempts to invert this compound to the \textit{R} sulfoxide (218) or indeed to synthesise the \textit{R} sulfoxide thermally were unsuccessful, but the inversion was successfully carried out by irradiation in acetone with light of wavelength longer than 290 nm.\textsuperscript{105}

Certain aromatic sulphur compounds are well known to be photochromic. The structure of the coloured compounds in some cases has now been assigned, and the photochemical processes have been shown to be highly efficient.\textsuperscript{106} The examples given in Scheme 7 are typical for this class of reaction. A photochromic effect has also been observed with acetonitrile solutions of phenothiazine (219) and anhydrides.\textsuperscript{107} Irradiation (charge-transfer?) of the system produces a green colour, which is destroyed by phenothiazine, as well as a colourless product of unreported structure.

A. G.

Photoelimination Reactions

Many organic molecules on photolysis undergo processes of molecular elimination of small molecules such as nitrogen or carbon monoxide, or massive fragmentation, *i.e.* complete decomposition into two or more sizeable polyatomic molecules. Such processes, excluding those observed with ketones (see Part III, Chapter 1) are reviewed in this Chapter. It is unusual for hydrocarbons to fragment in such a manner, and the overwhelming majority of examples reported every year involve compounds containing a heteroatom.

1 Nitrite Photolysis—Barton Reactions

Nitrite esters are known to undergo fission into nitric oxide and alkoxy-radicals which, like most radicals, have several paths by which they may yield stable products. The quantum yield for such decompositions is often thought to be unity, or very close to this; but it is not always so since the vapour-phase irradiation of isopropyl nitrite in the 366 nm banded region leads to decomposition into nitric oxide and alkxy-radicals with a quantum yield reported to be 0·36 at 26°C.¹ The major products of the

\[
\text{Me}_2\text{CHONO} \xrightarrow{h\nu} \alpha\text{Me}_2\text{CHO}^* + (1-\alpha)\text{Me}_2\text{CHO} + \text{NO} \\
\text{Me}_2\text{CO} + \text{HNO} \text{ (or NOH)}
\]

photolysis are acetone and acetaldehyde, but methyl nitrite, methyl nitrate, nitrogen, nitric oxide, and water are also formed. The *cis*- and *trans*-conformers of the nitrite apparently decompose with the same quantum yield, and the primary yield for photodetachment of HNO and NOH is <0·06.

It is known from e.s.r. studies that photolysis of alkyl nitrites in hydrocarbon media can lead to the formation of dialkyl nitroxides and alkoxoyl alkyl nitroxides.² The reaction has now been examined by e.s.r. spectroscopy with ethyl and t-butyl nitrites in alcoholic solvents.² Generally the spectra of the nitroxide radicals predominate over those of the alkoxyl alkyl nitroxides at high temperatures and slow flow rates, but the radicals

observed are derived from the photolysis of the solvolysis products of the original nitrite. Thus photolysis of RONO in R'OH gives R'ON(S)—O· where (S) is a solvent-derived fragment. No evidence for RON(S)—O· radicals was obtained. A scheme proposed for this reaction is shown in equations (1)—(6).

\[
\begin{align*}
\text{RONO} + \text{R'OH} & \quad \longrightarrow \quad \text{R'ONO} + \text{ROH} & (1) \\
\text{R'ONO} & \quad \xrightarrow{\text{hv}} \quad \text{R'O}· + \text{NO}· & (2) \\
\text{R'O}· + \text{R'OH} & \quad \longrightarrow \quad \text{R'OH} + \text{S}· & (3) \\
\text{S}· + \text{NO}· & \quad \longrightarrow \quad \text{SNO} & (4) \\
\text{SNO} + \text{S}· & \quad \longrightarrow \quad \text{S}_2\text{NO}· & (5) \\
\text{SNO} + \text{R'O}· & \quad \longrightarrow \quad \text{R'ON(S)O}· & (6)
\end{align*}
\]

In cases of nitrite photolysis where intramolecular hydrogen abstraction by the alkoxy-radical occurs to generate another radical which then recombines with the nitric oxide to yield nitroso-dimers or oximes, the process is known as the Barton Reaction after D. H. R. Barton who discovered and developed the reaction into one of great synthetic utility. Mechanistic features of the reaction have in the past been intensively studied. Photolysis of dissimilar nitrite esters, one of which contained \(^{15}\text{N}\), has shown that the nitric oxide formed is not held within a solvent cage; and since the quantum yield is never higher than unity, the process is no longer considered to be a chain reaction. Activation of non-activated sites is achieved, and many useful examples have been published of this type of reaction in the steroid series. Barton has presented some new data on the reactions of nitrites, particularly their gas-phase pyrolysis, and has reported the use of nitrite photolysis in the synthesis of a natural product, \(\beta\)-amyrin (1).\(^5\) Here the use of the reaction is to introduce a ketonic group into the A ring of \(\beta\)-amyrene (2).

The smooth fragmentation of an alkyl diphenyl carbinol nitrite (3) has been reported, giving in this case benzophenone and acetoxime.\(^6\) It was at first considered from this model compound that such reactions would be general since it was envisaged that the driving force for fragmentation was the gain in resonance energy in the formation of benzophenone. However, attempts to use the reaction in the synthesis of 18-hydroxyoestrone (4) from the diacetate (5) failed. Instead of breaking the (17)—(20) bond, and restoring the carbonyl function at C(17), the n.m.r. evidence indicated that C(18) was substituted by the usual abstraction mechanism, and that no benzophenone was liberated. Successful reaction has, however, been

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observed in the conversion of 3β-acetoxylanostan-11β-yl nitrite (6) to 3β-acetoxy-19-hydroxyaminolanostan-11β-ol (7). By-products of the reaction are 3β-acetoxylanostan-11β-ol and the corresponding 11-ketone. 3β-Acetoxy and 3β-benzoxyloxy-lanost-24-en derivatives of (8) similarly yield the corresponding 19-oximino derivatives, and irradiation in the presence of iodine leads to the 19-ido compound which by further thermal transformations is converted into the triterpenoid cycloartenol (9), making the total synthesis of this compound complete.

Masamune and co-workers have examined the photolysis of cyclopentyl nitrites in the veratrobasine series. The major product from photolysis of the diacetyl derivative (10) is the oximino-compound (11) while both 3-ON-diacetylveratrobasine (12) and the cyclic ether (13) are formed in addition to a compound of unknown structure. The formation of (13) is analogous to similar transformations in the steroid series. Although a number of results of the photolysis of nitrite esters of cyclopentanol have been reported, this work would appear to be the first example, although somewhat specialised, in which the Barton Reaction is the major pathway without appreciable cleavage of the 5-ring or epimerisation of the relevant alkoxy-radical. Photolysis of the dibenzoyl nitrite (14), on the other hand, leads to the formation of the parent 3-ON-dibenzoylveratrobasine, two unidentified compounds, and the nitrate (15). This latter compound must have arisen by oxidation (air) of an intermediate nitroso compound before

---

Photoelimination Reactions

$$\text{Ph}_2\text{C} = \text{CHMe}_2 \xrightarrow{hv} \text{Ph}_2\text{C} = \text{O} + \text{Me}_2\text{C} = \text{NOH}$$

$$\text{AcO}$$

(3)

(4)

(5)

(6)

$$\text{AcO}$$

$$\text{H}$$

$$\text{Ph}$$

$$\text{Me}$$

$$\text{H}$$

$$\text{C}_8\text{H}_{17}$$

$$\text{H}$$

$$\text{H}$$

$$\text{H}$$

$$\text{H}$$

$$\text{H}$$

(7)

(8)

$$\text{R}$$

$$\text{H}$$

$$\text{Me}$$

$$\text{H}$$

$$\text{H}$$

$$\text{H}$$

$$\text{AcO}$$

(9)

(10) $$\text{R} = \text{OAc}$$

(14) $$\text{R} = \text{OCPh}$$

(11)

(12)

(13)
rearrangement of the oximino-compound had occurred. Further investigations in this series with compounds (16), (17), and (18), all containing a 22,27-imino-17,23-oxidojervane framework, show that competition among the reactions of the 11-alkoxy-radicals gives a variety of products. However, cleavage of the carbon–carbon bond $\alpha,\beta$ to the nitrite group in these compounds is not a major course of reaction.\footnote{10} Whenever sterically possible [e.g. with (16)] the 11-alkoxy-radical achieves a Barton Reaction to yield relatively few products. In two of the cases examined, the reaction is accompanied by epimerisation of the relevant alkoxy-radical.

2 Elimination of Nitrogen from Azides

Photolysis of azides is well known to lead to the elimination of nitrogen with the resulting electron-deficient nitrene fragment undergoing inter- and intra-molecular reactions. Typically these reactions are insertion into an ethylenic bond, hydrogen-abstraction from the solvent, and coupling to form azo-compounds. Carbon–nitrogen cleavage has also been observed. Thus by e.s.r. spectroscopy triphenyl methyl radicals have been detected in the photolysis of triphenyl methyl azide.\footnote{11} It has also been reported that when the terminal nitrogen in this azide is labelled ($^{15}$N), isotopic position rearrangement occurs in a way which suggests that recombination of triphenylmethyl and azide radicals is very probable. On pyrolysis, however, no radicals were detected, and in this case the isotopic position rearrangement occurs either \emph{via} an intramolecular process or by ion-pair recombination. The lack of selectivity in migration aptitude in triarylmethyl azide

\footnote{11} F. D. Lewis and W. H. Saunders, \emph{J. Amer. Chem. Soc.}, 1968, 90, 3828.
photoysis, and the formation of triarylmethylamine in the presence of such efficient hydrogen donors as tri-n-butyltin hydride, are suggested to support the idea of a discrete nitrene intermediate.\textsuperscript{12} Triple-sensitised decomposition demonstrates a triplet azide reaction, and presumably a triplet nitrene, but efforts to detect a triplet azide in direct photolysis by quenching experiments with cis-piperylene failed. But this failure and the high quantum yield for decomposition indicate that a large part, if not all, of the direct photolysis of such azides probably occurs via singlet excited azide and singlet nitrene.

Studies have been conducted into the sensitised photolysis of several alkyl azides, phenyl azide, and ethyl azidoformate, and a possible case of non-classical energy transfer is reported.\textsuperscript{13} The rates of triplet energy transfer from sensitiser to azide are very similar for all the alkyl azides; greater rates are found for phenyl azide, and smaller ones for the azidoformate. Transfer of energy to the alkyl azides approaches the diffusion-controlled rate only as the sensitiser energy approaches 70—80 kcal/mole, suggesting a triplet energy in this range for the azide. Thus in the earlier work on the direct photolysis,\textsuperscript{12} cis-piperylene should have been an efficient quencher for these triplets. Sensitisation with compounds of lower triplet energies was found to be considerably more effective than expected for a classical endothermic energy transfer process, and it is suggested that energy transfer is accompanied by bending of the N—N—N bond angle from the normal 180° in the ground state. Extended Hückel theory calculations on methyl azide in the first excited state show two energy minima at angles of 140 and 220°, the former having the slightly lower energy. The transoid configuration (19) of the methyl azide is slightly more stable than those in

\[
\text{Me}^+\overset{1}{\text{N}}-\overset{2}{\text{N}}^2
\]

which the methyl group lies out of the N\textsuperscript{1}N\textsuperscript{2}N\textsuperscript{2} plane. Such bending would result in a ‘non-spectroscopic’ triplet state and thus account for the present sensitisation results.

Other workers have been concerned with the photolysis of aromatic azides where the excited states are essentially those of the parent hydrocarbon plus an \(\pi\pi^*\) long wavelength absorption of low intensity, and where energy is absorbed by the aromatic system as a whole.\textsuperscript{14} Quantum yields for a group of aromatic azides are reported at 25 °C and 77 K in hydrocarbon matrices. From these results, particularly for 1-azidonaphthalene, and earlier published work,\textsuperscript{15} it is concluded that bond dissociation occurs

via a 'hot' ground-state molecule by vibrational excitation of a critical stretching mode of the azido-group. The quantum yields for decomposition of the majority of examples of aromatic azides examined were greater than 0.4 and in several cases were unity at both 25° C and 77 K. The transients in the flash photolysis of several aromatic azides have been identified by their spectra as triplet nitrenes.\textsuperscript{16} The half-lives of the nitrenes have been determined over a range of concentrations in hexane, ethanol, and several polymer matrices, and are accounted for in terms of three processes; \textit{viz.} nitrene recombination, reaction with an azido-group, and hydrogen abstraction from the solvent. The former two processes are diffusion controlled while the latter is a relatively slow reaction.

The first instance is reported of the formation of a 1-azabicyclo[1,1,0]-butene by photodecomposition of an allylic azide and intramolecular nitrene insertion.\textsuperscript{17} The reaction is initiated by light of wavelength longer than 290 nm and may be compared with the formation of bicyclobutane and butadiene from allyl carbene.\textsuperscript{18}

Terminal vinyl azides (20) are known to undergo both thermal and photochemical reaction to give 3H-azirines (21) and N-alkyl ketenimines (22).\textsuperscript{19} Now for the first time a case in which the reaction path is dependent upon the activation processes is reported.\textsuperscript{20} Thus \textit{trans-β}-azidovinyl-p-tolyl sulphone (23) on pyrolysis yields toluene-p-sulphonyl acetonitrile (24) only, while the sole product from the photolysis of (23) in aqueous ethanol or wet solvents is 2,3-di-(toluene-p-sulphonyl)aziridine (25). The photolysis of 4(5)-toluene-p-sulphonyltriazole, isomeric with (23), is believed to form 3-toluene-p-sulphonyl-3H-aziridine (26), some of which is hydrolysed to toluene-p-sulphinic acid which then condenses with the remaining aziridine to yield (25). In support of the intermediacy of azirine (26) in these reactions, the former photolysis was examined under anhydrous conditions in the presence of benzenesulphinic acid and was found to form 2-benzene- sulphonyl-3-toluene-p-sulphonylaziridine. The \textit{cis-β}-azido-compound gave quantitatively the same reaction as the \textit{trans}-derivative. Attempts to isolate the 3H-azirine compound in the present work gave material with an i.r. spectrum characteristic of the 3H-azirine system, but rapid polymerisation occurred; this behaviour is typical of such compounds when there is no 2-substituent. This new addition reaction of the 3H-azirine system was further demonstrated by the addition of toluene-p-sulphinic acid to 2,3-diphenyl-3H-azirine and to 2-phenyl-3-methyl-3H-azirine.

