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Highlights of organic photochemistry – 1978

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Abstract

Chemical literature of 1978 has been surveyed and the articles presenting significant results in the area of organic photochemistry have been highlighted in this paper.

Key words: Organic photochemistry, synthetic applications, mechanistic organic photochemistry.

1. Introduction

The standard chemical literature was surveyed to cover the period—January to December 1978 (over fifty journals)[1–3]. Papers which presented either significant mechanistic or synthetic information or disclosed novel or interesting observations were selected for this article. The choice reflects the interests of the author and naturally result in a somewhat non-uniform coverage of all areas. This article is split into the following sections :

1. Theoretical organic photochemistry.
2. Physical aspects of organic photochemistry.
3. Photochemistry as a synthetic tool.
4. Photochemical reactions under unusual conditions.
5. Wavelength and temperature dependent photochemistry.
6. Mechanistic organic photochemistry.
   (1) Aromatics and alkenes,
   (2) Carbonyl compounds

(3) Heterocyclic chemistry and

(4) Singlet oxygen.

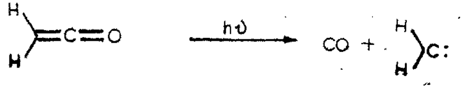
8. Reviews and books.

2. Theoretical organic photochemistry

Theoretical organic photochemists in the recent years have been concentrating their efforts on the calculation of energy surfaces for reactions and defining the terms involved in the decay of excited intermediates to ground state products. The development of a unified theory of photoreactions, which is occupying the central attention of theoretical chemists, is expected to have a large impact on organic photochemistry in the coming years. The potential energy barriers in the excited surface which govern the kinetic feasibility of photochemical reactions result from avoided crossing between states of similar symmetry. Devaquet[4] has shown how these come about due to allowed crossings of MO's of different symmetry or as a direct consequence of avoided crossings between MO's of identical symmetry.

Epiotis[5-9] has published a series of papers on potential energy surfaces which may be handy to photochemists to explain the many puzzling features of photochemical reactions. Here, the linear combination of fragment configurations approach (LCFC) is used in order to construct qualitative potential energy surfaces. The factors which control the heights of barriers and the stabilities of possible intermediates in thermal and photochemical reactions are discussed. More importantly, the LCFC approach with inclusion of spin-orbit coupling parts in the effective one electron Hamiltonian operator, has been used to formulate mechanisms of spin-inversion in triplet photoreactions and stereo selection rules for radiationless decay of triplet complexes to singlet ground state products.

Potential energy surfaces for a variety of dissociative processes have been reported. For example, photodissociation of ketene to methylene and carbon monoxide has been attempted by Morokuma using SCF method (eqn. 1)[10]. Devaquet has reported energy surfaces for the photodissociation of azo alkane and imines based on ab initio SCFCI calculations (eqns 2–4)[11-14]. Similarly Eveleth[15] has published detailed surface diagrams for the photodissociation of cyclobutane, water, ammonia, hydrogen peroxide and hydrazine calculated using semi-empirical method. The above model may find use in the hands of experimental chemists to rationalise various observations.



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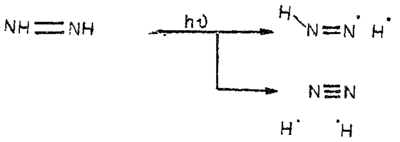

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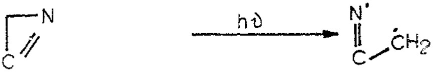

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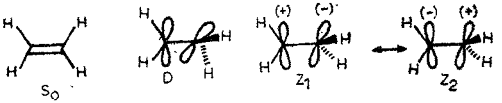
Correlation diagrams developed by Salem often involve Zwitter-ionic and diradical states. The simple theoretical description of diradical states in olefins gives rise to a pair of closely lying Zwitter-ionic states Z_1 and Z_2 which can be highly polarisable (eqn. 5). In the case of olefins the sudden polarisation effect offers a possible explanation for the existence of ionic intermediates. The above mentioned Z_1 and Z_2 states can become highly polar with opposite polarisations via the perturbation caused by any very small asymmetry of two radical sites. Calculations yielding the 'sudden polarisation' effect have been reported in the past for twisted ethylene, terminally-twisted butadiene and N-retinylidene. This year two papers have appeared on the 'sudden polarisation effect' in hexatriene[16,17]. These involve open shell SCF calculation and orthognal VB treatment. The calculations on s-cis/s-trans hexatriene (1) twisted around the central bond at values of θ between 86 and 94° yield two exicted states only slightly differing in energy.



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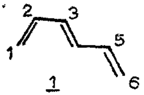

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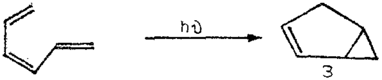
The disymmetry of the skeleton necessary for the sudden polarisation effect has been introduced into electron calculations by the non-nearest neighbour β's *i.e.*, $\beta_{1,5}$ and $\beta_{2,6}$ that are not equal. The rules for the relative energy of two oppositely polarised diallylic forms when substituted by methyls at different positions are given. These rules are used to predict the stereochemistry of cyclopropane ring closure in photochemical rearrangement of 1, 3, 5-hexatrienes to bicyclo (3, 1, 0) hex-2-enes (eqn. 6).



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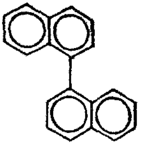
(6)

In this connection it should be noted that Fukui[11] has formulated a certain set of rules for cross-bicyclisation in these trienes based on perturbation treatment in the framework of Hückel MO's. Fukui has demonstrated that the 'symmetry disfavoured' reactions inferred from the usual cycloaddition mechanism can be interpreted as the *concerted* cross-bicyclisation reactions. It is important to realise that the earlier non-concerted mechanism originally due to Dauben is the one favoured by Salem's group from their theoretical calculations (the first step, *viz.*, cyclopropane ring closure is concerted and second step is non-concerted).

3. Physical aspects of organic photochemistry

This section reviews papers on radiative and radioationless transitions, energy transfer and excited state complex which may be of interest to organic photochemists. Turro[19, 20] has published a detailed paper on the spectroscopy of azoalkanes. Azoalkanes are often used as precursors for the construction of strained organic molecules. In this regard the knowledge of their photophysical properties is of interest. Most of the nineteen cyclic and bicyclic azoalkanes studied show fluorescence at room temperature and none show phosphorescence even at low temperature. Both emission quantum yield and singlet lifetime are found to be dependent upon the solvent and on isotopic substitution (OH → OD). A mechanism involving specific deactivation of the fluorescent state from a hydrogen bonded complex is proposed to rationalise the data (Table I).

