

TILDEN LECTURE

The Photochemistry of Some Allylic Compounds

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Although the importance of organic photochemistry has always been obvious, as the ultimate basis of all life, and of the oldest and still the largest industry, it is only in the last ten or fifteen years that its interest and potentialities have caught the imagination of organic chemists. Not only are the journals and lecture rooms increasingly full of accounts of old and new photochemical reactions, and speculations (or even experiments) on their mechanisms, but photochemical processes are beginning to be accepted as another normal laboratory technique, rather than the esoteric secret of the specialist that they seemed a few years ago.¹ After all, it is just as easy to plug in a u.v. lamp as a heating mantle.

The present intense activity can probably be traced to several causes. (a) Improved instruments and experimental methods have greatly simplified the work, (b) the physical chemists and spectroscopists have now established the important fundamental processes, (c) the molecular orbital theory, especially the brilliant popularisation of orbital symmetry rules by Woodward and Hoffmann, has provided a useful qualitative way of thinking about primary photochemical processes, (d) the extraordinary structures formed by many photochemical reactions have emphasised the potential of photosynthesis, and (e) even the sceptics have been impressed by the Toyo Rayon Co.'s demonstration of the possibility of large-scale industrial photochemistry² with its photochemical nitrosation of cyclohexane on a plant to produce 1.1×10^8 lb. a year of nylon-6. To these temptations one can add the further inducement that some traditional fields of organic chemistry have become over-grazed or, like the determination of structures of natural products, have become obsolete. Some interested in molecular

¹ In providing, rather belatedly, this written version of an unwritten lecture, apart from some abbreviations, I have kept to the original, particularly in not giving references. Anyone interested in learning more about photochemistry can be referred first of all to the comprehensive and authoritative gospel by J. Calvert and J. N. Pitts, 'Photochemistry', Wiley, New York, 1966.

² The direct use of sunlight for industrial photochemistry on a large scale (apart from agriculture and the smog over Los Angeles) seems as far off as when Giacomo Ciamician, one of the pioneers of organic photochemistry, made his prediction in 1912: 'Solar energy is not evenly distributed over the surface of the earth; there are privileged regions, and others that are less favoured by the climate. . . . On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere.'

structure and stereochemistry, refugees from the X-ray crystallographers, have turned to photochemistry. Those interested in reaction mechanisms too have found many thermal reactions increasingly well explored, and now enjoy the intricacies of electronically as well as vibrationally excited states: there is a limit to the number of alkyl halides one can solvolyse. Indeed one of the attractions of photochemistry is the way it brings together all we know about molecular structure and behaviour.

Before considering a few reactions that have interested my colleagues and me recently it may be helpful to remind ourselves of some relevant features of molecular energy states, as summarised in the familiar Figure 1. The energy level G in this diagram represents the ground state of molecule X, and S_1 and S_2 the first and second electronically excited states, each with its vibrational sub-levels. The arrow (a) represents the excitation of X by absorption of a photon of appropriate energy to the second excited state S_2 . Usually the equilibrium geometry of the excited state will differ, sometimes drastically, from that of the ground state, and the Frank-Condon principle ensures that S_2 is reached at a high vibrational level. In the liquid state at room temperature the excess vibrational energy is usually lost so quickly ($k > 10^{12}$ sec.⁻¹) that the lowest vibrational level is reached before anything else can happen to the molecule. Since fluorescence (b) can be observed from S_1 but not S_2 , conversion of S_2 to S_1 must also be extremely fast. Photochemical reactions in solution that proceed through the singlet will almost always therefore involve S_1 rather than higher excited states, even when light of short wavelength is used which initially produces a higher excited state. A 'forbidden' transition (f) with inversion of the spin of an electron can occur from S_1 to the corresponding triplet state T_1 , forbidden emission from which causes phosphorescence (c). The other, and usually more important way for T_1 to get back to the ground state G is, of course, by switching spin without emitting radiation and going over to a high vibrational level of G .