Such intramolecular cyclisation to give azirines is not, however, observed with \textit{β}-azidovinyl ketones. Phenyl \textit{β}-azidovinyl ketone on photolysis yields the ketonitrile (27) while the cyclic derivative (28) of this system, in aqueous

Photoelimination Reactions

\[
\begin{align*}
\text{C} &= \text{CH}_2 \\
\text{R} &\xrightarrow{h\nu} \text{N}^+ \\
\text{R} &+ \text{RN} = \text{C} = \text{CH}_2 \\
&\text{(20)} \hspace{2cm} \text{(21)} \hspace{2cm} \text{(22)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ts} &\xrightarrow{\Delta} \text{TsCH}_2\text{CN} \\
\text{H} &\xrightarrow{h\nu} \text{N} \hspace{0.5cm} \text{Ts} \\
\text{H} &\xrightarrow{\text{C}_6\text{H}_5\text{SO}_3\text{H}} \\
&\text{(23)} \hspace{2cm} \text{(24)} \hspace{2cm} \text{(25)} \\
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Ts} \\
\text{N} \\
\text{H}
\end{array} &\xrightarrow{h\nu} \\
\begin{array}{c}
\text{Ts} \\
\text{N} \\
\text{H}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} - \text{C} - \text{CH} &= \text{CHN}_3 &\xrightarrow{h\nu} \text{C}_6\text{H}_5 &\xrightarrow{h\nu} \text{Ph} - \text{C} - \text{CH}_2 - \text{CN} + \text{N}_2 \\
&\text{(26)} \hspace{2cm} \text{(27)}
\end{align*}
\]

tetrahydrofuran, gives (29). The reaction in this case is said to involve methylene migration to the nitrene with formation of a seven-membered cyclic ketenimine which is subsequently hydrolysed; such an intermediate would be drastically strained. In benzene solution (28) would seem to be photochemically stable since no nitrogen is eliminated, and there is no reference to other reactions.

Earlier work on the photolysis of 2-azidobiphenyl indicated that the major path was for carbazole formation via a nitrene. The sensitised reaction has now been studied and as well as carbazole, the ring-closure product, azo-2-biphenyl (30), an expected nitrene dimer, but nevertheless a new compound, is formed. A re-examination of the unsensitised reaction

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with higher concentrations of the azide revealed that in this case too, small amounts of the azo-compound (30) are formed.

Solvent-derived products are obtained from the photolysis of \( N \)-benzhydrylidene azido benzhydrylamine (31), in benzene and methanol. In benzene solution, \( N \)-phenyl-\( N' \)-benzhydrylidene benzamidine (32) is formed, but none of the expected product, benzophenone azine, could be isolated. The products of the photolysis of (31) in methanol are ammonium azide and benzophenone dimethyl acetal. This latter compound is also formed in low yield in the dark reaction, a fact which suggests that benzophenone imine and hydrazoic acid are the initial products from the photolysis of (31) in methanol. Dark reaction of the imine with methanol then leads to the dimethyl acetal, and photolysis of hydrazoic acid yields ammonium azide. In support of this, the latter reaction was demonstrated experimentally.

\[
\begin{align*}
\text{Ph}_2\text{C} & \quad \text{N} = \text{CPh}_2 \quad \xrightarrow{-\text{N}_3 \text{C}_\text{H}_5} \quad \left[ \text{Ph}_2\text{C} \quad \text{N} = \text{CPh}_2 \right] \\
\text{Ph}_2\text{C} & \quad \text{N}_3 \quad \xrightarrow{\text{hv} \text{MeOH}} \quad \text{Ph}_2\text{C} \quad \text{N} = \text{CPh}_2 \quad \xrightarrow{\text{Dark} \text{MeOH}} \quad \text{Ph}_2\text{C} \quad \text{OMe} \quad \text{OMe} \\
\text{NH}_4\text{N}_3 & \quad \xrightarrow{\text{hv} \text{MeOH}} \quad \text{NH}_4\text{N}_3
\end{align*}
\]

A photochemically induced Curtius degradation has been observed in the irradiation of methyl azidof ormate in alkenes; the reaction gives, in addition to the expected \( N \)-methoxycarbonyl aziridine, 10—11\% of 1,3,5-trimethoxy-2,4,6-trioxohexahydro-5-triazine (33), the Curtius product. Not surprisingly, methoxycarbonyl nitrene and methoxy isocyanate are suggested as intermediates for the reaction.

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Photoelimination Reactions

Photolyses of azides in both the carbohydrate and steroid series have been reported. In the former example a 6-azido-5-deoxyhexose derivative (34) was converted photochemically into the corresponding 6-aldehyde. The aldehyde imine is presumed to be the intermediate which readily undergoes mild hydrolysis yielding the desired product. In the steroid series the photolysis of 20α-azido-5α-pregnane has been studied for the first time. The isolated product from the photolysis is a bis-steroidal Schiff’s base (35).

---

The mechanism proposed for the formation of (35) is dimerisation of the initially formed nitrene to an azo-compound, and conversion of this into a hydrazone which subsequently undergoes fragmentation into two radicals with the elimination of acetaldehyde; the detection of this in the reaction is, however, not clearly indicated. Finally, radical combination yields the isolated product.

Sulphonyl azides (RSO$_2$N$_3$) in isopropyl alcohol, by either direct or benzophenone-sensitised irradiation, yield the corresponding sulphonamides, acetone, and nitrogen.$^{28}$ Detailed studies with methanesulphonyl azide show high quantum yields, and rates of reaction which have a complex dependence on the light intensity, and concentrations of the azide and benzophenone. A radical chain mechanism with two propagation sequences is suggested. The chains appear to be terminated by radicals derived from isopropyl alcohol and benzophenone. The reaction also occurs thermally at 80° or, very interestingly, on addition of small amounts of iron(II) chloride, and hydrochloric acid to a solution of the azide in alcohol.

Sodium, barium, and silver azides are all reported to form the corresponding nitrides on photolysis in the solid state, whereas potassium and lead azides would seem to be photostable.$^{29}$ The nitrides undergo further decomposition with light of long wavelength, and acceleration of rate of photolysis of metal azides in the latter stages of decomposition is attributed to the nitride decomposition, and to photoionisation of metal atoms if light of sufficient energy is present. (See Part II.)

3 Elimination of Nitrogen from, and Decomposition of, other Compounds with N—N Bonds

Nitrogen may be readily expelled photochemically from a variety of organic compounds which contain N—N bonds, particularly azo- and diazo-compounds. Such examples are reviewed in this section.

The photochemistry of simple aliphatic azo-compounds has been studied in some detail. The compounds chosen in this study were the cis- and trans-isomers of azoisopropane.$^{30}$ Photolysis in both the liquid and vapour phases was examined. In the gas phase, the quantum yield for decomposition at 350 nm is unity for both isomers. Increase of the pressure by added gases such as carbon dioxide causes the quantum yield for the decomposition to decrease, and the isomers begin to exhibit cis$\rightarrow$trans isomerism. Iso-octane solutions of the azo-compounds provide a solution pressure of ca. 1000 atmospheres, and in this case isomerisation is the major reaction pathway, with a quantum yield of 0.50. The quantum yield for decomposition in solution is much lower at 0.025. From these data it may be suggested that both cis- and trans-isomers dissociate from the

singlet state, and that collision aids intersystem crossing to the $\pi\pi^*$ triplet state. From the latter state there is equal probability for cis$\rightarrow$trans isomerism to occur, and it may be considered that no decomposition would arise. However, the decrease in the quantum yield of dissociation from 1.0 to 0.18 on addition of carbon dioxide shows that the lifetime of the state from which decomposition occurs must be $>0.5 \times 10^{-9}$ sec. On the other hand, the lifetime of the singlet state, as judged from fluorescence measurements, is $<0.5 \times 10^{-10}$ sec. Thus singlet-state decomposition is most unlikely. It is therefore considered that rapid intersystem crossing occurs from the singlet state to vibrationally excited levels in the $\pi\pi^*$ triplet manifold, and it is from these high vibrational levels that dissociation occurs. Collisional deactivation within the triplet manifold gives lower vibrational levels, but still those of the $\pi\pi^*$ triplet state, and it is from these lower levels that isomerism proceeds.

It has been found that the quantum yields for nitrogen and intramolecular ethane formation from azomethane are independent of temperature within the range 63—218$^\circ$. This result implies that collisional deactivation of electronically excited molecules is insignificant in this case. The same workers point out that the photodissociation of 2,2'$\prime$-azoisobutane is a good source of t-butyl radicals for a study of their reactions below 100$^\circ$.

The fate of the cyclo-C$_3$H$_8$N$=\cdot$N$\cdot$ radical from photolysis of 1,1,1-trifluoromethylazocyclopropane (36) has been investigated. The gas-phase photolysis of (36) with 2,3-dimethylbutane as diluent is reported to yield nitrogen, trifluoromethane, 1,1,1-trifluorobut-3-ene, and propylene, with only a trace of cyclopropyl derivatives and no combination products. In addition, 2-pyrazoline was isolated. Liquid-phase photolysis of (36) in either 2,3-dimethylbutane or carbon tetrachloride produced, among other products, the radical combination compound, trifluoromethylcyclopropane (37). Photolysis undoubtedly forms the trifluoromethyl radical, but researches show that the sum of products involving these radicals exceeds the total amount of nitrogen formed. Thus at least some of the intermediate radical species, cyclo-C$_3$H$_8$N$=\cdot$N$\cdot$, or the product of their rearrangement, do not eliminate nitrogen. Quantitative analysis of the system shows that the 2-pyrazoline : nitrogen ratio is ca. 0.15, and this result is consistent with the anomalous trifluoromethyl material balance. It would certainly seem reasonable that the radical (38) is a precursor to the 2-pyrazoline which is finally formed by hydrogen abstraction from the diluent. The question remaining is whether the radical (38) arises directly from decomposition of the excited azo-compound or by rearrangement of the diazonium radical, cyclo-C$_3$H$_8$N$=\cdot$N$\cdot$.

There are many examples in the literature of the loss of nitrogen from cyclic azo-compounds to yield cycloalkanes and their derivatives. The

---

process is still, however, being intensively studied with a wide variety of compounds, and interest lies particularly in the preservation or loss of stereochemistry in proceeding from reactants to products. The direct and sensitised irradiation of the 6-methylated-1-pyrazolines (39) and (40) has been reported. Examination of the product stereochemistry suggests that direct photolysis occurs via a singlet excited trimethylene whereas the sensitised reaction involves triplet states, i.e. the direct irradiation preserves the stereochemistry while in the sensitised reaction a mixture of stereoisomers is formed.

Studies complementary to those of Andrews and Day for the direct and benzophenone-sensitised irradiations of the 4-alkylidene-Δ(1)-pyrazoline-3-carboxylates (41) and (42) have been reported. The loss of nitrogen from (41) in the direct irradiation yields a methylenecyclopropane (43) as the major product, and a mixture of cis- and trans-isomers of (45) as the minor products. Similarly (42) forms (44) in good yield, and (43) and (45) in low yield. On the other hand, both (41) and (42) yield (44) as the major product from the sensitised reaction together with much smaller proportions of the other three isomers. Thus it is concluded that (44) rather than (43) is the favoured isomer from both the kinetically and thermodynamically controlled processes.

Andrews and Day have continued this line of research and have published full details of their earlier work on the photolysis of 4-chloromethylene-3,3,5,5-tetramethyl-1-pyrazoline (46). The compound photolyses at wavelengths longer than 290 nm by a singlet mechanism to give 3-chloromethylene-1,1,2,2-tetramethylcyclopropane (47) as the major and 2-chloro-3-isopropylidene-1,1-dimethylcyclopropane (48) as the minor product.

The latter product predominates in the presence of high-energy triplet sensitisers, and it is deduced that the triplet energy of (46) is greater than 55 kcal/mole and possibly as high as 65 kcal/mole. The data are interpreted in terms of diradical intermediates including a planar delocalised π system of the tris-methylenemethyl(2-methylene-trimethylene) type: the proportions of the two cyclopropanes are governed by competition between bond rotation and intramolecular cyclisation. Of course, cyclisation from the triplet case necessitates a spin inversion, and hence the photosensitised reaction yields a more nearly statistical distribution of products than the direct photolysis.

The primary processes in the photochemistry of bicycloazo-compounds have also been investigated with 2,3-diazobicyclo[2,2,1]hept-2-ene (49) and 2,3-diazobicyclo[2,2,2]oct-2-ene (50). The quantum yields for decomposition in the gas phase are 0.85 and 0.5 respectively. In iso-octane solution, the relative quantum yields change dramatically, and are reported.

to be unity and 0.08 for (49) and (50) respectively. Both compounds fluoresce in the vapour phase, but in solution (49) does not, thereby suggesting in this case a pressure-induced dissociation \([(49)^* + x \rightarrow \text{Product} + x]\); this can also be observed in the vapour phase by the addition of inert gases. Compound (50), on the other hand, fluoresces strongly in solution, and inert gases do not quench the vapour-phase reaction. Oxygen, dienes, and mono-olefins, however, all quench the emission from (50) in both phases. There is no evidence for triplet intermediates in either case in the direct photolysis, although molecules excited to their triplet states by sensitisation are observed to dissociate.

Two reports have appeared on the photolysis of the 2,3-diazabicyclo[3,2,0]heptene system to yield bicyclo[2,1,0]pentanes.\(^8\),\(^9\) The dichloro-compound (51) in ether gave a mixture of three compounds with the cyclopropane derivative (52) as the major product; but the decomposition did not proceed to completion because of the formation of insoluble polymeric materials.\(^9\) Irradiation in acetone (in which the polymer is soluble) led to complete reaction, but still a mixture of products was formed. But the use of benzophenone as sensitisier led to a quantitative yield of (52). Similarly (53) is converted into (54) on sensitised irradiation.\(^9\)

![Chemical structure](image)

The 1-pyrazoline (55) formed by photochemical or thermal addition of 9-diazofluorene to norbornadiene has been subjected to thermal and photodecomposition.\(^4\) Thermally, 2-(9-spirofluorenylidene)bicyclo[3,2,1]octadiene (56) is formed, whereas photochemically the ‘normal’ spirocompound (57) is obtained, and undergoes thermal rearrangement to (56). Further investigation of the addition reaction of 9-diazofluorene in neat norbornadiene shows that photochemically the 1,3-dipolar addition product, the 1-pyrazoline (55), is formed, whereas in ether solution the major products are 9,9′-bifluorenyl and 9,9′,9″-terfluorenyl.\(^4\) These

---


data suggest that reactions between diazo-compounds and olefins to yield cyclopropane derivatives may in fact proceed via the pyrazoline and loss of nitrogen, rather than loss of nitrogen, formation of the carbene, and addition of this to the olefin. However, in the photolysis of the exocyclic azo-compounds (58) and (59) in norbornadiene the spiro-compounds, e.g. (60), were formed free from the pyrazolines.\(^{41}\) Direct formation of the spiro-compounds of type (60) is suggested to be due to the low tendency of (58) and (59), compared with 9-diazafluorene, to undergo 1,3-dipolar addition, and it is concluded that carbenes are intermediates in these reactions. In benzene solution compound (58) yields the expected rearrangement products (61), (62), and (63) via the intermediate (64) from carbene addition.\(^{42}\)

The aza-compound (65) is reported to eliminate nitrogen both thermally and photochemically as expected.\(^{43}\) The former reaction yields bicyclo-[4,2,2]deca-2,4,7,9-tetraene (66) and bullvalene (67) while products of the photochemical elimination are (66), (67), and tricyclo[5,3,0,0^4,8]deca-2,5,9-triene (68). It was shown in the photolysis that the bullvalene arises by rearrangement of (66), and (68) is also formed from (66).

Quantitative elimination of nitrogen from \(\delta(3)-1,3,4\)-oxadiazolines (69) forms the epoxide (70) which subsequently rearranges to (71).\(^{44}\) The intermediate (72) in the cleavage of (69) was shown to undergo the usual cycloaddition reaction to norbornadiene. Where \(R = Me\) and \(R' = Ph\), the same products are formed thermally as photochemically, but for the spiro-compound where \(RR' = (CH_2)_5\), the photochemical reaction yields PhCO—O—CO—Me and the carbene \((CH_2)_5C:\).

