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Techniques and Applications of Far-UV Photochemistry in Solution. The Photochemistry of the C_3H_4 and C_4H_6 Hydrocarbons

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I. Introduction

Far-UV light sources have been employed in studies of the photochemistry of small molecules in the gas phase for many years, but their use in solution-phase studies has become common only relatively recently. There are a number of special considerations which come into play in studies of this type, but in spite of this, solution-phase far-UV photochemistry is now a well-established field and the special techniques involved are becoming routine. Far-UV techniques make it possible to study the photochemistry of molecules which contain simple chromophores, unencumbered with conjugating substituents that delocalize the lowest excited state and lower its energy. In short, they make it possible to photolyze systems which absorb only at wavelengths less than ca. 200 nm—the practical cutoff wavelength for "conventional" photochemical studies with medium-pressure mercury lamps and ordinary quartz reaction vessels.

The use of far-UV techniques for the study of photochemical processes in condensed phases was pioneered independently by N. C. Yang and C. von Sonntag in the late 1960s, in studies of the photochemistry of aliphatic alcohols and ethers in the neat liquid phase.[1] The extension to studies of small molecule photochemistry in dilute solution (principally alkenes and cyclopropanes) was brought about later by Y. Inoue[2] and R. Srinivasan,[3] who demonstrated (among

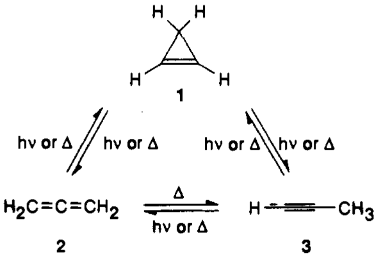
William J. Leigh was raised in Chatham, Ontario, and attended the University of Western Ontario, where he received an Honours B.Sc. in 1976 and the Ph.D. degree in 1981 under D. R. Arnold's supervision. He underwent postdoctoral training with R. Srinivasan at the IBM Research Center in Yorktown Heights, NY, and later with J. C. Scaiano at the National Research Council of Canada in Ottawa. He accepted an appointment with McMaster University in 1983 as Assistant Professor and NSERC University Research Fellow and was promoted to the rank of Professor in 1992. In addition to his ongoing interest in the far-UV photochemistry of small molecules in solution, Leigh's current research interests include the study of reactive intermediates in organosilicon chemistry using nanosecond laser flash photolysis techniques and the effects of ordered media such as liquid crystals and cyclodextrins on thermal and photochemical reactions.

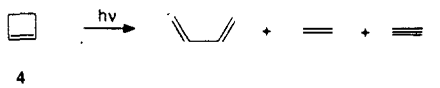
other things) that UV light of energy high enough to break *any* bond in an organic molecule does in fact usually result in fairly clean and selective photochemistry. In addition to laying out the basic experimental requirements and establishing a reliable actinometer for use in experiments of this type,[4] they reported comprehensive investigations of the photochemistry of simple aliphatic alkenes and cyclopropanes[5,6]—studies which have provided invaluable comparisons with the photochemistry of more highly substituted analogs. This work was quickly extended to encompass more complex, bichromophore and mixed chromophore systems such as nonconjugated dienes, allyl- and vinylcyclopropanes, bis-cyclopropyl systems, and enol ethers. All of this work has been comprehensively reviewed, and the reader is directed elsewhere for descriptions of the photochemistry of these systems.[5,6]

Out of these studies emerged one of the most significant recent developments in the use of pulsed UV lasers—the ablative photodecomposition (APD) of polymeric materials, which was originally discovered using the ArF excimer line at 193 nm.[7] This technique is now used widely in technological and medical applications[8] and employs lasers of wavelengths in both the far- and mid-UV ranges (193, 248, and 308 nm).

The focus of the present review is on the use of solution-phase far-UV techniques to study the photochemistry of organic molecules which are distinguished by their particular theoretical importance. Indeed, the ability to study directly—under conditions of complete thermalization of the excited state—the photochemistry of molecules small enough to lend themselves to independent ab initio theoretical study at the highest levels of sophistication is arguably the most significant aspect of the contribution that solution-phase far-UV techniques can make to the field of organic photochemistry. In recent years, the excited-state behavior of several such systems has been studied in detail experimentally and theoretically. These are the C_3H_4 hydrocarbons [cyclopropene (**1**), allene (**2**), and propyne (**3**); Scheme I] and the cyclic members of the C_4H_6 hydrocarbon family [cyclobutene (**4**), bicyclobutane (**5**), and methylenecyclopropane (**6**)] (eqs 1–3).

Scheme I. The C_3H_4 Hydrocarbons





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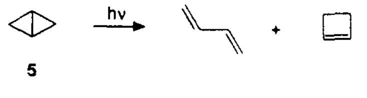

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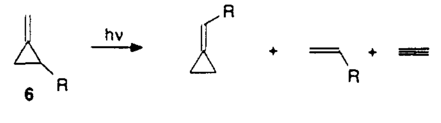


[3]

II. Far-UV Photochemistry in Solution: Techniques

A. Light Sources and Filters

Early studies in the area employed unfiltered low-pressure mercury lamps, whose main emission lines arise at 184.7 and 253.8 nm in an intensity ratio of about 1:7. These lamps are still the most economical sources of far-UV radiation for solution-phase studies and are particularly convenient for applications where the substrate and its photoproducts are transparent at 254 nm. For quantitative and semipreparative (100–300 mg) work, small U-shaped lamps (10 or 20 W) are ideal,[9] although larger lamps (up to ca. 1 m in length and power 40 W) are available for larger scale preparative photolyses.[10]

The smaller lamps can be used in conjunction with an interference filter (at the sacrifice of most of the lamp's radiant energy) to reduce the intensity of the 254-nm component (to 1–2% of its normal value) in cases where it is absorbed by photoactive products.[11] Commercially available interference filters have lifetimes of about 200 h with a 10-W lamp. As an alternative, we have employed 3-mm-thick lithium fluoride windows (vacuum-UV grade) which have been irradiated with γ-rays from a ^{60}Co source.[12,13] The irradiated windows exhibit strong absorption centered at 249 nm (OD > 5 for 3-mm windows) with very little absorption at 185 nm.[13] The color centers giving rise to the 249-nm absorption degrade upon UV irradiation and must be monitored closely, but they can be regenerated repeatedly by resubjecting the window to ^{60}Co radiation. Unfortunately, the "stability" of these filters (toward UV bleaching of the 249-nm absorption) varies substantially from crystal to crystal. Good quality crystals can provide filters stable for dozens of hours of UV irradiation, but acquisition of "good quality" crystals is evidently a matter of providence. Filters made using seemingly identical windows obtained from the same supplier have showed very poor UV stability, and for this reason we have abandoned this approach to obtaining monochromatic light in the far-UV range.

Zinc and cadmium resonance lamps (16 W) provide monochromatic radiation at 214 and 228 nm,[14] respectively, with insignificant output at other wavelengths below ca. 275 nm.[15] These lamps are marketed as spectroscopic sources and are about the same size as the 10-W low-pressure mercury lamps. They can thus be used with the same apparatus (vide infra).

A somewhat more expensive source of monochromatic far-UV radiation is the ArF excimer laser, which should be operated at low power (<10–20 mJ) and with the beam unfocused in order to avoid potential problems from two-photon processes. Quantitative work should be carried out at low repetition rates (<0.5 Hz) and with vigorous stirring of the photolysate so as to avoid product photolysis with solutions of high absorbance at the exciting wavelength. For preparative scale photolyses, it is usually possible to operate at higher laser power and faster repetition rates.

A fairly recent development is that of the plasma discharge lamp (or "excimer lamp"),[16] which is derived from excimer laser technology. The lamps are constructed from Suprasil quartz and are filled with the

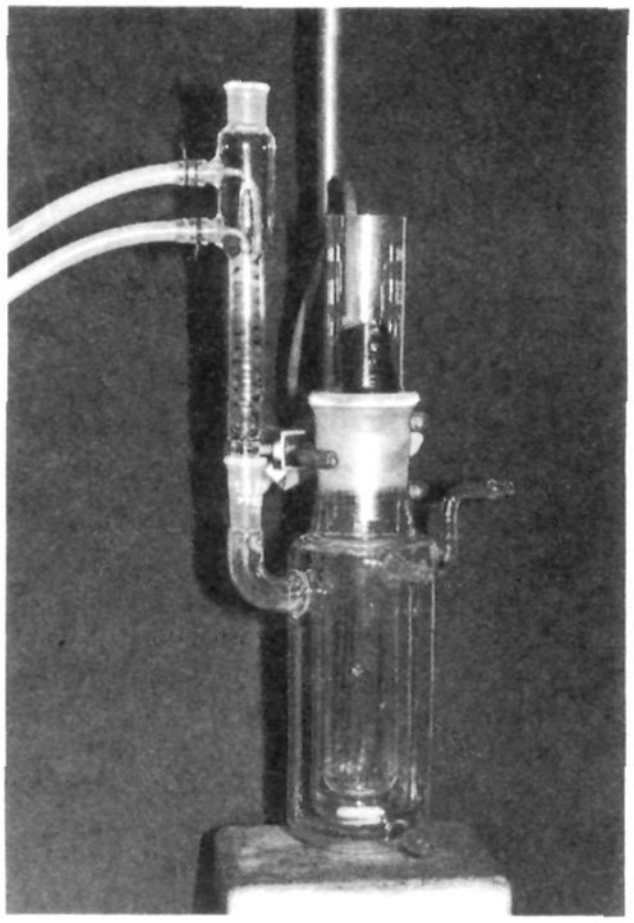


Figure 1. Immersion well apparatus incorporating a 10-W low-pressure mercury lamp, for semipreparative-scale far-UV photolyses in solution.

same gas mixtures as those employed in excimer lasers.[17] Initial developmental work on these lamps was carried out with the Xe_2 excimer, which emits at 172 nm,[16a] but has been extended to ArF (193 nm), KrBr (207 nm), KrCl (222 nm), and KrF (248 nm), XeCl (308 nm), and a number of other gas mixtures emitting at various wavelengths throughout the UV range.[16b,c] They provide reasonably intense, steady-state monochromatic light (of 2–4-nm bandwidth) and may hold great promise for preparative far-UV work, especially as a relatively inexpensive alternative to the excimer laser.

B. Apparatus, Solvents, and Procedures

Semipreparative scale photolyses with the 10- or 20-W Hg and 16-W Zn or Cd lamps can be carried out in a simple immersion well setup constructed largely from Pyrex with a Suprasil quartz inner sleeve. The lamp is cooled with nitrogen gas (water absorbs slightly at 185 nm)[18] and the solution is water cooled by an external jacket (the inner Suprasil sleeve is in direct contact with the photolysis solution). The jacketed Pyrex vessel has a nitrogen inlet for deoxygenation and is dimensioned so that a magnetic stirrer can provide solution agitation. An apparatus of this type is shown in Figure 1.

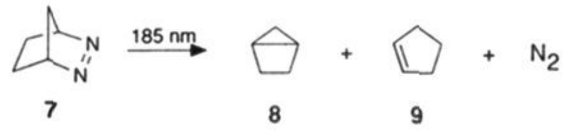
For quantitative work with a lamp or with the laser, we employ standard 2-cm cylindrical UV cells which are either clamped in front of the laser beam or mounted in a side port of a metal cylinder housing the Hg, Zn, or Cd lamp. In the latter case, an interference filter can be inserted in the side port along with the sample cell if desired. Larger cells with Suprasil windows can be employed for semipreparative scale laser photolyses, using a magnetic stirrer or mechanical shaker to agitate the solution during photolysis.

