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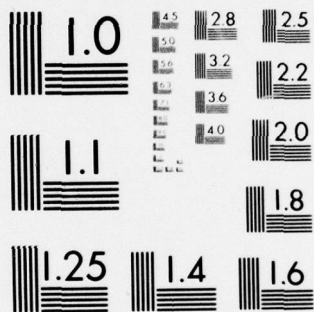
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PHOTOCHEMISTRY OF ALKENES

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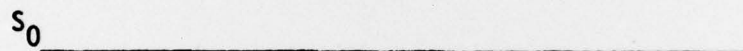
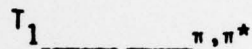
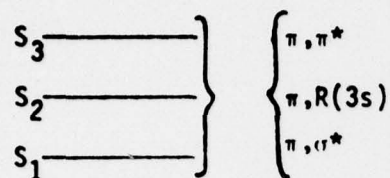
RESULTS

MONOENES

The principal goal of our work in this area has been a complete characterization of the chemical properties of the various excited states of alkenes. During the course of this work important insight into the number and electronic nature of the excited states of alkenes and the effect of structure on their relative energies has been gained which both confirms and extends earlier conclusions from theoretical and spectroscopic studies.

The current status of our understanding of the photochemistry of alkenes was summarized in detail in our renewal proposal and will be covered more extensively in two review articles which the principal investigator has been invited to prepare for Molecular Photochemistry and Reviews of Chemical Intermediates. The salient features are outlined below, with particular emphasis given to those aspects which have been elaborated most recently.

Excited States. Chemists have traditionally associated only the π, π^* excited state with alkenes. As can be seen from the Jablonski diagram below, this is reasonable for the triplet manifold, at least from a photochemical viewpoint, since one state is clearly low lying and its assignment as π, π^* is widely accepted.¹ By contrast, however, there are at least three low-lying excited states in the singlet manifold, and it is not clear from spectroscopic or theoretical studies how widely they are separated in energy or which is lowest lying.^{1,2} As indicated below, our studies, aimed at elucidating the chemical properties of each state, have afforded additional evidence for the electronic configurations of these states and have revealed that the ordering of the states is a subtle function of such structural features as the number



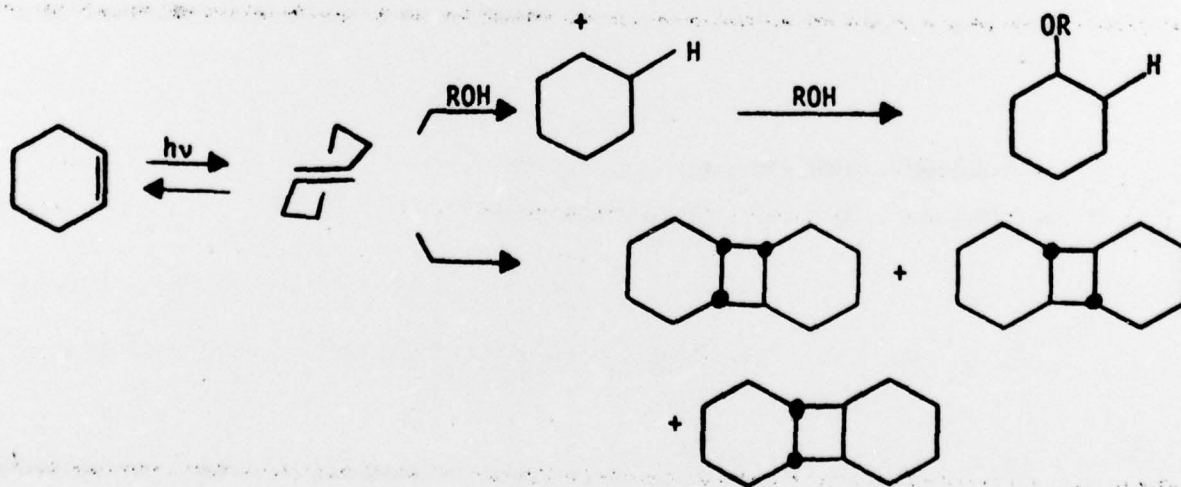
of alkyl substituents and the presence or absence of sigma strain about the double bond.

Singlet vs. Triplet Behavior. Because of the existence of just one low-lying excited state in the triplet manifold, sensitized irradiation of alkenes affords a single mode of behavior, that described below for the π, π^* state. By contrast, because of the closeness in energy of several excited states in the singlet manifold, direct irradiation of alkenes usually affords mixed behavior. However, one or another of the various modes frequently dominates -- depending upon which excited state is lowest lying, as determined by the structure of the olefin and the type of medium in which the irradiation is carried out.