The thermal reaction of diazoesters such as 4-diazo-4-phenyl butyrate with phenylacetylene give the expected 1,3-dipolar addition product (73).

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Photoelimination Reactions

Photolysis of this 3H-pyrazole does not, however, produce the expected cyclopropene derivative, but instead a mixture of methyl esters of trans- and cis-styryl-2-phenylcyclopropene-1-carboxylic acid (74) and 5,6-di-(2’-carbomethoxyethyl)-2,3,5,6-tetraphenylbicyclo[2,2,0]hex-2-ene (75).\textsuperscript{45} The formation of both these compounds may be explained by the mechanism outlined in Scheme 1. Heat treatment of (73) at 160° leads again to an

\begin{center}
\textbf{Scheme 1 Rearrangement of 3-(2’-carbomethoxyethyl)-3,5-diphenyl-3H-pyrazole (73)}
\end{center}

unexpected product by rearrangement of the phenyl group and the hydrogen, without side-chain loss or nitrogen elimination, to give the isomeric 3H-pyrazole (76). Photolysis of a mixture of a terminal acetylene and ethyl diazoacetate does, however, produce cyclopropenes;\textsuperscript{46} but in the light of the previous work, it would be more reasonable to suggest the intermediacy of a carbene than a 1,3-addition followed by nitrogen elimination. Secondary products from this reaction are acetylenic esters which are formed by carbene insertion in the acetylenic C—H bond.


Two examples of the photolysis of diazo-compounds have already been given in this section (see refs. 41, 42), but many more accounts of such reactions have appeared within the year.

It has been reported that the carbene-olefin addition reaction following the photolysis of 1-phenyl diazomethane (77) in olefins is not completely non-stereospecific since more cis-cyclopropane derivative is formed from a cis-olefin than from a trans-olefin, and vice versa.\(^4\) Styrene is also formed in appreciable amounts, indicating that hydrogen migration, as expected, competes with addition. In the reaction photosensitised by benzophenone, there is a decrease in the observed small measure of stereospecificity of the unsensitised addition, and the amount of styrene decreases markedly. These data are consistent with the assumption that hydrogen migration occurs in the singlet carbene, but not to a significant extent in the triplet carbene.

The interesting observation that diphenyl diazomethane decomposes with a quantum yield of ca. 2 has been explained by assuming the intermediacy of diphenylcarbene and formation of benzophenone azine (78) with another molecule of diphenyl diazomethane.\(^4\)

\[
\begin{align*}
\text{Ph}_2\text{C}=\text{N} - \text{N}=\text{CPh}_2 \\
\text{Ph}_2\text{C} + \text{N}_2
\end{align*}
\]

Several reports have appeared concerned with the photolysis and thermolysis of exocyclic azo-compounds.

The elimination of nitrogen both photochemically and thermally from anthracene(2,3 : 9,10)diquinone 3-diazide (79) in aromatic hydrocarbon solutions, results in an arylation reaction.\(^4\) Similar photolysis of 3-diazoo-2,4,5-triphenylpyrrole (80) in benzene yields tetraphenylpyrrole, while in

Photoelimination Reactions

\[
\begin{align*}
\text{(79)} & \quad \xrightarrow{\text{ArH}} \quad \text{(80)} \\
\text{Ph} & \quad \xrightarrow{hv, \text{C}_2\text{H}_6} \quad \text{Ph} \\
\text{Ph} & \quad \xrightarrow{hv, \text{CH}_3\text{OH}} \quad \text{Ph} \\
\text{Ph} & \quad \xrightarrow{hv} \quad \text{Ph} \\
\text{N} & \quad \xrightarrow{hv} \quad \text{N} \\
\text{H} & \quad \xrightarrow{hv} \quad \text{H} \\
\end{align*}
\]

methanol solution, 2,4,5-triphenylpyrrole is formed;\textsuperscript{50} these reactions are all consistent with the expected behaviour of carbene intermediates.

The \(\alpha\)-diazoketone (81) in aqueous solution undergoes photochemical ring-contraction with loss of nitrogen to yield the oxetancarboxylic acid (82) in a Wolff rearrangement.\textsuperscript{51} Likewise, even in the presence of an olefin, the cyclic diazo ketone (83) still undergoes an intramolecular Wolff rearrangement on direct irradiation.\textsuperscript{52} It is considered that the triplet carbene should find this intramolecular pathway more difficult than the singlet carbene, and in support of this view, the Wolff reaction is found to be avoided or diminished in the benzophenone sensitised decomposition of (83). A similar state of affairs is reported for diazoacetone where the singlet carbene formed by direct irradiation finds an accessible pair of electrons in the adjacent \(C—C\) bond and reacts with these faster than with the \(\pi\) electrons of an olefin. In the sensitised reaction, the triplet carbene would have to rearrange to a triplet keten to follow the same reaction path.


\textsuperscript{52} M. Jones and W. Ando, \textit{J. Amer. Chem. Soc.}, 1968, 90, 2200.
This keten is many kcal/mole above the ground-state singlet. Thus in this case reaction with the olefin occurs, and the loss of stereochemistry of the olefin is consistent with a triplet carbene reaction.

Rearrangement analogous to the photochemical Wolff reaction of diazoketones is also shown in photolysis of ethyl and phenyl diazoacetates, and N-methyl diazoacetamide, in aqueous or methanol solutions. In all cases, two major products are found: one by carbene insertion into the water or hydroxyl of the alcohol, and the other by rearrangement. A minor product from photolysis of ethyl diazoacetate is formed from carbene insertion into C—H to yield ethyl β-hydroxypropionate. The methyl phenoxyacetate formed by photochemical rearrangement of phenyl diazoacetate is reported to undergo further light-induced rearrangement to form methyl esters of α- and p-hydroxyphenylacetic acids.

It has, however, been shown that photolysis of diazoesters in alcohols may also proceed by a pathway not involving carbenes to give 'exchange' products (84) as well as the normal 'insertion' (85), 'addition' (86), and 'rearrangement' (87) products. The importance of this type of reaction depends inversely on the number of α hydrogen atoms on the alcohol. The formation of products of type (84) is suggested to involve ion-pairs (88) produced by light-induced heterolysis.

\[
\text{N}_2\text{CHCO}_2\text{R} \xrightarrow{hv} \text{R'R''CCH}_2\text{CO}_2\text{R} \quad \text{R'R''CHOCH}_2\text{CO}_2\text{R} \\
\text{Insertion} \quad \text{Addition} \\
\text{ROCH}_2\text{CO}_2\text{CHR'}\text{R''} \quad \text{R'R''CHOCH}_2\text{CO}_2\text{CHR'}\text{R''} \\
\text{Rearrangement} \quad \text{Exchange} \\
\left[ \text{N}_2-\text{CH}-\text{C}=\text{O} + \text{OR'} \right] \xrightarrow{\text{R'OH}} \left[ \text{N}_2-\text{CH}-\text{C}=\text{O} + \text{OR''} \right] + \text{R'OH} \\
\text{Exchange product} \xleftarrow{\text{R'OH}} \text{R'OCH}=\text{C} =\text{O} \\
\text{(88)} \quad \text{(88)}
\]

The photolysis of 5-diazo-3-caren-2-one (89) has also been studied. This diazoketone cannot undergo Wolff rearrangement after nitrogen elimination, and is interesting since it has the diazo-group γ to the α,β-unsaturated carbonyl function. Thermally, (89) gives the corresponding

azine (90) in 93% yield while irradiation of the aqueous dioxan solution yields both the azine and 3-carene-2,5-dione (91) as may be expected. In methanol solution, photolysis again gives both (90) and (91), but in addition a small amount of a third product is formed. Elemental analysis is consistent with a dimer of (89) but no structural assignments are made. Formation of (90) thermally and photochemically is interesting since it formally involves the intermolecular loss of nitrogen. Photolysis of the isomeric diazoketone (92) in aqueous dioxan produces small amounts of (91) and the oximino-ketone (93), while thermal treatment of (92) gives only polymeric material.

\[
\begin{align*}
\text{N}_2 &= \text{[Diagram]} \rightarrow \text{[Diagram]} \\
\text{(89)} &\rightarrow \text{[Diagram]} \\
\text{O} &= \text{[Diagram]} \\
\text{[Diagram]} &\rightarrow \text{[Diagram]} \\
\text{(91) + (90)} &\rightarrow \text{[Diagram]} \\
\text{(92)} &\rightarrow \text{[Diagram]} \\
\text{[Diagram]} &\rightarrow \text{[Diagram]} \\
\text{(93)} &\rightarrow \text{[Diagram]}
\end{align*}
\]

It has been reported that the principal products from the direct photolysis of \(\alpha\)-diazooacetophenone in isopropyl alcohol are isopropyl phenylacetate (57%) and acetophenone (23%).\(^{56}\) The reaction has now been examined in anhydrous isopropyl alcohol with \(\alpha\)-diazoo-p-methoxyacetophenone (94), and yields \(p\)-methoxyacetophenone (91%) and isopropyl \(p\)-methoxyphenylacetate (6%), as expected, although the relative yields are somewhat different from those earlier reported.\(^{57}\) Irradiation of (94) in anhydrous ethanol, on the other hand, gave ethyl \(p\)-methoxyphenylacetate and \(p\)-methoxyacetophenone in relative yields (63 and 13% respectively) more in line with those reported with the unsubstituted diazo-acetophenone. \(p\)-Methoxyphenylacetic acid (66%) was obtained from photolysis of an aqueous tetrahydrofuran solution of compound (94).

The effects of substituents, wavelength of exciting light, solvents, and temperature on the quantum yield for decomposition of diazonium salts in acid media, have been reported.\(^{58}\) The results show that photocleavage

---

of the C—N bond into nitrogen and a carbonium ion is the primary step in decomposition; the carbonium ion then rapidly reacts with the solvent. The thermal and photochemical hydrolyses of diazonium salts have also been studied.\textsuperscript{59} In the presence of chloride ions, aryl chlorides and phenols are produced from the photolysis of arenediazonium salts in aqueous solution, as in the thermal reaction. \textit{p}-Methyl and \textit{p}-chlorobenzene diazonium salts give a significantly higher yield of the chloride photochemically than thermally. Labelled compounds \textsuperscript{95} and \textsuperscript{96}, exposed to insufficient light to complete photolysis, give diazonium salts which are partly rearranged to \textsuperscript{97}; here the relative extents of rearrangement and

\[
\begin{align*}
\text{MeO} & \quad \text{COCHN}_2 \\
(94) & \\
\text{Me} & \quad \text{Me} \\
(95) & \\
\text{OMe} & \quad \text{Me} \\
(96) & \\
\text{Ar}^+ \text{N}≡\text{N} & \quad \text{Ar}^+ \text{N}≡\text{N} \\
(97) & 
\end{align*}
\]

hydrolysis are significantly more than in the dark hydrolysis. The conclusion is reached that there is no common intermediate for the thermal and photochemical reactions. The photolysis of 2-methoxybenzene-trans-diazosulphonate has been reported.\textsuperscript{60} The reaction involves \textit{trans} → \textit{cis} isomerism and photochemical conversion of the \textit{cis}-isomer to diazonium and sulphite ions. This process is followed by photolysis of the diazonium ions with a quantum yield of 0·39 (313 nm) and 0·56 (254 nm). The quantum yield for the isomerisation of the \textit{trans}-diazosulphonate is also wavelength-dependent, being 0·29 (at 245 nm) and 0·42 (at 436 nm).

The photolysis of both dimethyl ketazine \textsuperscript{98} and the perfluoro-derivative \textsuperscript{99} have been reported. Vapour-phase photolysis of \textsuperscript{98} yields acetonitrile and \textit{N}-methyl dimethylketimine \textsuperscript{100}, and minor amounts of ethane. Variation of various reaction parameters and the effects of added oxygen and nitrogen indicate an intramolecular reaction for the formation of the major products. The intermediate of the reaction would seem to have an appreciable lifetime since deactivation by nitrogen is possible to some extent. The quantum yield for decomposition is very much greater at shorter wavelengths, and the increased production of ethane under these conditions suggest that several excited states may participate in the overall decomposition mechanism. Formation of the major products from \textit{trans}-dimethyl ketazine and the minor from the \textit{cis}-isomer may be readily

envisaged. It has been previously reported that the perfluoro-compound (99) gives CF$_3$=N· radicals, and the ease with which these radicals add to fluoro-olefins suggests that in the presence of photolytic sources of fluoro-alkyl radicals, azomethines would be formed. The only previous method for the preparation of azomethines of this type was the pyrolysis of oxazetidines (e.g. 101). Irradiation of the perfluoro-compound (99) in

\[
\begin{align*}
\text{CF}_3 & \quad \text{N} \quad \text{CF}_2 \quad \Delta \\
\text{O} & \quad \text{C} \quad \text{F} \quad \text{Cl} \\
\end{align*}
\]

(101)

the presence of perfluoroacyl fluorides did indeed yield the desired azomethine (102) in addition to trifluoromethyl isocyanate (103), carbonyl fluoride, and non-condensable material suggested to be carbon monoxide and nitrogen. The yield of isocyanate is ca. 25%, and the azomethine yield is of the same order, depending on the acyl fluoride employed. The reaction may be rationalised by the following mechanism:

\[
\begin{align*}
\text{CF}_3=\text{N}=\text{N}=\text{CF}_2 \quad (99) & \xrightarrow{\text{hv}} 2\text{CF}_3=\text{N}. \\
\text{R}_F\text{COF} & \xrightarrow{\text{hv}} \text{R}_F^+ + \cdot\text{COF} \\
\text{R}_F^+ + \text{CF}_3=\text{N}. & \longrightarrow \text{R}_F\text{N}=\text{CF}_2 \quad (102) \\
\text{CF}_3=\text{N}. + \cdot\text{COF} & \longrightarrow \text{CF}_3=\text{NCOF} \\
\text{CF}_3=\text{NCOF} & \longrightarrow \text{CF}_3\text{N}=\text{C}=\text{O} \quad (103) \\
\end{align*}
\]

(7) (8) (9) (10) (11)

Irradiation of the related system, benzalazine in methanol or benzene, gives trans-stilbene as a minor product, plus benzonitrile and benzaldehyde imine which on work-up is isolated as benzaldehyde. The excited state responsible for this decomposition is not yet known, but the absence of reaction at wavelengths longer than 280 nm (the compound has an absorption at 303 nm), and the lack of product formation in the presence of triphenylene which should have triplet energy greater than the azine, lead to the unusual conclusion that the reactivity of the azine is derived from excited states other than the normal lowest excited singlet or triplet states.

The photolysis of compounds containing three and four nitrogen atoms in five- and six-membered rings is considered below.

A marked increase in the photosensitivity of 4-phenyltriazole has been noted by the introduction of a C-bromo-substituent. Thus, while the parent compound in methanol yields phenylacetonitrile only slowly, the bromo-derivative under the same conditions rapidly forms acetophenone,

methyl benzoate, phenylacetonitrile (104), and \(\alpha\)-methoxy-phenylacetonitrile (105). That the first step is C—Br cleavage is confirmed by irradiation of the bromo-derivative in anhydrous ether to give the parent triazole as its hydrobromide. The genesis of acetophenone and methyl benzoate is as yet unknown but the formation of the products (104) and (105) may be accounted for by the mechanism outlined in Scheme 2. This report seems

![Scheme 2](image)

**Scheme 2** Photolysis of vic-triazoles

to be the first account concerned with photolytic cleavage of a *vic*-triazole ring unsubstituted on nitrogen.

