

Introduction and Review of the Year

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We may perhaps be pardoned for feeling some sense of personal satisfaction and achievement in reaching the twentieth of these annual reviews of photochemistry; though it must also be said that we have been unsuccessful in persuading the Royal Society of Chemistry that a celebratory banquet for the hard-working Reporters would be in order.

The coverage this year is much the same as in Volume 19, with one major exception. Circumstances beyond our control have necessitated omission of Part V dealing with photochemical aspects of solar energy conversion. We hope that it will prove possible to reinstate this section in future Volumes. Some of the Reporters have been feeling that constraints on length have been preventing them from doing full justice to the work reviewed. Changes designed to ameliorate this problem are now under discussion, and we hope to be able to give details in Volume 21.

We start this Review by referring to some of the more interesting developments on the theoretical side of photochemistry.

Kusba has solved the diffusion equation for long range energy-transfer by dipole-dipole interaction accompanied by material diffusion. Fractal models are increasingly being used to explain some energy transfer processes (von Borczyskowski and Kirski; Tamai *et al.*; Pines and Huppert; Newhouse and Kopelman). Attention is drawn to Najbar's important treatment of heavy atom effects.

Very short time-resolution techniques are being increasingly applied to the study of very fast processes, for example solvent relaxation and electron-transfer to and from electronically excited species (Peters *inter alia*). Real time femtosecond techniques now provide a probe for the study of transition states (Dantos *et al.*). This is a very promising development. The First International Laser Conference was held in 1987 - in part a

reflection of the growing use of laser techniques in photochemistry and photophysics. A valuable survey giving access to Russian laser work on picosecond spectroscopy and biological photochemistry has been provided by Letokhov. Amongst numerous applications of fibre optics in luminescence studies, we would pick out the ingenious oxygen sensor which uses fluorescence decay time as the information carrier (Lippitsch *et al.*), and the use of liquid-core fibres in laser fluorimetry (Fujiwara *et al.*). The information available from steady state luminescence studies can be increased by a computer-based multidimensional fluorescence technique which has been reviewed by Patonay *et al.* Cundall in Part I of this Volume has identified chirality changes on electronic excitation as a fruitful area for further research. Brauchle's novel phase-modulated holographic grating technique has been successfully applied to excited molecules in polymer matrices.

A pioneering study by Chatzidimitriou-Dreisman and Brandas has been concerned with photochemical effects in molecules situated in amorphous environments, including liquids: thermal motion can generate local coherent or dissipative structures which affect the behaviour of neighbouring molecules. Bulska has proposed 2,2'-bipyridyl-3,3'-diol as an advantageous new fluorescence standard, and Wintgens *et al.* have described a fulgide actinometer particularly useful for work on laser excitation.

Locke and Lim have reported the first example of a species formed by the combination of two electronically excited molecules: they term this a 'bicemer'.

Alkane photochemistry, normally a rather inaccessible field, has been studied using an ionizing excitation source (Yoshida and Lipsky). Much still remains to be understood about the photochemistry and photophysics of benzene, and this hydrocarbon and its derivatives, including diphenylpolyenes, continue to provide perennial challenges. Doublet-doublet fluorescence of free benzyl radicals in solution has been observed by Tokumura *et al.*: non-radiative decay also occurs. Azulene continues to attract photochemical admirers, including Hopkins and Rentzepis, *inter alia*. Attention is drawn to a two-photon study of pyridine using a thermal lensing technique (Salvi *et al.*). The fluorescence decay kinetics of 1,2-di(1-pyrenyl)propane are the subject of strong disagreement between two groups (Siemiarezuk and Ware; Zachariasse and Striker).

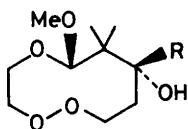
Mialocq has studied the formation of solvated electrons by photoexcitation of inorganic anions and the biphotonic excitation of water. Gartstein and Zakhidov have proposed that charge-transfer states in mixed stack donor-acceptor compounds couple with crystal lattice phonons to form comparatively stable solitons. Examples of competing singlet and triplet pathways for photochemical trans + cis isomerization of certain stilbenes having intramolecular donor-acceptor character have been described by Gorner. Several other interesting studies in the field have appeared this year.