The main disadvantage in far-UV work is the limited choice of solvents. With 185-nm irradiations, the possibilities are confined to spectroscopic or HPLC grade hydrocarbons (most commonly) and water,[19] but with 193-nm work, one can also use carefully purified acetonitrile. With the 214-nm light source, the list is extended to include methanol and other simple alcohols,[20] and with the 228-nm source, 1-alkenes.[21] In general, a solvent (impurity) absorbance of up to about 0.8 (1-cm pathlength) at the excitation wavelength is tolerable (and practically impossible to avoid with 185- or 193-nm photolyses), so long as the substrate concentration is high enough to absorb most of the light.

In mechanistic studies where the primary photoproducts are strongly absorbing and photoactive, it is particularly important to minimize secondary photolysis effects. This can normally be accomplished by working with substrate solutions at least 0.02 M in concentration, and monitoring product formation as a function of photolysis time between 0.2% and 3–4% conversion. Secondary photolysis effects can be quantified by carrying out control experiments in which the substrate is photolyzed in the presence of low concentrations of an unrelated standard which exhibits similar absorption characteristics and photoreactivity as the primary products of interest, and monitoring for photolysis of the standard.[22] Depending on the substrate and its excited-state lifetime, effects of this type may be extremely difficult to detect when using a laser as the excitation source, even by carrying out the normal product yield vs laser intensity analysis. Often, the best evidence one can obtain for the absence of secondary photolysis effects in laser irradiations is to compare the results to those obtained with a lamp.

C. Actinometers

There are a limited number of actinometers available for far-UV studies. Although as far as we know, none have yet been accurately characterized at 193 nm,[12] the formation of hydrogen from photolysis of ethanol/water (the Farkas actinometer)[23] and the cis $\rightleftharpoons$ trans photoisomerization of *cis*-cyclooctene[4] have been quantified at 185 nm and are the most commonly used actinometers for far-UV work. In addition, Adam and Oppenlander have accurately measured the quantum yield of nitrogen extrusion from 2,3-diazabicyclo[2.2.1]hept-2-ene (7; $\phi_{N_2} = 0.95$) at 185 nm.[24] None of these actinometers absorb at 254 nm; hence the light source need not be filtered. The uranyl oxalate actinometer has been characterized at 214 and 228 nm,[20c,25] but since both the Zn and Cd lamps have weak output at other wavelengths above ca. 275 nm, an interference filter is required for actinometry at these wavelengths.

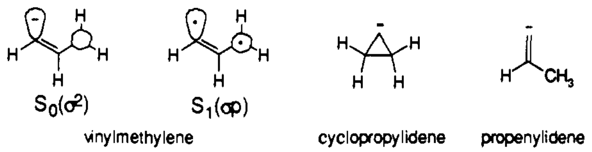


7 8 9

(4)

III. The Photochemistry of Cyclopropenes, Allenes, and Alkynes: Interconversions of the C_3H_4 Hydrocarbons

The properties of the ground- and excited-state potential energy surfaces which link the C_3H_4 hydrocarbons (Scheme I) have been of considerable theoretical and experimental interest for many years.[26] Early theoretical[27] and experimental[26] studies concentrated on cyclopropene/vinylmethylene interconversions, particularly with phenylated systems. Recent studies have attempted to more fully define the relationships between the three stable C_3H_4 isomers (**1**–**3**) and the three divalent C_3H_4 species—vinylmethylene, cyclopropylidene, and propenylidene.[21,28-34]



A. Background

It has long been known that thermolysis or direct photolysis of cyclopropenes results in the formation of products consistent with initial ring opening to yield vinylcarbene intermediates.[26,35] The product distributions obtained from the two modes of activation generally differ substantially, because thermolytic ring opening yields the S_0 state (σ^2) while photochemical ring opening is thought to involve the S_1 state (σ_p; planar vinyl diradical) of vinylmethylene. In addition to vinylcarbene formation from the first excited singlet state, other decay pathways (such as side-chain cleavage leading to free radicals) can intervene if the system bears appropriate substituents.[36] The lowest excited triplet state of cyclopropene is unreactive toward ring opening and generally undergoes dimerization;[37] this has been proposed to be due to a substantial activation energy for the former process on the basis of theoretical calculations.[27,29]

Once formed, the vinylcarbene reacts by hydrogen migration (to yield conjugated dienes, allenes, and/or alkynes), intramolecular insertion, or closure to regenerate the cyclopropene.[26] Rearrangement to allenes and/or acetylenes is effectively blocked in 1,2-disubstituted cyclopropenes. In asymmetrically substituted phenylated systems, it is quite commonly observed that photochemical ring opening proceeds to yield the *less* stable of the two possible vinylcarbene intermediates.[26,30,35,37b] Thermolysis, on the other hand, tends to favor formation of the more stable vinylcarbene.[26] This has been explained in terms of Michl's "funnel" theory of excited-state to ground-state conversions;[38] the less stable carbene is formed photochemically because its ground- (or excited-) state surface comes in closer proximity to the cyclopropene's excited-state potential energy surface, allowing for more efficient internal conversion between states.[26]

In the case of alkylcyclopropenes which are mono- or unsubstituted at the cyclopropene C=C bond, thermolysis generally yields the isomeric alkyne as the major product, with minor amounts of the allene and conjugated dienes.[26,39] Similarly, thermolysis of allenes yields alkynes predominantly. For the parent hydrocarbons, the experimentally determined activation energies for the various interconversions are: cyclopropene → allene, 43.4 kcal/mol; cyclopropene → propyne, 37.5 kcal/mol; allene → propyne, 60.5 kcal/mol.[39]

B. Theory

Yoshimine and co-workers have reported extensive MCSCF (4-31G) ab initio calculations of the thermal interconversion pathways.[31] Figure 2 summarizes the results of their calculations for pathways involving vinylmethylene (Figure 2B) and for those involving cyclopropylidene and propenylidene (Figure 2C).[31c,d] Figure 2A shows the experimental activation energies for interconversion of the three stable isomers.[39] The calculations suggest that cyclopropene (1) and allene (2) interconvert via vinylmethylene, while the lower energy pathway linking 1 and propyne (3) involves propenylidene intermediates. The calculated activation energies for isomerization of 1–3 via these two pathways are in reasonable agreement with the experimentally determined values (vide supra).

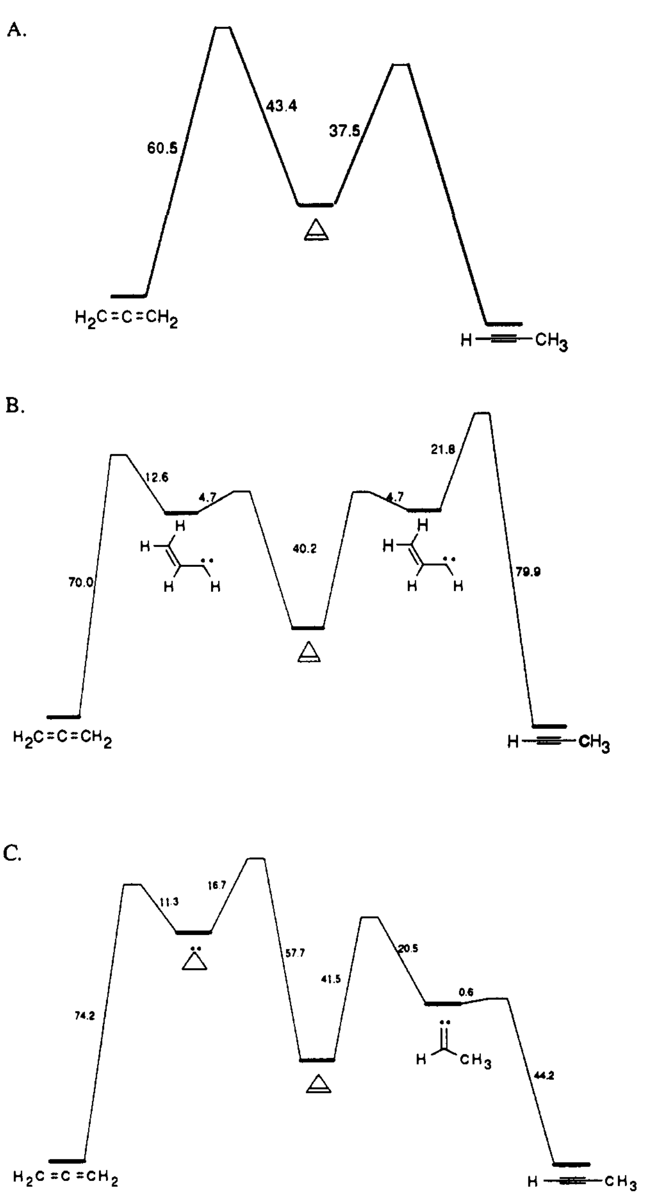


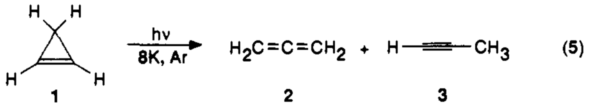
Figure 2. The ground-state C_3H_4 surface (experimental and calculated[28c,d]): (A) experimental activation energies for thermal interconversions of **1**–**3**; (B) interconversion of **1**–**3** via vinylmethylene; (C) interconversions of **1**/**2** and **1**/**3** via cyclopropylidene and propenylidene, respectively.

Sevin and Arnaud-Danon have reported ab initio SCF-CI calculations (STO-3G) of the ground- and excited-state behavior of cyclopropene with respect to vinylmethylene formation, C–H bond homolysis, and two-bond fragmentation to yield methylene and acetylene.[29] The formation of planar σ^2 vinylmethylene from cyclopropene on the ground-state surface occurs in stages.[29,31] The C_1–C_3 bond lengthens and then rotation about C_2–C_3 occurs; the transition state resembles the planar vinylmethylene diradical with the CH_2 group slightly twisted out of planarity.[31] In contrast, the lowest energy pathway for formation of planar σp vinylmethylene from the first excited singlet state of cyclopropene involves C_1–C_3 bond lengthening occurring in concert with C_2–C_3 bond rotation.[29]

Klett and Johnson have carried out ab initio calculations, at a similar level of theory, to probe the formation of propyne, cyclopropene, and vinylmethylene by in-plane [1,2]-hydrogen migration in the first excited singlet state of allene.[30] The calculations reveal two excited state minima with structures similar to the bisected vinyl diradical form of vinylmethylene; one which could lead to cyclopropene and one which could lead to propyne (both could yield planar vinylmethylene by bond rotation).

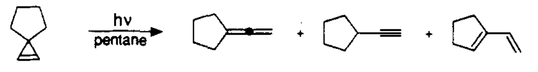
C. Photochemistry of Alkylcyclopropenes and Allenes

Photolysis of cyclopropene itself in an argon matrix at 8 K (eq 5) yields allene (**2**) and propyne (**3**),[40] although the relative yields of the two products have never been reported. Thermolysis of **1** at 190–240 °C yields **2** and **3** in yields of 1–2% and ca. 98%, respectively.[39] More recent reports of the photochemistry of alkyl-substituted cyclopropenes in solution have led to a better definition of the photobehavior of the system and how this compares to the ground-state chemistry.



1 2 3 (5)

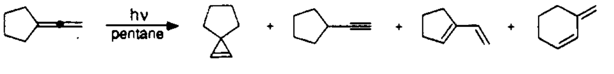
Photolysis of spiro[2.4]hept-1-ene (**10**) in pentane solution with an unfiltered low-pressure mercury lamp results in rearrangement to the isomeric allene **11**, alkyne **12**, and diene **13** with quantum yields of 0.11, 0.093, and 0.029, respectively (eq 6).[32] This should be compared to the results of thermolysis of **10** at 225 °C, which yields the alkyne **12** in 75% yield along with minor amounts of **13**. Allene **11** was not detected as a product in the thermolysis, even though it was shown to be thermally stable under the reaction conditions employed. Comparison of the thermolysis and photolysis results led the authors to suggest that ring opening of excited cyclopropene initially produces vinylcarbene in the S_1 (σp) state; decay of this species then produces mainly the product (**11**) corresponding to the *least favorable* thermal rearrangement pathway, which is thought to involve the S_0 (σ^2) state of the vinylcarbene.