The cleavage of \(N\)-substituted triazoles is known, and this process has been investigated as a possible route to the, as yet unknown, antiaromatic heterocycle 1-azene.\(^6\) Such hopes were, however, not realised. Irradiation of benzene solutions of the triazole (106), lead instead to the ketenimine (107) and 2,3-diphenyl indole. In contrast the benzotriazole (108) gives a quantitative yield of carbazole, and 1-benzhydrylaminobenzotriazole (109) in benzene solution forms (110) in 80% yield. Benzotriazoles similar to (108), but substituted in the 1-position by a heterocyclic moiety containing a nitrogen atom vicinal to the benzotriazolyl group (*e.g.* 111), have been subjected to thermolysis and photolysis.\(^7\) The thermal reaction of (111) in the presence of zinc chloride or acid yields 9H-pyrado[2,3,b]indole (112), and small amounts of pyrido-[1,2,a]-benzimidazole (113). Thus the

---

nitrogen in the heterocyclic moiety is not involved in the reaction except when the 'normal' position of attack is blocked. On the other hand, the photochemical reaction is carried out in neutral media, is inhibited by acid, and yields (113) in addition to a small amount of (112). Here cyclisation preferentially involves attack on the nitrogen.

The first step in the photochemical transformation of 3-phenyl-3,4-dihydro-1,2,3-benzotriazin-4-one (114) to 7-phenyl-7-azabicyclo[4,2,0]octa-1,3,5-trien-8-one (115) has been shown to involve the formation of (116), by trapping this intermediate with β-naphthol. The loss of nitrogen in this reaction has been shown to occur from the N(1) and N(2) positions by studying the photolysis of the compound 15N-labelled in the N(3) position.

The products derived from lithium 3-phenyl-3,4-benzotriazin-4(3H)-one (117), a compound related to (114), implicate ground-state benzocyclopropenone as a reaction intermediate. Nitrogen

---

is rapidly eliminated on irradiation of (117), and lithium toluene-\(p\)-
sulphonate, methyl \(p\)-chlorobenzoate, and the toluene-\(p\)-sulphonohydrizide
of 5-chloro-2-methoxybenzoic acid (118) are formed. The production of
(118) suggests the intermediacy of a species having the symmetry of a
benzocyclopropenone which subsequently yields (118) by the stages outlined
below. Benzocyclopropenones have also been implicated in the oxidation
of 3-aminobenzotriazin-4-one.\(^{72}\)

\[ \text{PhC}^+\equiv\text{N}^-\text{NH} \]

\[ \text{PhC}^+\equiv\text{N}^-\text{NH} \]
Photoelimination Reactions

A new source of phenylcarbene has been reported from a study of the photolysis of 5-phenyl tetrazolide anion (119). Two equivalents of nitrogen are eliminated on irradiation of (119), and products derived from the reaction of phenylcarbene with the solvent are formed. Insertion into (C—H, O—H, and N—H) and olefin addition products are all obtained. Photolysis of 5-phenyltetrazole, on the other hand, causes elimination of 1 mole of nitrogen and the formation of a transient species, formulated as the 1,3-dipole (120), which dimerises to yield a dihydrotetrazine (121). The dihydrotetrazine (121) also undergoes light-induced decomposition to benzonitrile and 3,5-diphenyl-1,2,4-triazole.

4 Fragmentation Reactions of Organosulphur Compounds

The vast majority of sulphur-containing organic compounds undergo photodecomposition and elimination reactions more readily than their oxygen analogues. This greater photolability is doubtless responsible for the increasing number of reports which appear each year concerned with the photolysis of sulphur compounds, particularly thiols and sulphides.

The primary process in the photolysis of methanethiol is reported to be S—H cleavage: the hydrogen atom produced abstracts sulphydryl hydrogen from the substrate, giving molecular hydrogen*. The quantum yield for hydrogen formation from ethanethiol is unity, and independent of pressure, whereas from methanethiol the quantum yield is less than unity, and increases with pressure. This behaviour is ascribed to an additional sequence of reactions involving decomposition of the substrate catalysed by CH₃S· radicals. The RS· radicals produced in such photolyses dimerise to give an excited disulphide molecule which attains the ground state by collisional deactivation. The nature of this excitation is at present unknown but it is highly improbable that the molecule is vibrationally excited. In the case of ethanethiol, this deactivation process can sensitise decomposition of the substrate to ethylene, ethane, and hydrogen sulphide. The decomposition of methanethiol has been studied in the presence of added gases such as ethylene and nitric oxide. In the first case, methyl ethyl sulphide is formed in addition to the usual products, and is suggested to arise from a chain reaction by attack of CH₃S· radicals on the ethylene to give a composite radical, followed by hydrogen abstraction from the thiol. The addition product from nitric oxide is CH₃SNO. At high nitric oxide pressures, a slow chain reaction becomes operative producing nitrogen and CH₃SNO.

Researches in this field have also been concerned with the wavelength dependence of the hydrogen atom energy. Recently evidence has been provided for important effects of translationally excited hydrogen atoms in

---


* See Part I, chapter 2.
the CH₃SH–C₂H₄ and CH₃SH–D₂ systems.⁷⁶, ⁷⁷ From an extension of this work on the latter system, it is concluded that the energy distributions of hydrogen atoms, produced in photolyses at 253·7 and 228·8 nm, differ significantly.⁷⁸ This conclusion is in disagreement with another report in which it is stated that the hydrogen atom energy distribution from the CH₃SH–C₂H₄ system is essentially the same at the two wavelengths.⁷⁷

The mercury-sensitised photolysis of methane and ethanethiol leads to both S—H (the sole process in the unsensitised reaction) and C—S bond cleavage.⁷⁹ Some evidence was obtained from ethanethiol for a small proportion of C—C bond cleavage, but C—H rupture was not detected in either compound.

The sole product from liquid-phase photolysis of dimethyl disulphide and diethyl disulphide mixtures is reported to be methyl ethyl disulphide.⁸⁰ The exceptionally high efficiency of the overall process is ascribed to the chain propagation step R'S⁺ + RSSR' → RSSR⁺ + RS⁻ which probably proceeds through attack of the thyl radical on the S—S linkage. Pure disulphides give predominantly the thiol.⁸¹ Addition of ethylene to the systems causes no significant alteration of the rate of methyl ethyl disulphide formation from the co-photolysis, thereby indicating a low efficiency of RS⁻ scavenging by the olefin. With the pure substrates, addition of ethylene causes a lower rate of thiol formation, and production of relatively small amounts of sulphides. The mercury-sensitised decomposition of disulphides shows two primary modes of rupture, viz. S—S and C—S.⁸² There is no reaction leading to hydrogen removal, and the subsequent reactions of the RSS⁻ and RS⁻ radicals are mainly combination and disproportionation. Sensitised reactions of dimethyl sulphide indicate only one pathway of C—S bond rupture as may be expected.

Photolysis of the disulphide linkages in insulin has also been examined and the results show that the three S—S bonds randomly undergo reaction to give thiols.⁸³

Cyclic mercaptoles (cyclic dithioacetals) give a variety of products by primary and secondary photolytic steps.⁸⁴ The products of the reaction are also dependent upon the ring size. Thus both compounds (122) and (123) eliminate the elements of ethylene sulphide photochemically and give, for example with (122), the cyclic thione (124) which is isolated as the dimer (125). The thione or its dimer undergoes secondary photolysis to give the corresponding disulphide (126), sulphide (127), mercaptan (128), and the olefin (129). On the other hand, photolysis of compounds (130) and (131)

Photoelimination Reactions

involves an overall 1,2-shift of one of the geminal sulphur atoms onto an adjacent carbon atom as shown, the ratio of cis- to trans-products in each case is ca. 8:1.

\[ \text{S} \cdot \text{S} \]

\[ \text{(122)} \quad \text{(123)} \]

\[ \text{hv} \]

\[ \text{S} \cdot \text{S} \]

\[ \text{(124)} \]

\[ \text{hv} \]

\[ \text{S} \cdot \text{S} \]

\[ \text{(125)} \]

\[ \text{hv} \]

\[ \text{S} \cdot \text{S} \]

\[ \text{(130)} \]

\[ \text{S} \cdot \text{S} \]

\[ \text{(131)} \]

Reactions analogous to the photolytic formation of dibenzyl, stilbene, and phenanthrene from dibenzyl sulphide have been observed on the irradiation of various alkyl aralkyl sulphides.\(^\text{55}\) Exceptions to this process are found with alkyl \(\alpha\)-alkylbenzyl sulphides [e.g. (132)] which contain a hydrogen atom at the \(\beta\)-carbon relative to the aromatic ring. Although a dibenzyl derivative is formed from such compounds, in place of stilbenes and phenanthrene, styrene is also produced. This reaction is explained by

the loss of ethanethiol from, for example, ethyl α-methylbenzyl sulphide (132), possibly in a solvent cage. Another explanation for the formation of styrene may be hydrogen abstraction from primarily formed 1-phenylethyl radicals (133). 1,2-Elimination of the elements of a thiol is also observed in compounds of type (134) which contain the structural feature

\[
\begin{align*}
\text{Ph} & \quad \text{C} \quad \text{S} \quad \text{C}_2\text{H}_5 \\
& \quad \text{H}_2\text{C} \quad \text{H}
\end{align*}
\]

(132)

\[
\begin{align*}
\text{PhCH} &= \text{CH}_2 \\
\text{C}_2\text{H}_5\text{SH}
\end{align*}
\]

(133)

\[
\begin{align*}
\text{O} & \quad \text{SR} \\
\text{SRR}
\end{align*}
\]

(134)

\[
\begin{align*}
\text{O} & \quad \text{OH} \\
\text{H}_2\text{C} \quad \text{H}
\end{align*}
\]

(135)

An enone (1-naphthol) (135) is produced together with a disulphide (RSSR).

The photochemical loss of sulphur monoxide from a sulphoxide has never been described. Doubtless in the hope of observing this reaction, Schultz et al. have irradiated cis- and trans-1,3-dihydro-1,3-diphenyl-2-thiaphenalene-2-oxides (136) in benzene solution in the presence of benzophenone. However, the compounds did not lose sulphur monoxide but suffered an unusual photodesulphurisation to give an 80% yield of (137).

\[
\begin{align*}
\text{Ph} & \quad \text{S} \quad \text{O} \\
\text{SPh}
\end{align*}
\]

(136)

\[
\begin{align*}
\text{O} & \quad \text{Ph} \\
\text{Ph}
\end{align*}
\]

(137)

The quantum yield for the decomposition of (136) for the sensitised reaction is reported to be 0.23 for the cis-isomer, but only 0.10 for the trans. The lack of quenching of the sensitised reaction by piperylene or cyclohexadiene implies that the initially formed triplet state of (136) undergoes rapid

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relaxation to a lower triplet state which cannot be effectively quenched. This type of relaxation is known for stilbenes.88

A stereospecific elimination process has been observed from 2,5-tosyl-oxyketones.89 Thus while the cis-isomer (138) in benzene forms the α,β-unsaturated ketone (139), and in dioxan a 4:1 mixture of (139) and (140), the trans-isomer (141) is almost photostable, and only on prolonged irradiation produces small amounts of (139) and (140) in a 1:1 ratio. It is therefore concluded that in the elimination of the tosyl group a non-eclipsed conformation of the carbonyl group and the C₆—O bond is required, as is the case with (138) but not with (141). In aqueous dioxan, the cis-isomer (138) yields the β-hydroxyketone (142) together with (139). Similarly, in the acyclic case, the elimination from (143) to yield (144) is suppressed in aqueous dioxan, and the hydroxyketone (145) is formed.

These results provide evidence for the intervention of cationic intermediates, and hence point to the occurrence of heterolytic photocleavage reactions in such molecules.

A new procedure for de-O-tosylation of sugar tosylates has been reported.90 De-O-tosylation is usually performed by catalytic reduction, a method which is somewhat limited by the formation of side-products. In the photolysis of sugar tosylates in methanol, the parent sugars are formed in yields which are typically 90%, and no side-reactions are reported.

In sulphonylated amino-acids and peptides, the S—N bond (of —SO₂NH—) is reported to be cleaved photochemically to give good yields of the amino-acids.91 At present the yields are not sufficiently high to make the process a serious contender against conventional de-blocking of

tosylated amino-acids. The drawbacks to the process lie in its side-
reactions of decarboxylation and deamination, and the tendency for
destruction of certain susceptible amino-acids such as tryptophan.

The photolysis of such symmetrical aroyl dixanthates as di-O-ethyl-SS-
phthaloyl dixanthate (146) might be an attractive route to benzocyclo-
butendione, particularly as it is known that CO—S bond fission in acyl
xanthates occurs to give xanthate and acyl radicals. But attempted
synthesis of (146) unfortunately gave only the lactone (147); thus the
authors were restricted to investigation of the photochemistry of this
compound. The product was a mixture of cis- and trans-biphthalyl (148).
It is uncertain whether the most obvious intermediate carbene (149), is
actually formed in this reaction since it is believed to be formed from
benzocyclobutendione en route to lactones (150) and (151). These com-
ounds were not found among the photolysis products of compound (147).

5 Miscellaneous Decomposition and Elimination Reactions

Each year a large number of photochemical elimination, fragmentation,
and decomposition reactions are reported which do not easily fit into any
system of classification. It is proposed to discuss such reports in the

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following section, and loosely group them according to the type of molecules eliminated or the class of compound under investigation.

A. Elimination of Nitric Oxide.—The loss of nitrogen from organic compounds is a well-known photochemical and thermal procedure, but while such elimination occurs readily on heat treatment from 3-substituted-2-nitrosamino-2,3-dihydrobenzothiazoles (152), nitric oxide is the light-induced elimination product. Diphenyl sulphide derivatives are formed in good yield from the resulting radical, and evidence for the intermediacy of (153) in the process is given by reaction of (152) in the presence of a

\[
\text{PhCOCl} \quad \text{H-atom donor}
\]

hydrogen donor and benzoyl chloride to give the N-benzoyl imine (154). Loss of nitric oxide is observed in the photolysis of nitrosamines generally. Thus the diterpene, 4-N-nitroso-4-N-methyl-12-methoxy-16-norpodocarpa-
8,11,13-trien-4-amine (155) in cyclohexane yields the corresponding amine (156) and provides yet another example in which homolysis to the radical (157), and subsequent disproportionation, occurs in preference to hydrogen abstraction from the C-10 methyl group.\(^\text{95}\)

The photochemistry of nitrosamines, and in particular dibenzyl nitros-
amine (158), has been studied for both neutral and acidic media.\(^\text{96}\) In methanol under air, N-benzylidene benzylamine (159), dibenzylamine, and dibenzylammonium nitrate are formed by a radical abstraction mechanism. Under acid conditions, nitroxy1 is eliminated to give alkylideamines (160). Recombination of these two fragments yields amidoximes (161). The latter reaction might in principle have been either inter- or intra-molecular, but was shown by photolysis of isotopically labelled nitrosamines to be an intermolecular process. Evidence is presented in favour of a non-stereo-
specific elimination of nitroxy1 from nitrosamines protonated at the amino nitrogen atom.

