depends upon the amount of impurity, i.e., the extent of the reaction; the degree of flattening that we observed in our experiments does seem to correlate qualitatively with our estimates of the reactivity.

It is interesting to note that the experimental discovery of symmetrical tricritical points in fluid mixtures dates from 1967, when Graf, Lee, and Reppy[53] established the correct phase diagram for the helium mixture and when we[49] determined the phase diagram for triphenylmethane + sulfur (Figure 14a), including the critical polymerization line (which is analogous to the superfluid transition line). Neither paper called the phenomenon a tricritical point.

I conclude by returning to the enantiomer diagrams. Before anyone can find these pseudobinary ternary diagrams, one has to find fluid–fluid phase separation in racemic mixtures. It is only very recently that thermodynamic measurements have finally given convincing evidence[54] of deviations from ideal-solution behavior in fluid mixtures of d–l isomers. Systems with much larger and positive deviations must be found. The model exists; substances that will fit it need to be found. Some think this virtually impossible. But macroscopic phase separation has to involve the whole molecule, not just a few segments, so I hope that construction of polymer chains from appropriate optically active monomers will amplify the monomer effect sufficiently to produce incompatibility. Only time will tell, and it is likely to be a rather long time; but what fun it will be to find it!

It has often been suggested that the study of phase equilibria, like the classical thermodynamics upon which it is based, is really a 19th century subject far from the frontier of modern science. I hope that this presentation shows that this is not so, that there is still much excitement in this field. Moreover, many new types of phase equilibria that are just beginning to be understood have not even been mentioned—areas to which I have made no contributions at all, but ones that are exciting and will continue to excite the next generation of physical chemists: liquid crystals, microemulsions, phase equilibria in two dimensions (surface films), and many others.

Most of the research reported here was supported by the U.S. National Science Foundation. I also thank the nearly 60 research collaborators—students (undergraduate and graduate), postdoctoral associates, and faculty colleagues—who have contributed to our research over the years.

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Organic Photochemistry with Far-Ultraviolet Photons. The Photochemistry of Allyl-, Vinyl-, and Alkylidenecyclopropanes

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The past 3 decades have witnessed a tremendous surge of interest in the photochemistry of organic compounds in solution. The studies that have been undertaken have encompassed a wide variety of chromophores which absorb in the near-ultraviolet (>300 nm) and the mid-ultraviolet (200–300 nm) regions of the spectrum. As a result, there is general understanding of the photochemical behavior of chromophores (e.g., carbonyl, phenyl) whose lowest electronic transitions lie in these spectral regions. Compounds such as alkenes, acetylenes, cyclopropanes, alcohols, ethers, and amines whose chromophores do not absorb in this region have been studied by extending their absorption by suitable conjugating groups or, where possible, by promotion to their lowest triplet states by sensitization.

Organic photochemistry in the far-ultraviolet (185–214 nm) offers opportunities to study the behavior of simple, unsubstituted chromophores in their singlet excited states in solution. It also makes possible excitation of the second upper singlet states of those chromophores (e.g., carbonyl) which absorb at longer wavelengths as well.

Photons of wavelengths in the far-ultraviolet region correspond to energies greater than 143 kcal/einstein, which is more than adequate to break almost any bond in a typical organic molecule. In the gas phase, secondary bond homolysis does occur, often randomly, as a result of the primary photoproducts being formed with excess vibrational energy.[1] In solution, however, irradiation with far-UV light usually results in highly

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R. Srinivasan is Manager of Photochemical Research at the IBM T. J. Watson Research Center.

[1] See, for example: (a) McNesby, J. R.; Okabe, H. *Adv. Photochem.* **1964**, *3*, 157 and references cited therein. (b) Currie, C. L.; Okabe, H.; McNesby, J. R. *J. Phys. Chem.* **1963**, *67*, 1494. (c) Lopez, E.; Doepker, R. D. *Ibid.* **1978**, *82*, 753.

selective, efficient photochemistry; product quantum yields in the 0.2–0.9 range are not unusual.

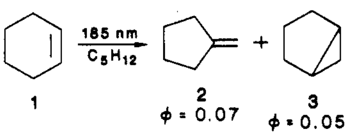
In this Account, we will describe the results of our investigations of the solution-phase photochemistry of hydrocarbons containing both cyclopropane and olefinic moieties. These encompass three systems with varying degrees and types of interaction between the two moieties: allyl-, vinyl-, and alkylidenecyclopropanes. As an introduction to this discussion, we will provide brief summaries of our and others' work on the photochemistry of cycloalkenes and alkylcyclopropanes. These summaries will not be exhaustive, and the reader is directed to two excellent reviews on alkene[2] and cyclopropane[3] photochemistry for more detailed information. The experiments described below were performed using the following wavelengths: 185 nm (mercury resonance lamp), 193 nm (argon fluoride excimer laser), and 214 nm (zinc resonance lamp).