Irie[21] in his classic paper has reported results that implicate the specific geometry requirement for the fluorescence quenching of 1, 1'-binaphthyl (4) by N, N-dimethyl α-phenethyl amine (5). Optically pure 1, 1'-binaphthyl (*R*)'s fluorescence was quenched by optical isomers 5 R and 5S. The different rates of quenching $\{[k_q(R)/k_q(S)] = 1{\cdot}90$ (hexane)$\}$ by these optical isomers reflect the specific geometrical requirement during the excited state interaction. The above results in the light of previous attempts to observe steric hindrance during excited state interaction is significant.



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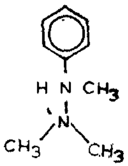

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Table I

Isotope effects on the spectroscopic properties of 3, 6-dimethyl-1, 2-diaza-(2.2.2) bicyclooctane.

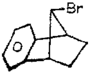
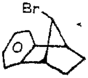
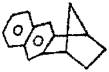
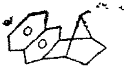
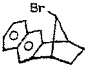
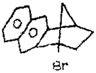
Solvent	ϕ_{fl}	τ_{ns}	τ_{fl} (ns)
Benzene	0·5	660	1200
Benzene-(d_6)	0·5	980	1960
Acetonitrile	0·7	780	1100
Acetonitrile—(d_3)	0·65	1000	1550
Methanol	0·01	14	1400
Methanol—(d_1)	0·1	165	1650
Water	0·25	335	1350
Water—(d_2)	0·55	700	1280

Chandra and Turro[22] have presented a theoretical basis for the specific geometrical requirement for the external heavy atom effect. They have suggested that the enhancement of phosphorescence (radiative rate K_p) process takes place through the second order mixing of triplet states of the chromophore with the singlet charge transfer states arising primarily from an electron transfer from the orbitals of the heavy atom perturber to the unfilled π^* orbitals of the chromophore. This specific orbital interaction brings in a geometrical requirement for the heavy atom effect (Table II).

Exciplex formation has been recognised to be a general mechanistic pathway in fluorescence quenching and has been suggested to precede photocycloadditions in a variety of reaction systems. In some exciplex formation systems, the increase in the concentration of a precursor results in the formation of a termolecular excited complex (triplex). Although termolecular complex is very unusual in ground state reactions the presence of such a complex in the excited surface is becoming common. Caldwell[23] has reported that exciplex resulting between phenanthrene and dimethyl-fumarate is quenched by a variety of electron rich olefins. Exciplex quenching efficiencies correlate with the electron donating ability of the quencher suggesting a charge transfer type of interaction (Table III). Similarly Pac[24] has reported that exciplexes formed between aromatic nitrile-2,5-dimethylfuran or 2, 5-dimethyl-2,4-hexadiene are quenched by pyridines. As the rate of quenching was dependent on the substituents at 2, 6-position of pyridine the exciplex quenching is discussed by the authors in terms of the inter-

Table II

Observed values of k_p (77° K) for a few- benzo- and Naphtho-norbornanes

Molecule	k_p ^{c} sec^{-1}
	0·15
	3·54
	16·70
	0·026
	5·1
	0·63
	0·95

action of the *n*-orbital of the quenchers with the positive charge developed on the electron donor side of the exciplexes (Fig. 1).

Table III

Stern-Volmer slopes for quenching of exciplex fluorescence (phenanthrene-dimethyl fumarate) by electron donors

Quencher	Ionisation potential (ev)	$K_a \tau\ M^{-1}$
2-methylbut-2-ene	8·89	0·1
Ethylvinyl ether	8·49	0·7
Dihydropyran	8·34	3·9
Trans-anethole	7·68	9·8
Triethylamine	7·50	9·7

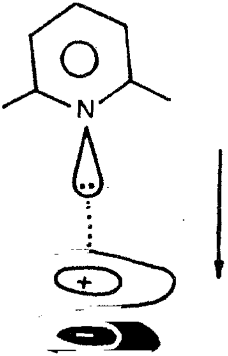
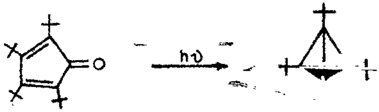


Fig. 1. Geometry of enterplex.

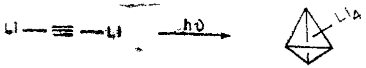
4. Photochemistry as a synthetic tool

Photochemistry continues to prove to be an invaluable tool to the synthetic organic chemists engaged in the construction of highly strained molecules and complex natural products. This year has witnessed the synthesis of tetrahedrane, the ultimate goal of chemists interested in strained molecules[25, 26]. Tetra-*t*-butyltetrahedrane has been synthesised by the photolysis of tetra-*t*-butyl cyclopentadienone at 77° K.

Surprisingly it is found to be stable at room temperature and for purification by chromatography. This feat was achieved by Maier. It is also interesting to note that irradiation on dilithioacetylene in liquid ammonia at − 45° yields a microcrystalline powder believed to be tetralithiotetrahedrane.

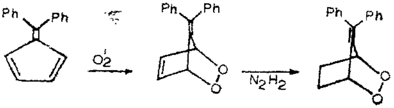


(7 a)



(7 b)

Adam[27, 28] has reported the synthesis of cyclic peroxides which involve the reaction of singlet oxygen with cyclic dienes (eqns. 8 and 9).



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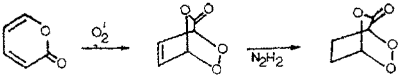
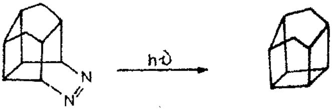


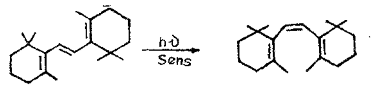
(9)

Photoextrusion of nitrogen, carbon monoxide, sulphurdioxide, etc., is often used to construct cage compounds. But there are several 'reluctant cyclic azo compounds' that resist photochemical elimination of N_2. Turro *et al*[29] have undertaken a detailed study of one of these and have shown that photoelimination of N_2 is still a valid tool for the creation of cage compounds (eqn. 10).



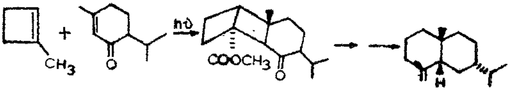
(10)

'One way sensitised geometric isomerisation' which has been efficiently utilised by Liu[30] to generate highly hindered isomers of retinyl polyenes is once again demonstrated to be a useful synthetic tool for the construction of highly hindered 'mini- β-carotenes' (eqn. 11).



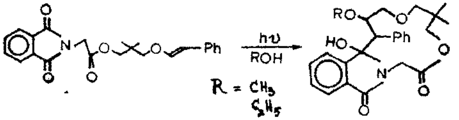
(11)

Photocycloaddition has yielded in the hands of Wender[31] a natural product as illustrated in eqn. 12.