10 11 12 13 (6)

ϕ = 0.11 ϕ = 0.093 ϕ = 0.029

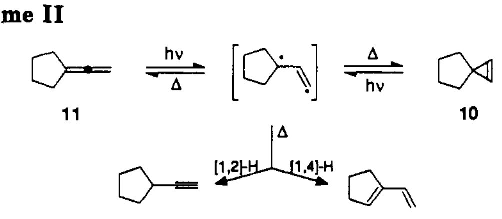
Photolysis (185 nm) of the exocyclic allene **11** yields the product distribution shown in eq 7.[33] Products **10**, **12**, and **13** were all suggested to arise from the σp vinylcarbene derived from [1,2]-H migration in the excited singlet state of **11** (Scheme II). Interestingly, diene **14** derives from the vinylcarbene resulting from [1,2]-alkyl migration (i.e., ring expansion). The formation of this product is enhanced by ring strain in the starting allene; thus, the analogous diene is the major vinylcarbene-derived product of photolysis of vinylidenecyclobutane (**15**), but is not formed in detectable amounts from photolysis of vinylidenecyclohexane (**16**).[33] The distributions of vinylcarbene-derived products from photolysis of these two exocyclic allenes are otherwise similar to that of **11**, but photolysis of **15** also yields appreciable amounts of 1,2,3-butatriene and ethylene by formal 2 + 2 cycloreversion.



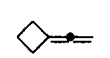
11 10 12 13 14 (7)

32% 18% 4.8% 4.9%

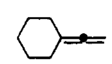
Scheme II



11 10 12 13

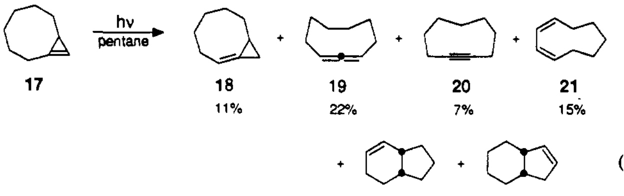


15



16

Direct photolysis of the bicyclic cyclopropene **17** in solution with broadband light of λ > 220 nm yields the complex mixture of products (**18–23**) shown in eq 8.[34]



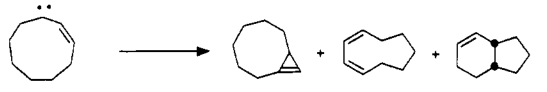
17 18 19 20 21

11% 22% 7% 15%

22 23 (8)

15% 18%

Photolysis of allene **19** under similar conditions yields **17** as the major product (94%), along with small amounts of alkyne **20** (3%) and a tricyclic hydrocarbon (3%) which was attributed to the formation of minor amounts of a cyclopropylidene intermediate. Independent generation of the two possible vinylcarbene intermediates **24** and **25** by photolysis of the corresponding tosylhydrazone salts demonstrated that **21** and **22** arise from **24** while **18** and **19** are due to competing formation of exocyclic vinylcarbene **25** (eqs 9 and 10). It was suggested that alkyne **20**, formed in the photolyses of both **17** and **19** but not from vinylcarbenes **24** and **25**, results from internal conversion to the ground-state surface at a bisected vinyl



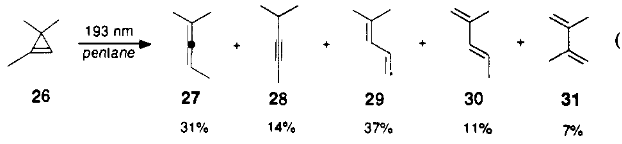
24 17 21 22 (9)

25 17 18 19 (10)

diradical geometry which is accessible from the S_1 states of both the allene and the cyclopropene.

The main pathway for excited-state decay in alkyl-substituted allenes is π-bond rotation. This was shown to be the case by monitoring photoracemization in an optically active sample of **19**; the ratio of photoracemization to isomerization was found to be about 70.[34]

In order to determine the preferred mode of photochemical bond cleavage (i.e. less vs more highly substituted) in simple alkylcyclopropenes, Leigh and Fahie studied the photochemistry of the simple monocyclic derivatives **26** and **32** in pentane, methanol, and 1-hexene solution using 185–228-nm light.[21] The products formed from these photolyses are summarized in eqs 11 and 12. Since only diene **31** is derivable from the vinylcarbene (**40**) formed by cleavage of the less substituted cyclopropene single bond in **26** (eq 13), they concluded that 70–90% of the observed products result from the more highly substituted of the two possible vinylcarbene intermediates formed from **26** (and **32** as well). Similar selectivities are observed in the thermolysis of the two compounds,[41] although the product distributions obtained are very different from those obtained with direct photochemical excitation. This contrasts the situation observed with most phenylated cyclopropene derivatives, which tends to yield the products of mainly the less stable of the two vinylcarbenes upon photolysis while thermolysis yields products of the more stable vinylcarbene.[26] It was suggested that this is because in the case of alkylcyclopropenes, there is a much smaller difference in the stability of the two vinylcarbenes and consequently less selection between the two as the cyclopropene excited-state funnels to the vinylcarbene σp state.[21]



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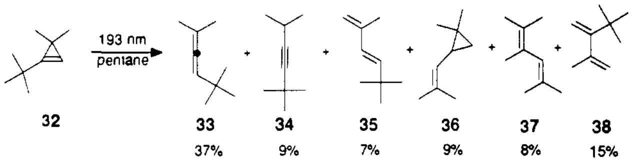

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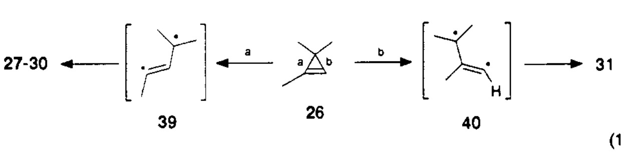
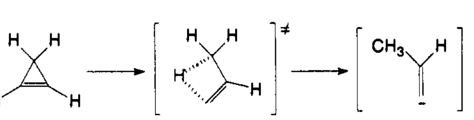
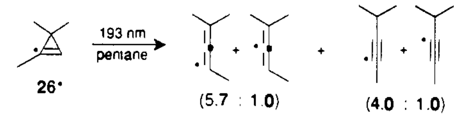


(13)

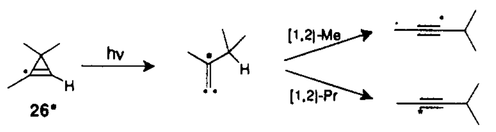
As mentioned earlier, the MCSCF calculations of Yoshimine and co-workers for the ground state C_3H_4 surface led to the suggestion that the lowest energy pathway for thermal formation of propyne from cyclopropene is via propenylidene rather than via vinylcarbene.[31c,d] Propenylidene formation was proposed to arise by a concerted pathway involving C_1–C_3 bond cleavage and concomitant H-migration from C_1 to C_3 (eq 14). In order to test for the possible involvement of alkenylidene intermediates in the photolysis of alkylcyclopropenes, Leigh and Fahie irradiated a ^{13}C-labeled derivative of **26**, and measured the distribution of the label in both the allene and alkyne products by ^{13}C NMR spectroscopy (eq 15),[21] using a technique developed to improve the precision associated with ^{13}C NMR integrations.[42] The distribution of the label in alkyne **28*** is such that at least 40% of this product must arise via the alkenylidene pathway, assuming equal migratory aptitudes for methyl and isopropyl groups in the alkenylidene intermediate (eq 16). It should be noted that the predominant isotopomer of the alkyne can also be formed via [1,2]-H migration in vinylcarbene **39**. The observation that ca. 15% of the label in allene **27** is located at C_3 led to the conclusion that a small amount of this product must arise from [1,2]-methyl migration in carbene **40**. Attempts to trap the suspected carbene intermediates by photolyzing **26** in methanol or 1-hexene solution failed, unfortunately. This study represents the first demonstration of the involvement of alkenylidene intermediates in cyclopropene photochemistry; it has yet to be investigated theoretically.



(14)



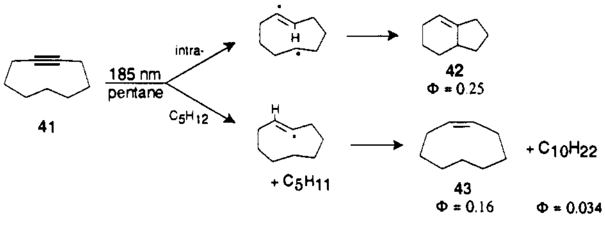
(15)



(16)

D. The Photochemistry of Alkynes

In general, it appears that alkyl-substituted alkynes do not rearrange to the corresponding allenes or cyclopropenes upon direct photolysis in solution. For example, photolysis (185 nm) of cyclononyne (**41**) in pentane solution yields products derived from competing inter- and intramolecular hydrogen abstraction by the triple bond (eq 17).[43] The photoreduction of acetylene to yield ethylene upon far-UV photolysis in hydrocarbon solution has also been documented.[44]

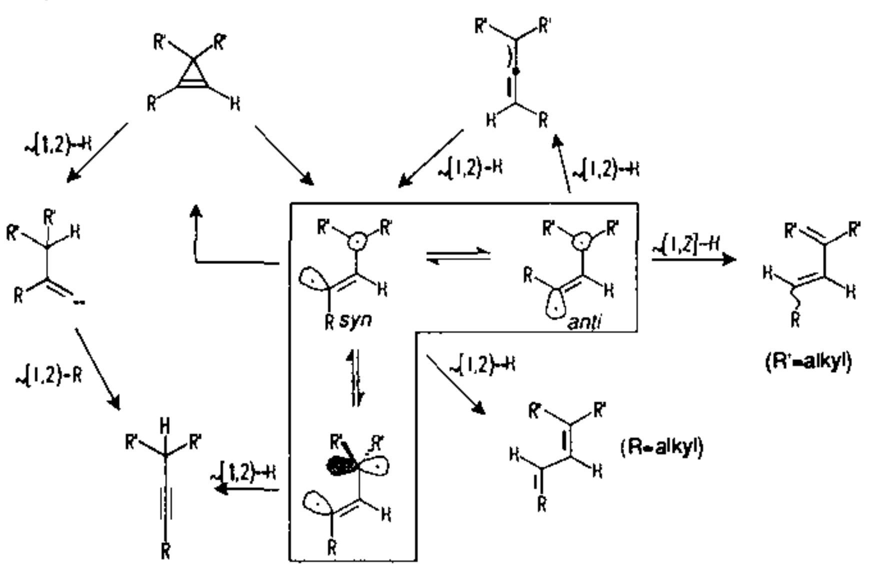


(17)

E. Summary

Scheme III summarizes the results of the theoretical and experimental investigations of the photochemistry of cyclopropenes and allenes discussed above, showing the role of vinylcarbene and alkenylidene intermediates in the C_3H_4 interconversions. The vinylcarbene is formed in the S_1 (σp) state from S_1 cyclopropene or allene, and decays to products by ring closure or

Scheme III. Interconversions of the C_3H_4 Hydrocarbons

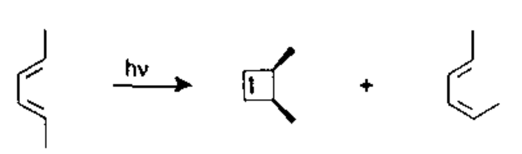


H-migration after internal conversion to the S_0 surface at the planar or bisected diradical geometries.

