

PHOTOCHEMISTRY OF ALKENES IN SOLUTION

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ABSTRACT

The direct and sensitized photochemical behaviour of cyclic and acyclic olefins is compared. Under either set of conditions cyclo-hexenes and -heptenes undergo photoprotonation in hydroxylic media, perhaps via a *trans* intermediate. By contrast acyclic, exocyclic, and larger-ring cyclic olefins fail to undergo photoprotonation on either direct or sensitized irradiation. However, both cyclohexenes and cycloheptenes, as well as larger-ring cyclic and acyclic olefins, undergo slow isomerization to positional and skeletal isomers on direct irradiation in either protic or aprotic media. Unique behaviour has been observed for tetraalkyl-substituted olefins, which exhibit behaviour on direct irradiation in alcoholic solvents suggesting the intervention of a cation radical intermediate. Mechanistic implications of these various types of photochemical behaviour are discussed.

INTRODUCTION

One of the most commonly occurring organic chromophores is that of the simple carbon-carbon double bond; and yet, despite its ubiquity, the ethylene chromophore has received relatively little attention by photochemists. In a parallel sense, despite its apparent simplicity, this chromophore has confounded spectroscopists and theoreticians alike, and even today there exist many questions concerning the location and configurational assignments of the various electronically excited states of ethylene and its simple alkyl derivatives¹. In view of the common occurrence of the ethylene chromophore in organic systems, its photochemical behaviour offers the potential of new, unexplored reactions which should have broad synthetic utility. Moreover, a systematic study of its photochemical behaviour should shed additional light on the nature and location of its various excited states. It was with these thoughts in mind that several years ago we undertook such an investigation.

BACKGROUND

The most current thinking among spectroscopists identifies four of the lowest lying excited states of ethylene and its simple alkyl derivatives as

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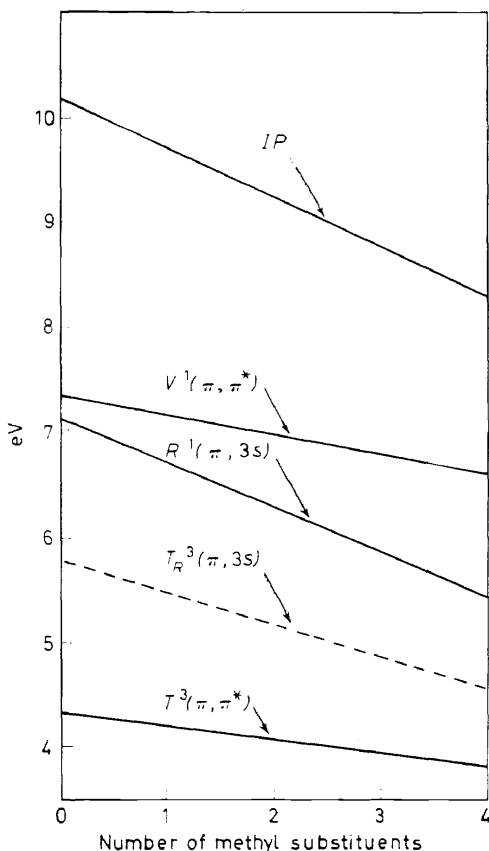


Figure 1. Observed (—) or predicted (---) vertical excitation energies for the π , π^* and Rydberg electronic levels of ethylene and its methyl-substituted derivatives and their ionization potentials (IP)^{1,2}.

shown in Figure 1¹. These are the singlet and triplet levels of the $\pi \rightarrow \pi^*$ and Rydberg transitions, which are frequently referred to as the V , R , T and T_R states, respectively[†]. Most of the photochemical investigations to date have been concerned with the lowest lying triplet level, which arises from the $\pi \rightarrow \pi^*$ transition. In this transition, one of the loosely bound π electrons is promoted to an unoccupied antibonding π^* orbital (see Figure 2). One of the consequences of such a transition is a weakening of the π bond to such an extent that the stability gained by parallel overlap of the π orbitals, a strong force in the ground state molecule, can no longer overcome the mutual repulsive forces of the π and π^* electrons. It is generally agreed that the result is a driving force to minimize these repulsive interactions by rotation about the carbon-carbon bond to afford an orthogonal geometry as shown

[†] Additional excited states, some of which lie close to those illustrated in Figure 1, have been predicted by theory but not yet located spectroscopically¹. However, transitions to these states from the ground state are forbidden.