Nitric oxide is also eliminated in the photolysis of nitrosobenzene in ethanol. Reactions subsequent to and competing with the elimination process are outlined in Scheme 3. Three pathways may be distinguished.

\[
\text{Nitrosobenzene} \xrightarrow{hv} C_6H_5^* + \text{NO}
\]

\[
\downarrow \text{hv}
\]

\[
\begin{align*}
\text{Photochemical disproportionation} & \\
\text{to nitrobenzene and azoxybenzene} & \\
+ \text{azobenzene} & \\
\end{align*}
\]

\[
\downarrow \text{hv}
\]

\[
\text{2-hydroxyazobenzene} \quad \xrightarrow{hv} \quad p\text{-nitrodiphenylamine}
\]

\[
\text{Nitrosobenzene} \xrightarrow{\text{reduced}} \text{Diphenyl nitrooxide} \xrightarrow{\text{by e.s.r. spectroscopy}} \text{Benzophenone imine}
\]

\[
\downarrow \text{hv}
\]

\[
\text{p-Nitroso-diphenylamines}
\]

\[
\downarrow \text{NO}
\]

**Scheme 3** *Photolysis of nitrosobenzene*

(i) Homolytic bond fission to a phenyl radical and nitric oxide, (ii) reduction to azoxybenzene, and a minor reaction, (iii) oxidation to nitrobenzene. These varieties of behaviour are also relevant to the reduction reactions of nitrobenzene reported in Part 3, chapter 5.

**B. Loss of Nitrogen-containing Groups.**—Cycloalkanone oximes generally are known to yield the corresponding alkanolic acid amides on irradiation in isopropyl alcohol. It has previously been reported that cyclohexanone oxime in methanol gives caprolactam, caproamide, and small amounts of cyclohexanone. In the case of $\alpha$-alkylated cyclohexanone oximes, products are formed which correspond to preferential cleavage on the side of the more substituted carbon atom, and isopropyl alcohol has been shown to transfer two hydrogens specifically to the excited oxime molecule, acetone being formed. In 1% aqueous solution, however, the oximes give the corresponding ketones, ammonia, and oxygen. These reactions are now rationalised by a mechanism which involves the intermediate formation of the spiro-oxazirane (162), as shown in Scheme 4. The photo-Beckmann rearrangement has been reported in Part 3, chapter 6.

Dimethylaniline hydrochloride is known to be decomposed through photosensitisation with aromatic compounds having high triplet energies. Triplet energy transfer and electron transfer are possible mechanisms for the process. Walsh has reported on the direct photolysis of anilinium salts, and now the decomposition sensitised by acetone has been investigated for

trimethylphenylammonium halides [PhN+Me₃X⁻].

Triplet intermediates for the reaction have been established from kinetic studies and quenching experiments with penta-1,3-diene. In Pyrex apparatus, 90—94% yields of benzene and trimethylamine (after alkali wash) are formed in compounds with X⁻ = Cl⁻ and Br⁻, but when X⁻ = I⁻ there is no significant decomposition since iodide ion quenches triplet acetone very effectively.

The photodecomposition of the acaricide, N-(4-chloro-2-methylphenyl)-NN-dimethylformamidine, has been studied both in solution and on silica gel chromatoplates at 254 and 364 nm. The major decomposition product is 4-formyl-4-chloro-o-toluidine. Similar experiments with 4-chloro-o-toluidine led to numerous uncharacterised products.

Photocyclisation of propenes indicates that 1,2-alkyl migrations may be induced from an excited state of an olefin. The related photoreaction of a β-amino-substituted keto-olefin (163) has now been reported; in aqueous dioxan the loss of a nitrogen-containing fragment to give the diketone (164) is observed. In cyclohexane the reaction takes a different course with production of the enamine (165) via secondary photoisomerisation (1,3-H-shift) of the first-formed product (166).

Photofragmentation of 16-unsubstituted 22,26-chloroepimino cholestan (167) into epimeric 20-chloropregnanes (168) in trifluoroacetic acid has

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Photoelimination Reactions

(163) \[ \text{Ph} \overset{\text{NH} - \text{CMe}_3}{\text{CHPh}} \rightarrow \overset{\text{hv}}{\text{Dioxan}} \overset{\text{Ph}}{\text{O}} \overset{\text{NHCCMe}_3}{\text{CH}_2} \]

(166) \[ \overset{\text{hv}}{\text{Cyclohexane}} \overset{\text{O}}{\text{H}} \overset{\text{Ph}}{\text{CH}_2\text{NHCCMe}_3} \]

(165) \[ \overset{\text{hv}}{\overset{\text{H}_2\text{O}}{\text{O}} \overset{\text{NHCCMe}_3}{\text{H}} \overset{\text{Ph}}{\text{CH}_2\text{Ph}}} \]

(167) \[ \overset{\text{hv}}{\text{CF}_3\text{CO}_2\text{H}} \]

(168) \[ \]

(169)
been reported.\textsuperscript{106} and the sodium salt of 2-deoxy-2-(2,4-dinitroanilino)-D-glucitol (169) has been shown to form the lower corresponding aldose, D-arabinose, by photolysis of its aqueous solution.\textsuperscript{107} From the latter reaction a yellow crystalline compound was also isolated, probably 4-nitro-2-nitrosoaniline.

C. Loss of Halogen Acids and Halogens.—Photolysis of trichlorofluoro-methane solutions of t-butyl iodide at $-100^\circ$ yields isobutylene and hydrogen iodide as the major products even in the presence of oxygen.\textsuperscript{108} The absence of isobutane and C\textsubscript{8}H\textsubscript{18} dimer indicates that isobutylene is formed by disproportionation of the radical pair in the solvent cage or by an independent molecular elimination, and that all the t-butyl radicals which escape from the cage are scavenged by oxygen.

The irradiation of cis- and trans-4-iodo-3-heptenes in pentane or chloroform solutions is reported to yield hept-3-yne and cis- and trans-hept-3-ynes as the major products.\textsuperscript{109} The iodides undergo cis--trans isomerisation, and at low conversions (<5\%) hepta-3,4-diene is formed. The diene is believed to be transformed into other products by hydrogen iodide at higher conversions. The results are considered in terms of primary formation of vibrationally-excited cis- and trans-hept-3-en-4-yl radicals, and secondary reactions of these.

Loss of hydrogen halide from allyl chloride in the liquid phase yields allene and propene in a 1:1 ratio (quantum yield = 0.01), while the irradiation of solid allyl chloride gives allene, propene, and cyclopropane.\textsuperscript{110} The proposed primary process is cleavage of the C—Cl bond to give an allyl radical, but the formation of a cyclopropyl radical may be a parallel primary process. In the liquid phase, radical disproportionation occurs, but in the solid, hydrogen-abstraction from allyl chloride is postulated as an additional reaction.

Latowski has measured the quantum yields for hydrogen chloride formation from the irradiation of NN-dimethylaniline in dioxan and methanol solutions containing chlorobenzene derivatives, and in chlorinated methane solutions.\textsuperscript{111} The mechanism proposed involves formation of a charge-transfer complex by electronic excitation.

Specific loss of the 2-chloro-substituent is reported from 3-amino-2,5-dichlorobenzoic acid in methanol when oxidation of the irradiated solution is prevented.\textsuperscript{112} A complex mixture results from photolysis in the presence of oxygen.

D. Decarboxylation.—Photodecarboxylation of organic acids is not a particularly general reaction. Even so, many examples of it have been

reported. Pyridine dicarboxylic acids seem to be particularly susceptible to monodecarboxylation.\textsuperscript{113} Thus the four isomers (170), (171), (172), and (173) give the monocarboxylic acids (174), (175), and (176), as shown in Scheme 5. Photolysis of 1-naphthylacetic acid in ethanol follows several

pathways, including decarboxylation, to yield naphthalene, 1-methyl-naphthalene, ethyl-1-naphthoate, 1-naphthoic acid, and phthalic acid.\textsuperscript{114}

The rates of thermal and photochemical decarboxylation of aliphatic acids have been studied in the presence of lead tetra-acetate.\textsuperscript{115} Photochemically at 30° pivalic acid (tertiary) decarboxylates 100 times, and iso-butryic acid (secondary) 20 times faster than n-butryic acid with 350 nm radiation. The thermal reaction at 80—100° shows a smaller spread of reactivity, and is complicated by oxidation of olefinic products by Pb\textsuperscript{IV}. The lead tetra-acetate undergoes rapid ligand exchange with the carboxylic acids, and in neat solution the equilibrium is displaced completely to the right in equation (12). Photolysis converts Pb\textsuperscript{IV} to Pb\textsuperscript{II} and in the case of sec-butryic acid for example, propane, propylene, and isopropyl isobutyrate are formed. The reaction is non-stoichiometric and thus equation (13) is not balanced.

\begin{equation}
\text{Pb}^{\text{IV}}(\text{OAc})_4 + n\text{RCO}_2\text{H} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{Pb}^{\text{IV}}(\text{OAc})_{4-n}(\text{O}_2\text{CR})_n + n\text{HOAc} \quad (12)
\end{equation}

\begin{equation}
\text{(Pr}^{\text{ICO}}_2)_2\text{Pb}^{\text{IV}} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{(Pr}^{\text{ICO}}_2)_2\text{Pb}^{\text{II}} + \text{CO}_2 + \text{propane} + \text{propylene} + \text{Me} \quad (13)
\end{equation}


\textsuperscript{114} D. A. M. Watkins and D. Woodcock, \textit{Chem. and Ind.}, 1968, 1522.

E. Elimination of Aliphatic Hydrocarbons.—Photolysis of tetrabutylammonium iodide in acidified aqueous solution, either direct or uranyl-sensitised, has been observed to yield a precipitate of tributylidooammonium iodide, and the elimination of butane. The reaction is represented by equation (14). Small amounts of butylene and octane are also formed. This

\[
R_4N^+ + 2I^- + H^+ \xrightarrow{\text{hv}} R_3IN^+I^- + RH
\]

reaction was reported four years ago, and has now been extended to the preparation of other trialkylidooammonium iodides including methyl, ethyl, propyl, butyl, and isopentyl compounds, with the concomitant elimination of the respective paraffins.

The mass spectrum of \(N\)-t-butyl-2,4-diphenylpyrrole (177) shows a loss of \(C_4H_8\) fragment, to leave an ion which is similar in structure to the molecular ion of 2,4-diphenylpyrrole. Similarly (177) shows a loss of \(C_4H_8\) moiety on photolysis of its alcohol solution at 253-7 nm, and 2,4-diphenylpyrrole is the sole product. Two fundamentally different pathways may be envisaged for the decomposition: these are homolysis and reaction of the radicals with the solvent to give the product (path A), and expulsion of isobutylene following rearrangement (path B). Since \(N\)-cyclohexyl- and \(N\)-phenethyl-diphenylpyrroles are photostable, it is suggested that the former mechanism (path A) operates, as the second mechanism should at least have allowed rearrangement to occur. Pyrolysis of (177) also yields the pyrrole and isobutylene, and it is thus tempting in this case to suggest a relationship between unimolecular reaction of ions in the mass spectrometer, photochemical, and thermal behaviour.

Ethylene is reported to be eliminated photochemically from cyclo-octa-1,5-dienes.\textsuperscript{119} The intermediacy of diradicals of type (178) is consistent with the results. Other processes of isomerisation and dissociation of this hydrocarbon have been previously reported.\textsuperscript{120}

**F. Photolysis of Lactams.**—Photolysis of $\alpha$-lactams causes fragmentation which formally resembles a Norrish Type I photodecarbonylation of amides, although in this case of $\alpha$-lactams the yields are much higher. The products of the reaction are the corresponding Schiff's bases, e.g. (179) and (180).\textsuperscript{111, 122} Thermolysis, on the other hand, causes a completely different cleavage to ketones and isocyanides.\textsuperscript{121} Attention is again drawn to the similarity of fragmentation induced photochemically and that caused by electron impact, since with compound (181) the mass spectrum shows a

\begin{equation}
\text{Me}_3\text{C}\cdots\text{C} \quad \text{Me}_3\text{C}\cdots\text{C} \quad CO + \text{Me}_3\text{CH} = N - C\text{Me}_3
\end{equation}

(179)

\begin{equation}
\text{H} \quad \text{Me}_3\text{C} \quad \text{Me}_3\text{C} - N \equiv C
\end{equation}

(181)

\begin{equation}
\text{CH} = N \quad \text{CH} = N
\end{equation}

(180)


weak or negligible parent ion, but the \((M - 28)^+\) peak is significant even at 10—12 eV.\(^{123}\) 

\(\beta\)-Lactams have been shown to fragment by two pathways, C or D. Generally the thermal course of reaction is D, and it has now been shown that whereas \(\beta\)-lactams unsubstituted in the 4-position [e.g. (182)] undergo C-type cleavage photochemically, compounds substituted in the 4-position [e.g. (183)] exhibit significant proportions of D-type fission.\(^{123}\) The quantum yield for the processes is in the range 0.01—0.04.

\[
\begin{align*}
R'\text{NCO} & \quad + \quad R''\text{CH}=\text{CHR} \\
\xrightarrow{D} & \\
R'\text{N}=\text{CH} - R'' & \quad + \quad \text{RCH}=\text{C}=\text{O} \\
\xrightarrow{C} & \\
\text{Ph} & \quad \xrightarrow{\text{hv, MeCN, PhNH}_2} \quad \text{Ph}-\text{N}=\text{CH}_2 & \quad + \quad \text{CH}_2=\text{C}=\text{O} \\
\quad \text{(182)} & \\
\text{Ph} & \quad \xrightarrow{\text{hv}} \quad \text{Ph}-\text{N}=\text{C}=\text{O} & \quad + \quad \text{Ph}_2\text{C}=\text{CH}_2 \\
\quad \text{Ph} & \quad \text{(183)} & \\
\text{Ph} & \quad \xrightarrow{\text{hv}} \quad \text{Ph}-\text{N}=\text{CPh}_2 & \quad + \quad \text{CH}_2=\text{C}=\text{O} \\
\end{align*}
\]

\(\delta\)-Hydroxylactams on photolysis in aqueous solution are reported to undergo replacement of the hydroxy-group by hydrogen.\(^{124}\) The reaction has been demonstrated for a number of other compounds of this type with chemical yields varying between 10 and 30%.