The Photochemistry of Alkenes

Alkenes have two low-lying excited singlet states, the π,π^* (valence) state and the π,R(3s) (Rydberg) state. The π,π^* state energy is less affected by the presence of alkyl substituents than the Rydberg state, so that for tri- and tetra-substituted alkenes the Rydberg state is the lower energy one in the gas phase[4] as well as in solution.[2]

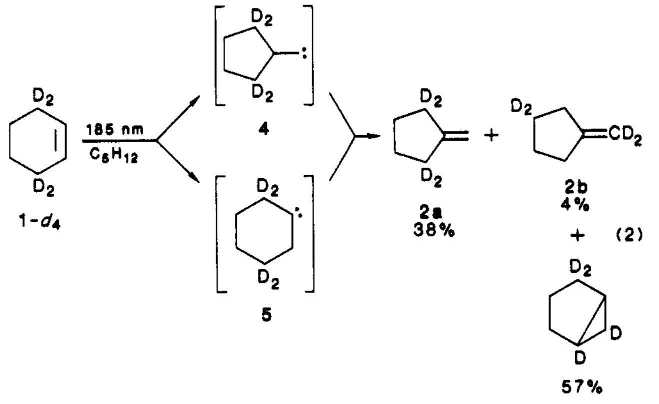
The photoreactivity of simple alkenes upon direct excitation is often observed to be complex, presumably as a result of population of both the valence and Rydberg states.[2] Cis–trans isomerization,[2] [1,3]-hydrogen migration,[2] unimolecular dehydrogenation,[5] and (possibly) hydrogen atom abstraction[6] have been identified as π,π^* reactions. [1,2]-Alkyl and [1,2]-hydrogen migrations (yielding carbenes or carbene-like intermediates) and photosolvolysis are common alkene photoreactions that have been attributed to the involvement of the Rydberg state.[2]

The photochemistry of cyclohexene (1) in solution illustrates the general photobehavior of cyclic alkenes (C_5–C_7)[6-8] as well as the nature of the carbene or carbene-like intermediates that are involved. Irradiation (185 nm) of **1** in pentane solution leads to two products, methylenecyclopentane (**2**) and bicyclo[3.1.0]hexane (**3**) (eq 1)[7]. The formation of these products is consistent



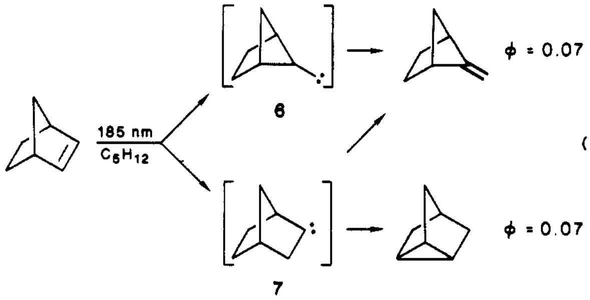
(1)

with the intermediacy of both cyclopentylmethylene (**4**), formed via [1,2]-alkyl migration, and cyclohexanylidene (**5**), formed via [1,2]-hydrogen migration,[7,8] since both **2** and **3** are formed when **4** and **5** are generated independently from diazo precursors.[9] Irradiation of 1-d_4 was performed in order to determine the relative involvement of the two carbenes **4** and **5**.[7] In this case, **2a** arises from either **4** or **5**, while **2b** can arise only from **5** (see eq 2). From the distribution of deuterium in the products, it has been determined that **4** is the major intermediate in the photolysis of **1**, with as little as 1/14 of total product formation arising via the intermediacy of **5**.



(2)

The competition between [1,2]-hydrogen and [1,2]-alkyl migration in the Rydberg state is more apparent in the case of constrained, bicyclic olefins such as norbornene[6,7] (eq 3). In this case, the efficient formation of nortricyclane indicates the intermediacy of norbornanylidene (**7**).[10]



(3)

An interesting generalization that has emerged is that for cyclic olefins [1,2]-alkyl migration resulting in ring contraction always appears to predominate over migration of other alkyl substituents, such as methyl groups.[2,11]

The Photochemistry of Alkylcyclopropanes

The excited singlet state behavior of alkylcyclopropanes can be considered superficially to be characterized by competition between formal one- and two-bond fragmentation.[12] The products of the former pathway correspond to [1,2]-hydrogen migration to yield olefins and can be rationalized in terms of the intermediacy of 1,3-biradical intermediates, although concerted pathways cannot be ruled out. Two-bond fragmentation[13] yields an olefin and a carbene, of which the latter proceeds to react further via [1,2]-hydrogen migration or C–H bond insertion. The two competitive

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(2) Kropp, P. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, p 1.

(3) (a) Hixson, S. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, p 191. (b) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537.

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(9) (a) Kirmse, W.; Pohlmann, K. *Chem. Ber.* **1967**, *100*, 3564. (b) Frey, H. M.; Scaplehorn, A. W. *J. Chem. Soc. A* **1966**, 968.

(10) (a) Powell, J. W.; Whiting, M. C. *Tetrahedron* **1959**, *7*, 305. (b) Reusch, W. DiCarlo, M. W.; Traynor, L. *J. Org. Chem.* **1961**, *26*, 1711.

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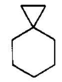
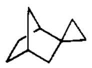
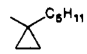
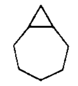
(12) (a) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 7089. (b) Srinivasan, R.; Baum, T.; Ors, J. A. *Tetrahedron Lett.* **1981**, *22*, 4795.

