

The Photochemistry of Olefinic Compounds

By J. D. Coyle

DEPARTMENT OF PHYSICAL SCIENCES, THE POLYTECHNIC,
WOLVERHAMPTON, WV1 1LY

1 Introduction

The extensive studies of photochemical reactions in recent years enable a systematic description of the photoreactions of organic compounds to be made on the same basis as for their thermal reactions. A compound with a particular functional group undergoes characteristic ground-state (thermal) processes and characteristic, often different, excited-state (photochemical) processes. The differences between thermal chemistry and photochemistry arise largely because the excited state has a higher internal energy than the ground state (and therefore a wider range of reactions is thermodynamically feasible), and because the electron distribution is different in the various electronic states.

An attempt is made in this review¹ to give a brief survey of the major classes of photochemical reaction of compounds containing the C=C functional group. Examples are taken mainly from the chemistry of alkenes and dienes. The photoaddition of such compounds as polyhalogenated alkanes and thiols to alkenes² is omitted, in which excitation of the non-olefin component causes homolytic cleavage of a bond in the excited state to give radicals which add to the alkene. Certain reactions of unsaturated carbonyl compounds are not dealt with, which involve mainly the C=O group.

2 Excited States

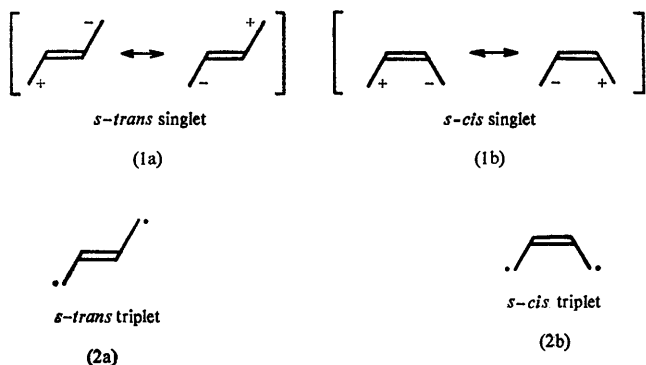
For compounds which contain only C=C chromophores the lowest energy electronic transition involves promotion of an electron from the highest occupied π molecular orbital to the lowest unoccupied π^* orbital. The intense absorption in the spectra of simple alkenes which corresponds to this allowed transition has its maximum around 170–180 nm in the vacuum u.v., and the singlet (π, π^*) excited state is of fairly high energy (~ 700 kJ mol⁻¹ for the planar singlet of ethylene). The corresponding triplet (π, π^*) excited state is considerably lower in energy (~ 350 kJ mol⁻¹ for the planar triplet of ethylene, ~ 250 kJ mol⁻¹ for the non-planar triplet), and the large singlet–triplet energy difference is the result of extensive spatial overlap of the π and π^* orbitals. This large difference in energy causes intersystem crossing from $S_1(\pi, \pi^*)$ to $T_1(\pi, \pi^*)$ to be very slow, so that direct irradiation of alkenes and dienes normally gives rise only to chemical reactions of the singlet excited state. Reactions of the triplet excited

¹ For a similar review for carbonyl compounds, see J. D. Coyle and H. A. J. Carless, *Chem. Soc. Rev.*, 1972, 1, 465.

² C. J. M. Stirling, 'Radicals in Organic Chemistry', Oldbourne, London, 1965, p. 75.

state must be brought about by the use of sensitizers. The reactions of the two (π, π^*) states (singlet and triplet) often differ considerably, partly because the states differ widely in energy, and partly because the triplet-state behaviour bears some resemblance to that of a carbon biradical whereas the singlet state is capable of undergoing concerted reaction.

Conjugated dienes and polyenes exhibit u.v. absorption at longer wavelength than simple alkenes, and the excited-state energy becomes progressively lower as the extent of conjugation increases.³ Of particular interest in the photochemistry of conjugated dienes is that the central bond of the diene, which is of largely single-bond character in the ground electronic state, has much more double-bond character in the first excited state, so that there are two geometrically isomeric excited states corresponding to the *s-cis*- and *s-trans*-conformations of the ground state. The singlet states are often represented in dipolar form (1) and the triplet states in biradical form (2), although undue significance should not be attached to such representations.



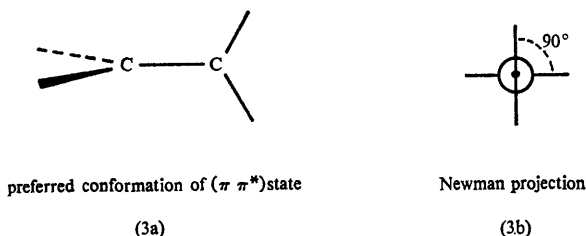
In the absorption spectra of ethylene and other alkenes there is a series of sharp bands superimposed on the broad $\pi^* \leftarrow \pi$ absorption envelope. The bands are the first members of a Rydberg series which corresponds to promotion of an electron from the π -orbital of the alkene to σ -type orbitals associated with the whole C_2H_4 unit (for ethylene itself). The series converges to the ionization limit. Rydberg excited states seem to play a part in the photochemistry of certain types of alkene, but their role is not yet fully established.

3 *cis-trans* Isomerization

In both the singlet and triplet excited states of an alkene, rotation about the central C=C bond occurs freely, since there is effectively no π -bond in the (π, π^*) state. The lowest-energy conformation of the excited states is normally

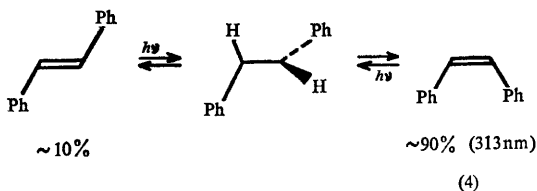
³ A. Streitwieser, 'Molecular Orbital Theory', Wiley, New York, 1967, pp. 208-214.

that in which rotation has occurred by 90° from the planar (ground-state) geometry (3). The existence of these 'non-vertical' ('phantom') states accounts



for the long, weak absorption tail in the u.v. spectrum of an alkene, the very short triplet lifetime (intersystem crossing from T_1 to ground state is rapid because the energy of the phantom triplet is very close to the ground-state energy in this particular geometry), and the lack of phosphorescence.

On direct irradiation the *cis* or the *trans* ground state of an alkene is excited to the first singlet excited state with the same geometry, and this relaxes to a common, lower-energy state of different geometry. For stilbene this is probably the non-vertical singlet state, though for 1-phenylprop-1-ene direct irradiation seems to lead to isomerization through a triplet state.⁴ The common intermediate decays non-radiatively to either *cis* or *trans* ground state. When a photostationary state is achieved, the composition of the *cis-trans* mixture depends on the extinction coefficients of *cis*- and *trans*-alkene at the wavelength employed and on the partitioning of the common excited state to *cis* or *trans* ground state. In the near-u.v. region *trans*-stilbene has a higher extinction coefficient than *cis*, and since the common excited state decays equally to *cis* or *trans* ground state the photostationary state contains a high proportion of *cis*-stilbene (4) as a result of selective isomerization of the *trans*-isomer.⁵



The triplet-sensitized *cis-trans* isomerization of alkenes follows a similar pattern, and if the sensitizer has a sufficiently high triplet energy (E_T) the photo-

⁴ C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, 1973, **58**, 3529.