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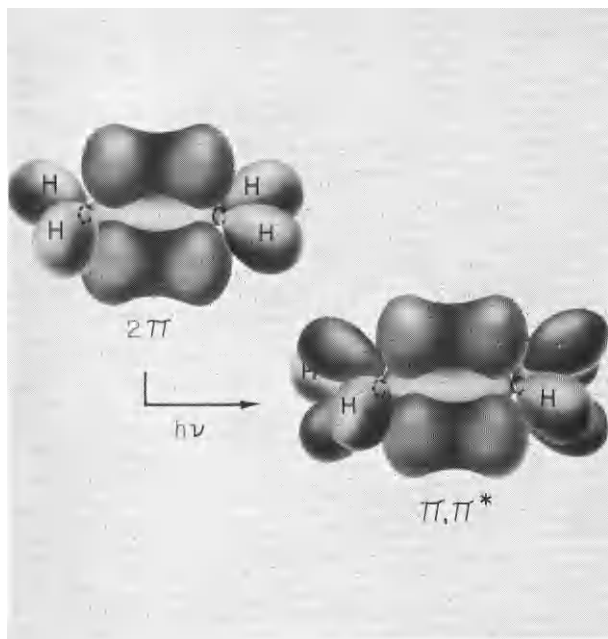


Figure 2. Orbital representations of the ground and π, π^* excited states of ethylene.

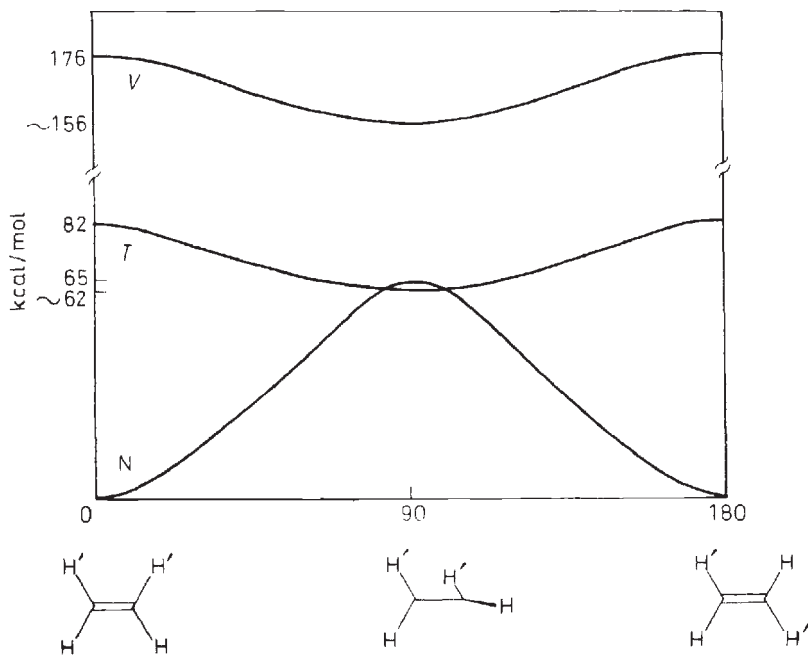


Figure 3. Potential energy curves for the twisting of the N, T and V states of ethylene.

in *Figure 3*. Thus, once formed, the planar π, π^* spectroscopic triplet of a simple ethylene derivative would be expected to undergo facile vibrational relaxation, accompanied by rotation to an orthogonal geometry. Intersystem crossing to either the *cis* or *trans* ground-state singlet manifold can then occur with approximately equal facility, resulting in *cis-trans* isomerization of the starting olefin. The planar spectroscopic π, π^* triplet can be populated by direct irradiation and has been located at 3.65–4.59 eV (270–340 nm), depending on the degree of alkyl substitution, as shown in *Figure 1*^{1,2}. However, being highly forbidden, the transition has a very low intensity and can be observed only by using such special spectroscopic techniques as long pathlength cells³, oxygen enhancement^{2,4}, or the heavy atom effect². Hence, the *T* level is more practically reached by the photochemist through the simple technique of photosensitization.