(13) This process is well-documented in the gas-phase photolysis of cyclopropanes. See: Currie, C. L.; Okabe, H.; McNesby, J. R. *J. Phys. Chem.* **1963**, *67*, 1494. Hill, K. L.; Doepker, R. D. *Ibid.* **1972**, *76*, 3153. Lopez, E.; Doepker, R. D. *Ibid.* **1978**, *82*, 753. Scala, A. A.; Ausloos, P. *J. Chem. Phys.* **1968**, *49*, 2282. Shibuya, K.; Obi, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1974.

Table I.
Effect of Substitution Pattern on One- vs. Two-Bond Cleavage and Fragmentation Pathway[a]

							
one-bond cleavage	3	3	3	3	4	1	0.5
olefin + R_1R_2C:	3	1	2	2	6	9	8
olefin + H_2C:	4	6	5	5	0	0	1
ref	12b	12b	12b	12b	12a	12a	16

[a] Relative product yields; 185-nm photolysis.

pathways are illustrated by the behavior of bicyclo[3.1.0]hexane-6,6-d_2 (**8**), shown in eq 4.[12a] This general behavior is followed by all members of the bicyclo[*n*.1.0]alkane family (*n* = 3–6),[12a,14] although bicyclo[4.1.0]heptane is apparently anomalous in that a one-bond cleavage product (cycloheptene) could not be detected in that case.[12a]

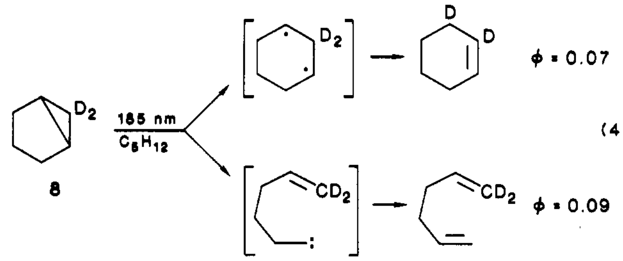
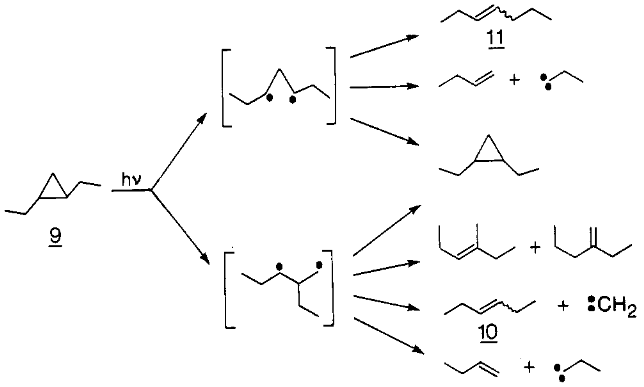


Table I illustrates the competition between one- and two-bond fragmentation pathways as a function of cyclopropane substitution. Two-bond fragmentation products clearly dominate the photochemistry in all cases, but the course of carbene extrusion is substituent-dependent. Of primary interest is the effect of substitution on the preference for methylene vs. substituted carbene elimination. While monosubstituted systems show roughly equal partitioning between the two fragmentation pathways, methylene elimination is strongly favored in 1,1-disubstituted systems and strongly suppressed in 1,2-disubstituted cases. The pattern that emerges from these results is most consistent with a stepwise mechanism for the two-bond cleavage process, involving initial one-bond cleavage to yield the most stable possible 1,3-biradical (predominantly). The biradical then decays by reclosure to starting material, [1,2]-hydrogen migration, or further fragmentation (which can proceed in two ways) to lead to carbene and olefin (see Scheme I). This mechanism is supported by theoretical calculations,[15] as well as by the observed loss of stereochemical integrity in olefinic products formed upon photolyses of *cis*- and *trans*-1,2-diethylcyclopropane (**9**) (Scheme I).[16]

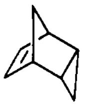
The lifetimes of the initially formed 1,3-biradicals are apparently long enough to allow partial loss of their stereochemistry, resulting in cyclopropane cis–trans isomerization (usually minor[14]), formation of both geometrical isomers of the olefin derived from [1,2]-H migration (**11**), and formation of both geometrical isomers of the olefin derived from methylene extrusion (**10**). It is interesting that the isomeric cyclopropanes (**9**) yield different proportions of the two olefin isomers in each case.

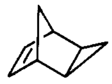
Scheme I.
One- and Two-Bond Cleavage Pathways in the Photochemistry of Alkylcyclopropanes

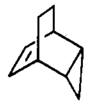


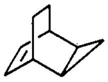
The Photochemistry of Allylcyclopropane Derivatives

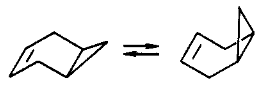
There is considerable interest in the possible interactions between nonconjugated olefin and cyclopropane moieties.[17–21] Photoelectron spectroscopy has revealed the presence of such interactions in the lower lying MO's of rigid tricyclic systems,[20,21] but little information exists regarding the excited state behavior of such compounds. Our studies of the photochemistry of **12–14** indicate that through-space interactions do exist in the excited state(s) of these systems and that the photobehavior is strongly dependent on both the relative conformations of the two chromophores and the rigidity of the ring systems.[22–24]


12N


12X


13N


13X



14

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(14) Srinivasan, R.; Ors, J. A.; Baum, T. H. *J. Org. Chem.* **1981**, *46*, 1950.