⁵ J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, 1972, **94**, 2742.

stationary-state composition depends only on the partitioning of the phantom triplet state. For lower energy sensitizers the photostationary-state composition depends on the actual value of E_T (Figure 1 for stilbene). A high-energy sensitizer

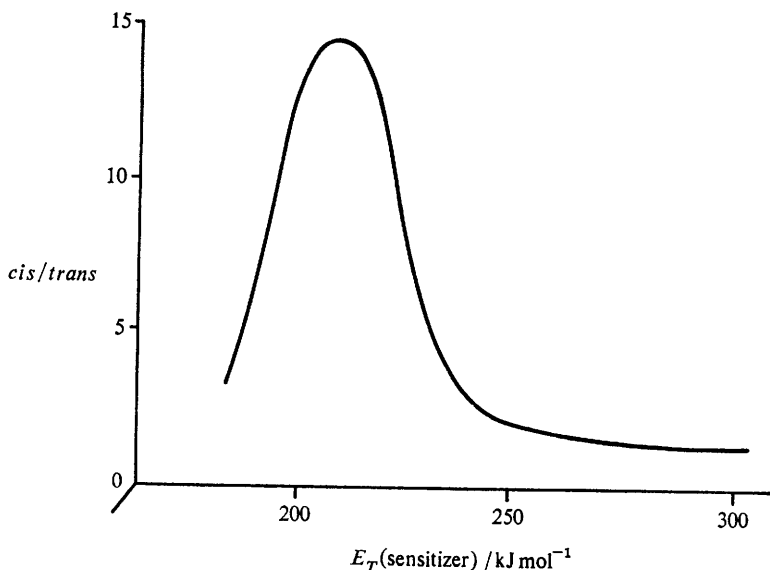


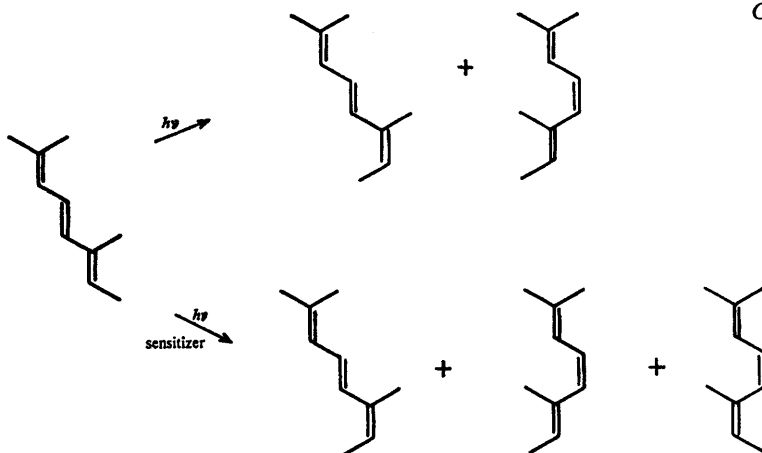
Figure 1 Photosensitized *cis-trans* isomerization of stilbene

populates both *cis* and *trans* triplet excited states efficiently, but as the sensitizer energy is reduced the efficiency of sensitization of the *cis*-isomer falls before that of the *trans*. As a result there is a region where the *trans*-isomer is selectively excited and the proportion of *cis*-isomer at photoequilibrium is greater. At even lower E_T values the efficiency of sensitizing the *trans*-isomer is also low, and the isomer ratio at equilibrium approaches the value obtained with high-energy sensitizers, probably because the energy transfer now produces a non-vertical excited state directly.⁶

cis-trans Isomerization of conjugated dienes and polyenes occurs on direct irradiation or in a sensitized reaction. Direct irradiation leads to isomerization about one of the double bonds, whereas triplet sensitization can lead directly to isomerization about two double bonds in a primary process, as shown in Scheme 1.⁷

⁶ S. Yamauchi and T. Azumi, *J. Amer. Chem. Soc.*, 1973, **95**, 2709.

⁷ R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, 1971, **93**, 1532.



Scheme 1

The effect of triplet sensitizer energy on the photostationary-state composition for the penta-1,3-dienes (Figure 2) is the reverse of that for stilbene.⁸ As E_T is

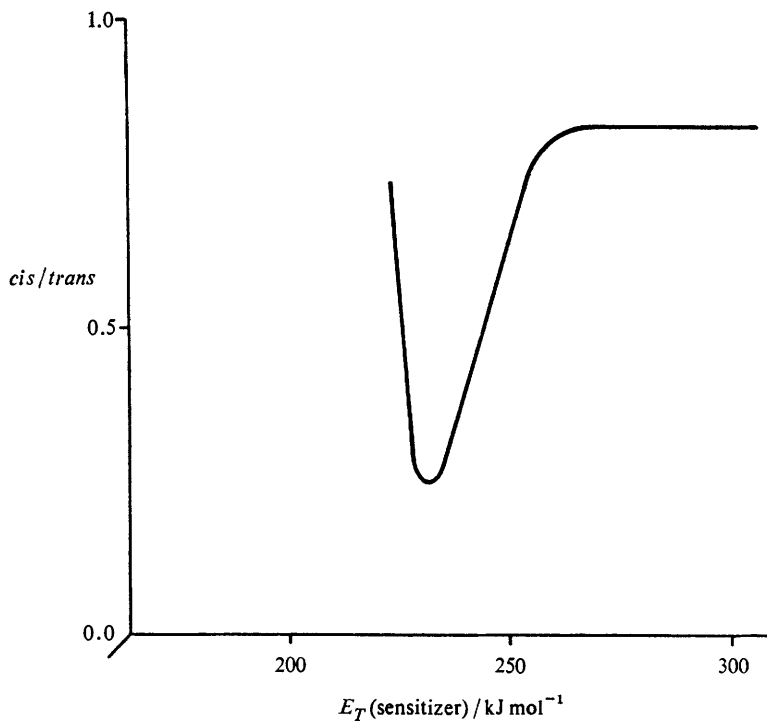
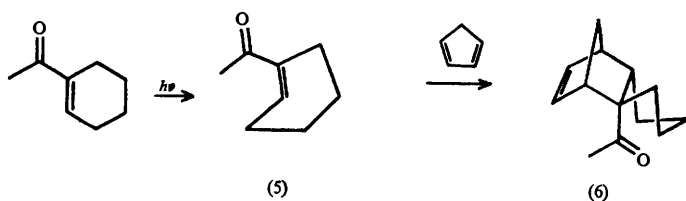


Figure 2 Photosensitized cis-trans isomerization of penta-1,3-diene

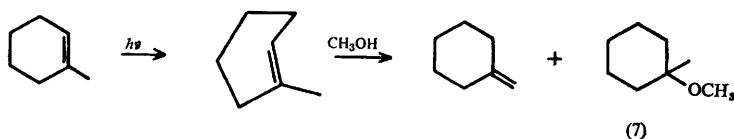
⁸ (a) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197; (b) J. Saltiel, L. Metts, A. Sykes, and M. Wrighton, *ibid.*, 1971, **93**, 5302.

reduced, energy transfer first becomes less efficient to the *trans*-diene, and only at lower E_T values is the efficiency of transfer to the *cis*-isomer similarly affected. The processes for conjugated dienes are complicated because different configurations (*s-cis* and *s-trans*) of each excited state can exist, and there are different possibilities for the non-vertical states because of the presence of two double bonds about which rotation can occur.