IV. Orbital Symmetry and the Photochemistry of Alkylcyclobutenes

A. Theory

The thermal and photochemical interconversions of cyclobutene and 1,3-butadiene play a central role in any textbook treatment of orbital symmetry selection rules and pericyclic reactions.[45–47] More rigorous theoretical treatments of the system have appeared over the years;[48–54] the ab initio results of Morihashi and Kikuchi[51b] are summarized in Figure 3. The highly selective conrotatory stereochemical course of the thermal interconversions is broadly exemplified[55] and has recently experienced renewed interest from the point of view of understanding "torquoselectivity" (the selection between the two possible conrotatory ring-opening pathways).[56] Similarly, there are literally dozens of examples that illustrate the preferred disrotatory stereochemistry of the photochemical ring closure of 1,3-butadiene derivatives to the corresponding cyclobutene.[57] For example, (*E,E*)-2,4-hexadiene (*E,E*-**44**) has been reported to yield *cis*-3,4-dimethylcyclobutene (*cis*-**45**) stereospecifically, albeit in low quantum yield, owing to competing cis ⇌ trans isomerization, upon direct photolysis in solution (eq 18).[57c]



(18)

E,E-44 cis-45 E,Z-44

On the basis of semiempirical valence bond calculations, van der Lugt and Oosterhoff proposed that the ring-closure reaction starts in the S_1 ($^1A''(1)$) state, crosses onto the $^1A'(2)$ potential energy surface, and proceeds to a well (the avoided crossing) from which internal conversion to the ground-state surface occurs.[48] The process cannot occur entirely on the $^1A''(1)$ surface because the cyclobutene excited singlet state is at least 50 kcal/mol higher in energy than that of the diene.[48,59] The geometry of the reacting molecule at the $^1A'(2)$ energy minimum is similar to that at the transition state for the thermal disrotatory process, so once the excited molecule has entered the ground-state surface, it can proceed to cyclobutene or revert to diene. The ab initio calculations of Grimbert et al. suggested that these general features are common to the ground- and excited-state energy surfaces for both the conrotatory and disrotatory ring-closure reactions. However, in the latter case the energy gap between the $^1A(2)$ and S_0 surfaces is substantially smaller so that the rate of $^1A(2) \rightarrow S_0$ internal conversion at the avoided crossing is greater for the disrotatory reaction pathway.[50] Morihashi and Kikuchi showed that the probability of the $^1A(2) \rightarrow S_0$ transition is 10^{12} times greater for the disrotatory pathway than for the conrotatory one.[51]

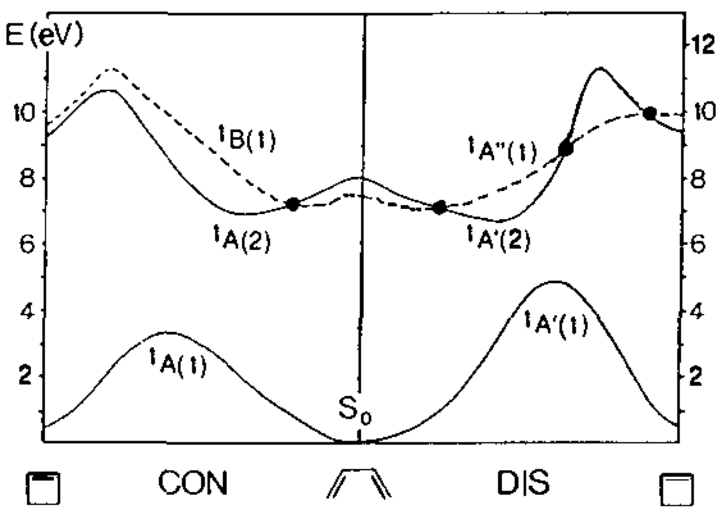


Figure 3. Calculated potential energy surfaces for ground and excited singlet state conrotatory and disrotatory interconversions of cyclobutene and 1,3-butadiene.[50,51b]

Each of the studies described above makes the classical assumption that orbital symmetry is conserved throughout the transformation; i.e., that C_s and C_2 symmetry is maintained in the disrotatory and conrotatory interconversions, respectively. More recent calculations have specified less stringent symmetry requirements for the excited-state reaction and explored the possibility that it proceeds asymmetrically. On the basis of semiempirical (MINDO/3) calculations, Pichko et al. have proposed that the photochemical ring closure of 1,3-butadiene proceeds by disrotatory closure of the *relaxed* butadiene singlet.[53] Thus, following Franck–Condon excitation, butadiene initially relaxes to the allylmethylene biradical geometry and then undergoes disrotatory terminal-group rotation (over an activation barrier of 8.4 kJ/mol) to reach the geometry at which internal conversion to the ground-state surface occurs.

Bernardi and Robb and their co-workers have reported MCSCF ab initio calculations which suggest that internal conversion to the ground-state surface during ring closure occurs via a conical intersection,[60] or a point where ground- and excited-state surfaces are degenerate. The calculated geometry of the molecule at the conical intersection for ring closure is described as a tetraradicaloid structure in which all π-bonds in the molecule are broken.[52]

B. The Photochemistry of Cyclobutene: Historical

Until recently,[12] the *only* example which demonstrates the stereochemistry of photochemical cyclobutene ring opening was that of Saltiel and Ng Lim, who reported the results of direct photolysis of the tricyclic, isomeric cyclobutene derivatives *cis*- and

Table I. Far-UV Photolysis of Alkylcyclobutenes in Hydrocarbon Solution[a]

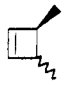
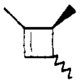
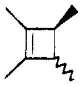
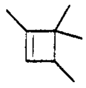
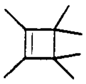
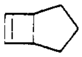
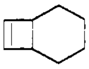
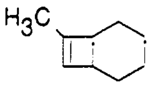
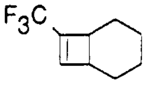
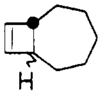
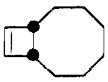
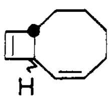
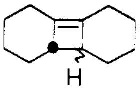
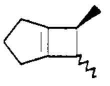
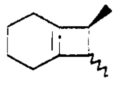
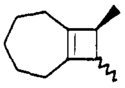
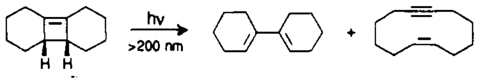
compound	products	isomers	diene isomer distribution	diene/ alkene	dienes: allowed/ forbidden	comments	ref
 (4)	1,3-butadiene + C_2H_2 + C_2H_4 + methylenecyclopropane			6.1		$\Phi_{diene} = 0.43$, $\Phi_{MCP} = 0.12$ with 185-nm excitation	44
 (45)	2,4-hexadienes + 2-butene	cis trans	*EE*:*EZ*:*ZZ* 3.2:4.9:1.0 2.5:3.2:1.0	nd nd	0.86 0.91	allowed/forbidden ratios lower for 185-nm excitation	12
 (50)	2-methyl-2,4-hexadienes + 2-butene + propyne	cis trans	*EE*:*EZ*:*ZE*:*ZZ* 15.8:5.5:2.9:1.0 1.6:1.9:3.6:1.0	nd nd	2.85 2.08	diene distributions different, but allowed/forbidden ratios identical with 214-nm excitation	22
 (51)	3,4-dimethyl-2,4-hexadienes + 2-butene + 2-butyne	cis trans	*EE*:*EZ*:*ZZ* 138:110:1.0 3.5:4.6:1.0	nd nd	1.26 1.04	allowed/forbidden ratio lower for cis, same for trans, with 214-nm excitation	22
 (52)	2,3-dimethyl-2,4-hexadienes + 2-methyl-2-butene + propyne + **53**		*E*:*Z* = 3.4	1.0		$\Phi_{dienes} = 0.13$, $\Phi_{53} = 0.015$ with 185-nm excitation; product distribution varies slightly with excitation wavelength	69
 (53)	2,4-dimethyl-2,4-hexadienes + 2-methyl-2-butene + propyne + **52**		*E*:*Z* = 3.4	1.2		$\Phi_{dienes} = 0.13$, $\Phi_{52} = 0.010$ with 185-nm excitation; product distribution varies slightly with excitation wavelength	69
 (54)	2,3,4,5-tetramethyl-2,4-hexadiene + 2,3-dimethyl-2-butene + 2-butyne			nd		quantum yield for ring opening is about half that of *cis*-**51** with 214-nm excitation	65
 (55)	1,3-cycloheptadiene + cyclopentene + C_2H_2	cis		1.0		essentially no wavelength dependence (185 vs 193 nm)	12
 (56)	1,3-cyclooctadienes + cyclohexene + C_2H_2	cis	*cc*:*ct* = 1.33	1.25	1.33	allowed/forbidden ratio = 3.0 with 185-nm excitation; diene/alkene = 0.91 with 214-nm excitation	12,73
 (57)	2-methyl-1,3-cyclooctadienes + cyclohexene + propyne	cis	*cc*:*ct*:*tc* 4.45:1.0:2.45	0.67	1.29	diene/alkene = 0.35 with 214-nm excitation	73
 (58)	2-(trifluoromethyl)-1,3-cyclooctadienes + cyclohexene + 3,3,3-tris(trifluoromethyl)propyne	cis	*cc*:*ct*:*tc* 4.54:1.0:1.58	10	1.75	diene/alkene = 17 with 214-nm excitation	73
 (59)	1,3-cyclononadienes + cycloheptene + C_2H_2	cis trans	*cc*:*ct* = 0.36 *cc*:*ct* = 0.25	1.05 2.73	0.36 4.0	product distribution independent of excitation wavelength (185–214 nm)	71
 (60)	1,3-cyclodecadienes + *cis*-cyclooctene + C_2H_2	cis	*cc*:*ct* = 0.40	>0.9	>0.5	thermally unstable product (*ttt*-diene) also formed	70
 (61)	1,3,5-cyclodecatrienes + 1,3-cyclooctadienes + C_2H_2	cis trans	*ccc*:*ctc*:*cct* 1.0:1.84:1.32 1.0:1.75:0.67	3.62 6.36	0.32 2.42		70
 (46)	1,1′-bicyclohexenyl + cyclododec-7-en-1-yne	cis trans		3.0 0.45	 <0.2	214-nm excitation only; *cis*-**46** tentatively identified in photolysis of *trans*-**46**	72
 (63a)	1,2-bis(ethylidene)cyclopentanes	cis trans	*EE*:*EZ* = 2.5 *EE*:*EZ* = 0.11	*b* *b*	2.5 9.1	Φ_{dienes}(total) ≈ 0.6 for 193-nm excitation; no wavelength dependence	74
 (62)	1,2-bis(ethylidene)cyclohexanes	cis trans	*EE*:*EZ*:*ZZ*[c] 3.43:1.0:0 0.18:1.0:0.09	*b* *b*	3.43 5.56[d]	Φ_{dienes}(total) ≈ 0.6 for 193-nm excitation; no wavelength dependence	58

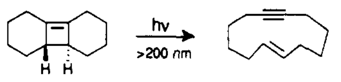
Table I (Continued)

compound	products	isomers	diene isomer distribution	diene/ alkene	dienes: allowed/ forbidden	comments	ref
 (63b)	1,2-bis(ethylidene)cycloheptanes	cis	*EE*:*EZ* = 9.1	*b*	9.1	Φ_{dienes}(total) ≈ 0.8 for 193-nm excitation; no wavelength dependence	74
		trans	*EE*:*EZ* = 0.29	*b*	3.45		

[a] All data obtained with 193-nm laser excitation, except where otherwise noted; nd = not determined. [b] No alkene formed. [c] *Z*,*Z*-Diene only tentatively identified. [d] *EZ*:*EE* diene ratio.



cis-46 47 Z-48 (19)



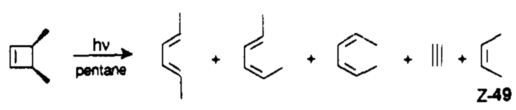
trans-46 E-48 (20)

trans-**46** (eqs 19 and 20).[61] Diene **47** is the product of (photochemically allowed) disrotatory ring opening of *cis*-**46**. The apparent failure of *trans*-**46** to yield this product is an indication that ring opening does *not* proceed by the formally forbidden, conrotatory pathway; in this case, the disrotatory pathway is effectively blocked since it must yield the highly strained cis, trans isomer of **47**.