π, π^ Behavior.* The principal chemical property associated with the π, π^* state of alkenes is cis \rightleftharpoons trans isomerization, which is readily explained in terms of a tendency of π, π^* states to undergo vibrational relaxation

by twisting about the weakened carbon-carbon bond to afford an orthogonal species to reduce the mutual repulsion of the π and π^* electrons. On returning to the ground state the orthogonal species has equal probability of going to either cis or trans olefin. Either direct or sensitized irradiation of acyclic and exocyclic olefins and cyclic olefins with ring sizes down to eight-membered affords a photostationary mixture of the cis and trans isomers. In the case of cycloheptenes and -hexenes the resulting *trans*-cycloalkene is highly strained and, hence, short-lived. When generated in protic media, the *trans*-cycloalkene undergoes facile protonation in a secondary, non-photochemical step; when generated in aprotic media *trans*-cyclohexenes (but not -heptenes) undergo secondary [2+2] cyclodimerization.

Scheme 1

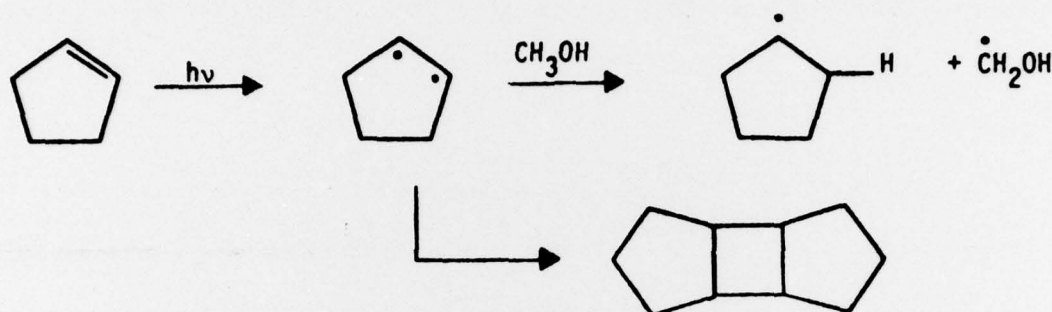


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Particular attention has been devoted in our laboratories to the photodimerization of cyclohexene. Three cyclobutane-type dimers -- the cis, trans, the trans-anti-trans, and the cis-anti-cis -- were obtained in an 8.3:3.3:1.0 ratio. Similar results were obtained over a wide range of concentrations and on both direct and sensitized irradiation. A previous claim that only one isomer, the trans-anti-trans, is a primary photoproduct and that this undergoes secondary photoisomerization³ was shown to be incorrect. All three stereoisomers are, in fact, primary photoproducts. The predominant formation of highly strained stereoisomers with one or more trans fusions support the proposed involvement of a trans intermediate. Moreover, if the cycloaddition process is concerted, or nearly so, orbital symmetry rules require that it be $[2_s+2_a]$ -- in which case the predominant cis, trans stereoisomer is that which would result from addition of a molecule of *trans*-cyclohexene with a second molecule of the trans isomer *rather than with the more abundant cis* isomer. This appears to indicate that *trans*-cyclohexene is surprisingly selective in its behavior despite the high degree of strain that might be expected. The two minor adducts, the trans-anti-trans and cis-anti-cis stereoisomers, are those which would be expected from addition of *trans*-cyclohexene with the cis isomer.

Cyclopentenes and other highly constrained cycloalkenes, which are structurally inhibited from undergoing cis \leftrightarrow trans isomerization, display a radical-type π, π^* behavior, as evidenced by abstraction of hydrogen atoms from the solvent. This is consistent with the biradical nature of the π, π^* excited state and its extended lifetime in these cases due to the inability to undergo twisting. Competing with hydrogen atom abstraction is $[2+2]$ cycloaddition to a ground state molecule of olefin to form a cyclobutane-type dimer. In contrast with the photodimerization of cyclohexenes, cycloaddition in this case probably involves attack of a π, π^* excited species on a ground state molecule of the olefin.