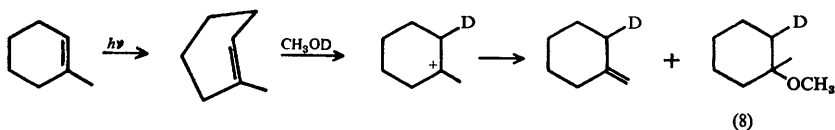
Simple acyclic alkenes also undergo *cis-trans* isomerization, through the (π, π^*) singlet triplet state on direct irradiation,⁹ or through a chemical intermediate with organic triplet sensitizers (rather than by energy transfer to give the alkene triplet state). Cycloalkenes behave in a similar manner, though the highly strained *trans*-isomers of cyclohexenes (5) and cycloheptenes cannot be isolated. These isomers can be trapped with added diene to give (6),¹⁰ by forming a dimer



with a ground-state molecule of *cis*-cycloalkene, or by protonation with an added reagent such as methanol to give (7).¹¹ The formation of a carbenium ion in the



reaction with methanol is supported by results with *O*-deuteriomethanol which gives (8).

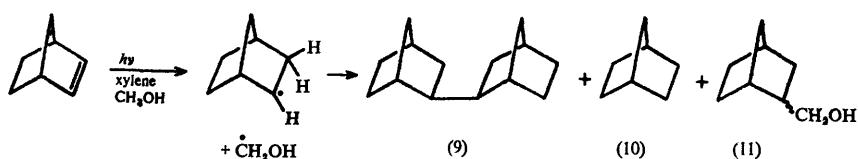


⁹ P. Borrell and F. C. James, *Trans. Faraday Soc.*, 1966, **62**, 2452.

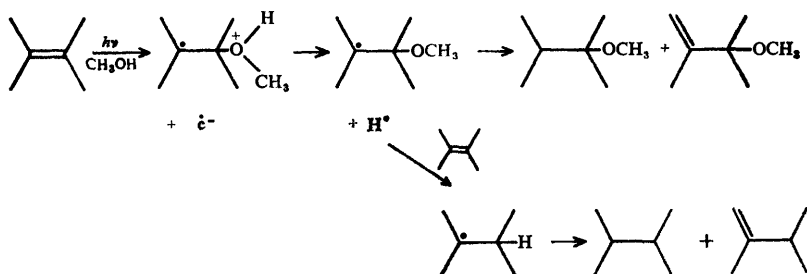
¹⁰ P. E. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50.

¹¹ P. J. Kropp, *Pure Appl. Chem.*, 1970, **24**, 585.

Cyclopentenes behave differently and lead to products (9)—(11) from radical



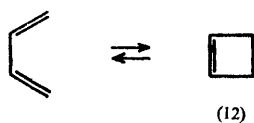
reactions, presumably because the *trans*-isomer is not formed at all. Tetra-alkyl-ethylenes are also different and react by a radical pathway.¹¹ In this case the lowest excited state is not (π, π^*) but Rydberg ($\pi, 3\sigma$), and the considerable electron deficiency near the carbon atoms invites nucleophilic attack by methanol as shown in Scheme 2.



Scheme 2

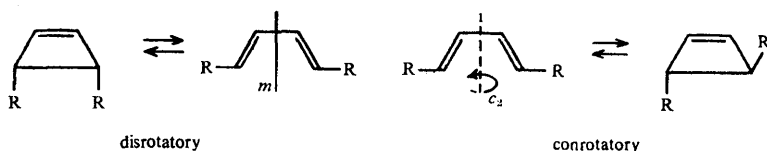
4 Cyclization Reactions

Concerted Cyclization.—The excited states of conjugated dienes and polyenes can cyclize to a monocyclic or bicyclic product. A major group of these cyclizations are electrocyclic reactions, in which a σ -bond is formed in a concerted process between the two ends of a conjugated π -system. The archetypal electrocyclic reaction is the cyclization of buta-1,3-diene to cyclobutene (12), and the



reverse ring-opening process. This reaction can occur in the ground state (*i.e.* thermally) or in the first singlet (π, π^*) excited state (*i.e.* on direct irradiation). The position of thermal equilibrium is determined by the difference in free energy between the open-chain and cyclic compounds, and in the butadiene reaction the equilibrium strongly favours the acyclic diene. The position of photochemical equilibrium is determined by the absorption characteristics of the two compounds at the particular wavelength of radiation employed, and since butadiene absorbs much more strongly than cyclobutene in the normal u.v. region, the photochemical reaction favours production of cyclobutene. The thermal and photochemical equilibria for conjugated trienes and higher polyenes are not always so favourable to one side of the equilibrium.

With substituted compounds, different geometrical relationships can exist between open-chain and cyclic compound. These are defined as conrotatory if a two-fold axis of symmetry is preserved in the transformation of one to the other, or as disrotatory if a mirror plane is preserved (Scheme 3). For a given



Scheme 3

reaction one particular stereochemical course of reaction is very strongly favoured over the other, and this is rationalized, as for all concerted reactions, on the basis of some concept of orbital interaction and conversion such as the concept of the conservation of orbital symmetry.¹² The 'Woodward-Hoffmann' rules for an electrocyclic reaction in which k electrons undergo major reorganization are set out in Table 1.

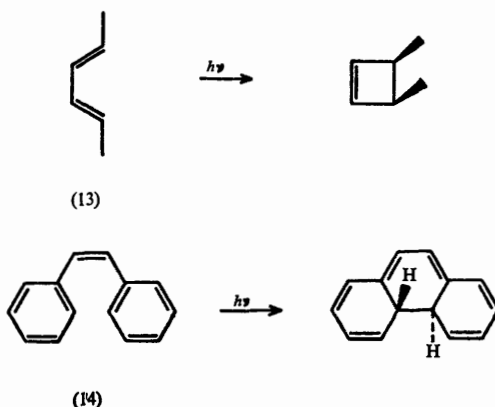
Table 1 Woodward-Hoffmann rules for electrocyclic reactions

k	thermal (S_0) reaction	photochemical (S_1) reaction
$4q$	conrotatory	disrotatory
$4q + 2$	disrotatory	conrotatory

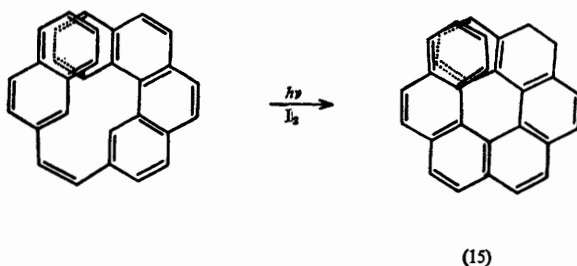
The stereoselectivity of the reactions is seen in the photochemical ring-closure

¹² R. B. Woodward, and R. Hoffmann, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1970.

of *trans,trans*-hexa-2,4-diene (13)¹³ and of *cis*-stilbene (14).¹⁴ The latter reaction



accompanies *cis-trans* isomerization on direct irradiation of *cis*-stilbene, and similar reactions provide a convenient route to the helicenes (15).¹⁵ The sequence



of thermal and photochemical reactions associated with ergosterol provides good examples of electrocyclic reactions.¹⁶

When a particular geometrical mode of ring-opening can lead to two different geometrical isomers of product, the major pathway is governed by steric effects in the product, or by conformational preferences in the reactant, as shown in Scheme 4.^{17,18}

¹³ J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, 1970, **92**, 3227.

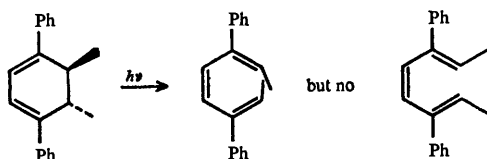
¹⁴ K. A. Muszkat and E. Fischer, *J. Chem. Soc. (B)*, 1967, 662.