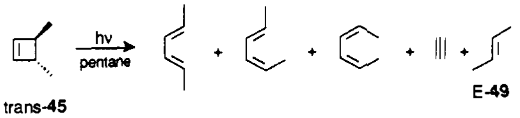
The apparent neglect of this important reaction by photochemists is presumably due to the fact that in general, phenylated cyclobutenes do not ring open upon photolysis in solution.[62-65] For example, 1,2-diphenylcyclobutene yields only the products of formal [2 + 2]-cycloreversion upon direct photolysis in hydrocarbon solution,[62,64] undergoes solvent addition upon photolysis in methanol solution,[63] and fluoresces efficiently (Φ_F = 0.9).[64] Evidently, conjugated cyclobutenes undergo ring opening upon photolysis only if the reaction is accompanied by the relief of ring strain, as for example with the cases of benzocyclobutenes[66] and Dewar aromatics.[67] Interestingly, the former have been reported to open nonstereospecifically, while Dewar aromatics yield the corresponding fully aromatic isomer adiabatically from both the singlet and triplet excited states.

C. The Photochemistry of Alkylcyclobutenes

Alkylcyclobutenes undergo two main competing reactions upon direct photolysis in solution with 185–214-nm light: ring opening to the isomeric, conjugated dienes and formal (2 + 2)-cycloreversion to yield the alkyne and alkene.[12,22,44,58,61,68-74] This is illustrated in eqs 21 and 22 for *cis*- and *trans*-3,4-dimethylcyclobutene (*cis*- and *trans*-**45**).[12,22] There are now well over a dozen systems reported which demonstrate that in general, ring opening proceeds *non*stereospecifically[12,22,58,70-74] while cycloreversion is stereospecific[61,70-72] (the stereochemistry in the product alkene being defined by the stereochemistry at the sp^3 carbons in the starting cyclobutene). While photolysis of cyclobutene itself also yields appreciable amounts of methylenecyclopropane (**6**) in addition to 1,3-butadiene, acetylene, and ethylene,[44] the formation of methylenecyclopropane derivatives in cyclobutene photolyses is not general.[12,71] Table I lists the particular systems which have been studied to date and which offer information on various aspects of the mechanisms of the ring opening and cycloreversion reactions. In the table, the product distributions observed in each case are expressed as the diene isomer distribution, the ratio of the yields of dienes (all isomers) relative to alkene, and the ratio of symmetry-allowed/symmetry-forbidden dienes.



cis-45 E,E-44 E,Z-44 Z,Z-44 Z-49 (21)



trans-45 E-49 (22)

1. Identification of the Excited State(s) Responsible for Ring Opening and Cycloreversion

It has long been known that population of the triplet state of alkylcyclobutenes through triplet sensitization results in (2 + 2)-dimerization and does *not* lead to unimolecular isomerization or fragmentation.[75] Thus, it is clear that both ring opening and cycloreversion arise from the excited singlet state manifold. Numerous workers have pointed out that there are two excited singlet states of similar energies in simple alkylcyclobutenes—the (valence) π,π^* and (Rydberg) π,R(3s) states[71,76]—and that in principle, both could give rise to ring opening and cycloreversion products.[12,44,68]

Leigh and co-workers identified the excited-state responsible for the two modes of reaction through a study of the spectroscopy and photochemistry of the series of substituted bicyclo[4.2.0]oct-7-enes **56–58**.[73] It was previously shown that trifluoromethyl substitution (at the C=C bond) has the effect of substantially raising the energy of the π,R(3s) state relative to that of the π,π^* state in simple alkenes such as norbornene. Thus, the latter is the lower energy excited state,[77] resulting in "classic" alkene π,π^*-state photobehavior in solution.[78] The gas- and solution-phase UV absorption spectra and gas-phase π-ionization potentials of **56–58** (Figure 4) show the expected trend; the π,R(3s) state is the lowest energy state in **57**, of similar energy to the π,π^* state in **56**, and higher in energy than the π,π^* state in **58**. It was further observed that the relative yields of ring opening and cycloreversion products from photolysis of the three compounds (eq 23) varies as a function of substituent and excitation wavelength in a manner consistent with the conclusion that ring opening arises (probably exclusively) from the π,π^* state, while "cycloreversion" results predominantly from Rydberg-state excitation.

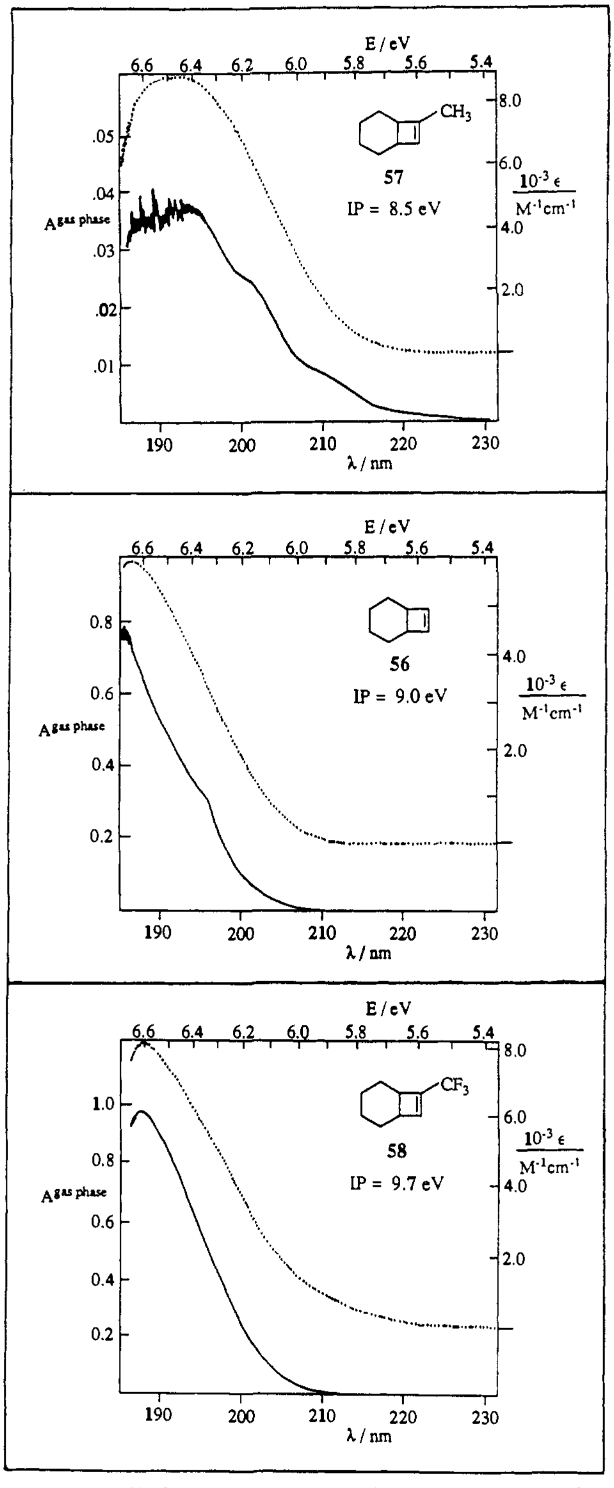
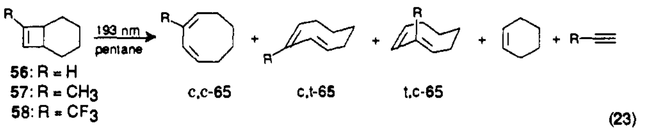


Figure 4. UV absorption spectra of **56**–**58** in the gas-phase (—) and in deoxygenated pentane solution (···). The left-hand axes refer to the gas-phase spectra, and the right-hand axes refer to the solution phase spectra. Reprinted from ref 73. Copyright 1991 American Chemical Society.

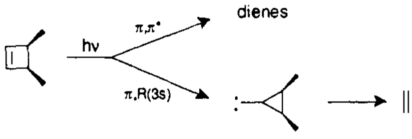


(23)

Since ring opening of all three derivatives is nonstereospecific, the apparent violation of orbital symmetry selection rules cannot be due to the intervention of more than one singlet excited state.

2. Scope and Mechanism of the Cycloreversion Reaction

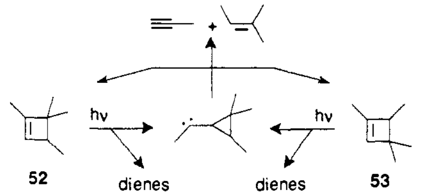
It has been suggested that Rydberg-derived cycloreversion proceeds by a mechanism involving initial (1,2)-alkyl migration (ring contraction) to yield a cyclopropylcarbene intermediate (with retention of stereochemistry) which then fragments to yield the corresponding alkyne and alkene, the latter stereospecifically (eq 24).[12,44,68] There is good precedent for such a suggestion. (1,2)-Migration (hydrogen or alkyl) to yield carbene intermediates is the most common reaction of alkene π,R(3s) states, and ring contraction is often the preferred migratory course for cycloalkenes.[5,6,79] Furthermore, it is well-known that cyclopropylcarbenes undergo stereospecific fragmentation to the alkene and alkyne, in addition to ring expansion to yield the isomeric cyclobutene.[80]



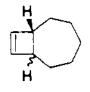
(24)

Evidence for the involvement of cyclopropylcarbenes in cyclobutene photochemistry was reported by Clark and Leigh, who reported a study of the photochemistry of the isomeric cyclobutenes **52** and **53**.[69] The two compounds were shown to interconvert in low yield upon photolysis in solution; the most reasonable mechanism for this process is via common cyclopropylcarbene intermediate(s), one of which is shown in Scheme IV.

Scheme IV



The cycloreversion reaction is suppressed when it must produce a relatively unstable alkene or alkyne product. Thus, photolysis of *cis*- and *trans*-bicyclo[5.2.0]non-8-ene (**59**) yields cycloheptene in both cases, but the quantum yield for formation of this product (185 nm) is ca. 5 times lower for the latter isomer (Φ = 0.26 from *cis*-**59** vs Φ = 0.05 from *trans*-**59**).[71] The difference is presumably due to the fact that in the latter case, stereospecific "cycloreversion" must produce *trans*-cycloheptene. Even more remarkably, the fragmentation reaction is completely suppressed in the photolyses of compounds **62**[58] and **63**;[74] in these cases, fragmentation would produce highly strained C_5–C_7 cycloalkynes.



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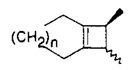
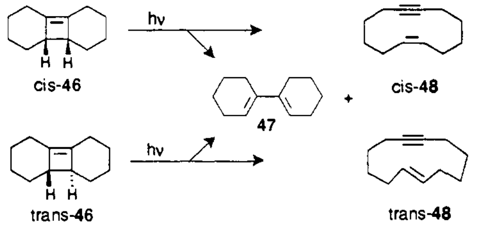


62: n=2
63: a; n=1
b; n=3

3. Scope and Mechanism of the Ring-Opening Reaction

It is clear from the numerous examples given in Table I that in general, the photochemical ring opening of cyclobutene does not follow orbital symmetry selection rules. Nevertheless, certain observations suggest very strongly that orbital symmetry does (or at least, *can* in certain instances) play a role in the reaction. The most compelling of these is the fact that compounds **62** and **63** consistently open with a high (although not complete) degree of disrotatory stereospecificity.[58,74] There are a number of structural features present in these compounds which set them apart from the monocyclic and other bicyclic systems which have been studied; the role that these features play in altering the general behavior of cyclobutenes with respect to ring opening will be discussed in more detail later.

