Photochemically Induced Ionic Reactions of Cycloalkenes

Cyclohexenes and cycloheptenes undergo cationic reactions upon ultraviolet irradiation in protic solvents.

James A. Marshall

The key role of olefinic substances in natural and synthetic chemical transformations can be attributed largely to interactions of the carbon-carbon double bond with electrophilic species (*1*). Such interactions control a variety of important processes such as the biosynthesis of steroids, terpenes, and other related natural substances, the polymerization of ethylene, and the commercial production of high-octane gasoline. Indeed electrophilic additions to olefins stand among the most useful reactions of organic synthesis. A less exploited aspect of olefin chemistry has to do with reactions involving electronically excited states of the carbon-carbon double bond. Such states can be conveniently attained through irradiation with ultraviolet light of appropriate wavelength (180 to 210 nanometers) to cause direct excitation of the π electrons, or by energy transfer from a relatively long-lived excited state of a sensitizer molecule whose excitation energy is equal to or greater than that of the olefin (*2*). In the first instance irradiation leads to the singlet excited state, whereas sensitized energy transfer usually produces the triplet state. Singlet-triplet conversion (intersystem crossing) is generally observed for ketones (*2*) but little is known about the analogous process in simple olefins. Figure 1 depicts both direct and benzene-sensitized excitation pathways for ethylene (*3*).

Olefin Photochemistry

Even though the carbon-carbon double bond is perhaps the least complex photoactive grouping known, few detailed photochemical studies have been carried out on simple olefins. Ethylene, and presumably substituted ethylenes as well, prefers an orthogonal excited state arrangement wherein the electrons occupying the π^* and π orbitals experience the minimum mutual repulsion (*4*). Accordingly, electronic excitation leads initially to a planar high energy species which reverts, through carbon-carbon bond rotation, to a lower energy, twisted conformer. The excitation energy of the planar excited state can be readily obtained from ultraviolet absorption data. The excitation energy of the perpendicular form cannot be determined in such a straightforward manner, however, and we must rely upon estimated values of this important parameter. A stabilization energy of roughly 20 kilocalories has been accorded to the twisting process (*4*).

One other important point, the orbital hybridization (sp^2 as opposed to sp^3) of the carbon atoms in these twisted conformers, is likewise not clearly established (*5*). Despite the lack of exact details with regard to certain aspects of olefin excited states, we can nonetheless construct a qualitative picture which helps to explain the photochemistry of these substances (Fig. 2). Thus photosensitized *cis-trans* isomerization most likely proceeds by way of unpairing of the π electrons in the T_1 state followed by 180° rotation about the carbon-carbon bond, through the lower energy, 90°-twisted conformer, and subsequent electron re-pairing and demotion to the ground state. The postulated photochemical unpairing of the π electrons in ethylene and its derivatives also explains the observed propensity of these compounds to undergo free radical reactions, such as hydrogen abstraction, in the presence of appro-