In solution exchange of energy between molecules is often very important, shown by absorption of light by molecules of one kind and emission or photochemical reaction from another. Exchange of energy between singlets may take place over relatively large distances by coupled dipole interaction. Exchange of triplet energy, requiring close contact of the two molecules with overlap of their outer electron orbitals, is particularly prevalent in organic photochemistry. In Figure 1 the process is shown by the dotted lines (e) in which the triplet of molecule Y undergoes a transition to the ground state coupled with the simultaneous transition of X, with which it is in contact, from the ground state to T_1 (with preservation of multiplicity of the complex). Y sensitises the phosphorescence or photochemical reaction of X through T_1 , while X conversely quenches the phosphorescence or reaction of Y. For efficient exchange the triplet excitation energy of Y naturally has to be greater than that of X ($e > c$). By irradiation of a solution containing a photosensitiser Y with light of wavelength absorbed by Y (d) but not by the reactant X [which would need light quanta of energy (b)] X can be put in the triplet state T_1 without going through any excited singlet state. Because of the small singlet-triplet splitting of the $n\pi^*$ excited states and

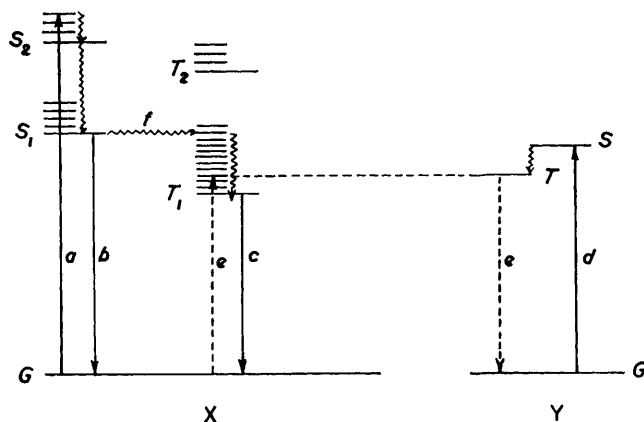
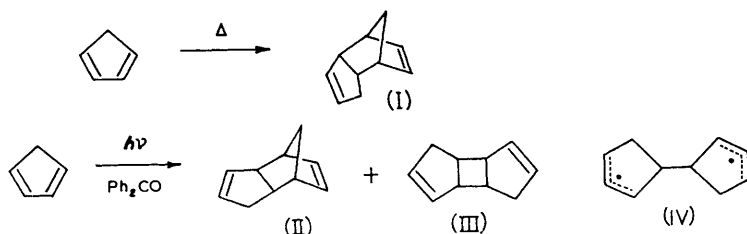


Figure 1 Partial energy diagram for two molecules *X* and *Y*
 (a) Excitation of *X* to second excited singlet state
 (b) Fluorescence from first excited state
 (c) Phosphorescence from lowest triplet state
 (d) Excitation of *Y* to first excited singlet state
 (e) Coupled transition of *X* from *G* to T_1 and *Y* from T_1 to *G*.

the high efficiency of crossing of the excited singlet to the triplet, ketones are very popular triplet photosensitisers.

G. S. Hammond has provided some nice examples involving dienes. Whereas thermal dimerisation of cyclopentadiene yields the *endo*-Diels-Alder dimer (I), irradiation of the diene in the presence of benzophenone (E_T 69 Kcal. mole⁻¹) with light absorbed only by the latter produces a mixture of dimers consisting mainly of the *exo*-isomer (II) and the cyclobutane-dimer (III). The $n\pi^*$ triplet of benzophenone, formed very efficiently from the singlet, produces the triplet diene, which adds to a molecule in the ground state to form the *dl* and *meso* allylic diradicals (IV). Spin-inversion and bond-formation lead to the structural and stereochemical isomers.

The behaviour of butadiene is more complicated, because it can exist in *s-cis* and *s-trans* conformations (V and VI) the latter with a higher triplet energy than the former. The two planar conformations are in rapid equilibrium in the