It has been pointed out that the relative quantum yields for ring opening of *cis*- and *trans*-**46** are consistent with the idea that orbital symmetry plays a role *in the initial stages* of excited-state ring opening.[58] In a reexamination of the photochemistry of these compounds, Leigh and Zheng found that in fact, both isomers yield ring-opening products upon photolysis (214 nm) in solution (eq 25).[72] However, *trans*-**46** yields diene with ca. 5 times lower efficiency than does the cis isomer. This would be the expected result if disrotatory motions are involved in the initial stages of ring opening; such motions are impeded in *trans*-**46** because the disrotatory pathway leads to the highly strained cis, trans isomer of 1,1′-bicyclohexenyl. Similarly, the permethylated cyclobutene **54** undergoes ring opening with less than half the efficiency of *cis*-**51**;[65] in this case, disrotatory motions are impeded because of the necessity of buttressing two of the methyl groups at C_3 and C_4 as the rotation occurs.



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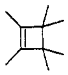
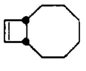
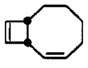

54

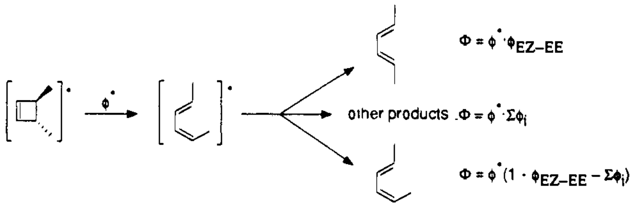

cis-51

It may also be pertinent to note that the efficiency of photochemical ring opening appears to depend on the bond strength of the C_3–C_4 bond,[71] just as is the case in ground-state electrocyclic ring-opening reactions.[55d] This is demonstrated by a comparison of the diene/alkene ratios obtained from photolysis of compounds *cis*-**60** (ca. 1.0) and *cis*-**61** (3.6).[70] Molecular models show that the π-system of the cyclooctenyl C=C bond in *cis*-**61** is almost perfectly coplanar with the fragmenting cyclobutenyl C–C bond. The weakening of the latter in *cis*-**61** compared to the corresponding bond in *cis*-**60** is also manifested in the relative rates of thermal ring opening of the two compounds.[70,81]


cis-60


cis-61

Scheme V. The Adiabatic Mechanism for Cyclobutene Ring Opening



Predicted: $(EE/EZ) = \phi_{EZ-EE}/(1 - \phi_{EZ-EE} - \Sigma\phi_i)$

If the above assessment of the initial stages of ring opening is correct, the ultimate loss of stereochemistry must then be due to intervening processes that occur after ring opening is initiated and which compete with the normal internal conversion processes that are thought to characterize photopericyclic reactions (i.e., internal conversion to the ground-state surface at the avoided crossing[47-51]). Several possibilities have been suggested:[12,71] (i) internal conversion to upper vibrational levels of ground-state cyclobutene, from which conrotatory ring opening occurs, (ii) internal conversion to ground-state biradical(oid) species, and (iii) adiabatic, disrotatory ring opening to yield diene in the first excited singlet state, from which cis ⇌ trans isomerization ensues. While the first possibility has not yet been investigated experimentally, the results of photolysis of compounds **59**[71] and **61**[70] are consistent with the second, biradical mechanism for ring opening; in both cases, the cis and trans isomers yield very similar distributions of cis,cis and cis,trans dienes, suggesting the involvement of a common set of intermediates or at least that reaction of the two isomers proceeds through a common point on the excited-state surface prior to product formation.[71]

The adiabatic ring-opening mechanism has been studied in the greatest detail, since in this case, it is a somewhat more straightforward task to design experiments with which to test the mechanism. If ring opening occurs exclusively to yield fully open, excited dienes by the disrotatory pathway, then the observed diene distribution from cyclobutene ring opening would be expected to be dictated by the decay characteristics of the excited dienes and thus predictable provided that the quantum yields for cis ⇌ trans isomerization and other photochemical processes of the dienes are known (Scheme V).[12] Analyses of this type have been reported for **45**–**53**[12,22,69] and **56**–**59**;[12,71,73] predicted diene distributions very rarely match those actually observed from photolysis of the cyclobutene derivative. In all of these cases however, the stable ground-state conformation of the diene is very different from the planar s-cis conformation in which the excited diene would be formed by disrotatory ring-opening, so that independent characterization of the excited state behavior of the dienes themselves may not provide a realistic indication of their behavior when formed by cyclobutene ring opening[12,71] (the photochemistry of dienes is known to be conformation dependent[82]).

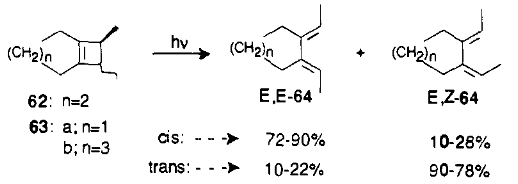
Leigh and Zheng therefore studied the photochemistry of the bicyclic cyclobutenes *cis*- and *trans*-**62**,[58] whose isomeric dienes are constrained to be s-cis (AM1 calculations predict a twist angle of ca. 36° in the parent diene, 1,2-bis(methylene)cyclohexane). The work has recently been extended to include the analogous bicyclo-

Table II. Comparison of Observed Diene Distributions from Photolysis (193 nm) of 62 and 63 with Values Calculated According to the Adiabatic Ring-Opening Mechanism[a]

isomer	compound	$(EE/EZ)_{obs}$	$(EE/EZ)_{calc}$[b]
cis	**63a**	2.5 ± 0.4	2.2 ± 0.4
cis	**62**	3.4 ± 0.6	3.7 ± 0.4
cis	**63b**	9.1 ± 1.3	3.7 ± 0.8
trans	**63a**	0.11 ± 0.02	0.71 ± 0.09
trans	**62**	0.18 ± 0.03	0.38 ± 0.05
trans	**63b**	0.29 ± 0.04	0.18 ± 0.08

[a] Photolysis at 193 nm in pentane solution, 22 °C. [b] Calculated from the quantum yields for photoreaction of the corresponding *E,E*- and *E,Z*-dienes (see eq 25), according to the equation in Scheme V.

[4.2.0]hept-1^5-ene (**63a**) and bicyclo[5.2.0]non-1^7-ene (**63b**) systems (eq 26).[74] Table II lists the observed



(26)

EE/*EZ* diene ratios from photolysis of these compounds, along with the corresponding ratios calculated from the independently determined quantum yields for cis ⇌ trans isomerization of the dienes according to the equation given in Scheme V.

Several interesting trends emerge from these data. First of all, the high degree of disrotatory stereospecificity observed for the ring-opening of *cis*- and *trans*-**62** is quite general within this special class of constrained systems. Secondly, these compounds undergo ring opening with considerably higher efficiency than other compounds with dialkyl substitution at the cyclobutene double bond (e.g. **51**). This might be explained by noting that the ancillary ring induces additional strain in the cyclobutenyl ring, as evidenced by the substantially lower activation energies for thermal ring opening of these compounds compared to those of monocyclics.[83] Thirdly, the *EE*/*EZ* diene ratios observed in the photolyses of the cis compounds are reproduced by the values calculated on the basis of the adiabatic mechanism defined in Scheme V in only two cases. We conclude that the adiabatic ring-opening pathway cannot account for the nonstereospecificity of the reaction.

If ring opening is not adiabatic, then the high degree of stereospecificity observed for these compounds may be the result of structurally induced suppression of internal conversion processes which normally occur with facility in less-constrained systems. Keeping in mind that the rates of internal conversion processes are affected by rovibrational factors, it is worth noting that the "alkyl substituents" on the C=C bond are more or less locked in **62**–**64**; furthermore, the isomeric dienes are highly constrained with respect to rotation about the central C–C bond. In principle, either or both of these factors could affect the rates of internal conversion processes at partially open geometries. Since the rigidity of these systems varies throughout the series, then accompanying variations in the degree of stereospecificity would be expected. However, it is difficult to understand why the variation observed within the series of *cis*-dimethyl compounds (increasing stereospecificity with increasing ancillary ring size) is *opposite* to that observed within the series of *trans*-dimethyl compounds (decreasing stereospecificity with increasing ancillary ring size).

D. Recent Theoretical Results

Bernardi and Robb and their co-workers have recently reported MCSCF calculations on the photochemical ring opening of 7-methylbicyclo[4.2.0]oct-7-ene (**57**),[54] experimental results for which were discussed earlier. This report follows an earlier study of the photochemical ring closure of 1,3-butadiene, in which was reported the existence of real surface crossings ("conical intersections") between the excited- and ground-state surfaces for disrotatory conversion of butadiene to cyclobutene (vide supra).[52] It was proposed that during the ring-closure reaction of 1,3-butadiene, funneling to the ground-state surface occurs at the conical intersection rather than at the avoided surface crossing. The geometry of the reacting species at this stage is one in which all the π-bonds in the molecule are broken—a tetraradicaloid species with the C_2–C_3 bond twisted by 78°. Excited-state ring opening of **57** was proposed to proceed through three such surface crossings; the three conical intersection structures have the common feature of having the (former) cyclobutene double bond twisted by an angle close to 90°. The formation of three isomeric dienes in the reaction is explained as being due to the fact that three different surface crossings exist, and at each one, the reacting species can further relax to give all three of the diene isomers after entering the ground-state surface.[54]

This theoretical model can adequately explain why ring opening leads to a distribution of isomeric dienes in most of the cyclobutene systems that have been studied experimentally. It might also explain why nearly common distributions of products are formed in systems such as *cis*- and *trans*-**59**, if there is a single conical intersection geometry which is accessible from both isomers of the cyclobutene. Compounds **62** and **63** are special in that they are prevented from achieving the 80–90° twist angle that characterizes the geometry of the system at the conical intersection. It is possible that in such cases, the system is forced to open largely via the avoided crossing, or perhaps adiabatically, or perhaps via other surface crossings[84] in a pathway which leads predominantly to the disrotatory product(s). It is clear that further study is required in order to develop a complete understanding of the remarkable complexities of this "prototypical" photoelectrocyclic reaction.

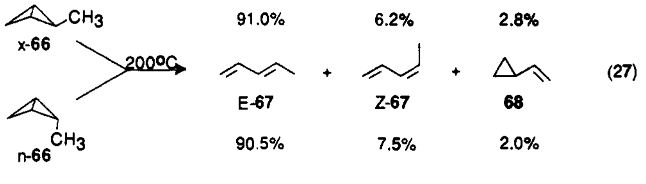
V. The Photochemistry of Bicyclo[1.1.0]butanes

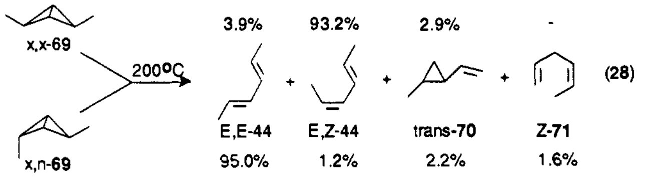
Related to the BD–CB interconversions are those between 1,3-butadiene and bicyclo[1.1.0]butane (**5**). While to our knowledge, there are no known examples of thermal formation of bicyclobutanes from butadiene derivatives the course of the reverse reaction is well known[85-88] and there are numerous examples of photochemical interconversion in both directions.[44,89-92]

A. Thermal Rearrangements

The stereochemistry of the thermal ring opening of bicyclo[1.1.0]butane was demonstrated by Closs and

Pfeffer with a study of the gas-phase thermolyses of *endo*- and *exo*-2-methylbicyclo[1.1.0]butane (**66**; eq 27) and *exo,exo*- and *exo,endo*-2,4-dimethylbicyclo[1.1.0]-butane (*exo,exo*- and *exo,endo*-**69**, respectively; eq 28).[87]





In particular, the distribution of isomeric 2,4-hexadienes (**44**) observed from thermolysis of the latter two compounds demonstrates that the reaction is best viewed mechanistically as a $(\sigma_{2s} + \sigma_{2a})$-cycloreversion in which two of the side bonds are cleaved (eq 29).