(15) Rossi, A. R. *J. Phys. Chem.* **1979**, *83*, 2554.

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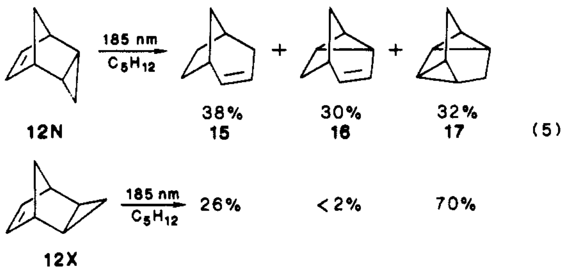
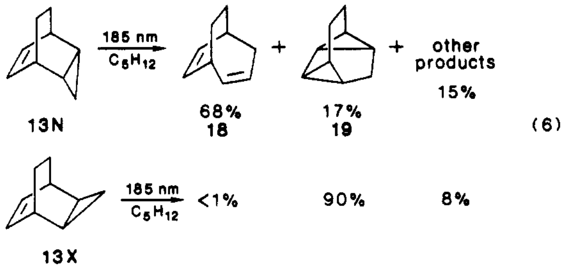
(22) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 3411.

Photolysis (185 nm) of **12** and **13** in pentane solution leads to the product mixtures shown in eq 5 and 6, respectively.[23] Several features can be noted in the results for these compounds. Products normally characteristic of the photochemistry of the isolated chromophores (viz., ring contraction from the olefinic group and two-bond cleavage from the cyclopropyl moiety) are *not* formed upon photolysis of these compounds, indicating that the two chromophores are strongly coupled in both the ground and the excited state(s). In both **12** and **13**, the endo isomers undergo predominantly cyclopropane bond rupture leading to dienes (the formation of **16** from **12N** has been attributed to the formation of diene **15** in the triplet excited state[23,25]), while the exo isomers undergo formal $2\pi + 2\sigma$ intramolecular cycloaddition. These features can be rationalized on the basis of the UV absorption spectra of **12** and **13** and ab initio calculations.



(5)



(6)

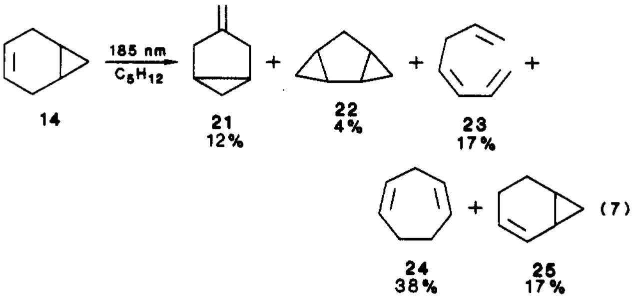
The absorption spectra are clearly different for the exo and endo isomers of both **12** and **13**; the exo isomers each exhibit two distinct absorption bands which apparently overlap in the endo isomers. Ab initio calculations indicate that the lower energy transition in the exo isomers corresponds to promotion of an electron from a molecular orbital that is antibonding beneath the carbon skeleton to one that is bonding in that region.[23] This transition is similar to the π,π^* transition in norbornadiene that leads to quadricyclane[26,27] and is identified as being responsible for internal cycloadduct formation in **12** and **13**. The higher energy transition involves removal of an electron from an orbital that is largely localized on the cyclopropane moiety, so that it weakens the cyclopropane C–C bond and leads to diene formation. In the endo isomers, the closer proximity of the two states should enable more facile population of the upper state by mixing or thermal population from the lower one, resulting in a relatively higher proportion of diene products than is obtained from the exo isomers.

Table II.
Effect of Excitation Wavelength on Product Yields from Photolysis of 14[a]

	yield, %				
λ, nm	21	22	23	24	25
185[b]	12	4	17	38	17
193[c]	13	13	27	32	16
214[d]	23	20	6	37	2

[a] All photolyses in pentane solution. [b] Mercury resonance lamp with 185-nm band-pass filter. [c] Argon fluoride excimer laser. [d] Zinc resonance lamp.

In contrast to **12** and **13**, the more flexible analogue **14** exhibits photobehavior typical of the *isolated* chromophores (see eq 7).[22,24] This is corroborated by deuterium-labeling studies,[22] which demonstrate that **21** is formed via an olefin-derived exocyclic carbene and **23** and **24** are the products of two- and one-bond cleavage of the cyclopropane ring, respectively. Unfortunately, **22** was overlooked in the original study, so it is not known whether the formation of this product is related to **21** or whether it occurs by internal cycloaddition. Compound **25** is the product of formal di-π-methane rearrangement of **24** and *not* that corresponding to the intermediacy of a cyclohexanylidene-type carbene or to [1,3]-H migration. The product distribution from **14** is strongly wavelength-dependent, as the data in Table II show.



(7)

Even though the photochemistry of **14** is apparently that of the isolated chromophores and the UV absorption spectrum of this compound bears a striking similarity to that of cyclohexene, the product distribution indicates that there is substantial interaction between the olefin and cyclopropane chromophores in the excited state(s) of **14**. Thus, products arising from reaction of the cyclopropyl group account for over 80% of the reaction mixture from 185-nm photolysis, even though the extinction coefficients of the isolated chromophores are such that the C=C group would absorb at least 90% of the incident light if no chromophoric coupling were present.