The photosensitized *cis-trans* isomerization of olefins has been rather widely studied and been found to occur with sensitizers having a broad range of triplet excitation energies, extending as much as 20 kcal mol below that of the spectroscopic triplet^{5,6}. It has been suggested that with the lower energy sensitizers a 'non-vertical' transition can occur⁷, perhaps via an initial bonding between the sensitizer and olefin^{8,9}, to give directly a twisted triplet species. Judging from the range of triplet excitation energies found to be effective for sensitizing *cis-trans* isomerization, it would appear that the relaxed, orthogonal triplet lies at about 62 kcal mol for dialkyl substituted olefins^{5,6}.

PHOTOSENSITIZED BEHAVIOUR OF ALKENES

Although lending credence to the concept of an orthogonal geometry for the π, π^* triplet, the occurrence of *cis-trans* isomerization actually reveals little about the chemical behaviour of the species. Indeed, it would appear that the high efficiency of *cis-trans* isomerization, probably due at least in part to a crossing of the *N* (ground state) and *T* state potential energy curves as shown in *Figure 2*, serves to mask any inherently slower intermolecular chemical processes. The interesting question arises as to what might happen if the ethylene chromophore were incorporated in a cyclic environment in which *cis* \rightarrow *trans* isomerization is either greatly impeded or even prohibited, depending on ring size. Recent work from these laboratories⁸ and others⁹ has shown that photosensitized irradiation of cyclohexenes and cycloheptenes in protic media results in photoprotonation of the olefin followed by a series of subsequent processes—including hydride shifts, skeletal rearrangements, nucleophilic trapping by solvent, and proton elimination—depending upon the chemical behaviour of the particular carbocation formed. Thus, for example, photosensitized irradiation of 1-methylcyclohexene (I) in methanol affords principally a mixture of methylenecyclohexane (II) and methyl 1-methylcyclohexyl ether (IV), accompanied by a small amount of methylcyclohexane (V)¹⁰. These products apparently arise via initial formation of the carbocation (III) since irradiation in methanol-*O*-*d* results in the incorporation of deuterium in the products as shown in *Figure*

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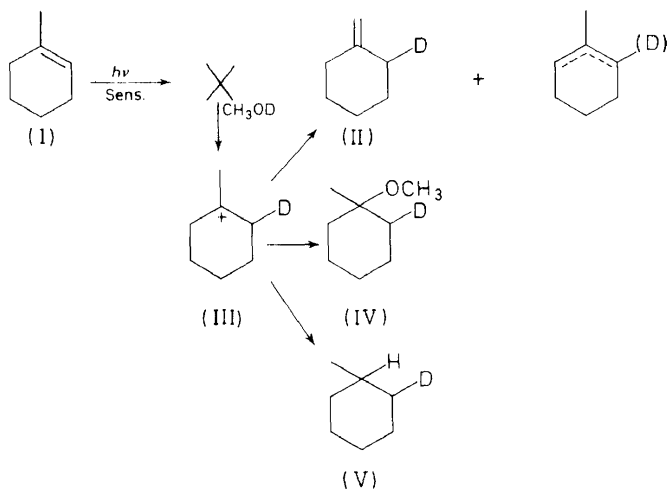


Figure 4. Photosensitized protonation of 1-methylcyclohexene.

4†. Photoprotonation has been found to be general for cyclic olefins having about the same conformational mobility as cyclohexene and cycloheptene^{10, 11}, but it is not shared by larger-ring cyclic, exocyclic or acyclic olefins, which undergo *cis-trans* isomerization under these conditions but show no evidence of undergoing photoprotonation^{†10}. Likewise, photoprotonation is not exhibited by cyclic olefins having a lower degree of flexibility, such as cyclopentene (VI) and norbornene (X), which afford, instead, radical rather than ionic products, as shown in Figure 5^{10, 13}. The radical nature of these products is highlighted by the fact that irradiation in methanol-*O-d* results in no detectable incorporation of deuterium in (VIII), (IX) or (XI), as well as in the recovered unreacted starting olefins (VI) and (X)^{10, 13}.

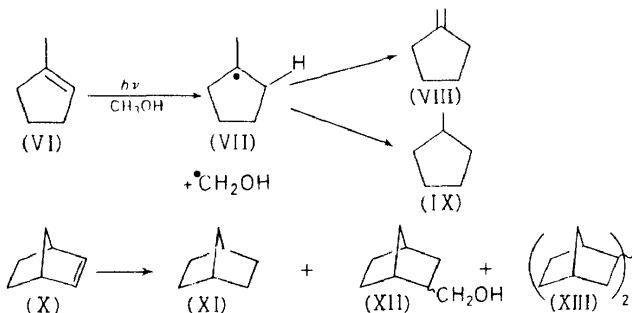


Figure 5. Photosensitized radical behaviour of 1-methylcyclopentene and norbornene.