¹⁵ R. H. Martin and J. J. Schurter, *Tetrahedron*, 1972, **28**, 1749.

¹⁶ G. M. Sanders and E. Havinga, *Rec. Trav. chim.*, 1964, **83**, 665.

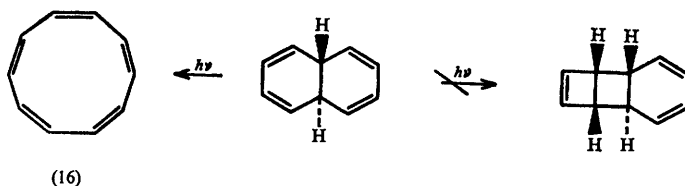
¹⁷ P. Courtot and R. Rumin, *Bull. Soc. chim. France*, 1972, 4238.

¹⁸ W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, 1973, **33**, 197.

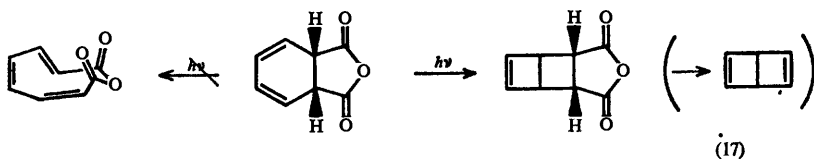


Scheme 4

Often there is a choice of different possible electrocyclic reactions. For instance, cyclohexa-1,3-dienes can in principle undergo six-electron ring-opening or four-electron ring-closure. Ring-opening is illustrated in the photochemical preparation of all-*cis*-[10]annulene (16).¹⁹ If the ring-opened product is highly



strained and absorbs strongly, ring-closure can predominate, and this is employed in the preparation of 'Dewar benzene' (17).²⁰

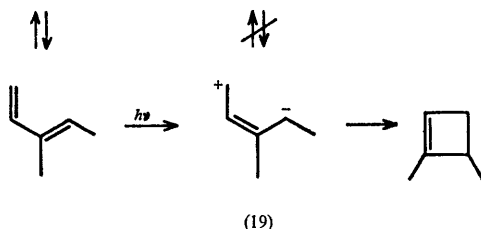
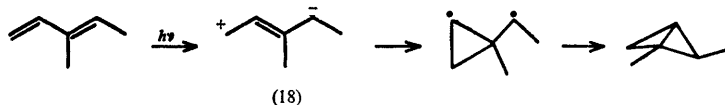


Non-concerted Cyclization.—Direct irradiation of conjugated dienes can give rise to bicyclo[1,1,0]butanes as well as cyclobutenes.²¹ The former seem to be formed in a two-step process from the *s-trans* excited state of the diene (18), whereas cyclobutenes are formed from the *s-cis* excited state (19). The bicyclobutanes can be isolated or converted *in situ* in to a mixture of cyclobutyl, cyclopropylmethyl, and homoallyl ethers by reaction with added alcohol.

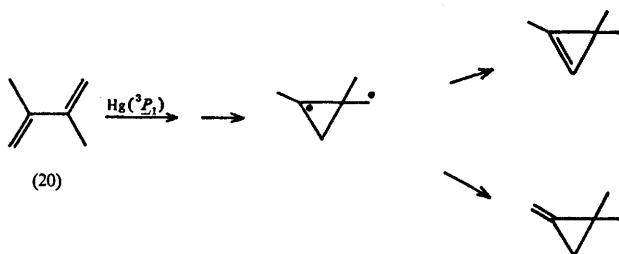
¹⁹ E. E. van Tamelen, T. L. Burkoth, and R. H. Greeley, *J. Amer. Chem. Soc.*, 1971, **93**, 6120.

²⁰ E. E. van Tamelen, S. P. Pappas, and K. Kirk, *J. Amer. Chem. Soc.*, 1971, **93**, 6092.

²¹ J. A. Barltrop and H. E. Browning, *Chem. Comm.*, 1968, 1481.



The same type of biradical intermediate is postulated²² to account for three-membered-ring products which are among those formed in $\text{Hg}(^3P_1)$ -sensitized reactions of dienes (20).



5 Cycloaddition Reactions

Concerted Cycloaddition.—Direct irradiation of a non-conjugated alkene can bring about a concerted cycloaddition between the (π, π^*) singlet excited state of one molecule and the ground state of another. The stereospecificity can be rationalized on the basis of the conservation of orbital symmetry or some equivalent concept. The geometrical relationship between reagents and product is defined by the mode of addition to each component, whether suprafacial (in which both new bonds are formed to the same face of the π -system) or antarafacial (in which the new bonds are formed to opposite faces of the π -system). The rules¹² for cycloadditions involving components with m and n π -electrons, respectively, are shown in Table 2. Most examples of concerted cycloaddition occur in a suprafacial-suprafacial manner, with an approach of reagents which

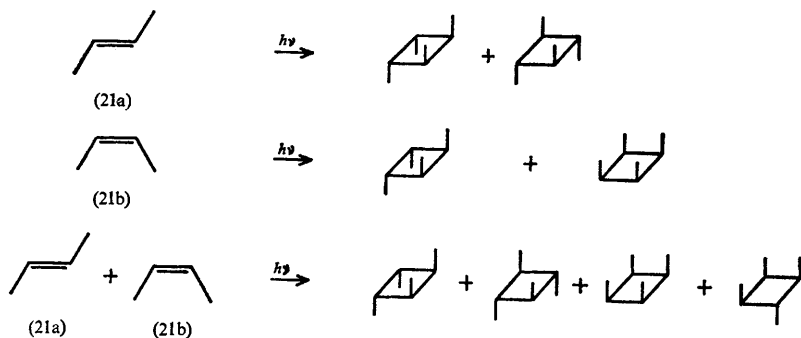
²² S. Boué, and R. Srinivasan, *Mol. Photochem.*, 1972, 4, 93.

normally allows maximum interaction of the π -systems. Hence many concerted thermal cycloadditions involve six π -electrons (e.g. the Diels-Alder reaction), and many concerted photochemical cycloadditions involve four π -electrons.

Table 2 Woodward-Hoffmann rules for cycloaddition reactions

$m + n$	thermal (S_0) reaction	photochemical (S_1) reaction
$4q$	suprafacial-antarafacial antarafacial-suprafacial	suprafacial-suprafacial antarafacial-antarafacial
$4q + 2$	suprafacial-suprafacial antarafacial-antarafacial	suprafacial-antarafacial antarafacial-suprafacial

Cyclodimerization of *cis*- and *trans*-but-2-ene (21) gives 1,2,3,4-tetramethyl-



cyclobutanes,²³ and the stereochemical course of the reaction strongly supports a concerted mechanism involving distinct *cis*- and *trans*-excited states. The formation of quadricyclane from norbornadiene (22) on direct irradiation is



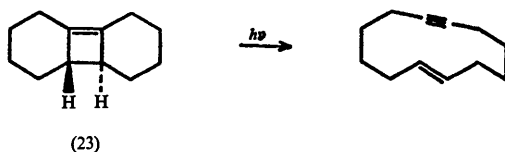
probably a concerted reaction, although it also occurs on triplet sensitization.²⁴

The reverse of a cycloaddition reaction follows the same stereochemical pattern, and an example of the stereochemical exclusiveness of these concerted

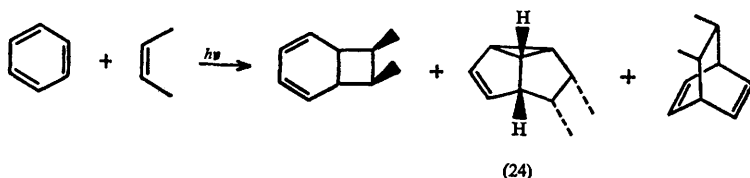
²³ H. Yamazaki and R. J. Cvetanović, *J. Amer. Chem. Soc.*, 1969, **91**, 520.