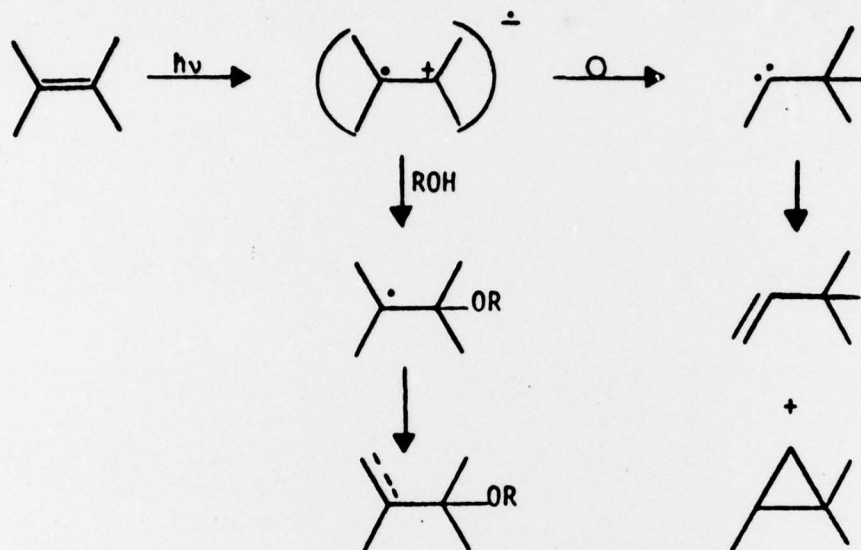
Scheme 2



$\pi, R(3s)$ Behavior. Rydberg excited states have been largely overlooked by photochemists. Prior to our work in the area,^{4,5} no observation had been made of the chemical properties of the $\pi, R(3s)$ excited state of alkenes in solution. A $\pi \rightarrow R(3s)$ transition involves promotion of one of the π electrons to a large molecular orbital that has a size and shape similar to that of a 3s carbon atomic orbital. In the case of tetramethylethylene the resulting molecular orbital has a maximum electron density at a radius similar to the distance of the allylic hydrogen atoms from the center of the molecule.¹ This imparts to the core of the molecule a radical-cation character. We have observed two novel modes of photobehavior for alkenes which we believe to be associated with the $\pi, R(3s)$ excited state, depending on the type of medium in which it is generated.

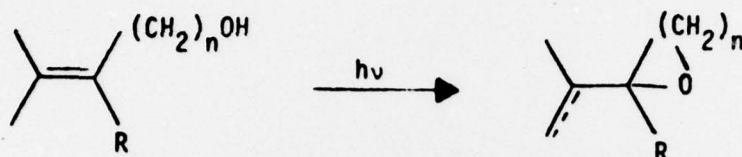
A. *Nucleophilic Trapping.* Direct irradiation of olefins in nucleophilic media such as alcohols or water results in the formation of an approximately 1:1 mixture of saturated and unsaturated ethers.⁴ This behavior can be most simply explained in terms of nucleophilic trapping of the $\pi, R(3s)$ excited state, followed by disproportionation of the resulting alkoxy radical (Scheme 3).

Scheme 3



A systematic study was made in our laboratories of the ease of *intramolecular* trapping of the $\pi, R(3s)$ state in unsaturated alcohols. Study of the two homologous series depicted in Scheme 4 revealed that the most suitable chain length for intramolecular trapping occurs when $n = 3$. No trapping was observed when $n = 1$ or 2, and trapping efficiency was less for $n = 4$ than for $n = 3$. Trapping always occurred at the end of the double bond closer to the hydroxyl group, to afford the smaller possible ring. Even in the most suitable cases, where $n = 3$, the yields of cyclized products were low. Apparently the $\pi, R(3s)$ state has a short lifetime and nucleophilic trapping can occur only if the hydroxyl group is already oriented in a suitable conformation. (Although somewhat reminiscent of the photoprotonation of cyclohexenes and -heptenes described above, this process is clearly different as it occurs in both cyclic and acyclic olefins and affords both saturated and unsaturated ethers.)

Scheme 4



B. Carbene Behavior. On irradiation in non-nucleophilic media alkenes display yet another mode of behavior, which involves rearrangement through a carbene intermediate, as shown in Scheme 3 for tetramethylethylene.⁵ In hydroxylic media of only mediocre nucleophilicity this pathway competes with the radical cation behavior described above. It is readily explained in terms of the $\pi, R(3s)$ state undergoing a 1,2-alkyl shift to afford the carbene. Those olefins which display dominant radical-cation behavior in nucleophilic media undergo rearrangement through a carbene intermediate in non-nucleophilic media.

The nucleophilic trapping process and the rearrangement to a carbene intermediate, both first observed in these laboratories, are the only chemical properties thus far attributed to the $\pi, R(3s)$ state in solution.