† Deuterium incorporation has not been explicitly demonstrated in the formation of 1-methylcyclohexane (V) but has been established for the photoreduction of another cyclohexene¹⁴ and is presumed to be general.

‡ However, it has recently been shown that on extended irradiation cyclooctenes exhibit a small degree of photosensitized protonation in acidic media¹².

The important question which at once emerges is what species is giving rise to the cationic or radical intermediates such as (III) and (VII). It seems clear that in the case of large-ring cyclic, exocyclic and acyclic olefins reaction involves initial formation of the π, π^* triplet followed by intersystem crossing to the *cis* and *trans* ground-state singlet manifolds (Figure 6). In the case of

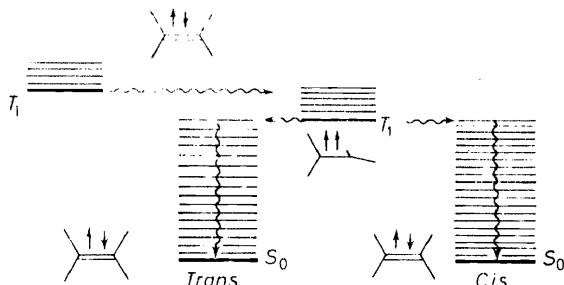


Figure 6. Acyclic and large-ring cyclic olefins.

cyclohexenes and cycloheptenes, it seems likely that the orthogonal triplet is again formed after energy transfer, since a study of models indicates that twisting to 90° should not cause undue strain on the molecule. It might be this orthogonal triplet species which is undergoing protonation, either in competition with or while undergoing intersystem crossing to the *cis* ground-state singlet manifold (Figure 7). However, a small additional twisting

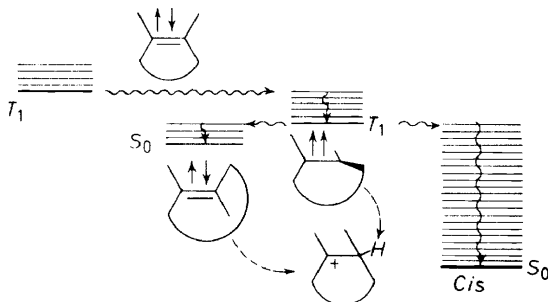


Figure 7. Six- and seven-membered ring olefins.

beyond the 90° of the triplet intermediate, accompanied by intersystem crossing, would afford a highly strained (and surely not planar) *trans* ground state singlet species[†]. This species, seeking rapid relief of strain, would be expected to undergo facile protonation, paralleling the behaviour observed for other highly strained olefins.

Of these two possible precursors to the protonated olefin, the orthogonal triplet or the *trans* olefin, we prefer the latter, but cannot claim that the former has been rigorously precluded. Since these two species are probably close in energy, particularly for cyclohexenes, it may become extremely

[†] There is abundant evidence to suggest that a *trans*-substituted double bond can be generated in a six- or seven-membered ring^{15,16}.

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difficult to distinguish between them. One reason for favouring the *trans* olefin as the species undergoing protonation is that the intermolecular chemical behaviour of the π, π^* triplet is more likely revealed by the behaviour of cyclopentenes and norbornenes, in which a partially twisted (but probably not orthogonal) triplet is probably formed but in which a ground-state *trans* species is difficult to conceive. Here radical behaviour is displayed.

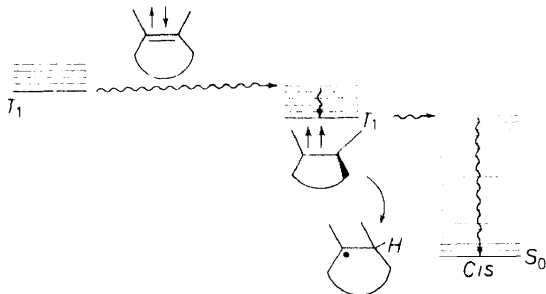


Figure 8. Five-membered ring olefins.

presumably by the triplet intermediate as shown in *Figure 8*: moreover, this is surely not unexpected behaviour for a triplet species, possessing unpaired electrons.