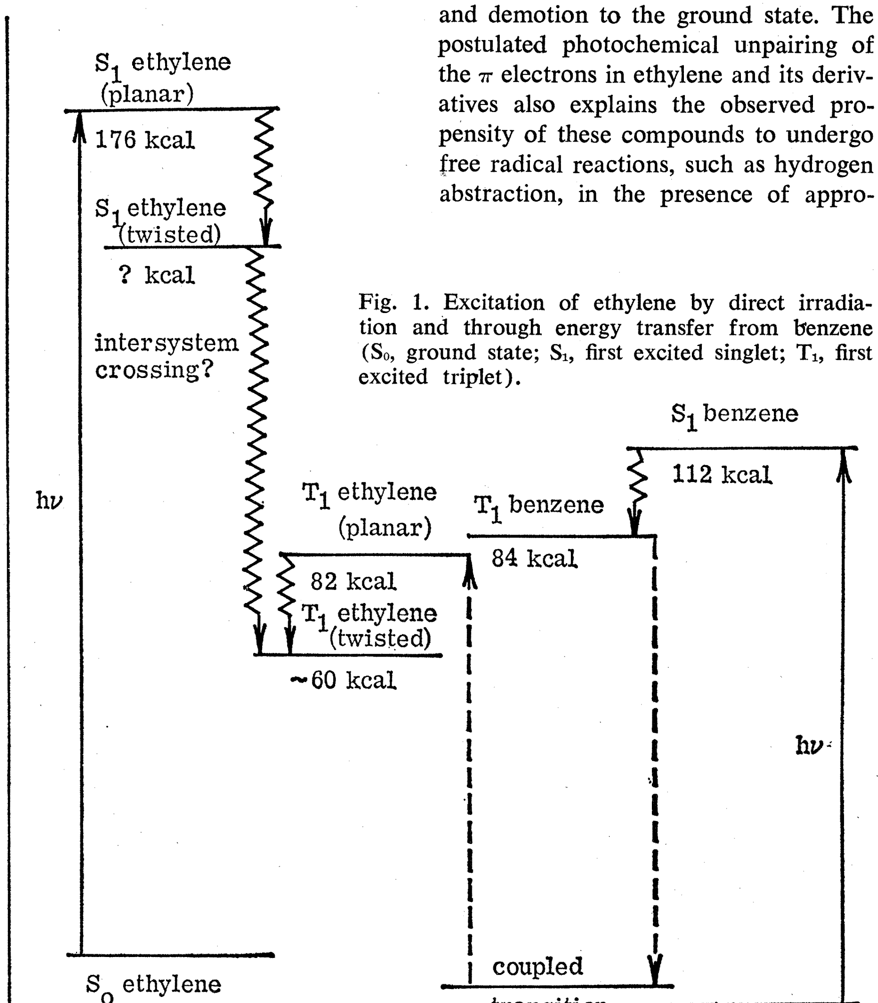


Fig. 1. Excitation of ethylene by direct irradiation and through energy transfer from benzene (S_0, ground state; S_1, first excited singlet; T_1, first excited triplet).

Dr. Marshall is professor of chemistry at Northwestern University, Evanston, Illinois.

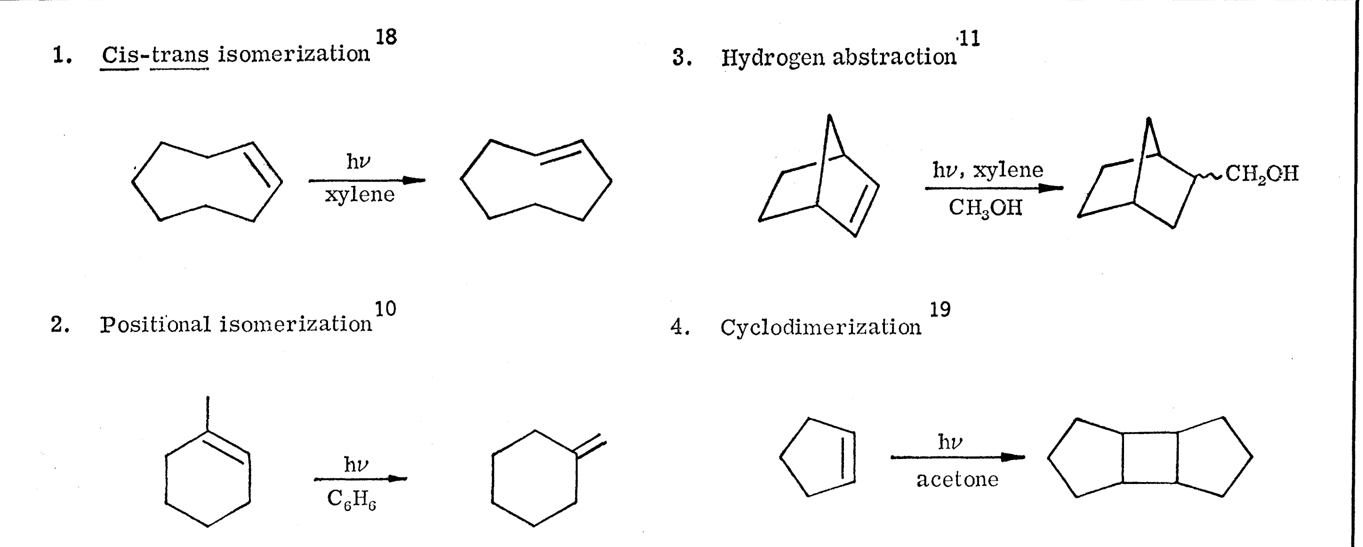


Chart 1. Nonionic photochemical reactions of olefins.

priate donor molecules. Dimerization by way of an electrocyclic 2 + 2 pathway constitutes a third type of photochemical reaction available to olefins (*6*). Examples of typical photosensitized transformations are shown in chart 1.