²⁴ W. G. Dauben and R. L. Cargill, *Tetrahedron*, 1961, **15**, 197.

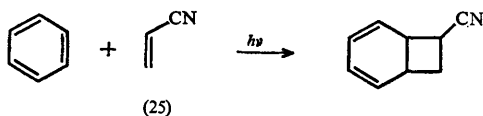
reactions is seen in the cycloreversion of the fused cyclobutene (23), where each isomer of the tricyclic compound forms only one isomer of the monocyclic enyne on irradiation.²⁵



Cycloaddition with Aromatic Compounds.—The irradiation of alkenes with benzenoid compounds gives rise to products of cycloaddition across the 1,2-, 1,3-, or 1,4-positions of the aromatic ring. Simple alkenes with benzene give all three types of product, the 1,3-adduct (24) normally predominating, and the reactions are stereospecific.²⁶



1,2-Cycloaddition is thought to occur in these simple systems through an exciplex (*excited complex*) formed from singlet-state excited benzene ($^1B_{2u}$ state) and ground-state alkene. It is an important reaction route when the alkene or the aromatic compound is electron-deficient, *e.g.* acrylonitrile (25),²⁷ but the mechanism of reaction is not always straightforward.

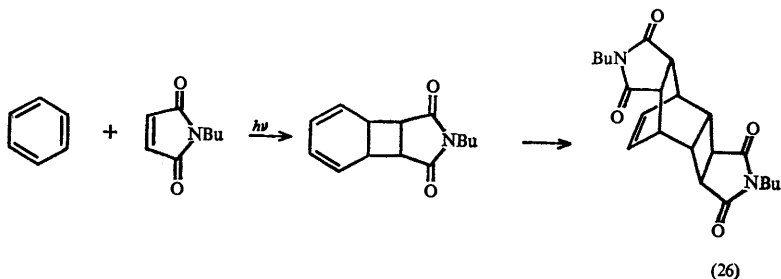


²⁵ J. Saltiel and L. S. Ng Lim, *J. Amer. Chem. Soc.*, 1969, **91**, 5404.

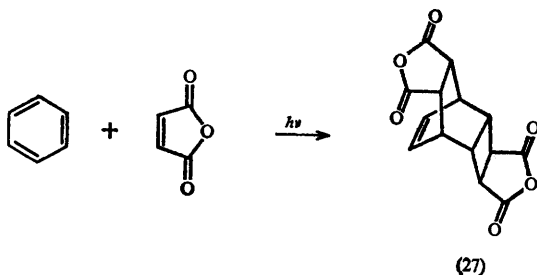
²⁶ (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073; (b) A. Morikawa, S. Brownstein, and R. J. Cvetanović, *J. Amer. Chem. Soc.*, 1970, **92**, 1471.

²⁷ B. E. Job and J. D. Littlehales, *J. Chem. Soc. (C)*, 1968, 886.

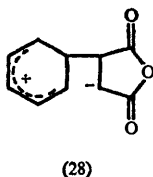
In the photocycloaddition of maleimides to benzene²⁸ a 2:1 adduct (26) is



produced as a result of a thermal Diels-Alder reaction of the 1:1 photoadduct. The photochemical reaction in this system begins with excitation of the imide. The reaction of maleic anhydride with benzene seems similar, affording (27),



but there is no evidence for the formation of an intermediate 1:1 cycloadduct. The initial excitation is of a complex formed between ground-state reagents to give a charge-transfer excited state of the complex. This gives a dipolar intermediate (28), which can go on to react with maleic anhydride to form the

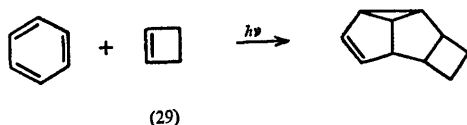


observed product.²⁹ The additions of both maleimides and maleic anhydrides occur on direct or sensitized irradiation.

²⁸ D. Bryce-Smith and M. A. Hems, *Tetrahedron Letters*, 1966, 1985.

²⁹ D. Bryce-Smith, *Pure Appl. Chem.*, 1968, 16, 47.

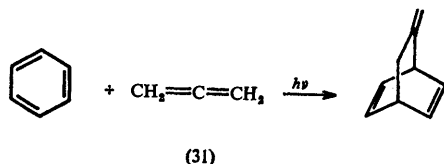
The reported examples of 1,3-photocycloaddition involve mainly alkyl-substituted ethylenes²⁶ or cycloalkenes (29).³⁰ It is the benzene which is initially



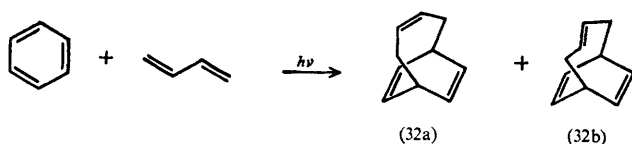
excited, but the subsequent steps may involve direct concerted addition to the alkene (this is the only cycloaddition of ${}^1B_{2u}$ benzene and ground-state alkene which is allowed on orbital symmetry grounds), or addition through an exciplex, or addition through an intermediate biradical (30).



1,4-Photocycloaddition is a major process for allenes (31),³¹ and for conjugated



dienes. With dienes ($4\pi + 4\pi$) addition products (32) may be formed instead of ($2\pi + 4\pi$) products.³²



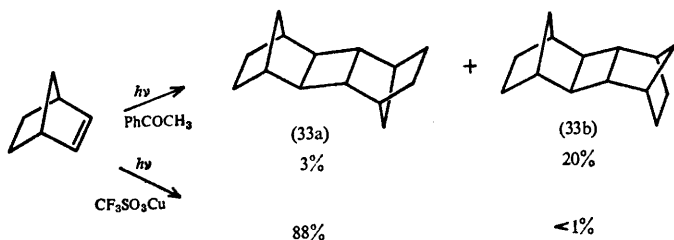
Non-concerted Cycloaddition.—There are many cycloaddition reactions of alkenes which are not concerted but which follow a two-step pathway through a

³⁰ R. Srinivasan, *I.B.M. J. Res. Develop*, 1971, **15**, 34; *J. Amer. Chem. Soc.*, 1971, **93**, 3555.

³¹ D. Bryce-Smith, B. E. Foulger, and A. Gilbert, *Chem. Comm.*, 1972, 664.

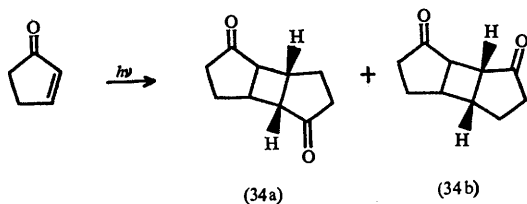
³² K. Kraft and G. Koltzenburg, *Tetrahedron Letters*, 1967, 4357, 4723.

biradical intermediate. These very often involve the triplet (π, π^*) state of one alkene molecule, and of the simple alkenes only three-, four-, and five-membered cycloalkenes give dimers such as (33) through their triplet excited state obtained

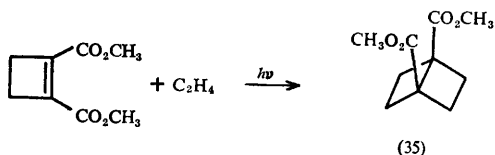


by energy transfer from organic triplet sensitizers.³³ Higher yields and greater selectivity result if a copper(I) catalyst is employed.³⁴ The triplet states of more flexible alkenes relax very rapidly to a non-vertical state and from this to *cis* or *trans* ground state.