DIRECT IRRADIATION

Since the singlet state V obtained from the $\pi \rightarrow \pi^*$ transition is expected to exhibit a potential energy curve for twisting rather similar to that of the corresponding triplet state T (*Figure 1*), it would be expected that direct irradiation of ethylene derivatives should again induce *cis-trans* isomerization. It is of interest that this, in fact, has been observed¹⁷, since it presents an opportunity in the case of cyclohexenes and cycloheptenes to test the question of protonation of a highly-strained *trans* intermediate versus protonation of an orthogonal triplet species in that intersystem crossing is probably not efficient in simple olefins and the triplet species should not be available by direct irradiation whereas the *trans* olefin should. Indeed, it has been found that direct irradiation of 1-methylcyclohexene (**I**) in methanolic solution affords the same products and in a similar, but not identical, ratio as are formed on photosensitized reaction (*Figure 9*)¹⁸. Similar behaviour is also exhibited by limonene (**XIV**), in which even the stereochemical consequences for products (**XVI**) and (**XVII**) are closely, but not identically, duplicated¹⁸. Moreover, parallel behaviour is exhibited by 1-methylcycloheptene on direct or sensitized irradiation¹⁸. However, neither the less flexible 1-methylcyclopentene, the highly flexible acyclic olefin (**XVIII**) nor the exocyclic olefin methylenecyclohexane (**II**) shows a similar ready tendency to undergo protonation on direct irradiation, again reflecting the patterns displayed in the photosensitized chemical behaviour of olefins¹⁸. In the case of methylenecyclohexane (**II**) no reaction was observed, whereas the acyclic olefin (**XVIII**) underwent slow rearrangement to the isomers (**XIX**) and

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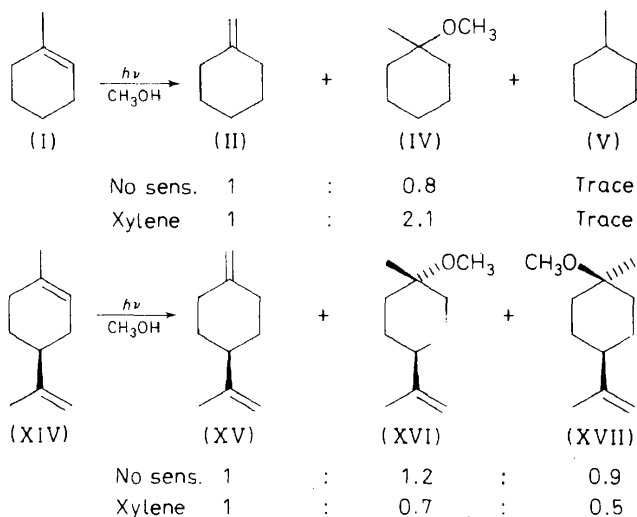
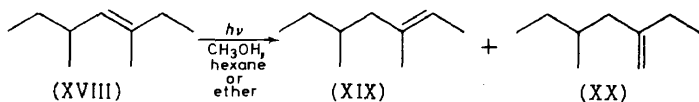


Figure 9. Comparison of direct and sensitized photoreactions of 1-methylcyclohexene and limonene in methanol.

(XX)¹⁸. In the latter case almost identical behaviour is displayed in aprotic solvents such as hexane and ether, as will be discussed below[†].



A simple interpretation of these results is that *cis-trans* isomerization of the olefin occurs followed, in the case of cyclo-hexenes and -heptenes, by protonation of the resulting *trans* olefin. The parallel correlation between olefin flexibility and direct or sensitized photochemical behaviour is of course a necessary, but not sufficient, condition for the proposal that photo-protonation involves a *trans* olefin intermediate. The origin of the slight variations in product ratios between the direct and photosensitized reactions is not yet clear, but may be related to the fact that the *trans* olefin is initially formed with a higher level of vibrational energy on direct irradiation. Also affecting the ratio is the fact that in some cases photosensitizers consume exocyclic olefin products through photoaddition processes.