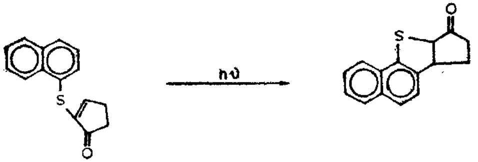
(12)

Markyama[32] has reported a photoreaction probably triggered by an electron transfer, which is expected to have enormous synthetic utility in the construction of macrocyclic compounds (eqn. 13).



(13)

Schultz[33, 34] has published full details on the hetero-atom directed photoarylation as a synthetic tool. For example, a ring C heterosteroid analogue is available from 1-naphthalenethiol in 78% yield (eqn. 14). Furthermore, he has developed a simple photochemical method for the conversion of 2-aryloxyenone to dihydrofuran (eqn. 15). These reactions are expected to prove useful in the synthesis of isoquinoline alkaloids.



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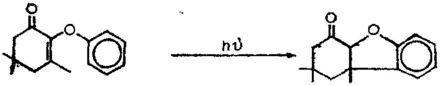

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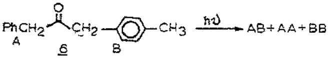
5. Photochemical reactions under unusual conditions

Photochemical reactions are most often conducted in solution phase for convenience and for their immediate utility in organic synthetic and mechanistic studies. On the other hand, systematic photochemical studies in micelles, monolayers and crystalline state has been quite scarce until recently. Last year a few publications have appeared in this area which speak for the importance of conducting studies in media other than solution.

5.1. *Micelles and monolayers*

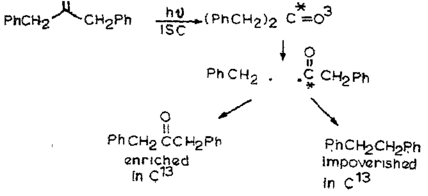
The photodecarbonylation of dibenzyl ketones in homogeneous fluid solution occurs via a free radical mechanism in which coupling products are produced in quantitative yield. For an asymmetric dibenzyl ketone the coupling products *AA*, *AB* and *BB* are formed in yields of 25, 50 and 25%, precisely the ratio expected for statistical, non-selective coupling of the free radicals *A* and *B* produced by decarbonylation. Turro[35] has shown that irradiation of *p*-(tolyl)-benzylketone (6) in HDTCl micellar phase brings about a drastic change in the ratio of products as illustrated in eqn. 16. The result is a dramatic enhancement of selectivity in the formation of *AB* relative to *AA* and *BB* as compared to homogeneous solution. This drastic change in photobehaviour of diarylketone in solution and in micellar phase is attributed to the difference in microviscosity between the two.



(16)

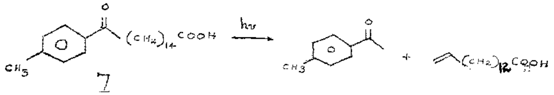
Homogeneous solution (benzene)	50%	25%	25%
Detergent solution (HDTCl – H_2O)	100%	0%	0%

Turro[35] has utilised the above principle of sequestering reactive species inside ' a super-hydrophobic cage ' to separate C^{12}/C^{13} isotopes. He has demonstrated that photolysis of dibenzyl ketones employing sunlight and ordinary mercury light as excitation sources brings about a measurable but small C^{12}/C^{13} isotope separation in homogeneous (benzene) solution. More importantly, C^{12}/C^{13} separation is greatly enhanced in soap solution (HDTCl) relative to homogeneous solution, the carbonyl carbon of dibenzyl ketone being specifically and exponentially enriched as photolysis proceeds (eqn. 17).



(17)

Whitten[37, 38] has studied the photochemistry of 16-oxo-16-*p*-tolyl hexadecanoic acid (7) in monolayer assemblies, anionic micelles and in solution. The results indicate that the micro environment can produce striking changes in reactivity. They report that the characteristic solution process—the type II photoelimination—is effectively eliminated in the highly condensed monolayer assemblies but enhanced compared with hydrocarbon solution in the more fluid micelles.

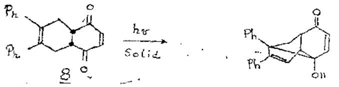


(18)

Monolayer assemblies	Φ 10^{-4}
Benzene solution	Φ 0·2
SDS-H_2O micelle	Φ 0·8.

5.2. *Crystalline phase*

Crystalline phase presents molecules in close proximity and in specific semi-rigid orientations with respect to reactive centres. This will exert an influence on the electronic states of molecules and on the stereo-chemical course of reactions. A few reports of photoreactions conducted in crystalline phase have appeared this year and interesting results are presented. Scheffer[39] has reported in detail the solid state photochemistry of *cis*-4*a*, 5, 8, 8-tetra-hydro-1,4-napthoquinone (8) and eight of its substituted derivatives. Of these, three underwent topochemically controlled (2 + 2) ene-dione double bond photocycloaddition. Others underwent intramolecular hydrogen abstraction. Bimolecular (2 + 2) photoaddition occurred only when the crystal lattice was such that adjacent molecules were oriented with centre to centre distance of less than ca 4·1° A; failing that unimolecular photoprocesses prevailed.



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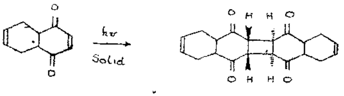
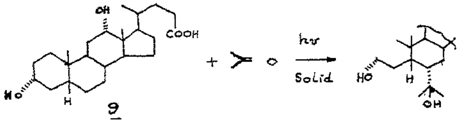


(20)

Lahav and Leiserowitz[40] have reported an elegant study on the photochemistry of molecular complexes of deoxycholic acid (9) with acetone. In crystalline phase 9 forms well defined 2 : 1 molecular complexes with acetone (m.p. 170–175° C). Irradiation of the solid leads to the formation of three major products as shown in eqn. 21. X-ray structure determination clearly reveals the presence of short contact between acetone and 9. The topochemical nature of these reactions are further supported by the results obtained on the 1 : 1 complex of apocholic acid (10) with acetone which upon irradiation is found to be inert.



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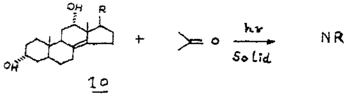
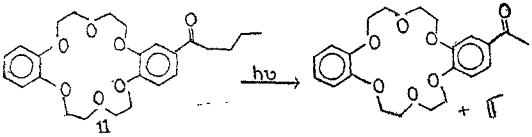


(22)

5.3. *Miscellaneous*

Photochemical reactions yielding drastically different results have also been carried out with the use of crown ethers. The specific binding of alkali metal ions to crown ethers is a well known phenomenon. Hautala[41] has reported the effect of metal ions on type II reaction of an arylalkyl ketone incorporated in crown ether 11.