Various photophysical techniques continue to be used in the study of polymers: some particularly interesting work on electrically-conducting polymers has been described by Roth and Bleier, inter alia. The photophysics of thin films and colloidal systems, including micelles, continues to be an important and active field of research: see e.g. Kalyansundaram; Debe. Cyclodextrins have been found to increase the chemiluminescence yields from aqueous peroxyoxalates by up to 300-fold (Woolf and Grayeski). Enzyme-generated excited states of acetone have been found to induce quasi-photochemical behaviour of riboflavin in the dark (Rojas and Silva). From studies of the luminescence of $^1\text{O}_2$, Schmidt and Brauer have concluded that most of the previously reported red emission does not come from this molecule. Delayed fluorescence has been observed in the deactivation of highly excited triplet states (Skvortsov and Alfimov; cf. McGimpsey and Scaiano). The photolysis of aryl azides, long used as a source of aryl nitrenes, has been shown also to produce a transient dehydroazepine (Shields et al.; Liang and Schuster).

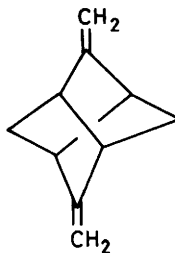
In a remarkable development, Nguyen et al. claim that they have been able to detect single molecules by a laser-induced fluorescence procedure.

Biochemists continue to be the main exploiters of photophysical techniques, though it should be pointed out that the coverage of these particular aspects is selective rather than comprehensive. Even processes in living cells are now being studied (Vigo et al., inter alia). Some aspects of biological photochemistry are undoubtedly an acquired taste. For example, a three-dimensional presentation of the total fluorescence from urine has enabled Leiner et al. to identify several fluorescent metabolites.

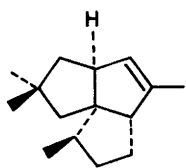
We now come to developments in inorganic photochemistry. Grätzel and co-workers have described a photoelectric device



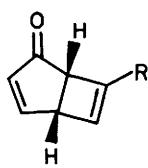
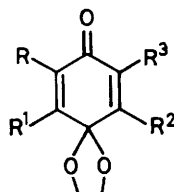
(1) R = Me or Et



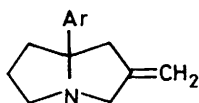
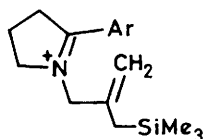
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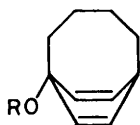
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(4) R = H or Buⁿ

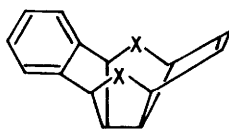
(5) R's = H or Me

(6) Ar = C₆H₅ or *p*-FC₆H₅ (7)

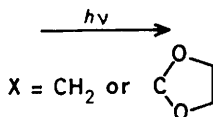
(8)

(9) R = Me, Et, or Prⁱ

(10)



(11)



(12)

responsive to the near-infrared, and with an efficiency of 37%. Carbon monoxide and hydrogen are produced by concurrent photo-reduction of carbon dioxide and water using visible light irradiation of solutions containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and various Co(II) species (Ziessel et al.). Photoexcitation of a system containing the same ruthenium complex, methylviologen, and quadricyclane can initiate a catalytic cycle for the valence isomerization of quadricyclane to norbornadiene (Kutal et al.). Ishida et al. report the photoreduction of CO_2 catalyzed by $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$. Bianchini and Meli have described an interesting new method for the introduction of sulphido, disulphur, and diselenium ligands into complex frameworks. Belmore et al. have described the first example of the photoactivation of a metal-carbon dioxide complex in solution. Dobson et al. have devised a procedure for the identification of co-ordinatively unsaturated substituted metal carbonyl transients which enable values of all rate constants for ligand displacement reactions to be obtained. Photoinsertion of isonitriles into the C-H bond of arenes produces aldimines, and is catalyzed by iron (Jones et al.). Messelhäuser et al. have described the photochemical insertion of an alkene into an S-S bond in a co-ordination complex. Sakakura and co-workers have described the regioselective carbonylation of aliphatic and aromatic hydrocarbons in the presence of a rhodium complex. In related work, these authors have used the same complex in an interesting chain-shortening synthesis of terminal alkenes from alkanes, e.g. pentane→but-1-ene.

Irradiation of the O_3/Br_2 complex leads to a new species which is believed to be Br_2O (Turner et al.).

In the field of organic photochemistry, greatly increased use is being made of photochemical procedures in the synthesis of natural products and other complex molecules. There is growing interest in the effects of novel environments on the course of photoreactions, e.g. zeolites, membranes, and cyclodextrin complexation.