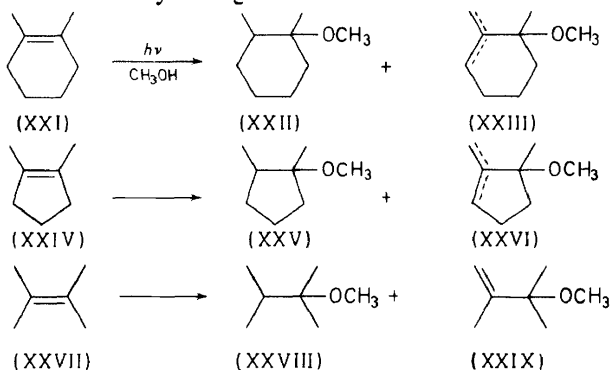
TETRASUBSTITUTED ALKENES

When the degree of substitution about the double bond is expanded from two or three as in the preceding examples, to four a surprisingly new behaviour emerges. For example, irradiation of 1,2-dimethylcyclohexene (XXI) in methanol or methanol-hexane affords not only an epimeric mixture

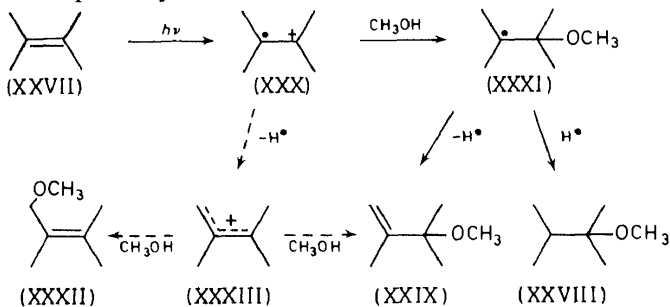
[†] An unidentified cyclopropyl derivative was also observed, as well as a trace amount of a methanol adduct. This latter product is probably related to the behaviour of tetrasubstituted olefins as discussed below.

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of isomers of the expected methanol adduct (XXII) but also a mixture of the *unsaturated* ethers (XXIII)¹⁸. Moreover, similar behaviour, leading to both saturated and unsaturated adducts, is exhibited by both the cyclopentyl analogue (XXIV) and the acyclic analogue (XXVII)¹⁸. This contrasts with the photosensitized behaviour of these olefins, in which only the six-membered ring analogue (XXI) affords a methanol adduct, and then only the expected *cis* and *trans* isomers of the saturated adduct (XXII) are formed. Thus a new type of behaviour has clearly emerged with the tetrasubstituted olefins.



This behaviour is perhaps most simply interpreted as involving the initial formation of a radical cation of the type (XXX), or at least a species displaying the properties of such a radical cation. This species would be expected to undergo nucleophilic trapping in the presence of methanol¹⁹ to afford a radical intermediate (XXXI), which could then either undergo hydrogen abstraction to afford the saturated ether (XXVIII) or loss of a hydrogen atom to afford the unsaturated ether (XXIX). In support of the mechanism, it has been found that irradiation of tetramethylethylene (XXVII) in methanol-*O*-d fails to result in the incorporation of deuterium into either of the photo-products¹⁸, in complete contrast to the photosensitized addition of methanol to cyclohexenes¹⁰. A minor variation of the mechanism would be for hydrogen atom loss to precede nucleophilic trapping by the solvent, to afford the allylic cation (XXXIII). However, this sequence does not account for the formation of the saturated product (XXVIII), and none of the isomeric allylic ether (XXXII), which might also be expected, has been observed. Hence, there is no reason at the present time to include the involvement of this mechanistic pathway.



Although the proposed intermediacy of the cation radical (XXX) is convenient in accounting for the products (XXVIII) and (XXIX), its formation raises a number of questions. Although light-induced ejection of an electron from a chromophore to the solvent medium has been widely observed with a number of aromatic derivatives with electron-donating substituents, as well as aryl carboxylic acids and heteroaromatic amines²⁰, to our knowledge this phenomenon has not previously been observed with simple alkyl derivatives such as the olefins (XXI), (XXIV) and (XXVII). Moreover, the ionization potential of tetraalkyl-substituted ethylenes (8.3 eV) is sufficiently high that substantial energy from solvation of the ejected electron is necessary for photoionization to occur under the experimental conditions (irradiation through quartz or Vycor).