Dimerisation of cyclopentadiene by heat and light

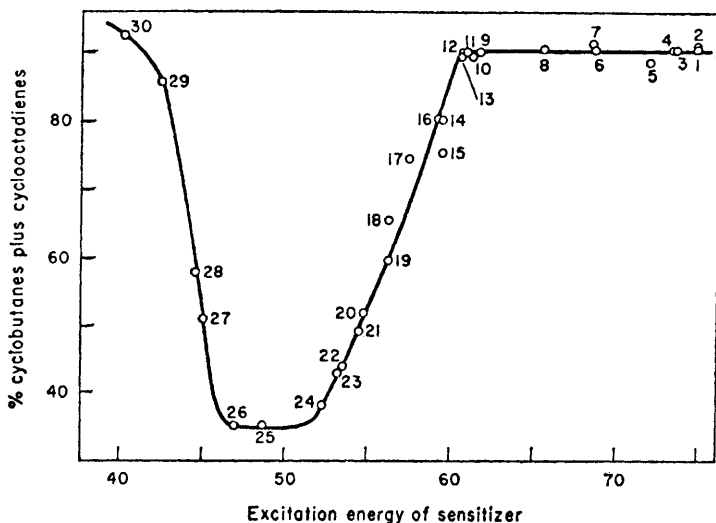
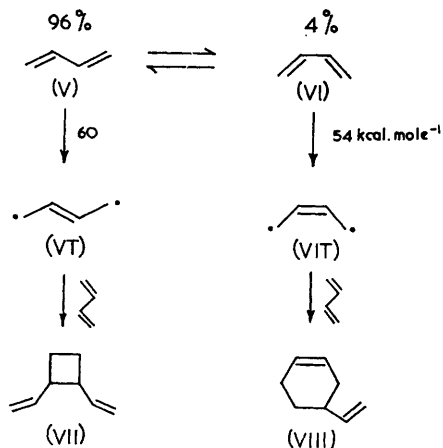


Figure 2 Variation of composition of mixture of photodimers of isoprene with triplet energy of photosensitizer



ground state, the *s-trans* predominating, but the triplets, with a higher 2,3 bond order, crudely depicted in (V T) and (VI T), are not. The composition of the photo-products therefore depends on the triplet energy of the sensitizer. Sensitisers with triplet energies greater than that of *s-trans*-butadiene (V) produce both *cis* (VI T) and *trans* (V T) triplets, but mainly the latter, since it comes from the predominant ground-state conformation. Sensitisers with triplet energies below that of planar *s-trans*-butadiene (about 60 Kcal. mole⁻¹) and above that of the *s-cis* (about 54 Kcal. mole⁻¹) produce only *cis*-triplets (VI T). The assumption that addition of *cis*-triplets to ground state *s-trans*-butadiene gives mainly

vinylcyclohexane (VIII), whereas *trans*-triplets give mainly *cis*- and *trans*-divinylcyclobutane (VII) and cyclo-octa-1,5-diene, then explains the variation of product composition with sensitiser energy, shown in Figure 2 (the points in Figure 2 actually refer to the very similar case of 2-methylbutadiene). Sensitisers with triplet energies above 60 Kcal. mole⁻¹ all give the same product composition, consisting very largely of cyclobutanes and cyclo-octadiene, the proportion of which falls sharply below 60, until at about 52 Kcal. mole⁻¹ it levels out again to become independent of the precise energy. But what is happening at very low sensitiser energies, where the curve rises steeply again? Hammond's answer is to point out that this type of energy transfer is not a spectroscopic transition and that the Franck-Condon principle need not apply: the exchange of electronic energy in the transient complex has long enough to allow simultaneous vibrational and rotational changes. The low-energy triplet of the diene may, for example, have one methylene group orthogonal to the remainder of the molecule, consisting essentially of an alkyl radical joined to an allyl radical.

We now turn to the main theme of this lecture, the thermal and photochemical rearrangements of diallyl and its derivatives. The behaviour of these compounds is particularly instructive because the three different accessible electronic states isomerise in three separate and unique ways, emphasising that the various electronic states of a molecule have quite distinct chemical properties.

Figure 3 shows an energy-level scheme for the six electrons associated with the two double bonds and the central C-C single bond of diallyl (IX). On the left are the energies of the uncoupled σ and π orbitals in the planar molecule, where the σ orbital is in the nodal plane of the two π orbitals, and in the middle those in the conformation where the 3,4-bond is in a plane at right-angles to the plane of both double bonds, and the π and π^* levels are therefore split by coupling through the σ bond. The resulting molecular orbitals shown in the right of the Figure are simply arranged in increasing numbers of nodes, from none to five (apart from the π nodes in the plane at right-angles). Whether the relative energies of the pairs of π and π^* levels, labelled as Symmetric (*S*) or Antisymmetric (*A*) about the dyad axis or mirror plane through the centre of the 3,4-bond, are correctly given by this zero-order approximation or should be reversed, does not affect the expectation that there should be a spectroscopic transition (of uncertain intensity) at longer wavelength in the coupled system than in the uncoupled one or in a normal olefin. We have now collected a large number of examples of molecules with three C-C single bonds separating two double bonds, or two atoms with unshared electron pairs (O, S, N) in various combinations. Only those with the necessary geometry show a new absorption band in the region 220–260 nm.