The photoisomerization of cyclobutanones to transient carbenes has been used as part of an interesting synthesis of muscarine (Pirrung and DeAmicis). Intramolecular oxetan formation has been used as part of novel syntheses of medium-ring ethers (1) and the tricyclo-octane (2) (Carless et al.; Gleiter and Kissler). Cossy et al. have employed the photoreductive cycliza-

tion of amides or unsaturated ketones in a new synthesis of hirsutene.

Pattenden and Teague have achieved the total synthesis of the angular triquinane (3) by procedures which include intramolecular $2\pi+2\pi$ photocycloaddition of an enone.

The use of circularly polarized light for irradiation has been little exploited in the past, so the synthesis of the optically active enones (4) in this manner by Cavazza and Zandomenighi is of particular interest. Wang and Paquette have described the photochemical route to 1,3-bridged cyclo-octatetraenes. The azomethine group is normally of low photochemical reactivity, but Kaneko *et al.* have described a system in which a CF_3 group appears to have an activating effect.

The oxa-di- π -methane photochemical rearrangement of β,γ -unsaturated systems normally occurs *via* a triplet pathway; but Fuchs and co-workers have described an example in which direct irradiation (presumably singlet) gives the oxa-di- π -methane product whereas triplet sensitization follows a different path. The oxa-di- π -methane rearrangement of bicyclo[2.2.2]octenones has been exploited by Schaffner and Demuth to produce tricyclo[3.3.0.0^{2,8}]oct-3-ones, and Raju and Deota have extended this procedure to a synthesis of linear triquinanes.

Nagamatsu *et al.* have shown that liquid crystal and various other media can greatly influence the stereochemistry of uracil photodimerization. Pirrung and Nunn have shown that irradiation of a series of quinone monoacetals (5) in acetic acid provides a flexible high-yield route to substituted cyclopentenones.

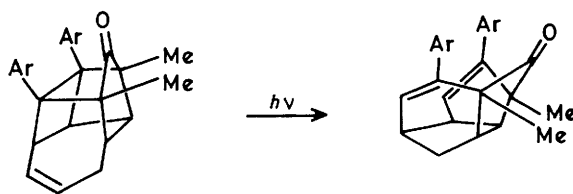
Tu and Mariano have described an interesting 1-step synthesis of the 1-azabicyclo[3.3.0]octane (6) by xanthone-sensitized irradiation of the pyrrolinium perchlorate (7). Mukai *et al.* have described the unexpected conrotatory ring-opening of a cyclobutene to the corresponding diene which occurs *via* charge-transfer excitation to give the radical-cation of cyclobutene. Tsuji and Nishida have reported that irradiation of the strained diene (8) in alcoholic solution gives the product (9) which is suggested to result from addition of the solvent to the photoisomer (10), spectroscopic evidence for which is provided. Attention is drawn to the extraordinary photoisomerization (11) \rightarrow (12) described by Prinzbach *et al.*

Cohen and co-workers have provided a valuable review of conformation effects in solid-state photoreactions. Mukai *et al.* have reported the remarkable desensitized photoelectron-transfer isomerization represented by (13) + (14).

Turro *et al.* have reported that irradiation of benzocyclobutene gives the dihydropentalenes (15) and (16). They propose the intermediacy of the prefulvene-type biradical (17): this type of intermediate was proposed earlier by the Senior Reporters to account for the photochemical formation of fulvene and benzvalene from benzene. It was once thought to be involved in the meta-cycloaddition of alkenes to benzene, but a different mechanism is now generally accepted. Lalley and Spillane have described a novel photochemical rearrangement of the sodium salt of m-aminobenzenesulphonic acid. Wagner and Nahm have described an intramolecular photochemical cycloaddition to the benzene ring that is unusual in occurring by a triplet pathway.

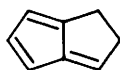
Cyclic osmic esters have long been known to be involved in the osmium tetroxide-catalyzed cis-dihydroxylation of alkenes, but not arenes. The isolation of compound (18) by Wallis and Kochi following irradiation of the charge-transfer complex between osmium tetroxide and benzene is therefore of particular interest. This suggests that the corresponding use of catalytic quantities of osmium tetroxide in conjunction with hydrogen peroxide could lead to the formation of polyhydroxylated cyclohexenes and -anes. A rare example of photochemical cycloaddition to a C≡N group is provided by the formation of benzoxazole (19) from pentachlorophenol in acetonitrile. The photoconversion of 2-methylbenzophenone into the anthrone (20) involves two sequential photo-processes via the E-enol (21) which under the influence of high intensity laser light absorbs a second photon to give the cyclized intermediate (22) which undergoes air-oxidation to (20) (Wilson *et al.*).