A special situation exists in the case of ethylene derivatives in that one of the lowest (if not the lowest, depending on the extent of stabilization gained by rotation in the V state) lying excited singlet states is the Rydberg state, in which a π electron is promoted to a molecular orbital so large that one may expect the properties of the excited species to be similar to those for the positive ion (note *Figure 10*)¹. Although little is known about the lifetime of

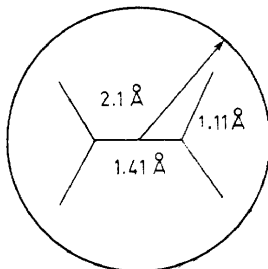
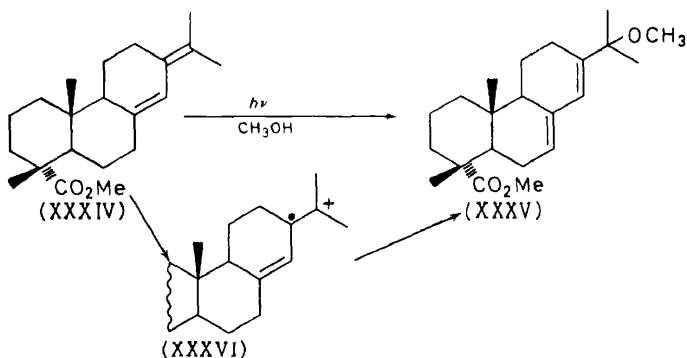


Figure 10. Maximum radial electron density for the 3s Rydberg MO¹.

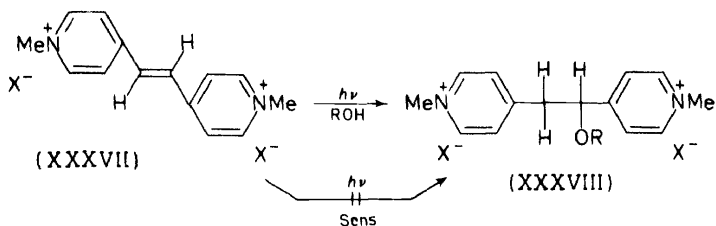
Rydberg state species, it is not unreasonable to expect that nucleophilic quenching by a hydroxylic medium can compete with electron demotion and return of the olefin to its ground state, particularly since the olefin and alcohol are undoubtedly oriented by hydrogen bonding in the ground state. The fact that the Rydberg system energies drop quite rapidly with increasing numbers of alkyl substituents (*Figure 1*), almost parallel with ionization potentials, whereas the V system energies drop more slowly, may at least partially explain the sudden emergence of the Rydberg mode of behaviour on going from tri- to tetra-substitution. Thus it is not clear at the present time whether the cation radical intermediate arises from photoionization or the Rydberg state.

It is also not yet clear how extensively ethylene derivatives will display cation-radical behaviour. However, one other example may be the recent observation that irradiation of the diene methyl neoabietate (XXXIV) in methanol affords the dienyl ether (XXXV) rather than the usual type of monosaturated product involving the formal addition of the elements of methanol across one of the double bonds²¹. In this case reaction may involve the cation radical intermediate (XXXV). It is noteworthy that addition occurred to a tetrasubstituted ethylene unit in this case.

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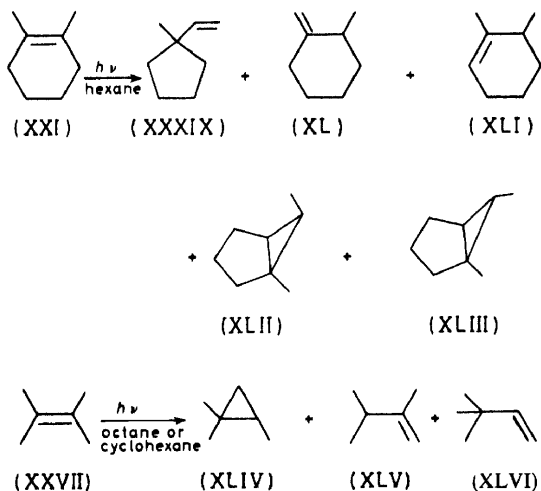


Nucleophilic quenching of singlet excited states of several aza-aromatics such as the 1,2-bispyridylethylene (XXXVII) has also recently been observed, both through fluorescence quenching and the formation of isolable adducts of type (XXXVIII)²². Although nucleophilic attack on an excited state singlet species is involved both with these electron-deficient olefins and with the more electron-rich olefins (XXI), (XXIV) and (XXVII), it is unlikely that they are mechanistically related.