He has shown that the quantum yield of type II of 11 is influenced by alkali metal cations and the enhancement of quantum yield is very specific to those which easily complex with the crown ether.

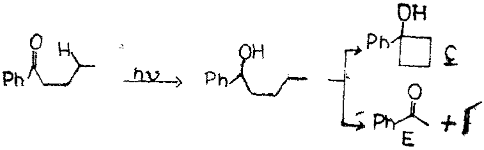


(23)

Salt added	Φ (*rel*)
None	1·0
NaCl	4·3
KCl	10·8

Though the effect of high pressure on thermal reactions is a well known phenomenon there are very few reports on the effect of pressure on photochemical reactions.

Neuman[42] has reported that high pressures (up to 1,500 atm.) have very little effect on type II cyclisation—elimination ratio of butyrophenone, valerophenone and α, α'-dimethyl-valerophenone (eqn. 24). Preliminary data reported suggest that in the case of α, α'-dimethyl valerophenone pressure effectively retards type I (α-cleavage) compared to type II (γ-hydrogen abstraction) process (eqn. 25).



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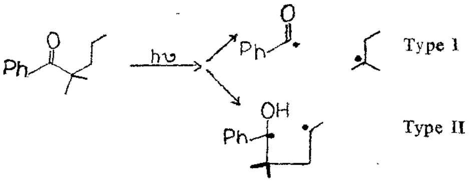
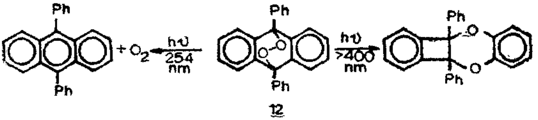


(25)

6. Wavelength and temperature dependent photoreactions

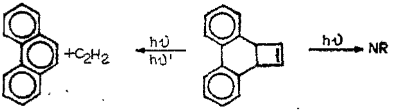
One of the most widely held and useful generalisations in solution phase photochemistry has been that reaction and luminescence occur from vibrationally relaxed molecules in their lowest singlet or triplet states. Reactions originating from higher vibrational levels of the lowest excited states (temperature dependent) and from higher electronic states (wavelength dependent) are being reported these days. This is expected to add a new dimension to the excited state chemistry.

9, 10-diphenylanthracene endo-peroxide (12) is reported to show different reactivity upon excitation with light of varying wavelength (eqn. 26)[43]. Short wavelength excitation induces cleavage of 'C — O' bond whereas long wavelength excitation induces that of 'O — O' bond. It is not clear whether the reaction originates from two different electronic states of the same chromophore (peroxide) or from electronic states of non-interacting chromophores namely peroxide and aromatic.



(26)

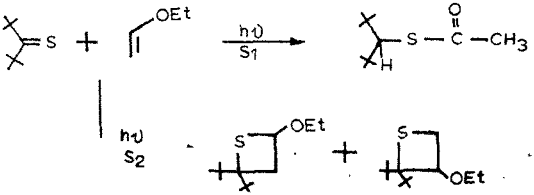
Michl[14] has reported another wavelength dependent reaction. Compound 13 is found to be inert upon irradiation with a single beam of low intensity light (310 nm). But irradiation of 13 at low temperature using two beams of different wavelengths (310 nm and 400 nm) is found to undergo photodissociation to yield phenanthrene and acetylene (eqn. 27). It is suggested that first excitation takes the molecule to the lowest excited state (triplet), and the second beam takes this excited molecule to a higher excited electronic state from where it undergoes dissociation.



13

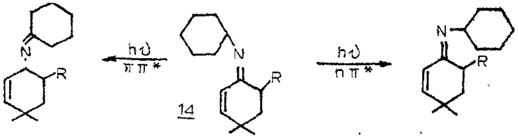
(27)

Thiones having large difference in excitation energy between S_1 and S_2 have been found to show wavelength dependent behaviour. For example, di-*t*-butyl-thione is reported to undergo photoreactions (reduction and addition to olefins) from higher excited singlet states[45].



(28)

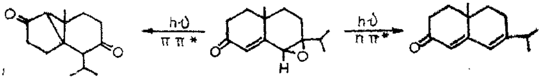
Margretha[46] reports that imines undergo reactions from $n\pi^*$ (S_1) and $\pi\pi^*$ (S_2) excited states. For example, 14 upon excitation to S_1 undergoes *cis*-trans isomerisation whereas excitation to S_2 yields a rearranged product (eqn. 29).



14

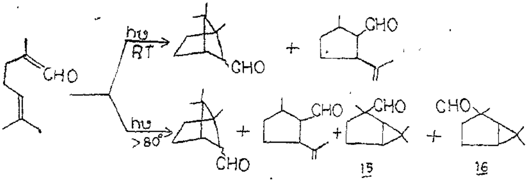
(29)

Wolf[47] has reported yet another α, β-enone which shows wavelength dependent behaviour (eqn. 30).



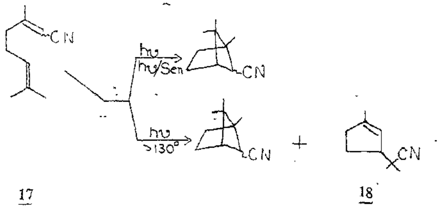
(30)

The above wavelength dependent reactions are examples of photoreactions originating from higher electronic states. Reactions originating from higher vibrational levels of their lower excited states are also known. This can be achieved by conducting reactions at higher temperatures. Agosta and Wolf[48] have reported that citral upon excitation at > 80°, yields 15 and 16 in addition to the usual low temperature products.



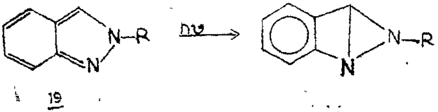
(31)

Similar to this they have also found that geranonitrile at > 130° furnishes 18, a new product, that is not observed at 30° C (eqn. 32).



(32)

Heizelmann[50] has reported that 2-alkyl indazoles (19) show a temperature dependent photochemical behaviour. In this case, unlike above examples, the temperature only enhances the product yielding process (eqn. 33).



$\phi(r)$	<200° K	0.00
$\phi(r)$	>300° K	>0.20

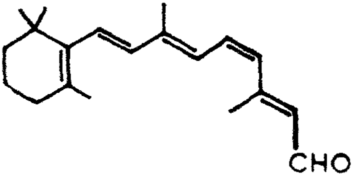
(33)

The temperature dependence of a photoprocess generally suggests the presence of a barrier for the reaction in the excited surface. The presence of such a barrier can be observed by monitoring the temperature dependent radiative process. This is detailed out in a paper by Turro[51].