The thermal Cope rearrangement (Xa \rightarrow Xb) of derivatives of diallyl is consistent with the overlap of the orbitals of C-1 and C-6 as the transition state is approached, which in the highest occupied level, π_{8s} , are of like phase (XI). As Woodward and Hoffmann, and others, have even more convincingly shown, correlation by their symmetry of all the affected levels of the reactant and product through the transition state requires no use of high-energy, anti-bonding

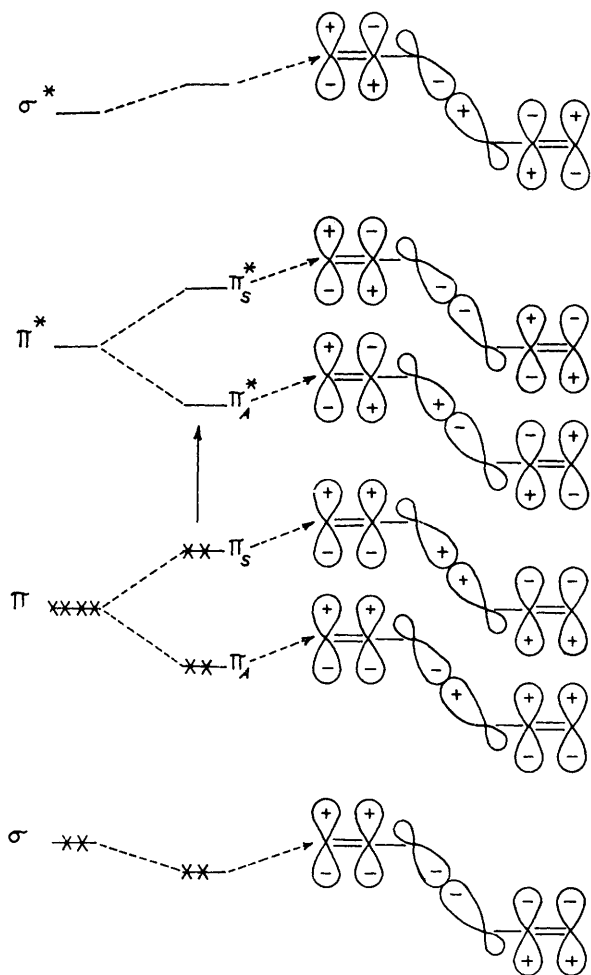
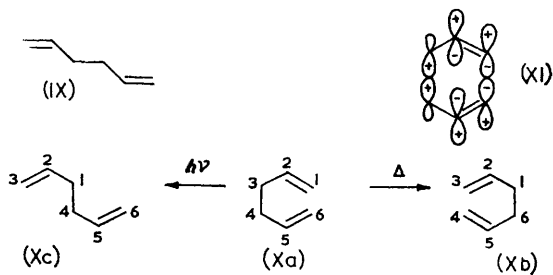
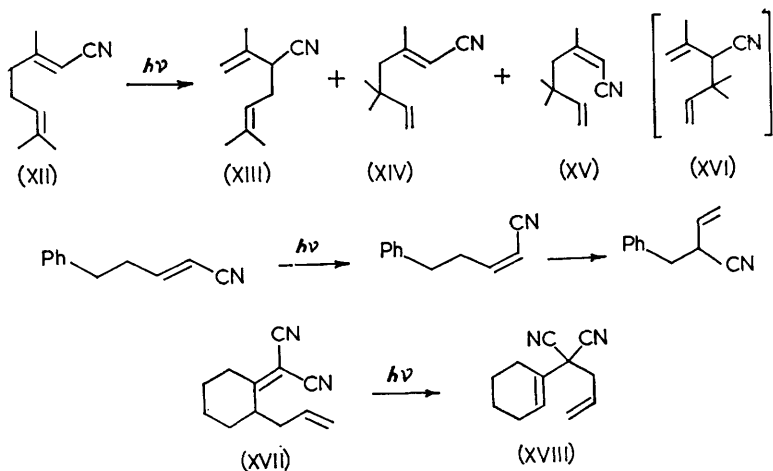