Correlation of π, π^ vs. $\pi, R(3s)$ Behavior with Structure.* In all of the cases which we have studied, sensitized irradiation of alkenes has induced only π, π^* behavior. It thus appears that in the triplet manifold the π, π^* state is invariably the lowest lying state (T_1) and that it is well separated in energy from T_2 . By contrast, direct irradiation has usually induced mixed behavior, with π, π^* and $\pi, R(3s)$ processes competing. However, the relative involvement of the two types of behavior varies as a function of the degree of alkyl substitution about the double bond, with increasing substitution favoring $\pi, R(3s)$ behavior. Indeed, it is only in tetrasubstituted alkenes that $\pi, R(3s)$ behavior dominates. It is generally assumed that alkenes do

not undergo singlet-triplet intersystem crossing since there are no heteroatoms present and the S_1-T_1 energy gap is large. Hence it appears that both types of behavior originate from singlet excited states on direct irradiation and that in the singlet manifold the π, π^* and $\pi, R(3s)$ states are similar in energy.

The increasing dominance of $\pi, R(3s)$ relative to π, π^* behavior with increasing alkyl substitution about the double bond is probably attributable to a greater stabilization of the former state by the presence of alkyl substitution. In a π, π^* state there is only a small degree of charge separation since the π and π^* orbitals are near-by in space. By contrast, there is considerably greater charge separation when a π electron is promoted to the large $R(3s)$ orbital. This is reflected in the radical-cationic behavior observed for the $\pi, R(3s)$ state. Hence the $\pi, R(3s)$ state should be substantially more sensitive than the π, π^* state to the electron releasing effect of alkyl substituents.

It thus appears that the effect of substitution on the relative energy levels for the two states is that depicted by Figure 1. In the case of ethylene the $\pi, R(3s)$ state is probably substantially higher lying. However, because of its greater cationic character, it decreases in energy much more rapidly than the π, π^* state with increasing alkyl substitution and either closely approaches or even drops lower in energy than the π, π^* state in tetrasubstituted alkenes.

The consistent display by alkenes of π, π^* behavior on sensitized irradiation, even when tetrasubstituted, indicates that in the triplet manifold the π, π^* state is consistently lower lying. Although the energy levels of $\pi, R(3s)$ triplet states are probably highly sensitive to the degree of alkyl substitution, in analogy with singlet states, the $\pi, \pi^* - \pi, R(3s)$ energy gap is

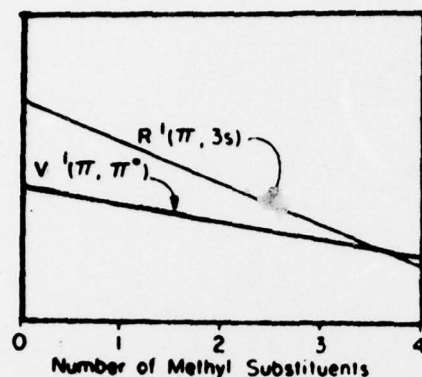


Figure 1. Proposed relative 0,0 energies for the π, π^* and $\pi, R(3s)$ electronic levels of ethylene and its methyl-substituted derivatives

greater in the triplet than in the singlet manifold of alkenes and the $\pi, R(3s)$ state is never lowered sufficiently in energy, even with tetra-alkyl substitution, to closely approach the π, π^* energy level. In other words, the S-T energy gap is greater for the π, π^* state. This is probably related to the fact that triplet states are lower in energy than the corresponding singlets because the unpairing of spins prevents the two electrons from occupying the same space simultaneously and, consequently, reduces electron-electron repulsion. This stabilizing effect is greater in a π, π^* than in a $\pi, R(3s)$ triplet state, in which the electrons are in more widely separated orbitals.

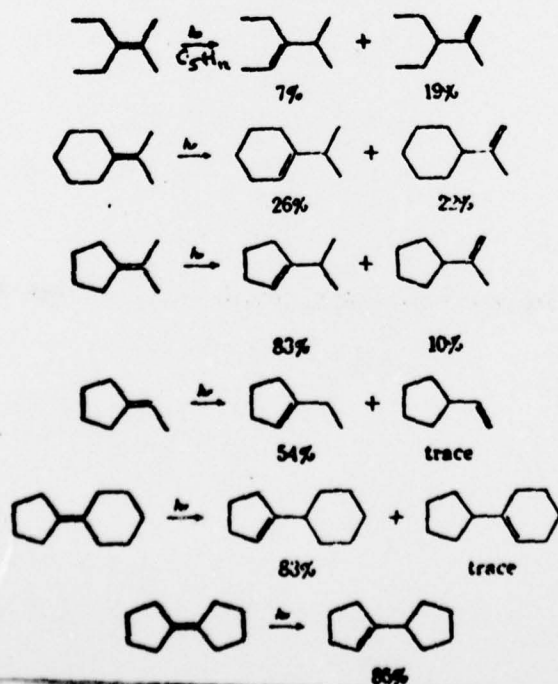
Double Bond Migration. In addition to the modes of photobehavior outlined thus far, there is yet another photochemical property of alkenes, which appears to be associated with neither π, π^* nor $\pi, R(3s)$ excited states. This reaction, involving a positional migration of the double bond, has been studied in detail in our laboratories.⁶