When one alkene group is part of a conjugated system, cycloaddition through the triplet state is much more readily achieved. If the conjugated system is an unsaturated carbonyl compound, direct or sensitized irradiation leads to the triplet state, and dimerization to give (34) or cross-addition with an alkene to



give (35) can be efficient.^{10,35} Intramolecular cycloadditions of this type provide



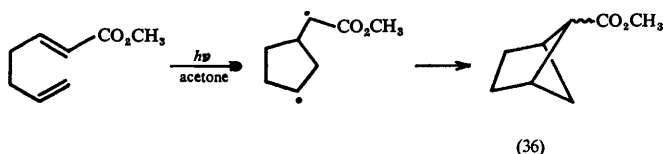
routes to bicyclic systems³⁶ such as bicyclo[2,1,1]hexanes (36).

³³ D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, 1965, **87**, 2596.

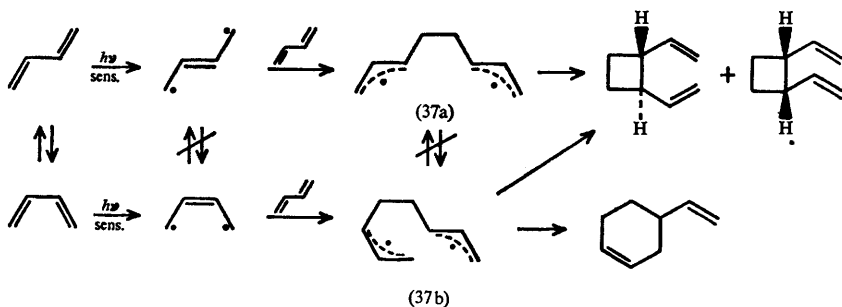
³⁴ R. G. Salomon and J. K. Kochi, *Tetrahedron Letters*, 1973, 2529.

³⁵ P. de Mayo, *Accounts Chem. Res.*, 1971, **4**, 41.

³⁶ J. R. Scheffer and R. A. Wostradowski, *J. Org. Chem.*, 1972, **37**, 4317.



If the conjugated system is a diene, triplet sensitization gives cycloaddition products together with products of *cis-trans* isomerization where appropriate. Diene dimers are produced by addition of *s-cis* or *s-trans* triplet-state diene to *s-trans* ground-state diene. This leads to di-allylic radicals (37), and ring-closure



gives either 1,2-divinylcyclobutanes or 4-vinylcyclohexene.³⁷ The participation of non-equilibrating configurations of the biradical is required to account for the variation of product ratio with the energy of the triplet sensitizer, since the *s-cis*- and *s-trans*-diene triplets are of different energy. Those dienes which have a rigidly held configuration, such as cyclohexa-1,3-diene, give dimers in a ratio which is independent of the sensitizer energy.

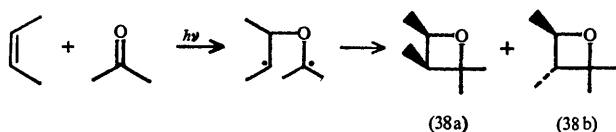
Heterocyclic Cycloaddition.—The formation of heterocyclic products can be a major reaction pathway when alkenes are irradiated with compounds containing groups such as C=O, C=S, C=N—, or NO₂. The reactions are usually initiated by excitation of the compound containing the heteroatom, and in many cases the formation of an exciplex involving both reagents is the next step in the process.

The irradiation of alkenes with carbonyl compounds gives oxetans as cycloaddition products.³⁸ Efficient reaction is associated with those carbonyl compounds which have a lowest (n, π^*) excited state. Simple alkenes (alkyl-substituted ethylenes) react with the triplet (n, π^*) excited state of aliphatic or aromatic

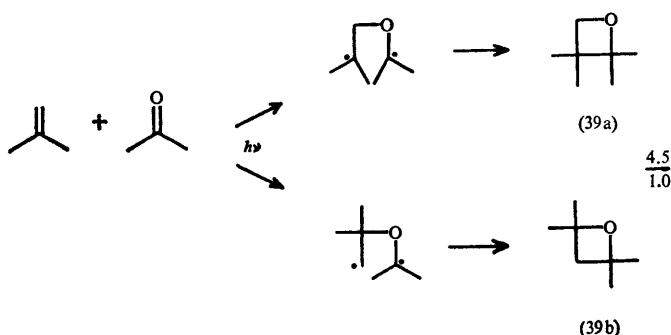
³⁷ G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, 1963, **28**, 3297.

³⁸ D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.

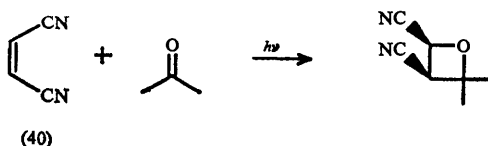
ketones to give products (38) in a non-stereospecific process. The intermediacy



of a relatively long-lived 1,4-biradical accounts for both the loss of stereochemistry and for the preferred orientation of addition to give the isomers (39).³⁹



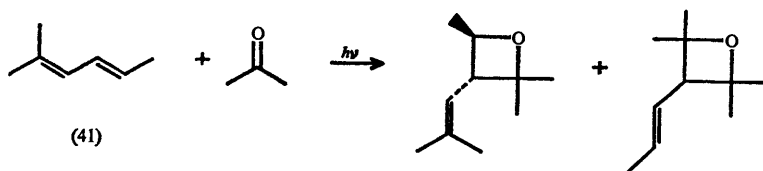
The ketone excited state and the alkene first form an excited charge-transfer complex. This exciplex in its triplet state gives the biradical, whereas the singlet state reacts stereospecifically to give oxetan either by a concerted process or through a short-lived biradical. Such singlet-state mechanisms predominate when the alkene, *e.g.* (40), is substituted with electron-withdrawing groups.⁴⁰



³⁹ H. A. J. Carless, *Tetrahedron Letters*, 1973, 3173.

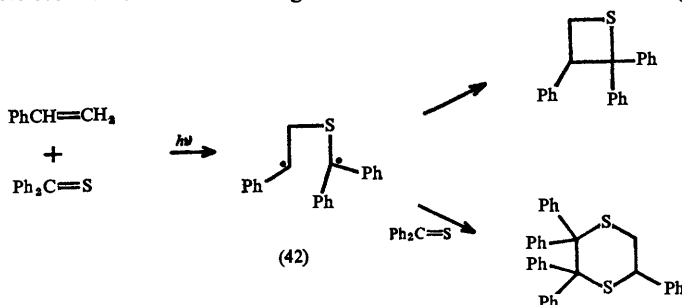
⁴⁰ J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 1318.

The reaction of conjugated dienes (41) with aliphatic ketones⁴¹ seems similar.



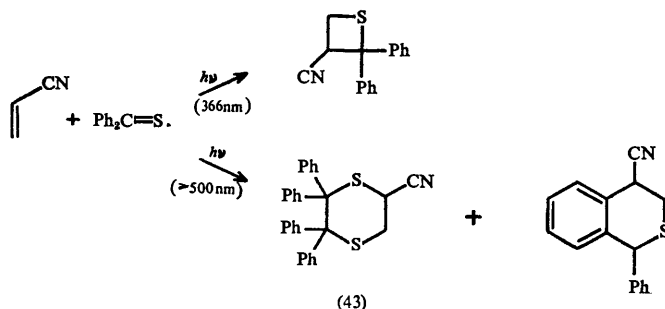
In this system energy transfer from the triplet state of the ketone to the ground-state diene is another major reaction pathway, though it is not in *direct* competition with the cycloaddition reaction of diene and singlet-state ketone.