What is the reason for the pronounced difference in the photobehavior of **14** compared to that of **12** and **13**? A close analogy can be made to norbornadiene and 1,4-cyclohexadiene. The dissimilarities in the photochemistry of these compounds have been explained in terms of the degree of interaction between the double bonds in the excited state.[28,29] These interactions are

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(23) Srinivasan, R.; Ors, J. A.; Brown, K. H.; Baum, T. H.; White, L. S.; Rossi, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 5297.

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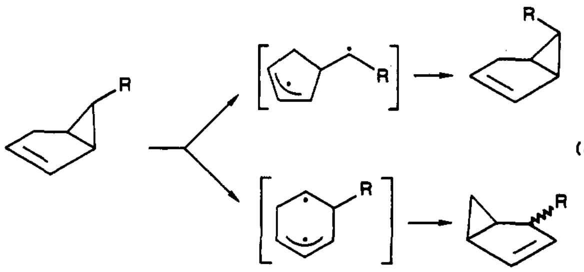
strongly dependent upon the dihedral angle at the carbons linking the two chromophores. The greater flexibility of 14 when compared to the rigid systems may also contribute to the observed differences in its photochemistry.

The UV absorption spectra and photoreactivity of the exo and endo isomers of 12 and 13 encourage the speculation that the wavelength dependence of the product mixture obtained from 14 may relate to the presence of two conformers in solution, if their absorption spectra differ to some degree. According to Table II, 3-methylenebicyclo[3.1.0]hexane (21) and tricyclo[4.1.0.0^{3,5}]heptane (22) can be identified as short-wavelength products, 1,3,6-heptatriene (23) and 2-norcarene (25) are long-wavelength products, and 1,4-cycloheptadiene (24) is both a long- and short-wavelength product. Thus, 21, 22, and 24 can be assigned as products of *endo*-14, and 23–25 as products of the exo conformer. If 25 is truly the product of an electronically excited state of 24, then the result that it must arise only from the endo conformer of 14 relates well to the behavior of 12.

The Photochemistry of Vinylcyclopropanes

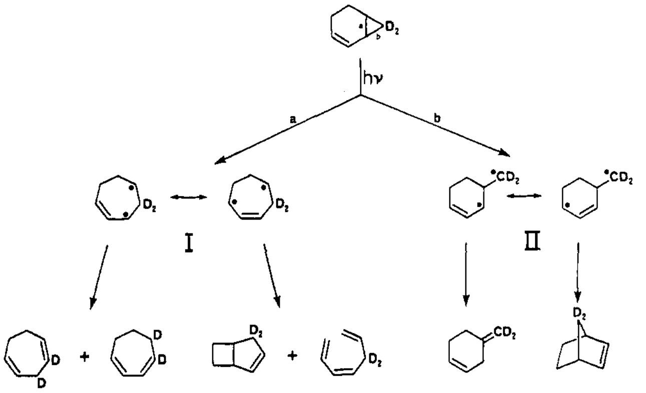
The limited number of alkyl-substituted vinylcyclopropanes that have been previously investigated[30–35] indicates that (in common with phenyl-substituted systems[36]) cyclopropane cis–trans isomerization and vinylcyclopropane rearrangement[37] are the dominant features of both direct and triplet-sensitized photolyses of these systems (see eq 8). In bicyclic systems, there is ample proof that cis–trans isomerization proceeds predominantly via cleavage and reclosure of the external cyclopropane bond, i.e., the one conjugated with, and which therefore overlaps best with the vinyl π-system.[34–36]



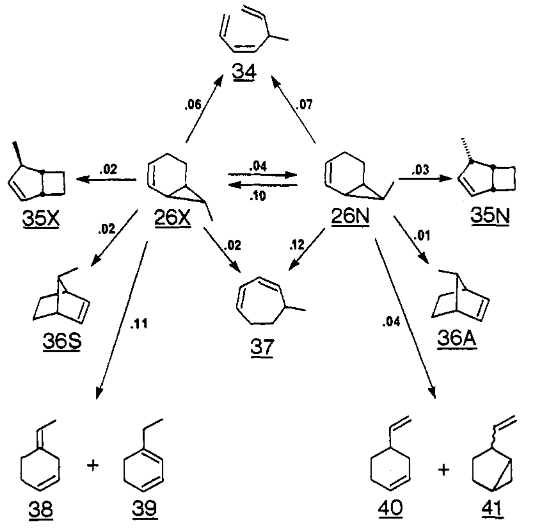
(8)

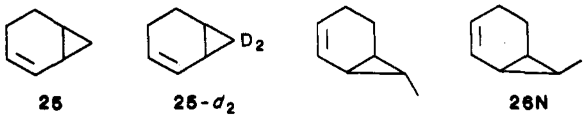
The UV absorption spectrum of 2-norcarene (25) exhibits a maximum at ~200 nm, revealing a lowest excited singlet state that is 15–20 kcal/mol lower in energy than those of either cyclohexene or alkylcyclopropanes. The photochemistry of 25 and the 7-methylated (26) derivatives is to a limited extent analogous to that typical of cyclopropanes,[3] with several additional features that are unique to the bicyclo[4.1.0]hept-2-ene ring system.[38,39]