Photoinitiated Ionic Reactions

A new photochemical reaction of olefins which seems to bridge the gap between the ground state and excited state chemistry of the carbon-carbon double bond has been discovered. This discovery was made during an investigation of the photochemical isomerization of 1-menthene (**1**) to 1(7)-menthene (**2**). When this reaction was carried out in alcohol solvents containing aromatic hydrocarbons as sensitizers, a mixture of the isomerized olefin **2** and the ethers **3** and **4** was produced (*7–9*). The appearance of these latter products came as a complete surprise and seemed to indicate that ionic rather than free radical reaction pathways were being followed. Indeed, the same two ethers were obtained through treatment of 1-menthene with methanolic sulfuric acid, under conditions clearly favoring ionic reactions. Since ether formation and olefin isomerization completely ceased upon discontinuation of the irradiation and commenced again only when irradiation was resumed, these products must not have arisen through fortuitous acid catalysis. Furthermore, the ratio of ethers **3** and **4** ($R = CH_3$) obtained in the photochemical (**3** : **4** = 1.5) and acid-catalyzed (**3** : **4** = 0.3) reactions differed markedly. In the latter case the isomer ratio reflects the relative stabilities of **3** and **4** as expected from a reversible reaction. The ratio of photochemically derived ethers, on the other hand, corresponds roughly to what would be expected on steric grounds for the attack of the alcohol nucleophile on the cation **5** in an irreversible reaction (chart 2).

Thus the cation **5** would appear to be a reasonable intermediate in the photochemically initiated addition of alcohols to 1-menthene (**1**). This cation could also lead to the isomerized olefin 1(7)-menthene (**2**) through loss of a methyl proton. Subsequent photochemical transformations of exocyclic olefins such as **2** do not occur to any significant degree under the reaction conditions (*10*). The absence of olefin **2** among the acid-catalyzed methanolysis products of 1-menthene (**1**) would be expected in view of the instability of the exocyclic as compared to the endocyclic double bond in this system.

Additional support for the postulated photoprotonation scheme was provided

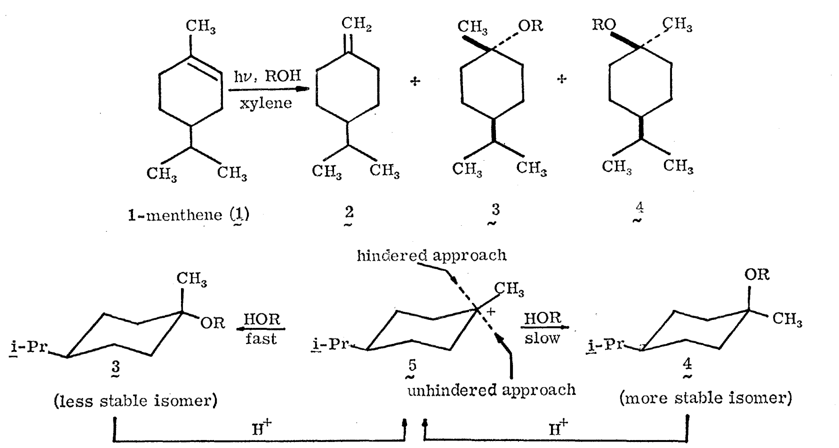


Chart 2. Additions to 1-menthene via cationic pathways.

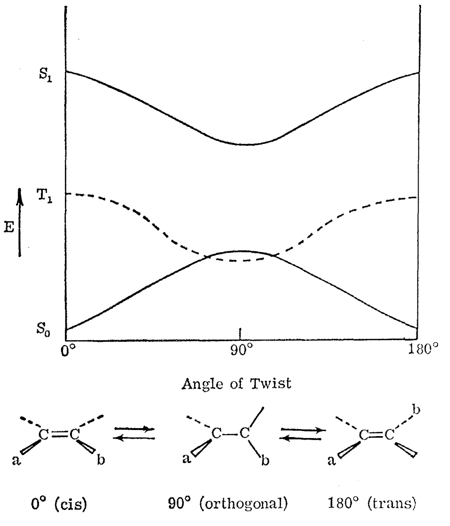
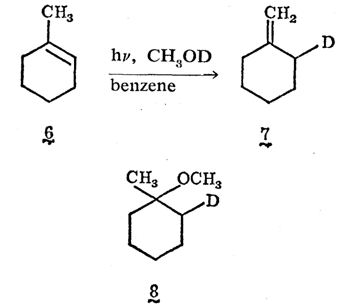