Alkenes also undergo photocycloaddition with thiocarbonyl compounds,⁴² and two types of product are formed, thietan and 1,4-dithian. With styrene the products seem to be formed through a common intermediate biradical (42),^{42,43}



and the ratio of products varies with the concentration of ground state thio-ketone.

The situation is more complicated with the electron-deficient alkene acrylonitrile.⁴⁴ The thietan is produced when radiation of shorter wavelength is employed, and the dithian (43) (together with another product) when longer



⁴¹ R. R. Hautala, K. Dawes, and N. J. Turro, *Tetrahedron Letters*, 1972, 1229.

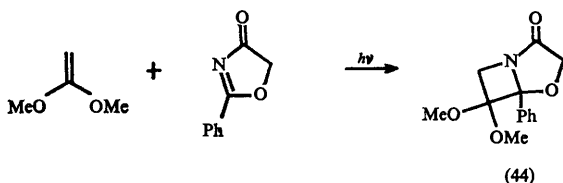
⁴² A. Ohno, *Internat. J. Sulfur Chem., B*, 1971, 6, 183.

⁴³ P. de Mayo and A. A. Nicholson, *Israel J. Chem.*, 1972, 10, 341.

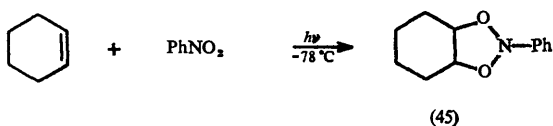
⁴⁴ P. de Mayo and H. Shizuka, *J. Amer. Chem. Soc.*, 1973, 95, 3942.

wavelength radiation is used. A possible explanation is that the lowest (n, π^*) excited state is responsible for dithian production, whilst a different excited state gives thietan.

Photocycloaddition between alkenes and C=N compounds has not been widely reported. One example of azetidine formation is shown for the product (44).⁴⁵



A different type of product results from irradiation of an alkene and a nitrobenzene. The excited state of the nitrobenzene reacts with alkene to give a dioxazolidine (45) at low temperature.⁴⁶



6 Sigmatropic Reactions

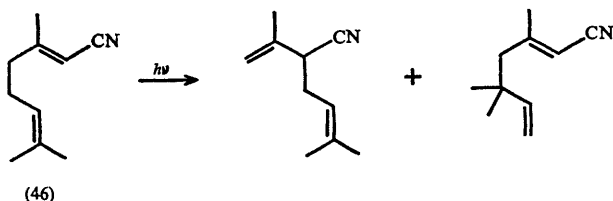
Sigmatropic Shifts.—A rearrangement reaction in which, formally, a σ -bond migrates across one or two π -systems is called a sigmatropic shift. If the termini of the σ -bond migrate over m and n atoms, respectively (inclusive of the initially and finally bonded atoms), the shift is said to be of order (m, n). Many of these rearrangements are concerted and are subject to stereochemical restrictions as a result of orbital interaction. The geometrical relationship between reactant and product is defined as suprafacial if the migrating group is attached to the same face of the π -system after migration as before, or antarafacial if it is attached to the opposite face after migration. The rules covering the 'allowed' modes of sigmatropic shift of order (m, n) are the same¹² as those for concerted cycloaddition (see Table 2).

As with cycloaddition reactions, many (though by no means all) of the examples reported involve the most straightforward geometrical relationship and are suprafacial(-suprafacial) shifts. Thus there are many photochemical (1,3)

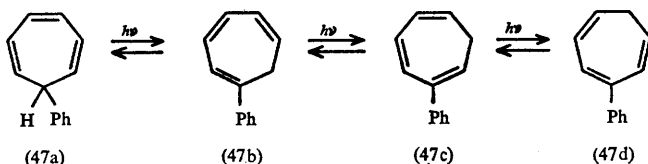
⁴⁵ T. H. Koch and R. M. Rodehorst, *Tetrahedron Letters*, 1972, 4039.

⁴⁶ J. L. Charlton, C. C. Liao, and P. de Mayo, *J. Amer. Chem. Soc.*, 1971, **93**, 2463.

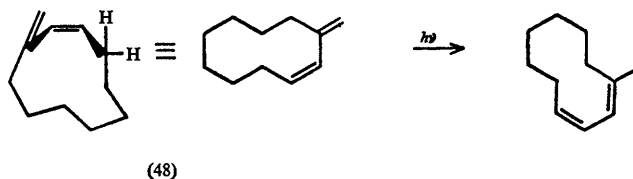
sigmatropic shifts such as⁴⁷ those of 1,5-dienes (46), and many photochemical



(1,7) shifts such as⁴⁸ those of cycloheptatrienes (47). Photochemical (1,5) hydrogen

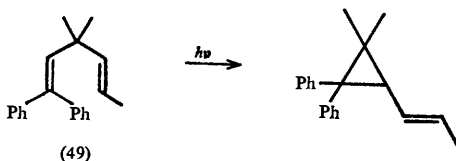


shifts are observed with some conjugated dienes (48),⁴⁹ when the geometry of



the system is favourable for an antarafacial migration.

Di- π -Methane Rearrangement.—Many 1,4-dienes and 3-phenylalkenes undergo a rearrangement in the excited state which involves a 1,2-shift accompanied by ring-closure to form a vinyl- or phenyl-cyclopropane.⁵⁰ With acyclic compounds (49) and most monocyclic compounds (50) the reactive excited state is the singlet,

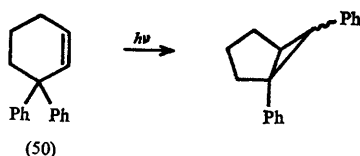


⁴⁷ R. C. Cookson, *Quart. Rev.*, 1968, **22**, 423.

⁴⁸ A. P. Ter Borg and H. Kloosterziel, *Rec. Trav. chim.*, 1963, **82**, 741.

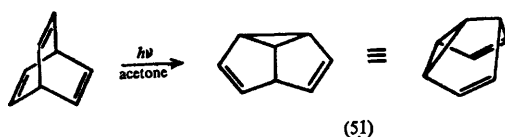
⁴⁹ W. G. Dauben, C. D. Poulter, and C. Suter, *J. Amer. Chem. Soc.*, 1970, **92**, 7408.

⁵⁰ H. E. Zimmermann and J. A. Pincock, *J. Amer. Chem. Soc.*, 1973, **95**, 2957.

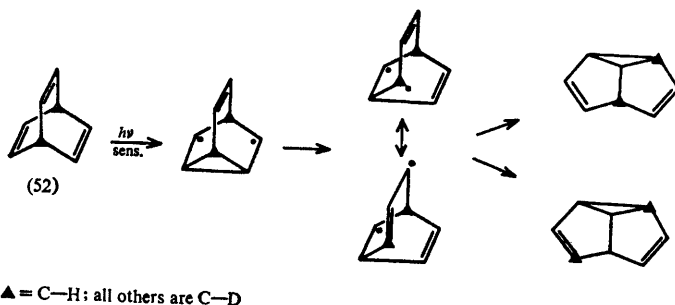


and the reaction is stereospecific with retention of configuration at C(1) and C(5) and with inversion at C(3) of the 1,4-diene unit. The triplet excited state of these compounds generally leads to *cis-trans* isomerization where it is possible.