Scheme II.
The Photochemistry of 2-Norcarene-d_2 (25-d_2)



Scheme III.
Products and Quantum Yields from Direct Photolysis of 26 (214 nm, Pentane Solution)





25 **25-d_2** **26X** **26N**

The photochemistry of 25 is most aptly demonstrated by the behavior of the deuteriated derivative (25-d_2), summarized in Scheme II. The variety of products formed have been grouped according to the biradical intermediates resulting from cleavage of the internal (C_1–C_6) and external (C_1–C_7) cyclopropane bonds, although these should not be considered as *discrete* intermediates in the excited singlet state photochemistry of 25. The photochemistry of *endo*- and *exo*-26 (**26N** and **26X**, respectively) affords information on the stereochemistry involved in the formation of some of the products and is summarized in Scheme III. The study of the latter compounds has also demonstrated the importance of cyclopropane cis–trans isomerization in this system and that the excited singlet state behavior of 25 can be altered quite dramatically by the presence of an endo substituent.

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(37) This is a well-known thermal reaction. See: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981; p 81.

(38) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 514.

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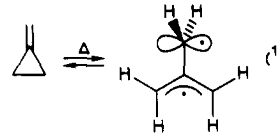
In contrast to the behavior typical of alkylcyclopropanes, two-bond cleavage, which would lead in this case to a vinylcarbene intermediate, does not occur to a significant extent in the photolyses of **25** and **26**.[40] This is indicated by the regiochemistry associated with the formation of **27**-d_2 and **34**, as well as the absence of cyclopropene products[41] in the photolysates (limit of detection: <2%). Compounds **27** and **34** arise from formal $2\pi + 2\sigma + 2w$ electrocyclic ring opening of the 2-norcarene skeleton (or β-scission of biradical I in Scheme II). This reaction is the homologue of the photochemical 1,3-cyclohexadiene → 1,3,5-hexatriene interconversion.[42] Products of [1,3]-alkyl migrations (viz. **28** and **29** in Scheme II) are formed in lower yields, but the behavior of **26** indicates that both these processes occur stereospecifically.

The product distribution obtained from photolysis of **26X** is similar to that from the parent compound **25**, and cis–trans isomerization is only of minor importance. Endo methyl substitution results in a dramatic alteration of the photochemical behavior. For example, **26N** undergoes cyclopropane cis–trans isomerization with high efficiency, presumably to relieve unfavorable steric interactions. Furthermore, the formation of compounds **37**, **40**, and **41** from **26N** can all be attributed to the specific geometry of the 7-methyl substituent with respect to the 2-norcarene C=C bond. The former product can arise from [1,2]- or antara, supra [1,5]-methyl migration coupled with disrotatory cyclopropane ring opening. Compound **37** is formed in only minor amounts from photolysis of the exo isomer. The latter two products (**40** and **41**) presumably arise via hydrogen migrations from the methyl group to C_1 and C_2, respectively.

The Photochemistry of Alkylidenecyclopropanes

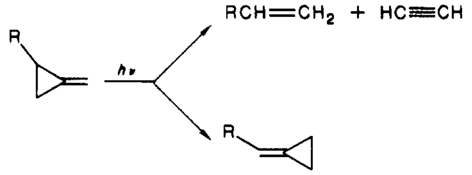
The interconversions between methylenecyclopropane (MCP) and the trimethylenemethane biradical (TMM) have been the subject of theoretical[43,44] and numerous experimental[45-50] investigations. Thermal interconversions have received the most attention,[45,48] and while several studies of the photochemistry of MCP's have been reported,[47-49] they offer little insight into the excited state MCP–TMM transformations.

The thermal interconversions have been explained as involving the orthogonal $^1B_1$ state of TMM which has been calculated to be 17.6 kcal/mol above the triplet ($^3A_2'$) ground state:[44]



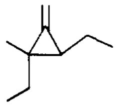
In substituted systems, thermal isomerization occurs with normally high regioselectivity and the radical-stabilizing abilities of the substituents determine which of the two possible ring carbons undergoes migration.[46]

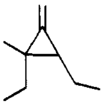
Direct photolysis studies of alkylidenecyclopropanes in solution have mostly concentrated on phenylated systems.[47] Photolysis results in a competition between fragmentation and MCP rearrangement (eq 9), the latter presumably involving a TMM intermediate(s). The fragmentation reaction has been shown to involve discrete vinylidene intermediates (as opposed to cyclopropylmethyl carbenes formed by [1,2]-H or alkyl migration) by trapping with olefins.[48] Direct UV photolysis of methylenecyclopropane itself in a low-temperature matrix reportedly does not yield the ESR spectrum of the ground state ($^3A_2'$) of TMM, although the spectrum can be generated under these conditions by irradiation of MCP with fast electrons[49] or by photolysis of 3-methylenecyclobutanone or 4-methylenepyrazoline.[51]



(9)

A study of the photochemistry of a simple monocyclic MCP system (**42T** and **42C**), suitably substituted with stereochemical labels, was undertaken to determine the course of the photochemical MCP isomerization and the stereochemistry of the fragmentation reaction.[52] This has been coupled with theoretical calculations on the electronic excited states of MCP and TMM, carried out using the INDO/S-CI method.[29,52]


42T


42C

Photolysis (185 nm) of **42T** and **42C** in pentane solution leads to fragmentation, cis–trans isomerization, and structural isomerization (eq 10 and 11). Fragmentation occurs stereospecifically in each case, which may be suggestive of a concerted, simultaneous two-bond rupture. This fragmentation is almost certainly not related to that of simple cyclopropane derivatives, which occurs with only partial stereoselectivity and for which the observed products are most consistent with stepwise two-bond rupture involving prior cleavage of the weakest of the three cyclopropane C–C bonds (vide supra). The analogous process in MCP would involve stepwise cleavage of the two C–C side bonds, which are obviously the stronger of the cyclopropane bonds.