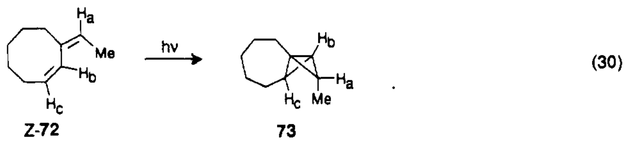
5

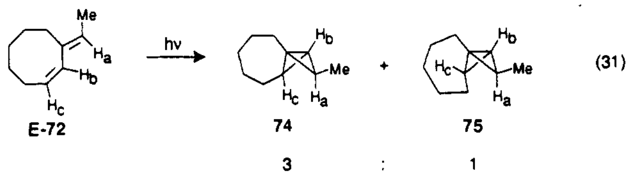
Becknell has recently reported the thermolysis of *endo,endo*-**69** at higher temperatures (254 °C) but otherwise under similar conditions as those employed for the thermolysis of the exo,exo and exo,endo isomers.[88] After correction for secondary thermal rearrangement of the initially formed products, the observed product distribution indicates that *endo,endo*-**69** yields *E,Z*-**44** with 98.6% stereospecificity.

There have been numerous theoretical studies of the thermal ring opening of bicyclo[1.1.0]butane.[94-96] The most recent ab initio calculations, carried out at the MP2/3-21G level, leads to an activation energy of 43.6 kcal/mol for the reaction,[96] in good agreement with the experimental value of 40.6 kcal/mol.[84c] The structure of the transition state has only one of the side bonds lengthened appreciably, so that it *resembles* the cyclopropylcarbinyl biradical, indicating a nonsynchronous (but concerted) mechanism for the reaction.

B. Bicyclo[1.1.0]butanes from Photolysis of 1,3-Dienes

The photochemical conversion of dienes to bicyclobutanes proceeds from the lowest excited singlet state of the s-trans conformer of the diene, in competition with cis ⇌ trans photoisomerization.[57c,89-91] The process is highly stereospecific, as demonstrated by the products of irradiation of the isomeric, s-trans dienes **72** (eqs 30 and 31).[91] The results were proposed to be incompatible with a $(\pi_{2s} + \pi_{2s})$-cycloaddition mechanism on the basis that the two isomeric dienes did *not* each yield a pair of bicyclobutanes epimeric at two centers. Rather, the reaction was proposed to proceed via the vibrationally relaxed (i.e., twisted), zwitterionic singlet excited state of the diene in a one-step (concerted) process. On the basis of the observation that photoisomerization of the endocyclic $C{=}C$ bond in **72** is 3-5 times faster than that of the exocyclic bond, it was proposed that ring closure in this system involves twisting of the former to an allylmethylene geometry (with the exocyclic $C{=}C$ bond part of the allyl system) along with conrotatory closure of the allyl system. Direct photolyses of 3-methylenecycloalkenes in methanol solution leads to the formation of methyl ethers with partial quenching of bicyclobutane formation.[89,90] In some cases, it could be shown that the formation of these products had to arise via quenching of an excited-state intermediate; this intermediate was proposed to be the zwitterionic excited singlet state of the diene.



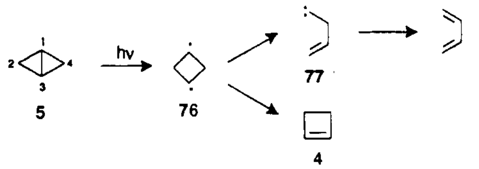


C. The Photochemistry of Bicyclo[1.1.0]butanes

The photochemistry of bicyclo[1.1.0]butane derivatives has received only recent attention. Spectroscopic studies show that **5** possesses at least four low-lying excited singlet states in the 5.6–6.7-eV range.[97-98] M. B. Robin has assigned the four low-lying absorption bands in the spectrum of **5** to Rydberg transitions (3s, 3p, and higher).[98] The lowest excited singlet states of **5** would thus be expected to have a certain amount of radical cation character,[93] which should lead to special ramifications on the photochemistry of the molecule.

Two studies in 1985 reported different results for photolysis (185 nm) of the parent compound (**5**) in hydrocarbon solution. Adam and co-workers reported that photolysis of **5** with the unfiltered output from a low-pressure mercury lamp (185 + 254 nm) yielded 1,3-butadiene and cyclobutene (**4**) in a 1:1 ratio along with minor amounts of acetylene, ethylene, and methylenecyclopropane.[44] In contrast, Becknell, Berson, and Srinivasan reported that photolysis of **5** under similar conditions afforded only butadiene and cyclobutene, in a ratio of ca. 10:1.[92] The latter results were later confirmed; furthermore, the butadiene/cyclobutene ratio was found to be unaffected by the presence of oxygen, photolysis temperature (0–25 °C), or reduction of the intensity of the 254-nm lamp component with an interference filter.[88] The reasons for the discrepancy between the two group's results have not been delineated, although Becknell has speculated that the sample of **5** used by Adam and co-workers in their studies was contaminated with cyclobutene.[88]

The most reasonable mechanism for the formation of butadiene and cyclobutene from **5** is via a mechanism involving initial cleavage of the bridgehead (C_1–C_3) bond to yield the 1,3-cyclobutanediyl biradical (**76**), which then fragments to carbene **77** or yields **4** by 1,2-hydrogen migration.[44,92] Once formed, **77** would be expected to yield 1,3-butadiene by hydrogen migration (eq 32). This mechanism has ample precedent in the photochemistry



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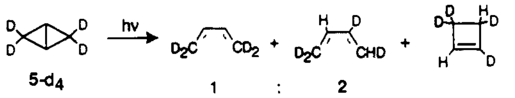
of alkylcyclopropanes, which undergo both one- and two-bond cleavage upon direct photolysis.[5b,6] The latter has been suggested to occur by a stepwise process initiated by cleavage of the weakest of the cyclopropane C–C bonds and ultimately yields a carbene and an alkene after cleavage of the 1,3-biradical. An alternative mechanism for the formation of butadiene is via a process analogous to the thermal rearrangement of bicyclo[1.1.0]butanes[85–87]—cleavage of two of the "side" bonds of the bicyclobutane ring system (eq 29).

In order to distinguish between these two possibilities, Becknell et al. photolyzed the deuterium- and ^{13}C-labeled derivatives **5**-d_4 and **5***, respectively (eqs 33 and 34).[88,92] From the distribution of the isotopic label(s) in the products from the two sets of experiments, it was concluded that both the cyclobutanediyl/allylcarbene and side-bond cleavage pathways contribute to the formation of 1,3-butadiene and in a ratio of about 2:1. It was further found that the stereochemical distribution of deuterium in the butadiene-1,1,3,4-d_4 was approximately equally weighted between *E* and *Z* across the C_3–C_4 bond, allowing the conclusion that the hydrogen-migration process in the allylcarbene intermediate proceeds nonstereospecifically. The precise positioning of the labels in the cyclobutene-d_4 obtained from photolysis of **5**-d_4 is uncertain, so the authors were not able to determine whether this product arises directly from 1,3-cyclobutanediyl or from the allylcarbene. Neither of these reactive intermediates, independently generated from diazenyl precursors (**78** and **79**) affords cyclobutene under thermolytic conditions.[84a,99]



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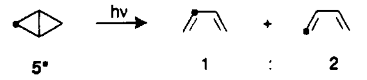

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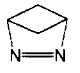

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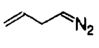

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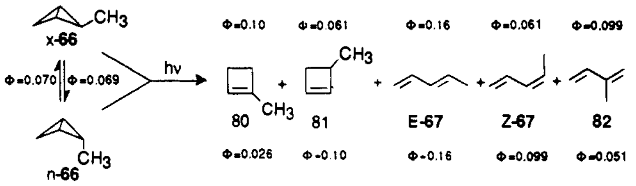
Photolysis of *exo*- and *endo*-2-methylbicyclo[1.1.0]butane (**66**) results in interconversion of the two isomers and formation of the five additional products shown in eq 35.[88] Quantum yields for the 185-nm photolyses were measured by cyclooctene actinometry and are included in eq 35. As was found to be the case in the thermolysis of these compounds (eq 27), irradiation of *exo*- and *endo*-**66** yields similar distributions of isomeric dienes.

In principle, exo ⇌ endo photoisomerization in **66** could occur by two pathways—an inversion process proceeding through the cyclobutanediyl biradical, or through a cyclopropyl–carbinyl biradical species formed by cleavage of the C_1–C_2 bond. A study of the photochemistry of the three isomeric 2,4-dimethylbicyclo[1.1.0]butanes (**69**; eqs 36 and 37)[88] successfully delineates the mechanism of this process. Quantum yields of product formation were measured using a filtered 185-nm light source so as to minimize secondary cis ⇌ trans photoisomerization of the dienes observed as products in the reactions. The observation that *exo,exo*- and *endo,endo*-**69** interconvert upon photolysis without yielding the exo,endo isomer, and *exo,endo*-**69** does not isomerize to *exo,exo*- or *endo,endo*-**69** provides convincing evidence that exo ⇌ endo photoisomerization proceeds by the 1,3-cyclobutanediyl inversion process.



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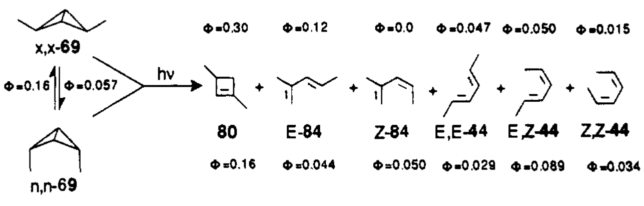

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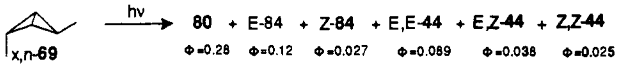

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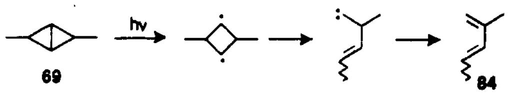
The photochemistry of **69** also affords information on the stereochemistry of the two competing pathways for the formation of dienes which were discussed earlier for **5**. In principle, the analysis is straightforward because the 2-methyl-1,3-pentadienes (**84**) must arise by the allylcarbene pathway (eq 38), while the 2,4-hexadienes (**44**) are necessarily formed via side-bond cleavage (eq 39). However, the experimental conditions employed for the quantum yield determinations were such that the 254-nm component of the light source was only *largely* eliminated; the photostationary state for **84** (254 nm) is 100% *E* isomer, while for **44** it is *EE*:*EZ*:*ZZ* = 2:1:1. The distributions of *E*- and *Z*-**84** from irradiation of the three isomers of **69** indicates that the allylmethylene pathway for diene formation proceeds with a low (but non-zero) degree of stereoselectivity. The side-bond cleavage pathway leading to **44** is clearly nonstereoselective, although it does show a preference for formation of the major *thermolysis* product in each case (*E,Z*-**44** from *exo,exo*- and *endo,endo*-**69** and *E,E*-**44** from *exo,endo*-**69**). Photolysis of *exo,exo*-**69** with an ArF excimer laser (193 nm) leads



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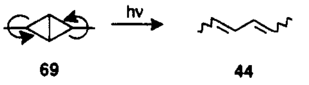