G. Decompositions into Several Small Fragments.—It is reported that four concurrent molecular processes arise from the photolysis of succinimide vapour.\(^{125}\) A common initial ring-opening step is suggested, followed by rearrangement and fragmentation. Thermolysis of succinimide favours reactions (17) and (18), whereas \(N\)-methylsuccinimide both thermally and photochemically exhibits fragmentation by reaction (15) mainly, but with reaction (16) occurring to some extent.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \xrightarrow{\text{O}} \quad \text{CO} + \text{HNCO} + \text{C}_2\text{H}_4 \quad (\sim 40\%) \\
\text{H}_2\text{C} & \quad \xrightarrow{\text{hv}} \quad \text{CO} + \text{HCN} + \text{C}_2\text{H}_4 \quad (\sim 40\%) \\
& \quad \xrightarrow{\text{hv}} \quad \text{CO} + \text{H}_2\text{O} + \text{CH}_3=\text{CHCN} \quad (\sim 10\%) \\
& \quad \xrightarrow{\text{hv}} \quad \text{CO}_2 + \text{MeCH}_2\text{CN} \quad (\sim 10\%) \\
\end{align*}
\]


**Photoelimination Reactions**

Results of the vapour-phase photolysis of isocyanic acid have been explained by a mechanism involving alternative primary dissociations (19) and (20). The ratio of (19) to (20) increases with decreasing wavelength,

\[
\text{HNCO} + \text{hv} \quad \rightarrow \quad \text{NH} + \text{CO} \quad (19)
\]

\[
\text{HNCO} + \text{hv} \quad \rightarrow \quad \text{H} + \cdot \text{NCO} \quad (20)
\]

and the subsequent reactions of the radicals lead to the formation of carbon monoxide, nitrogen, hydrogen, and polymer. The gaseous products are formed in the ratio 3:1:1.

The direct photolysis of hydrazine has been previously studied, and may be summarised by the equations \(\text{N}_2\text{H}_4 \rightarrow \text{NH}_2 + \text{NH}_3\), and \(\text{N}_2\text{H}_4 \rightarrow \cdot \text{N}_2\text{H}_3 + \cdot \text{H}\). In the vacuum-u.v. photolysis, other processes are postulated including \(\text{N}_2\text{H}_4 \rightarrow \text{NH} + \text{NH}_3\), and \(\text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2\). Mercury-sensitised decomposition of hydrazine has now been investigated in a fast-flow reactor coupled to a mass spectrometer. Direct evidence has been obtained for the participation of \(\cdot \text{N}_2\text{H}_3\), \(\cdot \text{N}_2\text{H}_2\), \(\cdot \text{NH}_3\), and \(\text{NH}\) in the decomposition, and the two unsensitised primary decomposition modes have been established in this case also.

Photolysis of tetrafluorohydrazine in the presence of alkanes is known to give \(\text{R} - \text{NF}_2\), and with olefins to produce \(\text{Me} \cdot \text{CH}:\text{CH} \cdot \text{CH}_2 \cdot \text{NF}_2\) and \(\text{Me} \cdot \text{CHF} \cdot \text{CH(NF}_2\cdot \text{Me}\). (See Part I, chapter 2.) The reaction has now been examined in the presence of cyclopropane; a variety of products is formed.

\[
\text{F}_2\text{NNF}_2 + \text{C}_3\text{H}_6 \quad \rightarrow \quad \text{FCH}_2\text{NF}_2, \quad \text{FCH}_2\text{CH}_2\text{NF}_2, \\
\quad \text{FCH}_2\text{CH}_2\text{CH}_2\text{NF}_2, \quad \text{FCH}_2\text{CH}_2\text{CN}
\]

Multiple fragmentations have been observed in the liquid-phase photolysis of both \(\gamma\)-lactones (184) and ozonides. A methyl group in the

\[
\begin{align*}
\text{R}_1 \quad \text{R}_2 \\
\text{O} \quad \text{O} \\
\text{R}_3
\end{align*}
\]

\(184\)

\[
\begin{align*}
\text{R}_1 \quad \text{R}_2 \\
\text{H} \quad \text{H} \\
\text{O} \quad \text{O} \\
\text{R}_1 \quad \text{R}_2
\end{align*}
\]

\[
\begin{align*}
\text{R}_1 \quad \text{R}_2 \\
\text{H} \quad \text{H} \\
\text{O} \quad \text{O} \\
\text{R}_1 \quad \text{R}_2
\end{align*}
\]

\(\alpha\)-position of the lactone increases the quantum yield of formate production from 0.23 (allyl formate) to 0.39 (crotyl formate) and for cyclopropane from 0.013 to 0.027; but the yield of aldehyde does not change.

---

substituent effects and the observed wavelength dependence are discussed in terms of vibrational effects in solution. The first publication concerning the photolysis of ozonides has appeared within the year.\textsuperscript{132} The study has been concerned with di-isopropyl ozonide (185) and cyclopentene ozonide (186) in pentane solution in Pyrex apparatus. Intermediates (187) and (188) in the

\[
\begin{align*}
\text{O} & \text{O} \\
\text{C} & \text{C} \\
\text{O} & \text{O} \\
\xrightarrow{\text{hv}} & \text{Isobutyraldehyde + isobutyric acid + HCO}_2\text{H} \\
& + \text{CHO} + \text{CO}_2\text{H}
\end{align*}
\]

reactions arise by O–O bond cleavage followed by two C–C ruptures. The good yield of cyclopropane from cyclopentene ozonide suggests that the process may be useful preparatively. The results of photolysis of ozonides of higher homologues in the cycloalkene series will clearly be of interest.

H. Massive Fragmentation.—Unlike other –N=N– compounds reported earlier, 2,2-diphenyl-5-diphenylmethylen-1,3,4-oxadiazoline (189) does not lose nitrogen on photolysis. Instead diphenylketene and diphenyl-diazomethane are formed. A mechanism has now been put forward to account for this reaction.\textsuperscript{133} The primary chemical process is suggested to be formation of the α-lactam (190), which being very reactive undergoes secondary reactions. Evidence for the intermediacy of (190) is found by studying the reaction in ethanol and diethylamine when (191) and (192) respectively are formed. However, despite the evidence for implication of the lactam, this has not yet been detected directly in such photolyses.

A light-induced retro-Diels–Alder reaction has been observed for styrene and indene adducts of anthracene.\textsuperscript{134} The dissociation is rationalised by assuming a stepwise mechanism involving a diradical intermediate, and again the similarity between photochemical reactions and electron impact studies is pointed out. Other Diels–Alder adducts of anthracene not

Photoelimination Reactions

\[
\begin{align*}
\text{Ph}_2\text{C}=\text{O} & \xrightarrow{\text{hv}} \text{Ph}_2\text{C}^{-}\text{N}=\text{N}^{+}=\text{CPh}_2 \\
(189) & \\
\xrightarrow{(a) \ \text{C}_2\text{H}_5\text{OH} \quad (b) \ \text{(C}_2\text{H}_5)_2\text{NH}} & \\
\xrightarrow{\text{Ph}} \text{Ph}_2\text{C}=\text{C}=\text{O} + \text{Ph}_2\text{CN}_2 \\
(191) & \\
\xrightarrow{\text{(C}_2\text{H}_5)_2\text{N}=\text{C}=\text{N}^{+}=\text{CPh}_2} & \\
(192) & \\
\end{align*}
\]

involving an aromatic residue on the dienophile are reported to be photo-

stable.

Two groups of workers report on the photoelimination of dimethylketen
from the benzobicyclo[2,2,2]octa-5,7-dien-2-one system to form hydro-
carbons (193) and (194).\textsuperscript{135} In the acetone-sensitised reaction, the re-
arrangement product (195) is also formed, together with these hydrocarbons.
The formation of (195) is somewhat analogous to the benzobarelene-
benzosemibullvalene rearrangement.\textsuperscript{136}


\textsuperscript{15*}
The rates of $p$-chloranil-sensitised monomerisation of the 1,3-dimethyluracil dimers are reported to be very dependent upon the dimer structure.\textsuperscript{137} Thus while the trans,anti-dimer is photostable under these conditions, the other three dimers form the monomer in yields varying between 8 and 50\%.

Phenylcyanocarbene is of interest since it could be tautomeric with phenylethynylnitrene Ph\(\equiv\)C\(-\)C\(-\)N\(^\circ\). Its generation from a variety of epoxides has been reported\textsuperscript{138} but an alternative, simpler, and more efficient method for its genesis has now been described from 1,3,2-dioxaphospholans (196), which may be prepared from benzoyl cyanide and triethyl phosphite. Irradiation in the presence of an olefin gives a cyclopropane corresponding to addition of the carbene form of the intermediate; no products derived from the hypothetical nitrene form are reported. By-products of the reaction are triethyl phosphate and benzoyl cyanide; the latter is photolabile and easily resinifies.

Part IV

POLYMER PHOTOCHEMISTRY
1 Introduction

Photochemical processes are of enormous industrial interest when applied to prepare and modify commonly used polymeric materials. The concern of industry may be divided into several areas. Firstly, addition polymerisations require initiation by free radicals. Commonly these are provided by the thermal dissociation of some convenient additive. However, use of a thermal initiator usually introduces end groups into the polymer which may be undesirable, such as ketonic species. In such cases production of free radicals may be facilitated by the photochemical breakdown of compounds which do not have this undesirable side-effect. Thus photo-polymerisation is of immediate industrial importance. Related to this are polymerisations photosensitised by the addition of compounds which do not immediately break down into free radicals upon irradiation, but which provide a source of radicals via secondary reactions. An example of this type would be benzophenone. It is well known that increase in the number of cross-links between polymer chains drastically alters the physical properties of macromolecules. Cross-linking is often achieved by high-energy irradiation of the sample, but the same effect may be obtained by use of lower energy photons; and thus photochemical cross-linking has technological importance. Absorption and emission spectra of polymeric materials provide useful information about their chemical and physical structure, and irradiation with u.v. light may also effect such structural changes. However, perhaps the widest industrial interest in the applications of photochemistry to macromolecules is in the photodegradation and photo-oxidation of high polymeric material. The destruction of man-made polymers and the change in their physical and optical properties wrought by sunlight presents a very serious industrial problem. Accordingly, vast industrial efforts have been applied to find a solution to the problem. Commonly, radical scavengers and u.v. absorbers are introduced into polymers to improve their stability to sunlight. Because of the large number of publications concerning industrial applications of polymer photochemistry, no attempt is made here to provide a comprehensive review of the field. Instead attention is focused on relatively few publications which may be of a more fundamental interest to workers in the field, although at the same time references are provided so that readers interested in any particular aspect may consult the original sources.
2 Photopolymerisation

Photopolymerisation has been reviewed recently.\textsuperscript{1, 2} As is pointed out in the latter article, the initiation of addition polymerisation via a light-initiated free radical process offers several advantages over that induced thermally. These are that the kinetics (including nonstationary state kinetics) of the polymerisation process may be studied in detail, since the light may be turned on and off readily. Moreover in many photochemical systems the primary production of free radicals is independent of temperature, and thus polymerisations may be induced at low temperatures where thermal initiation is impossible. A more recent application of one of the unique aspects of photopolymerisation is the confinement of polymerisation to local regions so as to produce relief images, \textit{i.e.} a type of photography. Addition polymerisation may be broken down into elementary steps: (i) the production of primary radicals; (ii) initiation of chain radicals from primary radicals; (iii) chain propagation, and (iv) chain termination. Assuming that step (i) involves the photolytic breakdown of a sensitiser, the steps may be written as follows:

\begin{align}
S + h\nu & \rightarrow R^* \quad (1) \\
R^* + M & \rightarrow RM^* \quad (2) \\
RM_{n^*} + M & \rightarrow RM_{n+1}^* \text{ etc.} \quad (3) \\
RM_n^* + RM_m^* & \rightarrow \text{termination} \quad (4)
\end{align}

where S is the sensitisier, R*, are the primary radicals, and RM* etc. the propagating radicals. For low intensities of illumination it can be shown that the rate of reaction (1) is given by

\[ \nu_{(1)} = I_0 \Phi \epsilon[S] \quad (5) \]

where \( I_0 \) is the intensity of incident radiation, \( \Phi \) the quantum yield of production of radicals, \( l \) the optical path length, and \( \epsilon \) the molar extinction coefficient of the initiator. If step (4) is the only termination step (\textit{i.e.} primary radicals are not involved), it can be shown that the rate of polymerisation is given by equation (6): (see ref. 2).

\[ \frac{-d[M]}{dt} = k_p \left( \frac{I_0 \Phi \epsilon[S]}{k_t} \right)^4 [M] \quad (6) \]

where the rate constants for propagation and termination are \( k_p \) and \( k_t \) respectively. It is the nature of the first reaction, (1), which is of principal photochemical interest. Certain monomers are themselves light sensitive, and thus no initiator is required to polymerise them. Thus visible light may be used to induce the photopolymerisation of pure methyl methacrylate,\textsuperscript{3, 4} and photo-irradiation of maleimide and its \( N \)-substituted derivatives in the

absence of sensitiser leads to polymerisation. It can be seen from equation (6) that in these cases, where \([S] = [M]\), the rate of polymerisation should have a three halves dependence upon monomer concentration. However, it is usual for sensitisers to be added to monomers to induce the photochemical reaction. These may be any convenient source of free radicals, e.g. ketones and other organic carbonyl compounds, peroxides, nitrogen compounds such as azo-compounds, halogen-containing compounds, sulphur compounds etc. The use of these materials is reviewed in reference 2, and further examples of compounds which decompose to give free radicals will be found in Part II. However, not all free radicals are capable of initiating polymerisation; indeed sources of large unreactive free radicals are frequently added to monomers as radical scavengers in order to prevent polymerisation.

The presence of sulphur-containing materials in petroleum products causes complications in radical oxidations and storage. Some recent examples of the use of sulphur-containing compounds to initiate radical polymerisations can be quoted. Sodium benzyl thiosulphate has been found to be a good photosensitiser for methyl methacrylate and acrylamide polymerisation, and equation (6) was obeyed well for this system. The activation energy for the methyl methacrylate polymerisation was found to be 5.1 kcal mole\(^{-1}\). \(\beta\)-Keto sulphides may also be used to sensitise methyl methacrylate, acrylonitrile, styrene, and vinyl acetate polymerisations. Sensitisers used were phenyl phenacyl sulphide, phenyl acetonyl sulphide, ethyl acetonyl sulphide, and ethyl phenacyl sulphide: their efficiency compared with azoisobutyronitrile was good with the exception of the last, and in the order presented. The difference in efficiency between phenyl phenacyl sulphide and ethyl phenacyl sulphide probably reflects a difference in photodissociation mechanism. The former almost certainly decomposes to give radicals by a rupture at the \(\text{CH}_2—\text{S}\) bond, whereas the latter probably decomposes via a molecular mechanism. Phenyl phenacyl sulphoxide and phenyl phenacyl sulphone may also be used as sensitisers, but their efficiency is less than that of phenyl phenacyl sulphide. The sulphone was found to be very inefficient, for although photodecomposition occurred in alcohol solution none occurred in methyl methacrylate. At high concentrations of the sensitisers, their efficiencies decreased owing to bimolecular quenching.

Halogen-containing compounds are also effective photosensitisers. Vinyl monomers may be polymerised rapidly in the presence of the tetra-chlorides of Group IV elements, \(\text{CCl}_4\), \(\text{SiCl}_4\), and \(\text{SnCl}_4\). A binary system of carbon tetrachloride and anthracene has been used to induce

---

photopolymerisation, but early results do not show the presence of CCl₃ or Cl end groups as might be expected from simple cleavage of the CCl₃. It is possible that this step is followed by rapid reaction of the CCl₃· and ·Cl species with the anthracene to form chain-initiating radicals. Other sources of radical initiation are tritolylphosphine and anthraquinone sulphonates.