Nishio *et al.* have described an interesting procedure for 'storing' singlet oxygen as an adduct with pteridin-2,4,7-trione, a solid which can be stored indefinitely at room temperature but which on warming reverts to the parent trione with liberation of singlet oxygen. Adam and co-workers have described a convenient one-pot synthesis of epoxy-alcohols via photo-oxygenation of alkenes in the presence of a Ti(IV) catalyst.

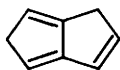


(13) Ar = *p*-MeOC₆H₄, *p*-MeC₆H₄,
or C₆H₅

(14)



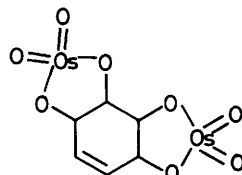
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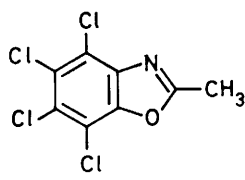
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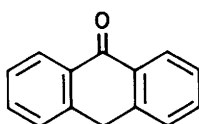
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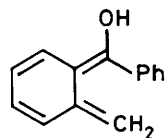
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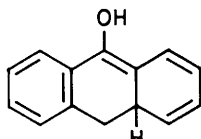
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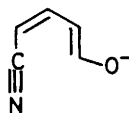
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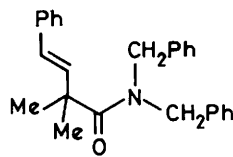
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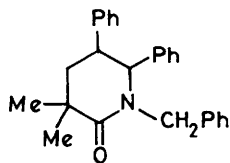
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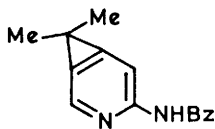
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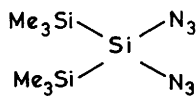
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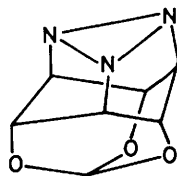
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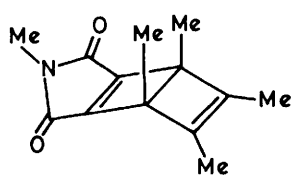
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(28)



(29)



(30)

Dürr *et al.* have described some novel complex cinnoline derivatives which show photochromic properties. Albini *et al.* have provided some new evidence on the mechanism for the photoisomerization of heterocyclic N-oxides. Simple pyridine N-oxides are exceptional. Thus irradiation of pyridine N-oxide in aqueous base affords the ring-opened product (23). Aoyama *et al.* have described the unprecedented photocyclization of the amide (24) to the lactam (25). The first examples of $[2\sigma+2\pi]$ photoreactions of a three-membered ring and an azo-compound have been described by Hunig and Schmitt. Nicolaou *et al.* have prepared the first stable example of a 1,2-dithiethane: the procedure involves $(2\pi+2\pi)$ photodimerization of C=S groups.

Transient triplet biradicals have been trapped by reaction with oxygen: the procedure is claimed to provide an effective method for estimating the lifetimes of these species (Adam *et al.*). Streith *et al.* have described the first example of a pyridino-cyclopropene (26).

The remarkable silanediimine (27) has been prepared by irradiation of the azide (28) (Klingler and Prinzbach). The unusually stable triaziridine (29) has been prepared by photolysis of the corresponding azide.

Delduc *et al.* have reported that the photolysis of S-alkyl and S-acyl xanthates provides a useful source of free alkyl and acyl radicals. Photolysis of the imide (30) gives tetramethylcyclobutadiene (Kashima *et al.*).

We conclude with references to developments in polymer photochemistry.

Polymer films have been obtained by plasma polymerization of hexafluorobenzene, N-vinylpyrrolidine, and chloracrylonitrile (Munro). Higuchi *et al.* have shown that irradiation of an azobenzene-modified poly(γ -methyl-L-glutamate-CO-L-glutamic acid) in bilayer membrane vesicles of distearyldimethylammonium chloride leads to trans-cis isomerization of the polymer: this leads to transfer of the polypeptide from the hydrophobic bilayer membrane interior to the hydrophilic surface. As a result, there was a decrease in the ion permeability through the bilayer membrane and the formation of intervesicular adhesion. Elsner and Ritter have prepared photosensitive membranes from an aromatic polyamide and a cinnamate that incorporates a liquid crystalline component.