Cis–trans isomerization and structural isomerization presumably occur through the intermediacy of TMM's. The most striking features of the observed product

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(40) Vinylcarbene-derived products have been isolated from the photolysis of other vinylcyclopropanes, however. See ref 3a, p 231 and references cited therein.

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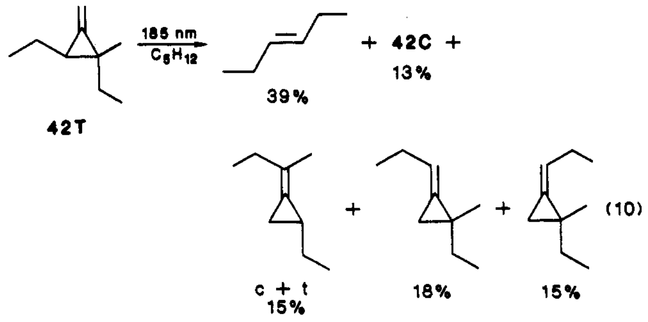
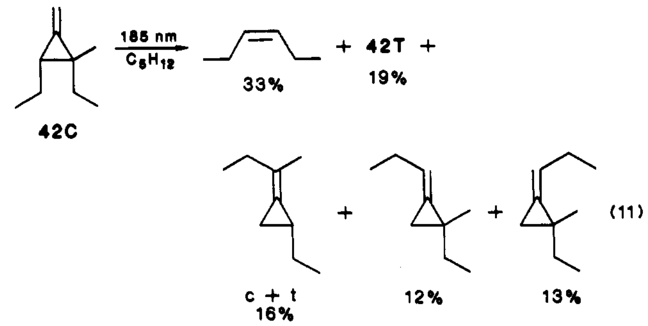
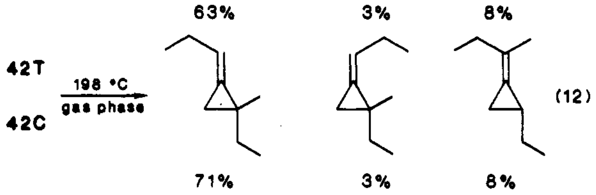


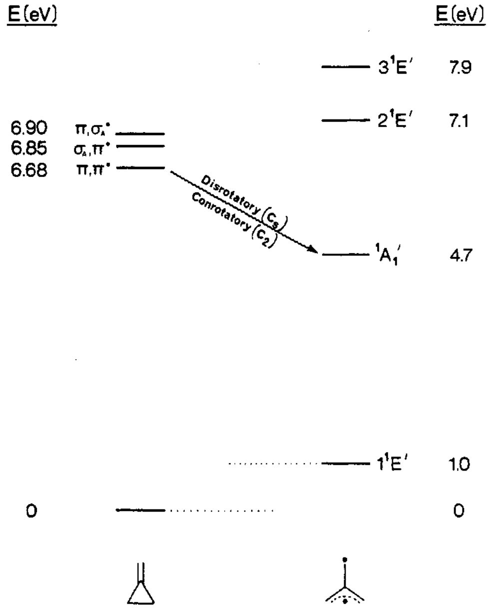


mixtures are the almost complete lack of regioselectivity in the formation of the various structural isomers and the virtually identical distribution of MCP isomers that are formed from **42C** and **42T**.[53] The photolysis results can be compared to the product mixtures obtained from thermolysis of the two isomers (eq 12). Clearly, photolysis of MCP involves excited states of TMM that are not accessible in the thermal reaction. Our results rule out the possibility of populating the $^1B_1$ state of TMM directly from MCP excited states, while those of Takeda and co-workers[49] demonstrate that the $^3A_2'$ ground state of TMM is also not involved. The near-statistical formation of all possible structural isomers of **42** upon photolysis strongly suggests the intervention of planar TMM excited states.



The calculated energy levels for MCP and planar TMM (D_{3h} symmetry) in the 6.7-eV region are shown in Scheme IV. The highest energy ($\pi,\sigma_A{}^*$) transition in MCP has a relatively low oscillator strength, and there is strong antibonding character between all three of the cyclopropane carbons and in the C–H bonds of the π-moiety. In the second highest energy (σ_A,π^*) excited state, both the C–C side bonds and the C–H bonds of the π-moiety are weakened, although this transition is calculated to have zero oscillator strength. Population of either of these states is predicted to result in fragmentation. The electronic characters of both the π, $\sigma_A{}^*$ and σ_A, π^* states are consistent with either the simultaneous or stepwise two-bond rupture mechanisms for fragmentation. However, the low calculated oscillator strengths of the two transitions, the expectation that reclosure of the initially formed 1,3-biradical should be at least as efficient as further fragmentation, the high degree of stereospecificity observed, and the relatively high efficiency of the reaction all argue convincingly for the concerted, simultaneous two-bond rupture mechanism, leading to olefin and vinylidene.