Not all photoinitiation involves the production of free radicals; ionic mechanisms may also operate in solution. Thus the uranyl ion can be used to initiate photopolymerisation of hydroxypropyl acrylate and tetraethylene glycol dimethacrylate in solution, and Bunte salts can also photosensitise the formation of addition polymers; and a new photoredox catalyst system has been described. In some systems, free radical and ionic mechanisms proceed concurrently. This is the case in N-vinylcarbazole (VCZ)—acrylonitrile (AN), VCZ—acetonitrile, AN—N-ethylcarbazole, and AN—ferrocene mixtures. The results clearly show that both cationic and radical polymerisations occur in these cases. The mechanism involves formation of a complex between donor and acceptor pairs, absorption of light by this complex to form radical anions and radical cations, and subsequent reaction of these to give diradical or ionic initiating species.

\[
D + A \xrightarrow{hv} \stackrel{(D \cdots A)}{\text{hv}} \xrightarrow{\text{hv}} D^+ + A^- \xrightarrow{\text{hv}} \cdot D - A^+ (7)
\]

The free radical-induced polymerisation of cyclohexene oxide or propylene oxide can be made to yield an acid adduct if maleic anhydride is added. This addition shows all the characteristics of a cationic polymerisation. Both cationic and free radical mechanisms are operative in the polymerisation of styrene, methyl methacrylate, and n-butyl vinyl ether using a tetrahydrofuran–maleic anhydride charge transfer complex as an initiator under u.v. irradiation.

As was stated earlier, photoinitiation of polymerisation provides a convenient means of studying the nonstationary-state kinetics of the reaction. From such studies data can be obtained which allow the ratio

---

of rate constants for propagation and termination, \( k_p/k_t \), to be determined. Conventionally, rotating sector techniques could be used, but flash photolysis has recently been employed to obtain this rate constant ratio for styrene and vinylpyrrolidone polymerisation.\(^{17}\) Styrene polymerisation has also been initiated by high-energy laser radiation.\(^{18}\)

The photopolymerisation of methyl methacrylate in the gas phase on magnesium oxide, alumina, SiO\(_2\), ZnO, and TiO\(_2\) surfaces has been investigated.\(^{19}\) It was shown that methyl methacrylate monomer was adsorbed only physically on the SiO\(_2\) surface, but chemisorption occurred in the MgO, Al\(_2\)O\(_3\), and TiO\(_2\) surfaces. I.r. spectra showed that the growth of the polymer occurred in the gas phase and between physically adsorbed monomers. Initiation occurred by absorption of light either by the oxide or by the adsorbed molecules of monomer.

### 3 Photochemical Cross-linking of Polymers

Cross-linking in polymers is frequently carried out using high energy radiation such as \( \gamma \)-rays. The same result can sometimes be obtained by less drastic photochemical means, although sensitisers may be required for polymers transparent in the near-u.v. and visible regions. For example, chemically pure polypropylene is transparent to radiation at wavelengths longer than 2000 Å. However, it has been shown that irradiation of ordinary polypropylene in vacuo at wavelengths longer than 2100 Å causes a significant degree of cross-linking.\(^{20}\) The fact may be explained by the presence of catalyst residues (mainly TiO\(_2\) and Al\(_2\)O\(_3\)) in the polymer. TiO\(_2\) absorbs radiation at wavelengths shorter than 4000 Å, and Al\(_2\)O\(_3\) at

\[
\text{(TiO}_2\text{)} + h\nu \rightarrow \text{(TiO}_2\text{)}^* \\
(8)
\]

\[
\text{(TiO}_2\text{)}^* + \text{CH}_2-\text{CH}-\text{CH}_2 \quad \rightarrow \quad \text{CH}_3
\]

\[
\text{(9)}
\]

\[
\text{TiO}_2 + \text{CH}_2-\text{CH}_2 \quad \rightarrow \quad \text{CH}_3
\]

\[ \text{TiO}_2 + \text{CH}_2-\cdot \quad \rightarrow \quad \text{CH}_3 \]

---


wavelengths shorter than 3000 Å. Thus the inorganic residue is probably acting as a photosensitiser for the cross-linking process.

\[
\begin{align*}
&\text{CH}_3 \\
&\sim\text{CH}_2-\text{C}^\cdots-\text{CH}_2\sim \\
&\sim\text{CH}_2-\text{C}^\cdots-\text{CH}_2\sim \\
&\text{CH}_3 \\
\end{align*}
\rightarrow
\begin{align*}
&\text{CH}_3 \\
&\sim\text{CH}_2-\text{C}^\cdots-\text{CH}_2\sim \\
&\sim\text{CH}_2-\text{C}^\cdots-\text{CH}_2\sim \\
&\text{CH}_3 \\
&\text{(10)} \\
&\text{CH}_3
\end{align*}
\]

Although reaction (9) was proposed as the source of radicals leading to cross-linking, it seems more probable that TiO\_2\textsuperscript{+} abstracts hydrogen to form a TiOH\textsuperscript{−} site which would abstract a further hydrogen to give a stable Ti(OH)\textsubscript{2} species.

A comparison between the radiation-induced and photochemical cross-linking of polyethylene has been made\textsuperscript{21}, and the effects of photosensitised cross-linking upon isotactic polypropylene have been described\textsuperscript{22}. Photochemical cross-linking of rubbers during the introduction of bis-azides has also been observed\textsuperscript{23}.

Associated with cross-linking is the photochemical grafting of one polymer on to a second. This has already been mentioned in the case of epoxide polymerisation in the presence of maleic anhydride. Photosensitisers may again be necessary, and the experimental aspects have been discussed\textsuperscript{24}. Dyes such as proflavine\textsuperscript{25} may be used as the sensitisers, and acrylic monomers may be grafted onto fibrous proteins by this method.

**4 Optical Properties of Polymers**

Macromolecules exhibit all of the optical properties associated with smaller molecules, including absorption of radiation, luminescence, radiationless dissipation of energy, electronic energy transfer etc. Saturated organic polymers absorb strongly only at wavelengths in the vacuum-u.v. region. The spectra observed in this region for polyethylene and polypropylene are remarkably similar to those observed in such varying compounds as diamond and simple alkanes. Molecular exciton theory has been applied to the $\alpha$-bond absorptions\textsuperscript{26}, and the calculated energy levels of the polymers and diamond give reasonable agreement with

\textsuperscript{21} A. A. Kachan, A. C. Sirota, G. V. Chernyavskii, and V. A. Shrubovich, Vysokomol. Soedin.\textsuperscript{21}, 1968, 10, A, 471.


experimentally determined levels. Exciton theory can explain the similarity in the spectra of the various compounds, and also the fact that change in conformation of the polymer does not change the absorption spectrum. The polarisation of optically allowed transitions can also be calculated. The absorption spectrum of polystyrene in this region has been related to the observed photoconductivity and fluorescence of this macromolecule.\textsuperscript{27} The results show that for excitation at wavelengths longer than 1400 Å (8.8 ev) there is no photocurrent, whereas below this wavelength the current increases regularly with decrease in wavelength, as does the ratio of photocurrent to fluorescence yield. Since the onset of photoconductivity (8.8 ev) is close to the ionisation threshold for a single benzene molecule (9.2 ev), it was proposed that the conductivity arises from simple photo-ionisation of the polystyrene molecule, rather than via the alternative exciton annihilation mechanism. Most polymers luminesce, and spectra of various types including acetylenic and siloxanes\textsuperscript{28} have been reported, together with a study of the polarisation of fluorescence of polymer solutions.\textsuperscript{29} The total emission spectrum of poly(1-vinylnaphthalene) contains peaks for fluorescence (3460 Å) and phosphorescence (4900, 5250, and 5660 Å) which are almost the same as those for the analogous small molecule 1-ethynaphthalene.\textsuperscript{30} The delayed emission spectrum of the polymer in a rigid glass at 77 K showed delayed fluorescence with a lifetime of ca. 80 msec in addition to phosphorescence with a lifetime of 2 sec. The phosphorescence could be quenched out by piperylene, a well-known triplet quencher. The observations can be explained conventionally by supposing that two photons are absorbed by the macromolecule, producing singlets which cross over to the triplet manifold. The triplet energy migrates along the polymer chain by way of the naphthalene rings until the two triplets are in close enough proximity for mutual annihilation to give a fluorescent singlet and a ground state singlet. Experiments with polymers prepared in different ways produced widely differing ratios of phosphorescence to delayed fluorescence under the same conditions. Chain length appears not to be the critical factor, but end groups may be of vital importance. Clearly any end group or defect in the polymer molecule with a lower triplet energy than the naphthalene unit will act as an energy trap or ‘sink’ for the triplet energy, and prevent its migration. The finding that intramolecular energy transfer occurs in polymers has important implications in the field of polymer degradation, where weak links and energy sinks in the chain or at chain endings may assume significance in polymers where intrachain energy migration might occur. Intermolecular energy

\textsuperscript{27} W. L. Buck, B. R. Thomas, and A. Weinreb, \textit{J. Chem. Phys.}, 1968, 48, 549; M. Ofran, N. Oron (Ohana) and A. Weinreb, \textit{ibid.}, p. 4805.


transfer has been observed in polypropionic acid,\textsuperscript{31} and other excited state interactions in macromolecules have been discussed.\textsuperscript{32} Racemisation of isotactic poly(methyl methacrylate) is possible by u.v. and $\gamma$-irradiation.\textsuperscript{33}

5 Photodegradation of Polymers

The breakdown of polymers under u.v. and visible radiation in the presence of atmospheric oxygen is a serious problem in the polymer industry. Some of the fundamental aspects of this degradation have been considered recently.\textsuperscript{34} The initial process is absorption of radiation, either by the polymer itself or by impurities arising from the initiator added to cause the polymerisation, or catalyst, or entities arising from the partial oxidation of the polymer, especially carbonyl groups. Subsequent to the absorption of radiation, the processes of interest include formation of free radicals, radical depolymerisation, chain scission, energy transfer, and others. Stabilisation of polymeric materials against photolytic degradation has been attempted generally by the addition to the polymer of radical scavengers, and also compounds such as 2-hydroxybenzophenone which preferentially absorb the radiation and degrade the light energy to heat without damage to the host material. The problem is a complex one, and since different polymeric materials have different characteristics with regard to stability to light, generalisations about photodegradation of macromolecules are difficult. Accordingly, the subject is treated by dividing polymeric materials into classes and considering each in turn.

Vinyl Polymers.—Poly(vinyl chloride) is known to show discoloration on irradiation with u.v. light. This has been attributed to the formation of conjugated diene bonds along the molecular chain by direct photochemical dehydrochlorination. The wavelength of light necessary to induce this change is in the vacuum-u.v. region, \textit{i.e.} shorter than 2000 Å. Similar changes can be induced by near-u.v. radiation if suitable sensitisers are added to the polymer. Benzophenone is remarkably efficient in this respect.\textsuperscript{35} Since this molecule intersystem crosses with almost unit efficiency to the first triplet state after excitation, the formation of polynes is presumably sensitised by the triplet state of the benzophenone, feasibly by hydrogen abstraction. Conjugated double bonds were formed with a quantum yield of \textit{ca}. 0.3. At room temperature the polylene chain was relatively short, containing less than ten double bonds, but when the poly(vinyl chloride) was heated above the glass transition temperature, the conjugated sequence propagated to form a polylene with more than twenty conjugated bonds.

\textsuperscript{34} \textit{A.C.S. Advances in Chemistry Series}, 1968, 85, 272.
double bonds. Production of polyene chains by this method in a uniaxially oriented PVC film caused marked dichroism in the film due to oriented polyene sequences. The photodestruction of poly(vinyl chloride) at longer wavelengths proceeds via the formation of chlorine atoms\(^\text{36}\) which may need a sensitizer such as minute amounts of ozone to initiate reaction. Chlorine atoms thus formed are highly reactive and probably act as radical sources in subsequent chain reactions. The photo-oxidation of PVC and the model compounds, \((\pm)\)-, and meso-2,4-dichloropentanes has been studied by high resolution n.m.r. spectroscopy.\(^\text{37}\) The light source used was a low pressure mercury arc, which emitted mainly 2537 Å radiation. At the outset of the reaction, the ratio of \(\text{CH}_2\) protons to CHCl protons in the polymer is 2:0. After a considerable induction period of irradiation of ca. 100 hr. this ratio begins to increase significantly, indicating the loss of \(\alpha\) protons from the CHCl group. At the end of an irradiation, structures of type (I) were found in the polymer. There was no evidence for structures of type (II).

\[
\begin{align*}
\text{CH}_2-\text{CO}-\text{CH}_2-\text{CHCl} & \quad \text{CHCl- CO-CHCl} \\
(\text{I}) & \quad (\text{II})
\end{align*}
\]

Similar results were obtained in the photo-oxidation of the model compounds, and it thus appears that the photo-oxidation of PVC follows a reaction mechanism similar to that in the chloropentanes. The induction period for the photo-oxidation is probably due to the slow initial build-up of carbonyl groups, as in (I), which then act as efficient photosensitizers for the reaction.

Poly(vinyl alcohol) undergoes photo-oxidation in water solution at 30° when irradiated with a high pressure mercury arc in the presence of disodium benzophenone 3,3'-disulphonate as a sensitizer.\(^\text{38}\) The reaction products are hydrogen peroxide, acids, and carbon dioxide. A mechanism has been proposed which involves reaction of the excited sensitizer with a hydrogen atom from a carbon atom in the chain which bears an OH group, leaving a \(-\text{C}--\) centre. This reacts with oxygen to give a hydroxyperoxy radical which immediately attacks an adjacent CH group in the chain, dehydrates it, and leaves a hydroxy hydroperoxide group having the structure of a ketone peroxide (III). The peroxide (III) may lose hydrogen peroxide to form a ketone (IV), or undergo the degradative sequence shown. Primary alcohols may be formed from (III) by an ionic mechanism [(22)–(24)]. A spectrophotometric study of photochemical changes in a coloured poly(vinyl alcohol) film during u.v. irradiation has been made,\(^\text{39}\) and flash


\[ \text{S} + h\nu \rightarrow \text{S}^* \]

(12)

\[ \sim\text{CH}_2-\text{C}-\text{CH}_2-\text{C}\sim + \text{S}^* \rightarrow \sim\text{CH}_2-\dot{\text{C}}-\text{CH}_2-\text{C}\sim + \text{SH}^* \]

(13)

\[ \text{OH} \quad \text{OH} \]

(14)

\[ \text{HOO} \quad \quad \text{H} \]

\[ \sim\text{CH}_2-\text{C}-\text{CH}_2-\text{C}\sim \quad \quad \text{H} \]

(15)

\[ \text{OH} \quad \text{OH} \]

\[ \text{O-O} \quad \text{H} \]

\[ \sim\text{CH}_2-\text{C}-\text{CH}_2-\text{C}\sim \]

(III)

(16)

\[ \sim\text{CH}_2-\text{C}-\text{CH}_2-\text{C}\sim \rightarrow \sim\text{CH}_2-\text{C}-\text{CH}_2-\text{C}\sim + \text{H}_2\text{O}_2 \]

(IV)

\[ \text{OH} \]

(17)

\[ \text{O} \quad \quad \text{H} \]

\[ \sim\text{CH}_2-\text{C} + \cdot\text{CH}_2-\text{C}\sim \quad \quad \hat{\text{O}} \quad \quad \text{H} \]

\[ \text{OH} \quad \text{OH} \quad \text{OH} \]