Figure 3 Correlation of molecular orbitals of planar and non-planar diallyl

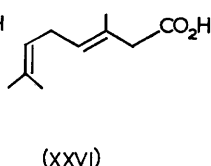
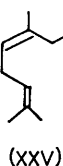
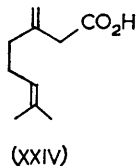
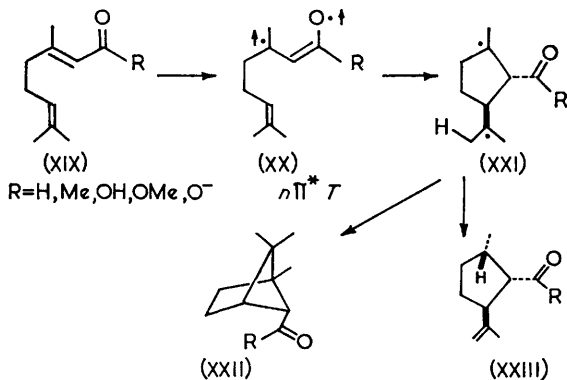
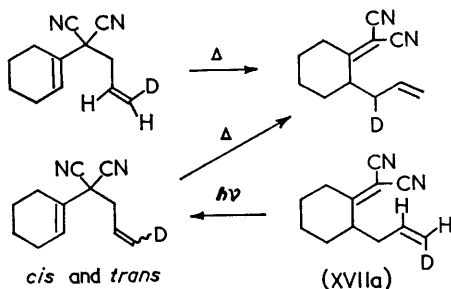
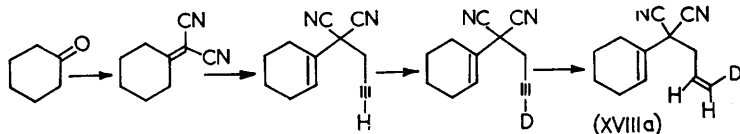
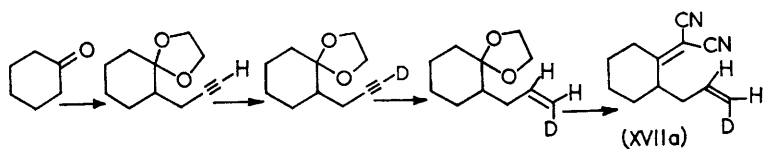


orbitals, consistent with the concerted, intramolecular, thermal reaction of relatively low activation energy, involving reversal of linkage in both allyl groups.

The photochemical rearrangement of several unsymmetrical substituted derivatives of diallyl with one double bond conjugated (to bring its u.v. absorption into a more easily accessible part of the spectrum) was investigated with great skill and efficiency by Dr. N. A. Mirza, who returned to the Pakistan Council of Scientific and Industrial Research in 1966. *cis*- and *trans*-Geranonitrile (XII), for example, rearranges with migration of the dimethylallyl group to give (XIII) or of the cyanomethylallyl group to give (XIV) and (XV), but not with migration of both, as in the Cope rearrangement which would have given (XVI). To check whether this was really a necessary feature of the photochemical path a simple allyl system was needed, free from the possibility of steric influences. The rearrangement of the allyl group in (XVII) to (XVIII) seemed a suitable case, and in a remarkably short time in 1966 Dr. R. F. C. Brown, on sabbatical leave from Canberra, devised and carried out the synthesis of the specifically deuteriated compounds (XVIIa) and (XVIIIa) as summarised in the flow sheet. Irradiation of (XVIIa) gave the product (XVIII) with the deuterium exclusively still at the 3-position of the allyl group, although it had lost its geometrical purity during rearrangement.



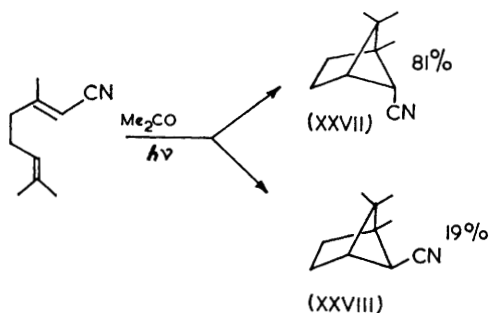
In striking contrast to this is the photochemical behaviour of the corresponding carbonyl compounds (XIX), such as citral (XIX, R = H), which give not products of allylic shift but instead form the isomers (XXII) and (XXIII). Here it is tempting to suppose that crossing of the $n\pi^*$ singlet (or of the $\pi\pi^*$ via the latter) to the $\pi\pi^*$ triplet, crudely represented by (XX), is faster than the allylic shift that occurs in the nitriles. (XX) then adds to the isolated double bond, producing the diradical (XXI) with the two substituents *trans*. After spin