REARRANGEMENT ON DIRECT IRRADIATION

Ethylene derivatives have also been found to undergo a number of interesting rearrangements on irradiation in either protic or aprotic solvents. This is illustrated by tetramethylethylene (XXVII), which on irradiation in a hydrocarbon solvent affords a mixture of the three isomers (XLIV)–(XLVI), and by 1,2-dimethylcyclohexene (XXI), which affords the isomers (XXXIX)–(XLI) and two cyclopropyl products tentatively assigned the structures (XLII) and (XLIII)¹⁸. Many of these products are also formed in low yield, along with the ether adducts described above, on irradiation in methanolic solution¹⁸. The same products are also formed from tetramethylethylene (XXVII) in neat solution, along with the previously²³ reported dimer, octamethylcyclobutane. Reaction of this type is not limited to tetra-substituted olefins, as shown by the behaviour of the olefin (XVIII)¹⁸. Control studies in the case of tetramethylethylene (XXVII) showed that each of the products (XLIV)–(XLVI) is apparently a primary product since none of these products underwent significant rearrangement on separate exposure to the reaction conditions¹⁸.



It is not yet entirely clear whether the excited state responsible for these rearrangements is the V or Rydberg singlet excited state. However, since these reactions occur readily with both tri- and tetra-substituted olefins, whereas Rydberg behaviour in alcoholic media is dominant only in the case of tetrasubstituted derivatives, it seems likely that the reactive species is the V state. One possible mechanism to account for these rearrangements is illustrated in *Figure 11* for tetramethylethylene (XXVII), in which reaction

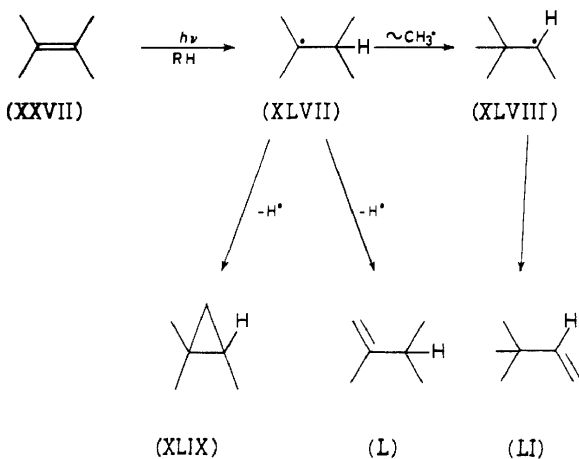


Figure 11. Possible mechanistic pathway for photoisomerization of olefins, disproved by deuterium labelling studies.

involves an initial abstraction of a hydrogen atom from the solvent RH by the excited olefin. However, this mechanism has now been shown not to be operative by the finding that irradiation in cyclohexane- d_{12} resulted in no incorporation of deuterium in any of the products as measured by n.m.r. It thus appears that rearrangement occurs intramolecularly, perhaps as

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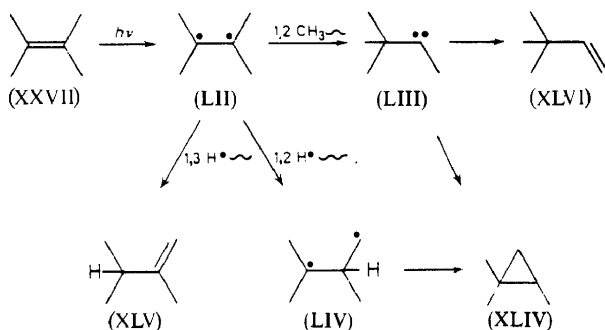


Figure 12. Alternative mechanistic pathway for photoisomerization of olefins.

outlined in Figure 12. Cyclopropane formation has been previously observed in 1,4-polvisoprene²⁴ and in phenyl-substituted allylic ethers²⁵, but it is of interest to note that it is apparently much more generally prevalent than these two observations would indicate.

Clearly much more remains to be done on the photochemical behaviour of ethylene derivatives. Many mechanistic parameters such as wavelength, solvent and substituent effects, quantum yields and structure-property correlations remain to be explored, but it is clear already that the ethylene chromophore offers a rich array of chemical behaviour on direct as well as sensitized irradiation and, moreover, it seems likely that many of the photochemical properties to be uncovered can be harnessed to provide unique synthetic capabilities.

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