Fig. 2. Energy of a substituted ethylene in various electronic states as a function of C=C twist angle (S_0, ground state; T_1, first excited triplet state; S_1, first excited singlet state).

by studies on the addition of CH_3OD to 1-methylcyclohexene (**6**) (*10*). Irradiation in the presence of benzene as the photosensitizer yielded the monodeuterated compounds, olefin **7** and ether **8**, almost exclusively. These findings show that the alcohol solvent donates a proton rather than a hydrogen atom to the carbon-carbon double bond. The observation of a substantial deuterium isotope effect and a rate acceleration by added acids lend further credence to the protonation hypothesis (*9, 11*).



In the past several years additional examples of photochemically initiated olefin reactions which seemingly proceed via carbocations have been reported (*12*). A few of these are shown in chart 3. Reactions of this type were formerly associated only with intermediates generated through solvolysis reactions or by protonation of olefins in strong acid. However, the photochemical pathway now provides a means for effecting such reactions from certain olefins under mildly acidic, neutral, or even basic conditions. Furthermore, the observed propensity for cyclohexenes and cycloheptenes to undergo these reactions provides a means for effecting the selective protonation of such olefins in polyunsaturated systems (*13*).

Mechanistic Considerations

Significantly, only cyclohexenes and cycloheptenes have shown any tendency to undergo photochemically initiated ionic reactions. Cyclopentenes afford free radical and cyclodimerization products, whereas cyclooctenes and larger ring olefins, and acyclic olefins undergo *cis-trans* isomerization, cyclodimerization, or free radical reactions. Thus, ring size appears to be one crucial aspect of photoinitiated ionic reactions. This limitation implies that steric factors may be responsible for the observed photoionic behavior of cyclic olefins. As noted above (Fig. 2), an electronically excited olefin should prefer a twisted conformation in order to minimize electron repulsion stemming from populated antibonding π orbitals. Such a species could decay by way of rotation and intersystem crossing to the *cis* or *trans* isomer. With cyclopentene and smaller ring olefins, steric constraints limit the angle of twist to 40°; further twisting leads to considerable molecular distortion (*10*). Thus, twisted orthogonal triplets would experience extraordinary strains in such cases and, needless to say, *cis* → *trans* isomerization would be effectively precluded. Cycloheptenes and cyclohexenes, on the other hand, can adopt a 90° twisted conformation with only modest molecular distortion and the orthogonal excited states could thus be attained photochemically without excessive strain. In fact, further twisting to *trans* or, more likely, *transoid* isomers (*14*) might conceivably occur in these cases and, in that event, protonation of the resulting intermediates would undoubtedly provide an effective strain-relieving reaction pathway. Thus, the chemically active species in the