Scheme IV.
Calculated (INDO/S-CI) Energy Levels for the Excited States of Methylenecyclopropane and Trimethylenemethane



The lowest energy (π,π^*) transition is calculated to be the most intense absorption, and this is presumably the one that leads to MCP rearrangement. The INDO/S-CI calculations show that this excited state of MCP correlates directly with the planar $2^1E'$ and $3^1E'$ excited states of TMM via con- or disrotatory ring opening. (The calculations are not sufficiently detailed to allow a distinction between the two pathways.) However, both these states appear to be somewhat higher in energy than the MCP π,π^* state, so that internal conversion to the lower $^1A_1'$ excited state of TMM upon ring opening must be invoked.[54] Random closure to all possible MCP isomers then occurs from the planar $^1A_1'$ state or from the $1^1E'$ state after internal conversion. Alternatively, internal conversion to the planar $^1A_1$ and $^1B_2$ states (these comprise the $1^1E'$ state in D_{3h} symmetry) could lead to four distinct planar TMM intermediates which could then close to yield six distinct products.

Concluding Remarks

Far-UV techniques make it possible to delineate the *intrinsic* excited state reactivity of simple chromophores by circumventing the necessity of attaching conjugating substituents that may drastically alter the excited state manifold of the system. Perhaps the biggest advantage of the technique is the ability to directly study the photochemistry of molecules for which sophisticated theoretical calculations can be conveniently carried out.

It may be surprising that irradiation with photons of such high energy more often than not results in fairly clean mixtures of only one or two products. This offers

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(53) Product yields were determined from concentration vs. time plots, extrapolated to zero conversion.

(54) Actually, considering the qualitative nature of the calculations, the $2^1E'$ state may in fact be energetically accessible from the π,π^* state of MCP.

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simple synthetic routes to strained hydrocarbons that may be difficult to prepare by conventional methods.[55] As is illustrated by some of the examples outlined above though, very complex product mixtures can be obtained, particularly with bichromophoric systems. What is remarkable, however, is the high degree of regio- and stereospecificity associated with many of the phototransformations.

In addition to the academic interest that these reactions provide, the advent of the excimer laser has introduced useful technological and medical applications[56] that involve interactions of far-UV photons with organic solids.[57] As a result, it can be expected that this field will develop rapidly in coming years.

We thank our co-workers, including T. Baum, J. A. Ors, and A. R. Rossi, whose ideas and experimental skill contributed a great deal toward the work described here.

Registry No. Cyclopropane, 75-19-4; allylcyclopropane, 4663-23-4; vinylcyclopropane, 693-86-7.

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Chemical Modification and Selective Fragmentation of Polysaccharides

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The fact that polysaccharides display an enormous variety of structures[1] may be obscured by the very abundance of starch and cellulose as chemically monotonous homopolysaccharides. In fact, the vast majority of polysaccharides are heteroglycans with two or more constituent sugars, frequently in several linkage types. The complete assignment of covalent structures still presents a major challenge to the organic chemist since it involves not only sequencing, as for proteins and nucleic acids, but also the determination of ring size, linkage type, and anomeric configuration for each of the monosaccharide units. Furthermore, repetitive features, which are always present, may be masked by departures from regularity. Some of these departures from strict regularity are of major importance since they provide the basis for the expression of desirable physical properties,[2] e.g., in gel formation, or give rise to the precise structural domains involved in specific biological activity.

Three broad classes of polysaccharides illustrate different balances between structural regularity and deviations from regularity. Many bacterial polysaccharides[3] (Figure 1, top), of the capsular type and in the *O*-antigenic regions of lipopolysaccharides, show a high degree of structural regularity resulting from the biosynthetic assembly on a lipid carrier of oligosaccharide repeating units of some 3–8 residues which are then polymerized. The presence of a regular repeating unit is a simplifying factor in structure determination. Consequently, with the use of two-dimensional NMR techniques and fast atom bombardment mass spectrometry, complete structures can be worked out with a minimum of chemical degradations.[4,5] Where degradations are required, specific bacteriophage enzymes are especially useful since they yield a single oligosaccharide closely related to the natural repeating unit.[6]

In contrast to most polysaccharides from bacteria, many of those from mammalian and plant sources show departures from simple regularity of structure. The mammalian glycosaminoglycans[7] (Figure 1, middle) are synthesized initially with rather simple repeating disaccharide structures of the AB type but then undergo postpolymerization changes in which each type of unit may be modified. The blood anticoagulant heparin provides an excellent example of one such polysaccharide in which very precise alterations to certain sequences of sugar residues produce the specific pentasaccharide region which binds to antithrombin III.[7]

Plant polysaccharides,[8] in addition to being essentially passive structural components of cell walls, may also be the source of biologically active fragments which are liberated by the action of specific enzymes.[9]

At first sight many plant glycans appear to be of a simple type in possessing repetitive interior chains, which form the basis for their structural classification

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