7. Mechanistic organic photochemistry

7.1. *Aromatics and alkenes*

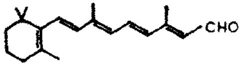
The photo-isomerisation of retinals has been investigated in numerous laboratories in the past. These studies included the measurement of photoisomerisation quantum yields for the direct excitation and triplet sensitised processes. Unfortunately, a few unequivocal mechanistic conclusions have resulted from these efforts. This year Weiss[32] has reported a study on the photoisomerisation of retinal using laser photolysis method.



11-cis retinal

An important outcome of this study is that the measured Φ (11-cis → all trans) 0·25 ± 0·03 and (all trans → mono cis) 0·07 ± 0·03 is consistent with the value reported earlier. Using pulsed laser photolysis at 347 nm it was shown that the transient absorption of 11-cis retinal is due to the triplet state of this isomer as well as that of *trans* retinal. This is in contradiction to the earlier proposal that 11-*cis*-retinal, *all-trans*-retinal and 7-*cis* retinal all produce the same equilibrated mixture of isomeric triplet-states. Based on the insensitivity of Φ_{iso} to oxygen, the evident lack of ground state *all-trans*-retinal production during the initial ~ 50nsec time interval Weiss concludes that isomerisation in hydrocarbon solvents occurs predominently from an internally excited first triplet state.

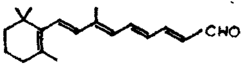
Waddell[33] has examined the photoisomerisation of four related retinals and has observed results which substantiate the photochemical isomerisation model of Kushick and Rice. The photochemical properties of retinals 20 to 23 have been examined in hexane solutions at room temperature and the results are shown below :



20

Φ

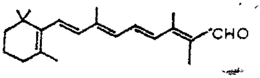
t → 9-cis	0·015
t → 13-cis	0·065



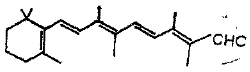
21

Φ

t → 9-cis	0.01
t → 13-cis	0.00



22



23

Φ

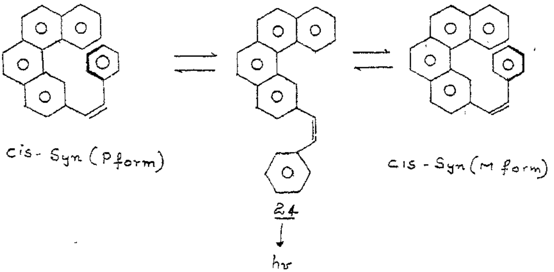
t → 9-cis 0·01
t → 13-cis 0·25

Φ

t → 9-cis 0·10-
t → 13-cis 0·30

The results show substantial variation in the Φ_{iso} of the concerned double bond where hydrogen has been replaced by methyl group. Waddell believes that as the number of available olefinic carbon-hydrogen stretching vibrations is reduced, torsional modes become important and the quantum yield of trans → cis photoisomerisation about that double bond is markedly increased.

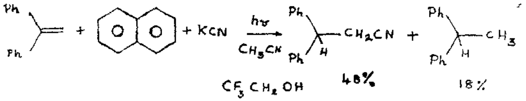
Laarhaven[54] has reported a chiral solvent-induced asymmetric synthesis of haxahelicenes. 2-styryl benzo-(c) phenanthrene (24) was irradiated in several chiral solvents in the presence of iodine as an oxidant. In all these cases optically active hexahelicene (not reacemic) was obtained. The role of the chiral solvents is ascribed to their influence on the equilibrium between enantiomeric conformation of cis 24 (eqn. 34).



(34)

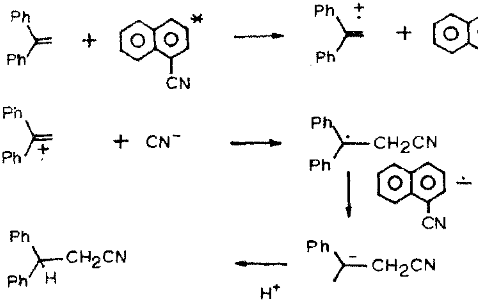
Solvent	*Optical yield*
± ethyl mandelate	0·00%
(RR) (+) diethyl-tartrate	1·1%
S (+) ethyl mandelate	2·1%

Electron transfer reactions in organic photochemistry has been gaining importance in the last few years. These reactions are especially useful in the synthesis of anti-



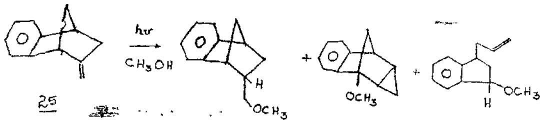
(35)

Markonikoff's addition products. Arnold[55] has reported that irradiation of phenyl olefins (*e.g.*, 1, 1-diphenylethylene eqn. 35) and potassium cyanide in acetonitrile in the presence of α-cyanonaphthalene gives good yields of nitriles having anti-Markownikoff orientation. The reaction is believed to involve an initial electron transfer from the olefin to the sensitizer as shown in scheme 1.

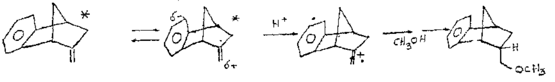


Scheme 1. Electron transfer mechanism for the anti-Markownikeff addition to olefins.

Similarly, Morrison[56] reports that irradiation of 2-methylene-benzonorbornene (25) in methanol gives the anti-Markownikoff's addition products (eqn. 36). As in the previous case, here also electron transfer process is suggested to be involved (eqn. 37).



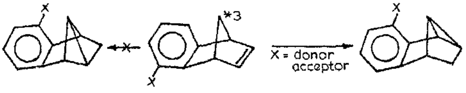
(36)



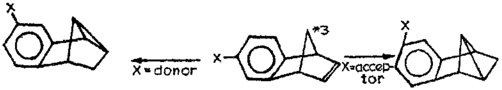
(37)

Houk and Paquette[57] have reported the ionisation potentials of sixteen aromatic ring substituted benzonorbornadienes measured by PES. They have correlated these

IP with the selectivity in triplet di-π-methane rearrangements as shown in eqns. (38) and (39).

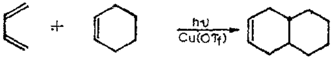


(38)

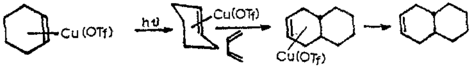


(39)

Cycloaddition reactions catalysed by metal salts are known in ground state chemistry. A report by Mackor[58] describes the use of copper(I) salts in the photocycloaddition reactions. It is reported that irradiation of butadiene and cyclohexene in the presence of copper(I) trifluoromethanesulfonate yields products which are otherwise not formed (eqn. 40). The suggested mechanism for the reaction involves excitation of the charge transfer complex between cyclohexene and Cu(OTf) (eqn. 41).