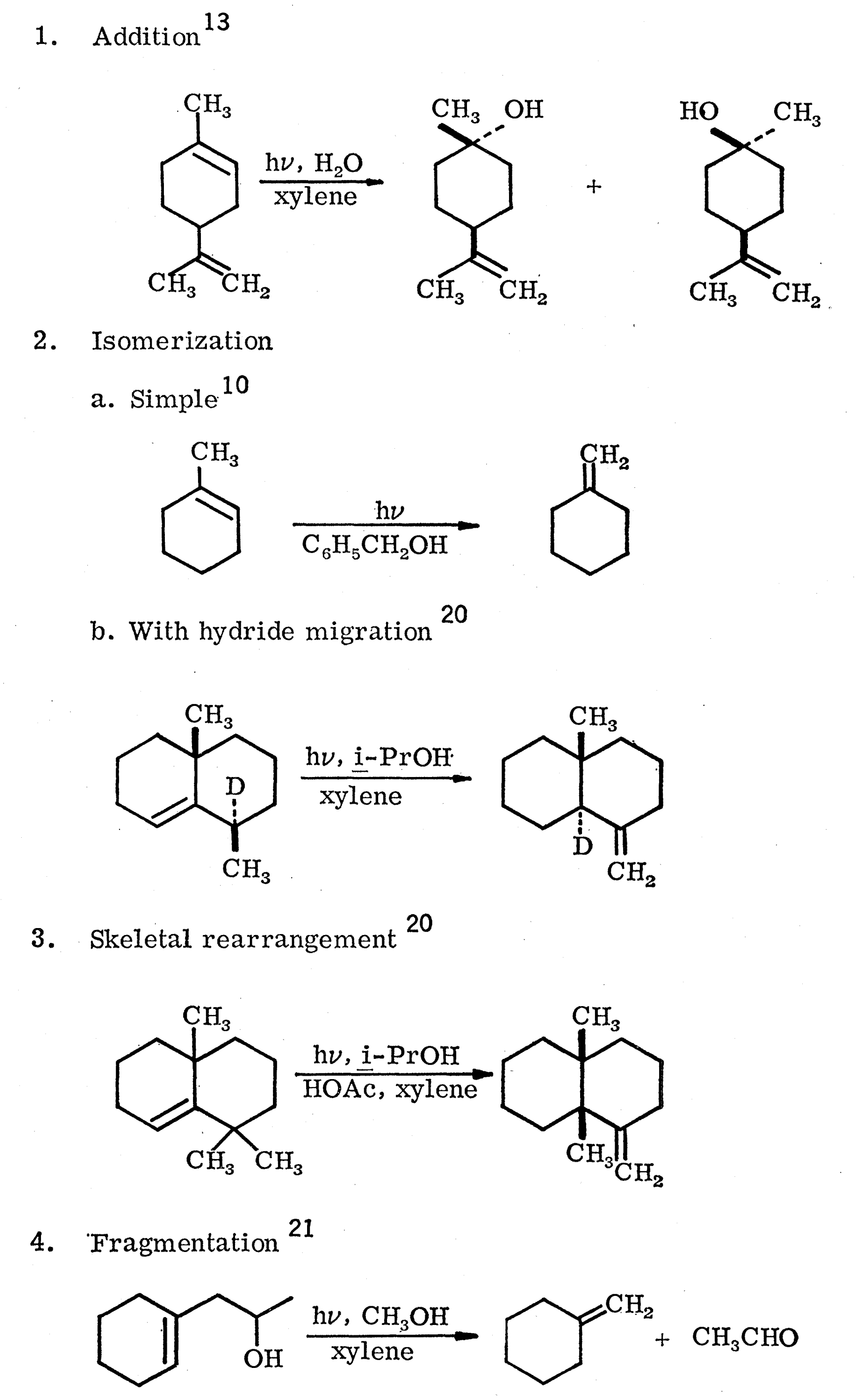


Chart 3. Ionic photochemical reactions of olefins.

aforementioned photoionic reactions may be a ground state transoid olefin formed via electronic excitation of the *cis* isomer. Of course, this hypothetical transoid cyclohexene or cycloheptene may possess a certain amount of vibrational excitation, at least initially, which would no doubt further enhance its reactivity.