The singlet excited state of more rigid (especially bicyclic) systems often undergoes some other reaction. However, a reaction is possible for the triplet state analogous to that observed with the singlet state of more flexible compounds. The triplet state of the rigid compound is unable to relax to a non-vertical geometry, and a non-concerted di- π -methane rearrangement occurs to give (51).⁵¹



The reaction pathway has been established by labelling studies, as shown for barrelene (52) (Scheme 5).⁵²



Scheme 5

7 Fragmentation Reactions

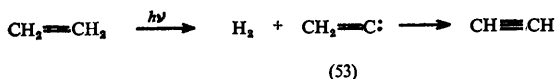
Monoalkenes are essentially transparent to near-u.v. radiation, and shorter wavelengths are required to effect direct photochemical reaction. The excited states formed on direct irradiation undergo fragmentation or rearrangement,

⁵¹ H. E. Zimmermann and G. L. Grunewald, *J. Amer. Chem. Soc.*, 1966, **88**, 183.

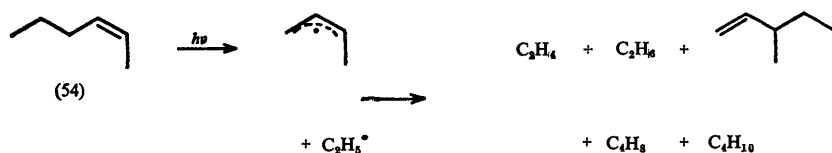
⁵² H. E. Zimmermann, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.* 1967, **89**, 3932.

and these processes are usually very efficient in the gas phase. In solution the efficiency is much lower, because energy dissipation is very rapid and reaction from vibrationally excited levels of the electronically excited state is suppressed. Solvent cage effects may also play a part in reducing the efficiency of reaction in solution.

Direct irradiation of ethylene leads mainly to intramolecular cleavage⁵³ to give acetylene and molecular hydrogen, possibly by way of a carbene (53).

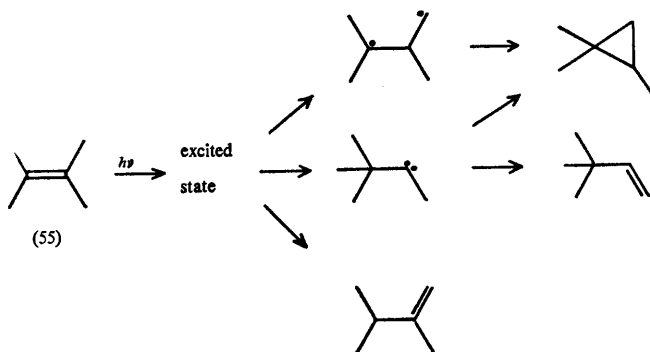


Smaller amounts of products from hydrogen atoms and vinyl radicals are also formed. With alkenes other than ethylene (*e.g.* 54), allylic C—H or C—C cleavage is the major process, apart from *cis-trans* isomerization, on direct



irradiation.⁵⁴ This is because these particular bonds are relatively weak.

The above processes derive from a (π, π^*) state, probably a singlet. For tetra-alkyl-substituted ethylenes, *e.g.* (55), different reactions occur which involve an



intramolecular (1,2)-hydrogen, (1,2)-alkyl, or (1,3)-hydrogen shift. These take place readily in solution as well as in the gas phase, and they may involve a Rydberg excited state.¹¹

The triplet states of monoalkenes can be obtained only by energy transfer since intersystem crossing is slow from the singlet states obtained on direct

⁵³ P. Borrell, A. Cervenka, and J. W. Turner, *J. Chem. Soc. (B)*, 1971, 2293.

⁵⁴ J. P. Chesick, *J. Chem. Phys.*, 1966, **45**, 3934.

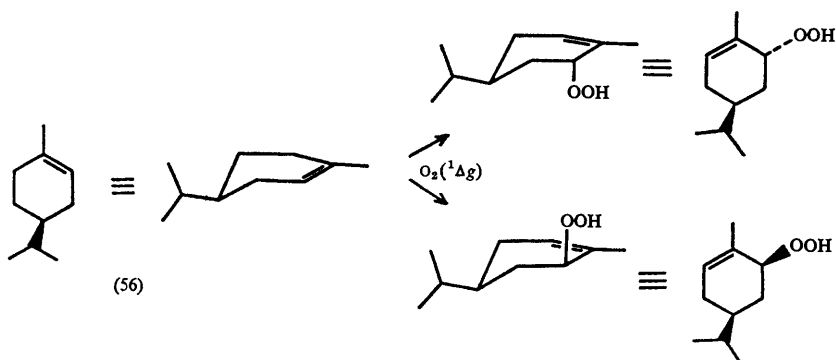
irradiation. In solution, acetone sensitizes the dimerization of rigid cycloalkenes (see Section 5). In the gas phase, sensitization of any alkene can be effected using $\text{Hg}({}^3P_1)$ or another triplet excited atomic species such as cadmium or zinc. The major quenching process of $\text{Hg}({}^3P_1)$ by an alkene goes through an intermediate complex (exciplex) and gives ground-state $\text{Hg}({}^1S_0)$ and triplet-state alkene.

The reactions of the triplet state resemble those of the excited singlet state except that a much higher degree of selectivity is found. Triplet-state ethylene gives acetylene and hydrogen by an intramolecular process (*cf.* ref. 53), and there is very little radical formation. Higher alkenes undergo allylic cleavage with considerable selectivity in their triplet excited states, though many minor rearrangement products are also formed, particularly at higher gas pressures.⁵⁵ This suggests that rearrangement is more important than cleavage from the lower vibrational levels of the excited state.

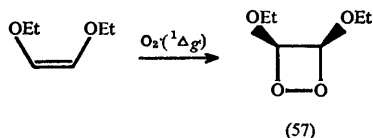
8 Photo-oxidation

Ultraviolet or visible irradiation of alkenes with molecular oxygen in the presence of a low-energy triplet sensitizer such as methylene blue leads to oxidation products. The role of the sensitizer is to generate singlet (${}^1\Delta_g$) oxygen.

Alkyl-substituted ethylenes with (${}^1\Delta_g$) oxygen give an allylic hydroperoxide as shown for (+)-limonene (56).⁵⁶ The reaction is concerted and stereospecific,



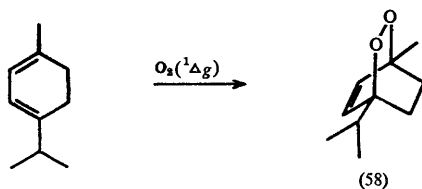
unlike thermal autoxidation, which gives racemic products by way of a symmetrical allylic radical.



⁵⁵ J. R. Majer, J. F. T. Pinkard, and J. C. Robb, *Trans. Faraday Soc.*, 1964, **60**, 1247.

⁵⁶ (a) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Letters*, 1972, 45; (b) N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *ibid.*, p. 49.

Alkenes such as dialkoxyethylenes give a 1,2-dioxetan (57) in a stereospecific cycloaddition reaction,⁵⁷ and conjugated dienes undergo a $(4\pi + 2\pi)$ cycloaddition which leads to a 1,2-dioxene (58).⁵⁸



⁵⁷ P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, 1970, **92**, 3223.

⁵⁸ K. Gollnick and G. O. Schenck in '1,4-Cycloaddition Reactions', ed. J. Hamer, Academic Press, New York, 1967, p. 255.