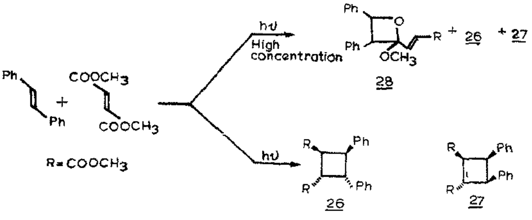


(40)



(41)

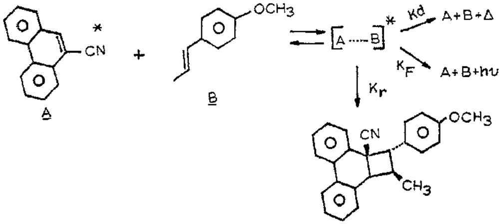
Lewis[59] has reported the formation of different cycloadducts upon quenching of singlet *trans*-stilbene and stilbene excimer by dimethylfumarate. For example, photolysis of *trans*-stilbene (10^{-2} M) and dimethylfumarate (10^{-2} M) in benzene results in the formation of dimethyl μ and neo-truxinate (26 and 27). On the other hand, irradiation of a more concentrated solution (0·2 M) gives an additional product 28 (eqn. 42). Since the formation of (28) depends mainly on the concentration of *trans*



(42)

stilbene it is suggested that stilbene excimer interacts with dimethylfumarate to yield 28. This divergent mode of cycloaddition for a singlet monomer and excimer are without precedent and offer a promising avenue for extending the synthetic scope of cycloaddition.

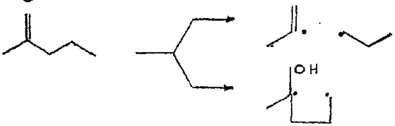
Caldwell[60, 61] in continuation of his studies on exciplexes and photocycloaddition reactions of phenanthrenes has undertaken a quantitative study on the photocycloaddition of 9-cyanophenanthrenes with anethole. Singlet exciplex fluorescence is observed in the case of 9-cyano-phenanthrene and anethole and this exciplex is demonstrated to be a product precursor. Based on the estimation of rates of various processes it is demonstrated that the rates of cyclobutane formation and internal conversion are affected by both substituents and temperature to a markedly greater extent than are fluorescence and intersystem crossing. Furthermore, the lifetime of exciplex is shown to decrease with temperature, indicating that its dominant decay processes are activated. Based on the available data he has suggested a model for the above photocycloaddition as shown in scheme 2.



Scheme 2. Mechanism for the cycloaddition of olefins to phenanthrene.

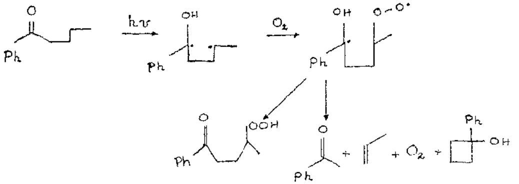
7.2. *Carbonyl compounds*

Lissi[62] has studied the photochemistry of several aliphatic ketones which decompose simultaneously by α-bond cleavage and α-hydrogen transfer (eqn. 43). The results obtained show that the rate of cleavage is completely determined by the α-substituent and that the rate of γ-hydrogen transfer is determined by the substituent at the γ-carbon. The solvent effect studied favour some amount of charge separation at critical configuration in both Type I and II processes.



(43)

Scaiano[63], in continuation of his studies on diradical, has trapped the diradical derived from Type II process in arylalkyl ketone using oxygen. He has studied the photochemistry of butyrophenones and valerophenones in the presence of oxygen. Typically oxygen is reported to quench the triplet state with rate constant of ~ 4×10^9 $M^{-1} sec^{-1}$ and interact with diradicals with rate ~ 7×10^9 $M^{-1} sec^{-1}$. The interaction of the diradical with oxygen results in the formation of an intermediate which decays to Type II products (75%) and to a stable peroxide (25%) (eqn. 44).



(44)

Scaiano[64] has also shown that triphenylphosphineoxide and organic phosphite $P(OMe)_3$; $P(OPr)_3$ interact with the diradical derived from valeropenone through Type II process. Unlike in the case of oxygen, no stable products were isolated during the above interaction. The interaction between the diradical and organic phosphites increases the yields of photofragmentation and cyclisation.

Quantum yields of formation of Type II products in the case of arylalkyl ketones is known to be solvent dependent. In the past, this has been attributed to the effect of solvent on the diradical behaviour. In fact, Scaiano[65] has provided confirmatory evidence for the above rationalisation. By laser flash photolysis studies he has measured

Table IV

Lifetime of the diradical derived from γ-methyl valerophenone through Type II process

Solvent	τ_B (n sec)	Solvent	τ_B (n sec)
Methylene bromide	16	Ether	68
Chlorobenzene	25	Acetonitrile-wet	76
Carbontetrachloride	26	Methanol	97
Cyclohexane	30	Triethyl-phosphite	119

Table V

Quantum yields of Type II and Type III products from substituted valerophenones (eqn. 45)

X	ϕ_{II}^{a}	ϕ_{III}^{b}	K_{-x} (rel)
Cl	0·58	0·10	1
Br	0·048	0·55	65
I	0·002	0·43	1260
SCN	0·003	0·25	490

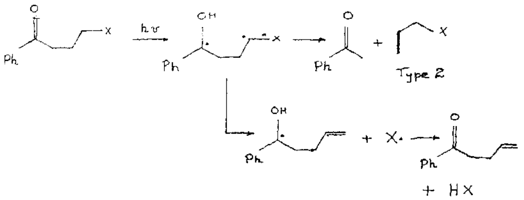
a Quantum yield of Type II products.
b Quantum yield of Type III products.

the lifetime of the diradical from γ-methyl-valerophenone and has shown that the diradical lifetime is very much solvent dependent (Table IV). Furthermore, the lifetime correlates with Φ_{II} of reaction, *i.e.*, longer lifetime favours larger Φ_{II}.

Wagner[66] has used the Type II process to generate the diradicals whose chemical behaviour is of current interest. He has attempted to study the elimination reactions of diradicals and has shown that these undergo elimination of H X to give Type III products (eqn. 45). The rate of elimination in general follows the usually known properties of 'X' (Table V).

Although hydrogen abstraction reactions of carbonyls is believed to originate from $n\pi^*$ state, there are several molecules which undergo the above reaction inspite of having $\pi\pi^*$ state as the lowest state. Steel[67] has provided a semi-theoretical rationalisation for the above observations as well as new data consistent with the rationalisation. Steel suggests that photoabstraction of acetophenones require a mixing between zero order $n\pi^*$ and $\pi\pi^*$ states with interaction energies $\geqslant 100\,\text{cm}^{-1}$. The extent of mixing and the energy separation of the resultant states are fundamental properties of the molecule. Variations in photoreactivity between compounds are then mainly manifested as activation energy differences and the reactivity of a given compound changes significantly with temperature. The above rationalisation is consistent with the data presented (Table VI) by Steel.