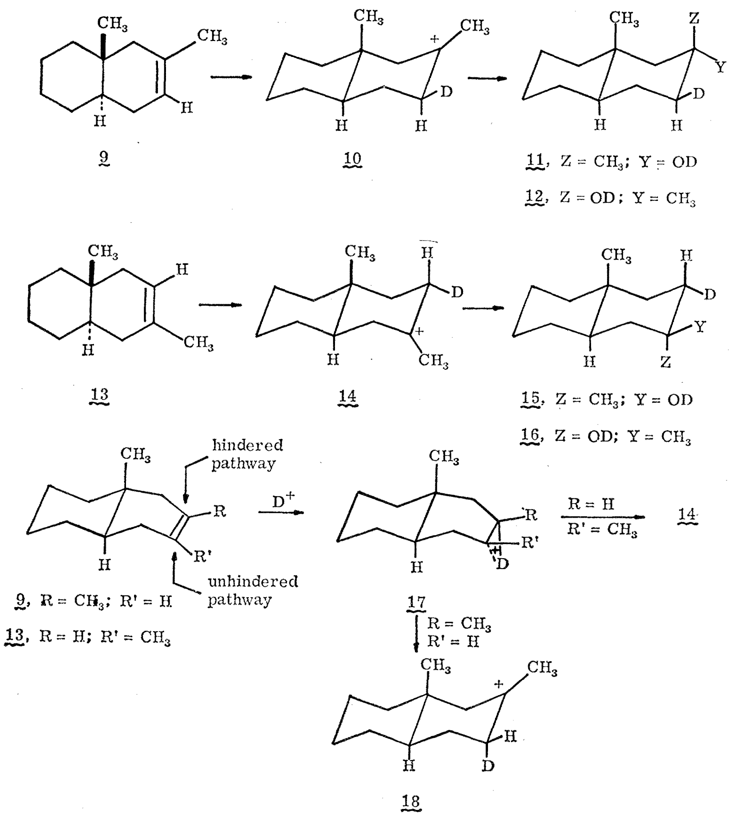


Chart 4. Stereochemistry of olefin protonation.

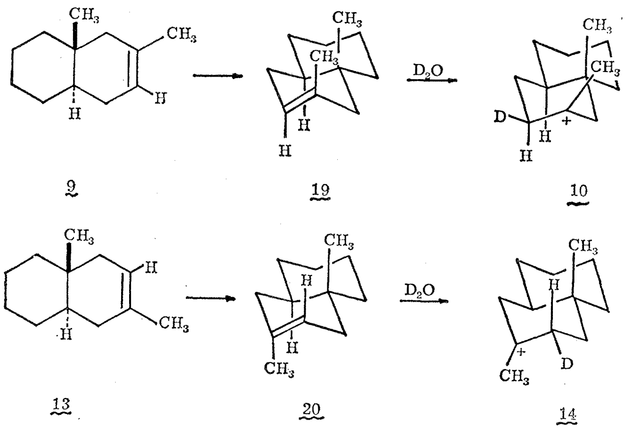


Chart 5. Stereochemistry of *trans*-cyclohexene protonation.

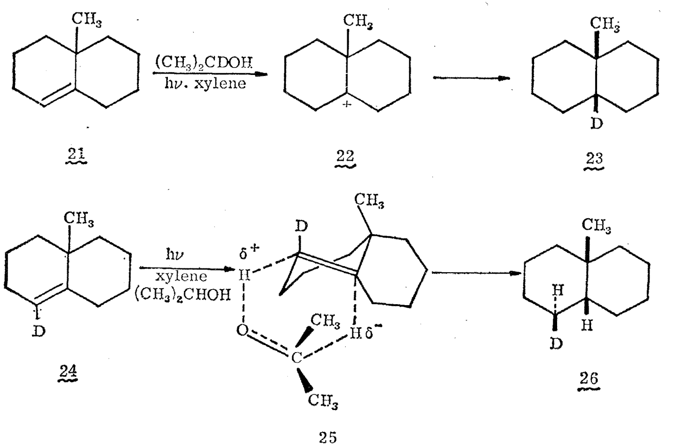
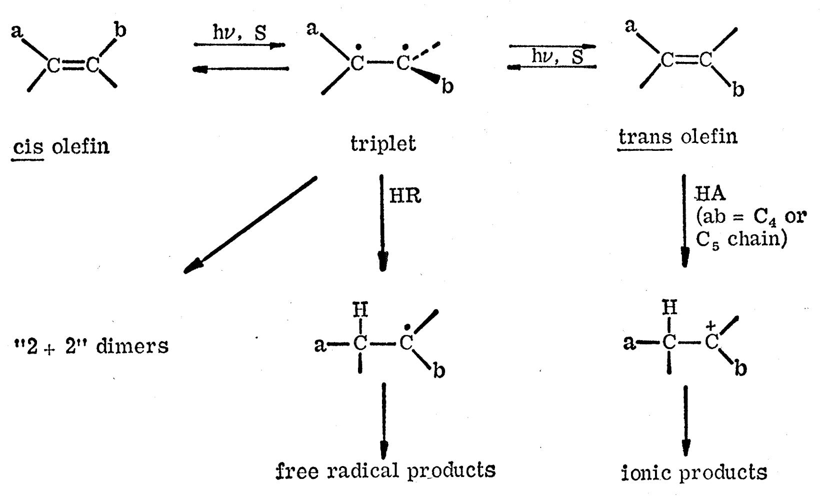


Chart 6. Stereochemistry of photohydrogenation.