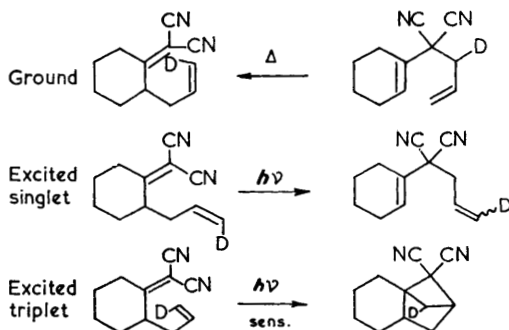
inversion the reaction can be completed either by formation of a bond between the two tertiary radical centres to give the bicyclohexane (XXII) or by hydrogen transfer to give the isopropenyl compound (XXIII). The two predominant products were proved by Dr. Mirza to have the configurations shown.

[The process cannot, in fact, be as simple as implied above, because of the variation with sensitiser of the proportions of products from geranic acid found by Dr. Mirza, which requires the intervention of at least two triplet states. These products include the $\beta\gamma$ -unsaturated isomers (XXIV), shown to be formed only from the starting isomer with the carbonyl *cis* to the methyl group, and (XXV), only from the one with the carbonyl *trans* to the methyl group, presumably arising from the enols produced by the familiar hydrogen shift.]

If the carbonyl compounds (XIX), which do not undergo the allylic shift, really do react through the triplet state then generation of the triplet of the nitrile (XII) in a way that avoids the excited singlet state should divert the reaction from the allylic shift. Sure enough, irradiation of (XII) in acetone, as a triplet sensitiser, with light not absorbed directly by (XII), gave none of the products of direct irradiation, only the bicyclohexanes (XXVII) and (XXVIII), mainly the former.



In summary, we can now show the separate forms of isomerisation exhibited by the three different electronic states, illustrated for the deuteriated dinitrile (XVIIa), each characteristic product, as far as one can tell, being quite free from contamination by either of the others:



Reactions of different electronic states

There remain some important stereochemical aspects of the 1,3-allyl shift, which can be clarified by following Woodward and Hoffmann's predictions based on the symmetry of the π orbitals of the allyl radical, shown in Figure 4. As illustrated in Figure 5, since the orbital of highest energy in the excited state (ψ_3) is symmetric about the mirror plane normal to the allyl group a saturated carbon atom can undergo a 1,3-shift while retaining bonding by simply presenting the same face to the allyl group throughout the movement. The same process in the ground state, however, would have to proceed through a transition-state with the symmetric alkyl carbon orbital overlapping the antisymmetric allyl orbital (ψ_2). Bonding can be maintained only by a clockwise rotation of the alkyl carbon atom through 90° in going to the transition-state, continuing through another 90° to reach the product. In short, a concerted 1,3-allyl shift should result in inversion of configuration of the migrating alkyl group in the thermal rearrangement but retention in the photochemical rearrangement.

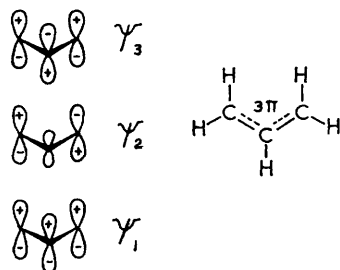


Figure 4 Molecular orbitals of the allyl radical

Berson and Willcott have just provided a well chosen example of the thermal rearrangement: the CHD group in (XXIX) moves from one end to the other of the cyclopentenyl group at about 500° , the isomer (XXIX) with deuterium

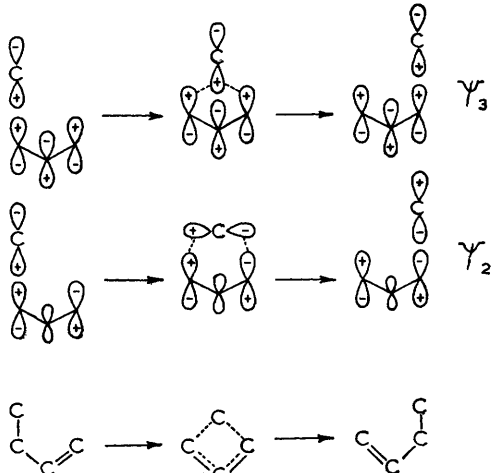
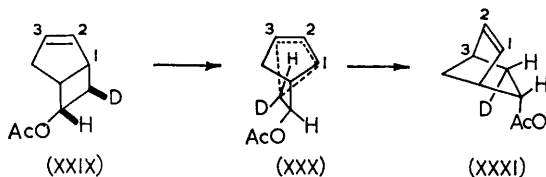