Most olefins -- regardless of the degree of alkyl substitution and regardless of whether they are cyclic, exocyclic, or acyclic -- undergo double bond migration on direct irradiation, although the π, π^* or $\pi, R(3s)$ modes usually

predominate. However, as can be seen in Scheme 5, when the double bond is exocyclic to a six- or, particularly, a five-membered ring, the positional isomerization becomes more dominant. Also noteworthy is that migration occurs preferentially into a five-membered ring. A deuterium labelling study has shown that the reaction is intramolecular, involving a [1,2]-sigmatropic hydrogen shift.

The reaction apparently does not involve the π, π^* excited state since it cannot be induced by sensitized irradiation. Moreover, direct irradiation of olefins at appropriately long wavelengths selectively induces π, π^* behavior with no concomitant double bond migration. Likewise, it does not appear to involve the $\pi, R(3s)$ state as it does not follow the pattern of being dominant only in tetrasubstituted olefins. It thus appears to involve yet a third excited state. On the basis of calculations it has been concluded that π, σ^* states are lowered in energy by the presence of sigma strain. In particular, the energy levels of alkylidenecycloalkenes were found by cal-

Scheme 5



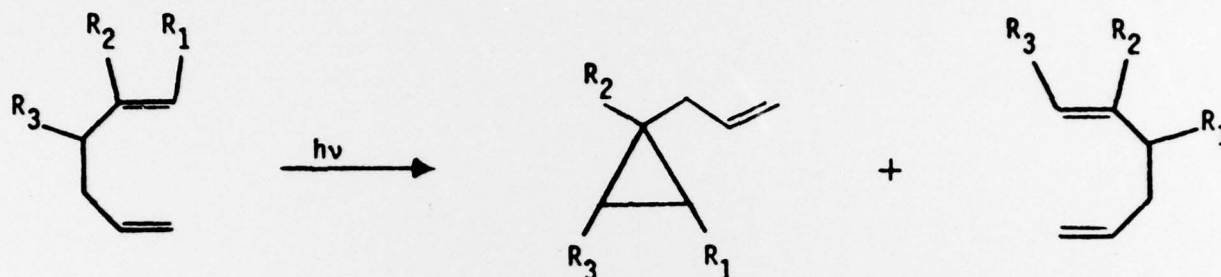
ulation to decrease with decreasing ring size. It is thus tempting to conclude that the [1,3]-sigmatropic hydrogen shifts involve π, σ^* states. However, the arguments for this assignment are perhaps not so strong as those available for the assignment of $\pi, R(3s)$ behavior described above, and additional study is warranted.

DIENES

Diene systems, particularly 1,5-dienes, are of interest as models for polybutadienes, polyisoprenes, and other elastomers -- all of which have residual double bonds. Previous photochemical studies in this area, which were concerned with polymer systems themselves, had afforded evidence for cyclopropane formation and the generation of vinylidene and vinyl double bonds.⁷ Since structural assignments in polymer systems are necessarily vague and mechanistic interpretations cannot be easily put to test, we undertook a systematic study of the photochemical behavior of a series of variously substituted 1,5-hexadienes as model systems. The study revealed that 1,5-dienes are in fact quite photolabile. As outlined in Scheme 6, each diene was found to undergo competing formation of an allylcyclopropane and a rearranged 1,5-diene. Allylcyclopropane formation was shown to occur via a stereospecific [1,2]-allyl migration in which cis olefin affords a cis-substituted cyclopropane and trans olefin a trans cyclopropane. The allyl group itself migrates with retention of stereochemistry. The rearranged 1,5-dienes were shown to be formed via a [1,3]-allyl migration.

In addition to the above two processes, which are apparently characteristic of the 1,5-diene chromophore, each diene also displayed behavior characteristic of isolated double bonds: cis \rightleftharpoons trans isomerization, double bond migration, and rearrangement via a carbene intermediate. These results concur with previous

Scheme 6



conclusions derived from studies based on polymer systems that cyclopropyl derivatives are formed but indicate a different mode of formation and indicate that other products are formed as well.

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