Stereochemistry of Photoadditions

Studies on the stereochemistry of photoinduced deuterium oxide addition to the olefins **9** and **13** have led to findings which support the postulated intermediacy of transoid cyclohexenes (*15*). Olefin **9** gave rise to the epimeric alcohols **11** and **12** and olefin **13** under identical conditions afforded a mixture of alcohols **15** and **16** (chart 4). In both cases the products appear to arise from carbocation precursors (**10** and **14**, respectively) containing only equatorially bound deuterium. Both reactions show remarkable stereoselectivity insofar as the deuteration step is concerned; none of the axially deuterated alcohol isomers related to **11**, **12**, **15**, and **16** could be detected. Since the olefinic bonds of **9** and **13** are situated in nearly identical environments, comparable stereochemical results might have been expected for both. In ground state reactions of these olefins the angular methyl grouping tends to shield one face of the double bond, and additions preferentially occur *trans* to this grouping. Thus, the kinetically controlled addition of DCl to olefin **13** yields mainly products with *trans*-related deuterium and methyl (*8*) presumably by way of the bridged ion **17**. Other electrophilic reagents such as peroxy acids exhibit comparable steric preferences with olefins **9** and **13**. However, this is clearly not the case for the photoinduced additions. Olefin **9** undergoes photoinitiated protonation in exactly the opposite stereochemical sense. Obviously, different transition states must be involved in ground state and photoinitiated protonation reactions of olefins **9** and **13**.

It can be readily seen from molecular models that *cis* → *trans* double bond isomerization in cyclohexene causes considerable molecular distortion. Of special interest from a stereochemical point of view is the requisite bridging of the four-carbon saturated chain across the inner face of the carbon-carbon double bond. Consequently, this inner face should be effectively shielded from external reagents and electrophilic



S = photosensitizer

Chart 7. Pathways of olefin photochemistry.

additions should take place exclusively by attack at the outside, unshielded face. In the case of the transoid chair isomers **19** and **20** of olefins **9** and **13** (chart 5) attack by deuterium oxide in this manner would lead to the equatorially deuterated cations **10** and **14**, respectively (*16*). Subsequent nucleophilic attack would yield the observed alcohol products. The same situation would prevail even if steric strain required the *trans* double bond to adopt a nonplanar, somewhat twisted conformation (*14*).

A related reaction, the photohydrogenation of olefin **21**, likewise exhibits stereochemical characteristics compatible with a transoid cyclohexene intermediate. The ionic nature of this reaction was first established by carrying out the irradiation in [2-D]propanol-2, whereupon *cis*-9-methyl[10-D]decalin (**23**) was obtained. The carbocation **22** would therefore seem to be a likely intermediate. Hydrogenation by way of a free radical pathway would have led to the isomeric hydrocarbon, *cis*-9-methyl[4-D]decalin. Irradiation of the deuterated olefin **24** in isopropyl alcohol afforded the *cis*-decalin **26** (*17*). The observed *trans* relationship of the added hydrogens can be accommodated on the basis of protonation and subsequent hydride transfer to the *trans* olefin intermediate **25** as depicted in chart 6.

Conclusion

The photochemistry of cyclohexenes and cycloheptenes has only recently been systematically examined and much remains to be done, particularly with the latter class of cycloalkenes. However, even in its present state, the reaction offers some exciting possibilities for novel synthetic applications whereby certain types of carbocations can be selectively generated in the presence of acyclic, exocyclic, or larger ring olefins under neutral or even basic reaction conditions.

With the findings to date it is possible to construct a unified picture of olefin photochemistry (chart 7) on the basis of the triplet state. Geometric considerations suggest that this state should exhibit a high degree of reactivity in the case of cyclopentene and smaller ring olefins. By the same token, the triplet states of cyclohexene and cycloheptene can sterically adopt the favored orthogonal geometry and unusual reactivity would not be expected in these cases. However, *cis* → *trans* isomerization could lead to highly strained species which might expectedly react through ground state ionic pathways. In this connection it should be noted that any olefin capable of photochemical isomerization to a highly strained isomer could, in principle, exhibit analogous ionic behavior. The remaining types of olefins (acyclic, large ring, and exocyclic), in which excitation does not lead to strained intermediates or products, show what might be considered normal photochemical behavior.