Figure 5 1,3-Allylic migration of an alkyl group

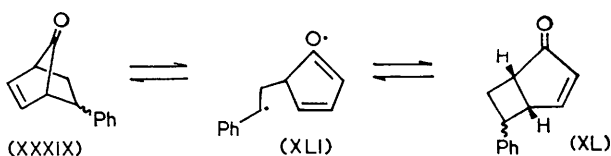
trans to the acetoxy-group giving the product (XXXI) with deuterium and acetoxy-group *cis*. The adoption of the transition-state (XXX) that forces the C-H bond against the allyl system, rather than of the more obvious and less compressed alternative involving the same side of the CHD group throughout, tells eloquently of the value of orbital symmetry in understanding concerted reactions.



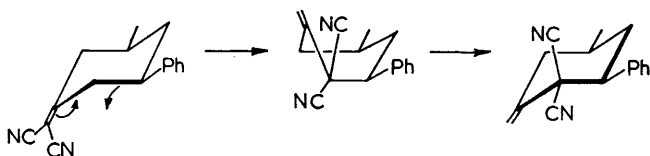
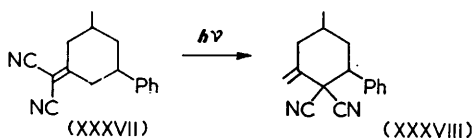
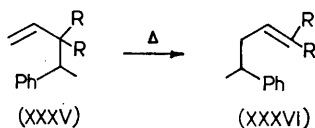
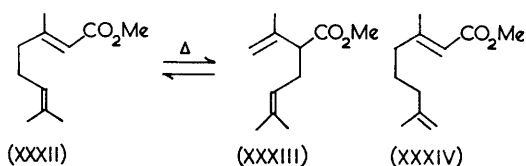
Such thermal 1,3-allylic shifts may well occur quite commonly in diallyl derivatives but have escaped recognition because the normal Cope rearrangement is usually much faster. Some possible examples have been investigated by Dr. J. E. Kemp in the geranyl system. For example, at about 530° for 5 seconds *trans*- or *cis*-geranonitrile (XII) and the isomer (XIII) give the same mixture of products, consisting largely of (XII) with a small amount of (XIII). The corresponding thermal conversion of *trans*- and *cis*-geranic ester (XXXII) into a mixture containing a few percent of (XXXIII) [which again reverts to (XXXII) when heated] misled earlier workers into claiming the conversion of the isopropylidene (XXXII) into the isopropenyl compound (XXXIV). We hope to test whether the thermal reaction does involve inversion and the photochemical one retention of configuration by use of a system such as (XXXV).*

An example of other systems under investigation is the dinitrile (XXXVII) which Mrs. M. Sharma finds rearranges on irradiation to the unconjugated isomer (XXXVIII). Unfortunately it has not been possible to reverse this rearrangement by heating the photo-isomer (XXXVIII), to see whether the *trans*-isomer of (XXXVII) would result. Such structures as (XXXVII) may, nevertheless, prove useful in testing the stereochemistry of the rearrangement at one end of the allyl group, after stereospecific deuteration of the appropriate methylene group in (XXXVII): the two olefinic methylene protons in the photo-isomer (XXXVIII) are easily distinguished in the n.m.r. spectrum by the strong shielding of the one *cis* to the nitrile groups.

* In some structures where the two allyl groups are highly conjugated, such as in derivatives of (XXXIX) and (XL), rearrangement is quite unsterespecific, the same mixture of isomers epimeric at the benzylic centre being formed from either epimer, whether by heat or light. These unconcerted rearrangements presumably occur through the diradical (XLI), which has time to undergo rotation about the bonds in the side-chain before recyclicising:



The Photochemistry of Some Allylic Compounds



Perhaps I shall be able to tell you the results of these and other experiments now under way on some future occasion. Meanwhile I would like to thank my past and present collaborators, some of whom have already been introduced by name, and to add that most of the work at Southampton is part of a joint project with my old friend and colleague John Hudec.