(18)

\[ \sim\text{CH}_2-\text{C}-\text{CH}_2-\text{C}\sim + \cdot\text{OH} \]

(19)

\[ +\text{O}_2 \]

\[ \cdot\text{OOCH}_2\sim \quad \quad \text{H} \]

\[ \text{OH} \]

(20)

\[ +\text{RH} \rightarrow \text{HOOC}-\sim \]

\[ \text{OH} \]

(21)

\[ -\text{H}_2\text{O} \]

\[ \text{H} \quad \text{OH} \]

\[ \text{OHC}-\sim \]
exposed dichromate-sensitised poly(vinyl alcohol) has also been investigated.\textsuperscript{40}

There is considerable industrial application for photosensitive polymers and resins. Poly(vinyl cinnamate) forms a thin lightly hardened film when exposed to light\textsuperscript{41, 42} and more recently a more sensitive analogue has been synthesised. This is poly(vinyl 2-furylacrylate) (V).\textsuperscript{43} The mechanism of the hardening by radiation is presumably dimerisation, as in the case of poly(vinyl cinnamate). The photolysis of poly(vinyl pyrrolidone) in oxygen-free aqueous solutions and in the presence of $O_2$ and $Cu^{2+}$ has been studied,\textsuperscript{44} and the role of hydrogen-bonding in the photochemistry of poly(t-butyl N-vinyl carbamate) discussed.\textsuperscript{45}

\begin{equation}
\text{(V)} \quad \text{CH} = \text{CH} - \text{COOR} \xrightarrow{h\nu} \quad \text{CH} - \text{CH} - \text{COOR}
\end{equation}

Polyethylene and Polypropylene.—Exposure of clear low-density polyethylene films to air and natural or simulated sunlight leads to the formation of carbonyl, hydroxyl, and vinyl groups, the evolution of acetone, acetaldehyde, water, and oxides of carbon, an increase in brittleness, the formation of crosslinks, and drastic changes in the physical properties of the

\textsuperscript{40} A. G. Leiga and R. A. Walder, \textit{Polymer Eng. Sci.}, 1969, 9, 35.
\textsuperscript{45} A. R. Monahan, \textit{Macromolecules}, 1968, 1, 408.
films. A careful study has revealed that the photodegradation separates into two stages. In the initial stage, irradiation with light of 2750 Å produces a species which absorbs in this region, whereas thermal treatment or irradiation at 4000 Å does not produce this species. Irradiation with light of 4000 Å prevents the formation of the species absorbing at 2750 Å, which also disappears thermally with an activation energy of 5.6 kcal mole⁻¹. After the disappearance of the species, carbonyl, hydroxyl, and carboxyl groups begin to be formed steadily. This is the second stage of the photodegradation. It seems probable from an inspection of the absorption spectrum of the species absorbing at 2750 Å that it is a conjugated triene. Light of 4000 Å does not destroy the triene, but the fact that it prevents the formation of further triene suggests that a precursor to the triene is destroyed by light of this wavelength. The sequence of events may be as follows. A collision complex of polymer and oxygen absorbs radiation at 4000 Å to give an oxygen adduct. This adduct may behave in two ways depending upon the wavelength of light used to destroy it. Absorption of a second quantum of 4000 Å radiation results in a stable product which is involved in cross-linking reactions. With the shorter wavelength light, the adduct forms a triene directly.

\[
\text{(Polymer-O}_2\text{)} + h\nu(4000 \text{ Å}) \quad \longrightarrow \quad \text{Adduct} \quad (26)
\]
\[
\text{Adduct} + h\nu(4000 \text{ Å}) \quad \longrightarrow \quad \text{Adduct}^* \quad (27)
\]
\[
\text{Adduct}^* \quad \longrightarrow \quad \text{X-linking} \quad (28)
\]
\[
\text{Adduct} + h\nu(2750 \text{ Å}) \quad \longrightarrow \quad \text{Triene} \quad (29)
\]

It is interesting that triene formation occurred only in polymers which had been formed by a radical process; linear polyethylene did not produce triene upon irradiation.

In the second stage of the degradation, carbonyl, hydroxyl, and carboxyl groups are formed. The focus of attack may be inferred from the behaviour of linear polyethylene and polypropylene under the same exposure conditions. Linear polyethylene fails physically quite rapidly, but the rate of oxidation to form hydroxyl and carbonyl groups is much slower than observed in branched polyethylene. The rate of polypropylene oxidation is much higher. These observations lead to the conclusion that attack occurs primarily at the branch points. The oxidation results primarily in destruction of the accessible amorphous regions which are also the regions subject to physical stress. Cross-linking which occurs on exposure to 4000 Å radiation does so relatively independently of formation of carbonyl and hydroxyl species, and thus different pathways are postulated, that of the formation of the carbonyl and hydroxyl arising from the short wavelength radiation associated with triene formation.

The photodegradation of polypropylene probably proceeds via a similar mechanism. The reason for the inhibition period in the photo-oxidation of isotactic polypropylene, and the effect of oxidation products on the photoactivity of polypropylene films, have been described. The action of a nickel oxime chelate photostabiliser was considered, and the effects of heat and u.v. radiation on the stability of a polypropylene–polyisobutylene ‘alloy’ described. The photolytic and radiolytic production of free radicals in polypropylene at 77 K have been investigated. The radicals were monitored using e.s.r. techniques, and the photolytically produced radicals were shown to arise via a process requiring the absorption of two photons.

Cellulose Materials.—Degradation of cellulose in atmospheric conditions by exposure to the unfiltered radiation from a high pressure mercury arc produced many volatile products, including oxides of carbon, hydrogen, acetaldehyde, propionaldehyde, methyl formate, acetone, methanol, ethanol, methane, and ethane. The kinetics of the depolymerisation process indicate that it is random, and the presence of low molecular weight sugars in the reaction products suggest that the initial reaction is mainly chain cleavage yielding glucose and oligosaccharides.

Further degradation of the resulting end groups yields carbon monoxide, carbon dioxide, and hydrogen. The chromophore weakly absorbing radiation at ca. 2650 Å may be the O—C—O species. Cellulose has also been degraded photochemically in solution. When cellulose is exposed

to 2537 Å radiation, the rate of its degradation is enhanced by the presence of anthraquinone. In this case, the first step in the photosensitised degradation is the abstraction of a hydrogen atom by the excited anthraquinone, which forms a semiquinone. The cellulose radicals thus formed undergo autoxidation, leading to chain scission. The photodegradation and photooxidation of acetyl cellulose have also been described.

**Miscellaneous.**—Polystyrene irradiated at liquid nitrogen temperatures produces free radicals which can be readily detected by e.s.r. techniques. It was found that poly(α-methylstyrene) gave the same e.s.r. signal as the unsubstituted compound, and that the radical responsible was probably (VI).

\[
-\text{CH}_2-\dot{\text{C}}-\text{CH}_3- \\
\text{Ph} \\
\text{(VI)}
\]

The reactions leading to the production of this species have been formulated as follows:

\[
\text{(a)} \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{Ph} \\
\text{H}
\end{array} \xrightarrow{h\nu} \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{Ph} \\
\text{H}
\end{array}^* \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{Ph} \\
\text{H}
\end{array} + \text{H}^* \quad (31)
\]

\[
\text{(b)} \quad \begin{array}{c}
\text{H} \\
\text{H}_2\text{C} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{Ph} \\
\text{H}
\end{array} \xrightarrow{h\nu} \quad \begin{array}{c}
\text{H} \\
\text{H}_2\text{C} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{Ph} \\
\text{H}
\end{array}^* \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{Ph} \\
\text{H}
\end{array} + \text{CH}_3^* \quad (32)
\]

[The methyl ejection proposed in sequence (b) has no obvious precedents in small-molecule photochemistry: its feasibility could be tested by the use of t-butylbenzene as a model compound.]

An increase in temperature from ca. 77 K to 118 K resulted in the disappearance of these radicals, indicating rapid reaction. In the absence of oxygen, the formation of cyclohexadienyl-type radicals was also observed. In the presence of oxygen, photo-oxidation occurs; and a study has been made of the effect of change of wavelength upon the photo-oxidation of polystyrene.

The chemical transformations of rubbers in the absence of oxygen have been little studied. However, a recent investigation of 1,4-polyisoprene

---


has revealed some novel reactions. Absorption of light by the rubber in the form of a thin film occurs either through traces of sensitisers adventitiously present, from which energy transfer to the double bond in the isoprene follows, or through weak direct singlet–triplet absorption. Excitation leads to cis-trans isomerisation, and 1,2-hydrogen migration followed by ring closure to give cyclopropane rings. A common biradical species is probably involved in both reactions (equation 33).

\[
\begin{align*}
\text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \xrightarrow{h\nu} \quad \sim \text{CH}_2-\text{C} &= \text{C} \sim \text{CH} \sim \text{CH}_2 \\
\text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \xrightarrow{\text{H migration}} \quad \sim \text{CH}_2-\text{C} &= \text{C} \sim \text{CH} \sim \text{CH}_2 \\
\text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \xrightarrow{\text{relaxation}} \quad \sim \text{CH}_2-\text{C} &= \text{C} \sim \text{CH} \sim \text{CH}_2 \\
\end{align*}
\]

\[\text{cis or trans}\]

Vinylidene and vinyl double bonds are also formed in the irradiation of polyisoprene, presumably via rupture of the weak C–C bond connecting two isoprene units (equation 34). The radicals formed may rearrange, then

\[
\begin{align*}
\sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \\
\text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \xrightarrow{h\nu} \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \\
\text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \\
\text{CH}_3 & \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \quad \sim \text{CH}_2-\text{C} &= \text{CH} \sim \text{CH}_2 \\
\end{align*}
\]

\[34\]

recombine or add to double bonds to produce some endlinks or crosslinks, and some new vinylidene and vinyl double bonds (equations 35 and 36). The photolysis and temperature decay of species in rubbers and the accelerated oxidation of rubbers in solution have also been investigated.

The effects of u.v. irradiation upon a wide variety of the following further polymer systems have been studied: poly(methyl methacrylate) in solution in the absence\(^{63}\) and presence\(^{64}\) of dye sensitisers; polyurethanes mono\(^{65}\) and di-photonic\(^{66}\) processes); polyethers;\(^{67}\) polyesters;\(^{68}\) ketones poly(vinyl benzophenone);\(^{70}\) polyformaldehyde;\(^{71}\) and polysulphones.\(^{72}\) Other interesting aspects of the photochemistry of polymers not directly concerned with photodegradation include the synthesis of two new nitrogen-based photosensitive polymers,\(^{73}\) a photochromic spiro-pyran polymer,\(^{74}\) and the creation of a polymer of acetylene which is highly photoconductive.\(^{76}\) This when introduced into poly(vinylcarbazole) or other polymers can act as a highly sensitive electrophotographic layer. Dyestuffs can extend the range of photoelectrical sensitivity by acting as photosensitisers.

**Photostabilisers.**—It can be seen from the preceding section that photodegradation of most polymeric materials occurs through the production of reactive free radicals in the system. The species which absorb radiation to produce the radicals responsible for the initiation of the degradation processes vary from system to system, but include units within the polymer chain itself, adventitious impurities, residues of polymerisation initiators, and more commonly, species arising from partial oxidation of the polymer

---


chains. Attempts to prevent the degradation alluded to have generally relied upon addition to the polymer of two classes of material. These are absorbers, compounds with high extinction coefficients which will preferentially absorb the radiation incident upon the polymer, and radical scavengers, which react efficiently with any free radicals produced in the system and thus prevent the occurrence of radical depolymerisation and oxidations. In the case of the former class of compound, care must be taken to ensure that the energy absorbed by the added compound does not itself initiate reaction, i.e. it must be harmlessly removed either as luminescence or by radiationless conversion to heat. Sometimes a single substance may be added to polymers which acts as an additive in both classes, e.g. carbon black is frequently added to polyethylene where it acts as both absorber and radical scavenger. Since additives to polymers are of great commercial interest, in general little is published on the precise nature and mode of action of these compounds in Western scientific journals. A number of publications appear on this subject in the Soviet academic press, however, and a brief account of these will now be given.

As has been stated above, the purity of the polymer may be critical in determining firstly whether or not the macromolecules absorb radiation, and secondly the mobility of the excitation energy within the polymer. A study has been made on the migration of triplet excitons in polymers, and the effectiveness of the sensitisation of reversible photochemical reactions.77 Since the effect of stabilisers in polymers in preventing photo-oxidation is likely to be similar to that in photo-oxidation of solutions of hydrocarbons, a study of the effectiveness of stabilisers in the latter case may yield results pertinent to polymers. In the case of a photosensitiser oxidation, the following reactions may occur,

\[
\begin{align*}
S + h\nu & \longrightarrow ^1S^* \\
^3S^* & \longrightarrow ^3S^* \\
^3S^* & \longrightarrow S \\
^3S^* + RH & \longrightarrow R^* + SH \\
R^* + O_2 & \longrightarrow RO_2^* \\
RO_2^* + RH & \longrightarrow ROOH + R^* \\
RO_2^* + RO_2^* & \longrightarrow \\
2R^* & \longrightarrow \text{termination} \\
R^* + RO_2^* & \longrightarrow 
\end{align*}
\]

(37) (38) (39) (40) (41) (42) (43) (44) (45)

In the above scheme, S is the photosensitiser (usually benzophenone in the studies below), $^1S^*$ is the first excited singlet state and $^3S^*$ the first triplet state of the sensitiser, and RH is the hydrocarbon being oxidised. It should

be noted that reaction (43) leads to weak chemiluminescence in the solution. Similar effects have been observed in polymer matrices.78

With the addition of an inhibitor Q, the following additional reactions may occur.

\[
\begin{align*}
Q + hv & \rightarrow Q^* \\
Q^* & \rightarrow Q \\
^1S^* \text{ or } ^3S^* + Q & \rightarrow Q^* + S \\
RO_2^\cdot + Q & \rightarrow ROOH + Q^* \\
Q^* + RH & \rightarrow QH + R^\cdot
\end{align*}
\]

(46) (47) (48) (49) (50)

It can be seen that in (46), the inhibitor is acting as an absorber and in (49) a radical scavenger, provided \( Q^\cdot \) is relatively unreactive. Reaction (50) would lead to chain initiation, and is thus undesirable in an inhibitor. Reaction (48), energy transfer from either singlet or triplet excited sensitiser to the inhibitor, is an example of a process hitherto little explored which may have immense consequence in polymer stabilisation against light. From a kinetic study, values of \( k_{49^\tau} \), where \( \tau \) is the lifetime of the excited state, and also values of \( k_{49}/k_{49^1} \) can be obtained and compared. An ideal inhibitor/quencher would combine high values for both of these rate constant ratios. Many types of inhibitor have been studied. These include substituted benzophenones,79 salicylates,79 substituted cyanocelluloses,79 Schiff’s bases,80 bivalent metallic acetates,81 and manganese and cobalt complexes with ethylenediamine tetra-acetic acid.81 Varying degrees of success were recorded, although generally the Schiff’s bases were extremely effective inhibitors. The mechanism of the protective effect of photo-stabilisers in polymers82 and the stabilisation of polycarbonates with polymeric quinones83 have also been discussed.

D. P.

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