Givens[68] has reported a substituent effect study on the photorearrangement of bicyclo (3, 2·1) oct-2-ene-7-ones. Direct irradiation of 29 and 30 a–*c* result in 1, 3 acyl migration (eqn. 46) whereas triplet sensitisation result in both 1, 3 acyl migration



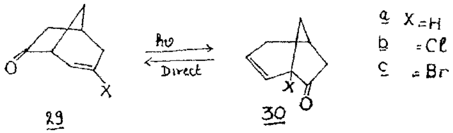
(45)

Table VI

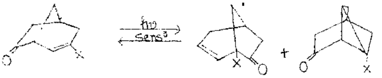
Rate constants, energy of activation and Arhenius factor for the photochemical hydrogen abstraction by carbonyl compounds

Carbonyl	$K \times 10^{-5}$ M^{-1} sec	Ea kcal/mole	log A M^{-1} sec
p-trifluoro methyl acetophenone	20·4	2·91±0·05	8·48±0·04
Acetophenone	3·9	3·54±0·09	8·23±0·07
p-methyl acetophenone	0·23	4·76±0·02	7·91±0·17

and oxadi-π-methane rearrangement to tricyclic ketone (eqn. 47). Detailed studies on the sensitised rearrangement showed that the two reactions (1, 3-acyl migration and oxadi-π-methane rearrangement) originate from separate excited states. It is suggested that a non-quenchable excited state possibly a higher $n\pi^*$ state is responsible for the 1, 3 acyl shift while a lower lying $\pi\pi^*$ triplet is the oxadi-π-methane precursor. Further more, it is shown that chlorine and bromine substituents do not alter the nature of product on direct irradiation. Evidence for the absence of intersystem crossing is provided by the absence of phosphorescence in all these cases at 77° K. The probable reason for the absence of heavy atom effect is suggested to be that the excited state surfaces funnel the reactant molecules into the ground state rearrangeemnt surface.

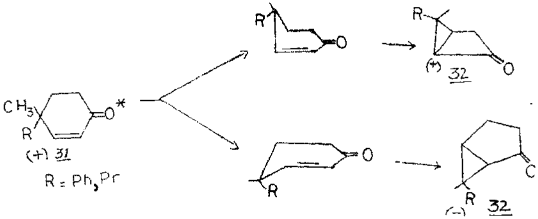


(46)



(47)

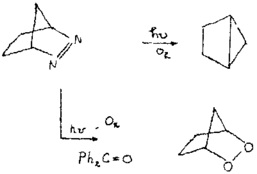
Schuster[69] has reported the photochemical behaviour of two chiral monocyclic enones. In both the systems it was found that the rearrangement to bicyclo (3.1.0) hexane-2-ones (32) proceeds stereospecifically with no loss in optical activity (eqn. 48). The results are consistent with synchronous mechanism for these rearrangements describable in term of ($\sigma_{2a} + \pi_{2a}$) cycloadditions originating from triplet excited states. It appears that the contour of the triplet surfaces, in so far as maxima and minima resulting from orbital symmetry and electronic correlations are concerned, resemble those predicted for the corresponding singlet excited states to a large extent.



(48)

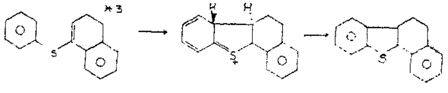
7.3. *Heterocyclic chemistry*

Wilson[70] has carried out an unique experiment in which he has trapped diradical intermediates derived from azo compounds using oxygen. This route, although serves as a synthetic method for the preparation of peroxides, will establish the presence of diradical intermediates in photochemical reactions (eqn. 49).



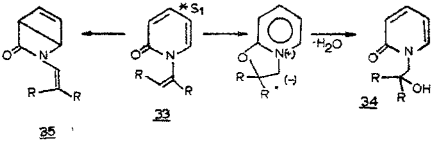
(49)

Wolf[71] has used flash photolysis method to establish the photochemical ring closure of S-aryl vinyl sulfides to substituted thiophenes. He has established that the reaction proceeds through the excited triplet state of the sulfides to colored Zwitterionic dihydrothiophene intermediates. This intermediate undergoes hydrogen shifts or abstractions to give the final product.



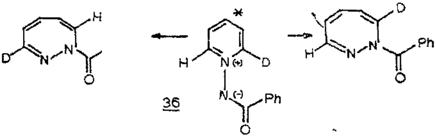
(50)

Marino[72] has reported a synthetically useful reaction of 1-vinyl-2-pyridones (33). 33 upon irradiation is found to give two products from excited singlet state as depicted in eqn. 51. Interestingly the efficiency for production of 34 is found to increase at the expense of 35 as water concentration in H_2O–THF solution is increased. Through detailed investigation he has demonstrated that the increased efficiency is due to an enhanced rate of ylide trapping by hydronium ion.



(51)

Kwart and Streith[73] have provided strong support for the presence of an intermediate in the photorearrangement of 1-imino pyridinium ylides. Photo-rearrangement of 2-deuterio 1-imino pyridinium ylide (36) show a very large, inverse, secondary deuterium isotope effect (eqn. 52). It is suggested that the large, inverse, secondary isotope effect is indicative of a thermal transition state in which the carbon seat of rearrangement is increasing its covalency. An intermediate is supported by kinetic isotope effect data.

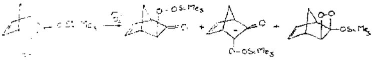


$$\frac{K_H}{K_D} = 0{\cdot}911 \pm 0{\cdot}003 \qquad (52)$$

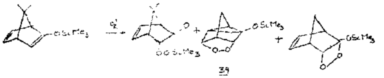
7.4. *Singlet oxygen*

Monroe[74] has reported the rate of interaction between singlet oxygen and olefins. These rates are consistent with the earlier data. The rate increases with the number of alkyl groups substituted on the olefin and decreases as the size of alkyl groups become larger. This trend may be related to the lower ionisation potential of the more highly substituted double bond. An increase in the size of the alkyl groups substituted on the olefin reduces the rate of O_2' addition proabaly due to steric hindrance as has been observed for aliphatic amine—O_2' interaction.