Summary

Sensitized ultraviolet irradiation of cyclohexenes and cycloheptenes in protic solvents causes reactions which seemingly proceed by way of carbocation intermediates. These intermediates, in turn, may arise from a photochemically produced *trans* cycloalkene which is so highly strained that protonation by even weak acids such as methanol may proceed readily. This picture is supported by product analysis, deuterium labeling experiments, and stereochemical studies.

References and Notes

1. For general background information on olefin chemistry, see J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry* (Benjamin, New York, 1964), pp. 169–206 and 1162–1170.
2. For general background information on photochemical excitation processes, see N. J. Turro, *Molecular Photochemistry* (Benjamin, New York, 1965), pp. 2–136.
3. R. S., Mulliken and P. G. Wilkinson, *J. Chem. Phys.* **23**, 1895 (1955); D. F. Evans, *J. Chem. Soc.* **1960**, 1735 (1960); D. F. Evans, *ibid.* **1959**, 2753 (1959).
4. R. S. Mulliken and C. C. J. Roothann, *Chem. Rev.* **47**, 219 (1947); A. J. Merer and R. S. Mulliken, *ibid.* **69**, 639 (1969).
5. A. D. Walsh, *J. Chem. Soc.* **1953**, 2325 (1953).
6. R. Hoffmann and R. B. Woodward, *Science* **167**, 825 (1970).
7. J. A. Marshall and R. D. Carroll, *J. Amer. Chem. Soc.* **88**, 4092 (1966); P. J. Kropp, *ibid.* **88**, 4091 (1966).
8. For a recent review, see J. A. Marshall, *Accounts Chem. Res.* **2**, 33 (1969).
9. J. A. Marshall and A. R. Hochstetler, *Chem. Commun.* **1967**, 732 (1967).
10. P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.* **89**, 5199 (1967).
11. P. J. Kropp, *ibid.* **91**, 5783 (1969).
12. H. Compaignon de Marcheville and R. Beugelmans, *Tetrahedron Lett.* 6331 (1968); *ibid.* 1901 (1969); J. A. Waters and B. Witkop, *J. Org. Chem.* **34**, 3775 (1969); J. A. Marshall and A. E. Greene, *Tetrahedron* **25**, 4183 (1969).
13. P. J. Kropp, *J. Org. Chem.*, in press.
14. A satisfactory *trans*-cyclohexene can be constructed from Dreiding models by effecting the following changes on the internal bond angles: C-1 and C-2 sp^2 atoms, compress from 120° to 100°; C-3 and C-6 tetrahedral atoms, compress from 109.5° to 90°; C-4 and C-5 tetrahedral atoms, expand from 109.5° to 120°. With these modified angles, the adjacent trigonal atoms of the double bond are twisted by about 30°. Such molecular parameters do not seem unreasonable in view of known isolable compounds such as cyclobutene and *trans*-cyclooctene where analogous bond angle distortion must exist.
15. J. A. Marshall and M. J. Wurth, *J. Amer. Chem. Soc.* **89**, 6788 (1967).
16. An alternative (boat) conformer of *trans*-cyclohexene can be envisioned wherein the backmost (C-4–C-5) carbon-carbon bond crosses the carbon-carbon double bond (C-1–C-2) at nearly right angles. Outside protonation of this species would lead to an axial orientation in the chair conformer of the cyclohexane ring for the newly introduced proton. However, the experimental findings on D_2O additions indicate a distinct preference for the chair *trans*-cyclohexene conformer. The reasons for this preference are not yet clear but steric factors undoubtedly play an important part.
17. J. A. Marshall and A. R. Hochstetler, *Chem. Commun.* **1968**, 296 (1968).
18. J. S. Swenton, *J. Org. Chem.* **34**, 3217 (1969); G. S. Hammond, N. J. Turro, P. A. Leermakers, *J. Phys. Chem.* **66**, 1144 (1962).
19. H. D. Scharf and F. Korte, *Chem. Ber.* **97**, 2425 (1964).
20. J. A. Marshall and A. R. Hochstetler, *J. Amer. Chem. Soc.* **91**, 648 (1969).
21. P. J. Kropp and H. J. Krauss, *ibid.*, p. 7466.
22. Financial support by the National Science Foundation, the Alfred P. Sloan Foundation, and the Hoffmann-La Roche Foundation. We thank Dr. P. J. Kropp for his interest and help and M. Wilder for stimulating discussions.