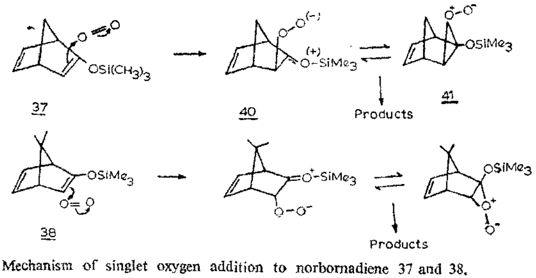
Jefford[75,76] continues to provide experimental support for the intermediacy of perepoxide/Zwitterionic peroxide during O_2' addition to olefins. Photooxygenation of norbornadiene 37 and 38 in $CDCl_3$ is reported to give the products described in eqns. (53) and (54). These results are rationalised in terms of the formation of ionic intermediates as the primary event as shown in scheme 3. Attack by O_2' on the parent norbornadiene 37 takes place preferentially on the less hindered exo-face of the molecule to give the Zwitterionic peroxide 40 or perepoxide 41. The action of gem-dimethyl grouping at C-7 is to force O_2' to approach the endo-face of the norbornadiene skeleton. This time the resulting intermediate has three avenues: (*a*) silatropic shift, (*b*) dioxetane formation and (*c*) closure to the endo-peroxy nortricyclane derivative. Thus the presence of extra double bond is suggested to trap the Zwitterionic peroxide/perepoxide intermediate intramolecularly to give 39.



(53)

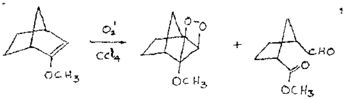


(54)

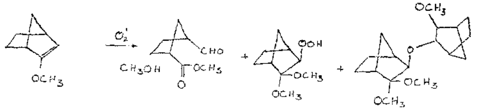


Scheme 3. Mechanism of singlet oxygen addition to norbornadiene 37 and 38.

Jefford[77] reports that 2-methoxynorbor-2-ene reacts with O_2' in aprotic and protic solvents as described in eqns. (55) and (56). In this report, he uses protic solvents to trap the perepoxide/Zwitterionic peroxide intermediates.

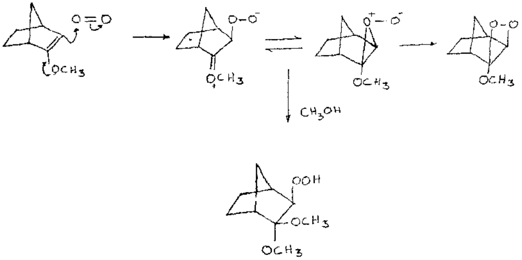


(55)



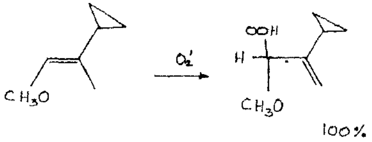
(56)

The chief finding in this investigation is that the products incorporating solvent can only be adequately explained in terms of primary Zwitterionic intermediate (eqn. 57). In the absence of interception by solvent, closure subsequently occurs to give dioxetane.

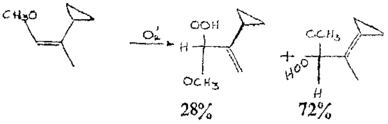


(57)

Ene reactions of O_2' with olefins is believed to be concerted in nature. Recently doubt has been cast on this and it is suggested to proceed through perepoxide/Zwitterionic peroxide intermediates. This year Goddard[78] has analysed the experimental data of Conia (eqn. 58 and 59) based on biradical peroxyl intermediate.

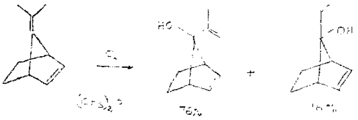


(58)

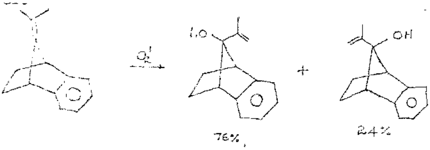


(59)

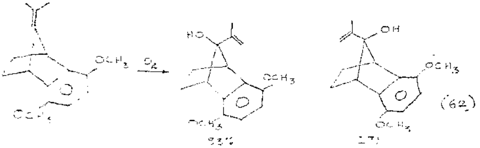
Okada and Paquette[79,80] have reported stereoselectivities in the addition of singlet oxygen to 7-isopropylidene norbornene derivatives. These interesting observations are described in eqns. 60-63. The observed variable selectivity is attributed to electronic effects and not to steric effect.



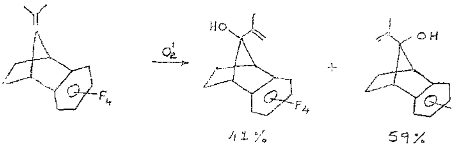
(60)



(61)



(62)



(63)

8. Reviews and books

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2. The effect of wavelength on organic photoreactions. Reactions from upper excited states. N. J. Turro, V. Ramamurthy, W. Cherry and W. F. Farnets, *Chem. Rev.*, **78**, 125
3. Mechanisms of photochemical transformations of cross conjugated cyclohexadienones. D. I. Schuster, *Acc. Chem. Res.*, **11**, 65
4. Radiationless transitions in molecules. K. F. Freed, *Acc. Chem. Res.*, **11**, 74
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6. Photoreactions of cyclic imides. Examples of synthetic organic photochemistry. Y. Kanoka, *Acc. Chem. Res.*, **11**, 407
7. Photolysis of organopolysilanes. Generation and reactions of silicon-carbon double bonded intermediates. M. Ishikawa, *Pure Appl. Chem.*, **50**, 11
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10. The problem of tetrahedrane. N. S. Zefloor, A. S. Kozmin and A. V. Abramenkov, *Russ. Chem. Rev.*, **47**, 163
11. The photochemistry of enamides. G. R. Lenz, *Synthesis*, p. 489
12. Photochemical and thermal reactions of porphyrins and organic surfactants in monolayer assemblies. D. G. Whitten *et al.*, *Ber. Bunseges. Phys. Chem.*, **82**, 858
13. Organic photochemistry I—General concepts. V. Ramamurthy, *Ind. J. Chem. Ed.*, **5** (3), 1
14. Photochemical rearrangements and fragmentations of alkenes and polyenes. G. Kaupp, *Angew. Chem. Int. Ed. Engl.*, **17**, 150
15. Industrial applications of photochemical synthesis. M. Fischer, *Angew. Chem. Ed. Engl.*, **17**, 16
16. Practical aspects of photochemistry. R. S. Davidson, *Chemistry and Industry* (March 18), p. 179
17. Energy storage via photochemical reactions. T. Laird, *Chemistry and Industry*, (March 18), 186
18. The development of photochromiccompounds for use in optical information stores. H. G. Heller, *Chemistry and Industry* (March 18), 195

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2. *Photochemistry of small molecules*, H. Okabe, John Wiley, New York.
3. *Modern molecular photochemistry*, N. J. Turro, Benjamin/Cumings Publishing Co., Inc., Menlo Park, California.

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