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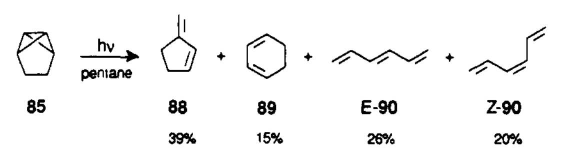
to slightly higher stereoselectivity with respect to formation of **44**: *EE*/*EZ*/*ZZ* = 28:56:16.[88]

It should be noted that in the cyclobutene product (**83**) formed from photolysis of **69**, the methyl groups are situated at C_1 and C_3, consistent with a mechanism involving [1,2]-H migration in the 2,4-dimethyl-1,3-cyclobutanediyl intermediate. No evidence for the formation of 1,2- or 1,4-dimethylcyclobutenes (which might involve alkyl migration) was reported.[88]

From the observed variation in product quantum yields throughout the series of compounds **5**-d_4, **66**, and **69**, it was concluded that bridgehead bond cleavage (leading to 1,3-cyclobutanediyl- and allylcarbene-derived products and exo ⇌ endo isomerization; see eq 32) and side-bond cleavage leading to dienes (see eq 29) arise from population of two different singlet excited states. RRKM calculations tentatively rule out the possibility that the side-bond cleavage pathway is a hot ground state reaction, in spite of the similarities between the photolytic and thermolytic diene distributions.[88]

Adam and his group have recently reported the photochemistry of the series of tethered bicyclo[1.1.0]butanes (**85**–**87**; eqs 40–42).[93] These experiments were all performed using an unfiltered low-pressure mercury lamp (185 + 254 nm) as the excitation source, which leads to complications owing to secondary photolysis of the highly photoactive (at 254 nm) 1,3-cycloalkadiene products (observed from **85** and expected from **86** and **87**). Control experiments in which 1,3-cyclohexadiene (**89**) was photolyzed with 254-nm light showed that this diene is converted to a mixture of *E*- and *Z*-**90**, in agreement with previous reports for the photochemistry of this compound.[100]



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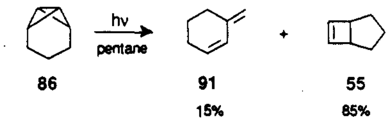

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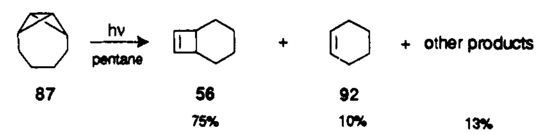
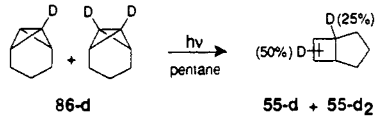


(42)

In the cases of **85** and **86**, the methylenecycloalkene products (**88** and **91**, respectively) are clearly those of allylcarbene intermediates. Adam and co-workers formulated the mechanism for allylcarbene formation as involving initial side-bond cleavage to yield a methylenecyclopropanediyl diradical, which then fragments to yield the carbene (this mechanism differs from the cyclobutanediyl pathway only in the order in which the central- and side-bonds are cleaved). The other products (**89**/**90** from **85** and the bicyclo[*n*.2.0]alkenes **55** and **56** from **86** and **87**, respectively) would seem most likely to arise from the side-bond cleavage pathway via secondary photolysis of the initially formed 1,3-cycloalkadiene, although Adam and co-workers recognized the additional possibility that they could arise via [1,2]-alkyl migration in the corresponding 1,3-cyclobutanediyl intermediate. This possibility was examined through deuterium-labeling studies, employing a 1:1 mixture of mono- and dideuterated **86** (eq 43) and monodeuterated **87** (eq 44). The bicyclo[*n*.2.0]alkenes were isolated after photolysis and analyzed by ^{1}H NMR spectroscopy. The presence of deuterium at the bridgehead position in **55**-*d* and **56**-*d* provides conclusive evidence that this pathway (eq 45) does indeed occur; surprisingly, it is a major contributor to the formation of these compounds in the photolyses of **86** and **87**. Presumably, [1,2]-H migration is blocked in these cases because such a process would yield anti-Bredt cyclobutenes of the general structure **93**. This conclusion is tentative however, since these compounds would be expected to undergo rapid ring opening to the corresponding methylenecycloalkenes, which were (coincidentally) observed as products from photolysis of **85** and **86**.



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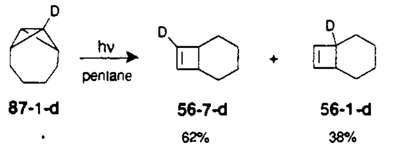

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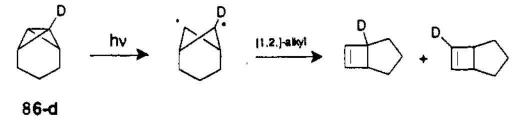

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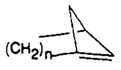


93

Isotopomers with deuterium at the double bond in **55** and **56** arise partly from the pathway discussed above, and also via side-bond cleavage pathways which may or may not involve the intermediacy of 1,3-cycloalkadienes (these undergo secondary photolysis under the experimental conditions employed). The thermolytic behavior of **86** is dominated by side-bond cleavage.[86] From the distribution of deuterium in the bicyclo[*n*.2.0]alkenes isolated from the photolysis of deuterated **86** and **87**, it was concluded that the central-bond cleavage pathway(s) account for 76% of that formed from **87** and 66% of bicyclo[*n*.2.0]alkene formed from **86**. In the case of **85**, central-bond cleavage accounts for less than 61% of the observed products. The trend toward decreasing central-bond cleavage with decreasing tether length was rationalized by consideration of variations in the ionization potentials and calculated (MNDO) structural parameters throughout the series of compounds. In bicyclo[1.1.0]butane itself (**5**), the C_1–C_3 and C_1–C_2 bonds are approximately equal in length, and the dihedral angle which defines the pucker of the ring system is 122°.[101] The calculated structure of the bicyclobutane moiety in **87** is very similar to that of **5** in these respects. Decreasing the length of the tether in **86** and **85** results in more pronounced puckering of the system, lengthening of the C_1–C_2 (side) bond and shortening of the C_1–C_3 (central) bond length. The lowest ionization potentials of the three compounds[102] show that the $\sigma(C_1–C_3)$ MO is stabilized accordingly. Thus, the proportion of side-bond cleavage products increases as the bicyclobutane moiety is increasingly distorted due to shortening of the tether linking C_1 and C_3.[93]

D. Theory

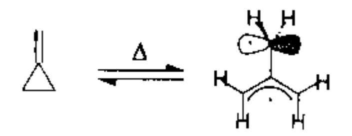
The main feature of the photochemistry of bicyclo[1.1.0]butanes is the dominance of central-bond cleavage processes, leading to 1,3-cyclobutanediyl- and allylcarbene-derived products with little stereoselectivity, and exo–endo isomerization. This contrasts the thermal behavior of these systems, which is dominated by concerted, highly stereospecific side-bond cleavage to yield 1,3-dienes. The dominance of central-bond cleavage processes in the photochemistry of the system has recently been explained by Bent and Rossi, on the basis of ab initio SCF and CI (4-31G) calculations of the low-lying excited states of bicyclo[1.1.0]butane (**5**).[103] The calculations confirm the conclusions of spectroscopic studies, which show that the four lowest excited states (2^1A_1, 1^1B_2, 3^1A_1, and 1^1B_1) have substantial Rydberg character (the 2^1A_1 state is a 3s Rydberg, while the other three are 3p Rydberg states),[97,98] and the calculated excited state energies agree rather closely with those obtained spectroscopically. The calculations also suggest that the 1^1B_2 state has substantial antibonding character between carbons 1 and 3—identifying this state as the one responsible for central-bond cleavage, in agreement with the assignment of Becknell.[88] The 3^1A_1 and 1^1B_1 states both have a strengthened C_1–C_3 bond and weakened side bonds, suggesting that one or both of these states are responsible for the formation of 1,3-butadiene by the side-bond cleavage pathway.[103]

VI. The Photochemistry of Methylenecyclopropanes

There has been intense theoretical interest over the past 25 years in the ground and excited states of the trimethylenemethane biradical[104–107] and the role of this species in the thermal[55d,108] and photochemistry[109–112] of methylenecyclopropane (**6**) and its derivatives.

A. Thermal Rearrangement

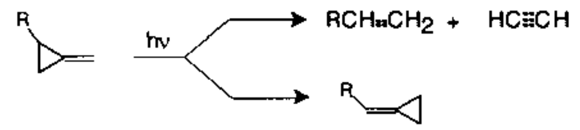
Thermal rearrangement of substituted methylenecyclopropanes occurs with high regioselectivity and with inversion of configuration at the migrating carbon.[108] The radical-stabilizing abilities of the substituents determine which of the two possible ring carbons undergoes migration.[108] The thermal rearrangements of derivatives of **6** have been explained as involving the orthogonal $^1B_1$ state of the corresponding trimethylenemethane biradical, which for the parent has been calculated to lie 17.6 kcal/mol above the triplet ($^3A_2'$) ground state (eq 46).[105] Theoretical evidence that the rearrangement is a concerted one, without involving the intermediacy of trimethylenemethane, has also been reported.[106]



(46)

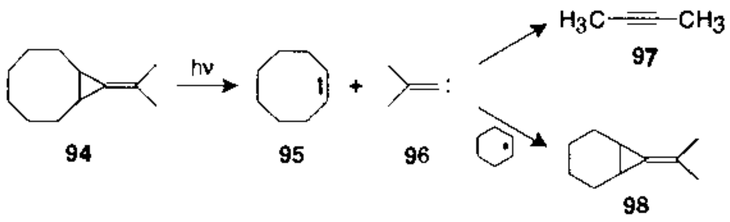
B. Photochemical Rearrangement

Early studies of the direct photolysis of alkylidenecyclopropanes in solution concentrated on phenylated systems.[109] Photolysis results in competing fragmentation and methylenecyclopropane rearrangement (eq 47). While the latter is presumed to involve



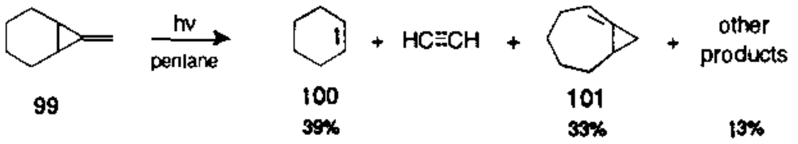
(47)

trimethylenemethane intermediates, the fragmentation reaction has been shown to involve discrete vinylidene intermediates by trapping with olefins.[111] Thus, photolysis of the nonconjugated derivative **94** with radiation > 200 nm results in the formation of cyclooctene (**95**) and dimethylvinylidene (**96**). The latter was identified by isolation of its rearrangement product (2-butyne; **97**) or by trapping with cyclohexene (yielding **98**; eq 48). Fragmentation products are formed upon thermolysis of methylenecyclopropanes only at extremely high temperatures.[113] The direct photolysis of alkylidenecyclopropanes such as **94** is thought to involve the lowest excited singlet state of the molecule, since photolysis of **6** itself in a low-temperature matrix does not lead to the ESR spectrum of the ground triplet state of trimethylenemethane.[110] The spectrum of triplet trimethylenemethane can be readily generated under similar conditions by irradiation of **6** with fast electrons[110,114] or by photolysis of other trimethylenemethane precursors.[115]



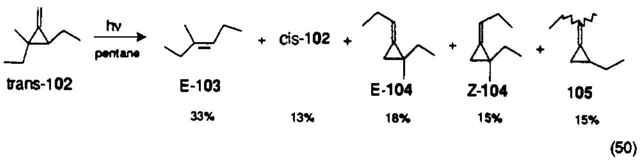
(48)

While no evidence was reported for the formation of the methylenecyclopropane rearrangement product from **94**, results for other alkylidenecyclopropanes suggest that as is the case with phenylated systems, the process competes effectively with fragmentation. Thus, photolysis (185 nm) of the bicyclic methylenecyclopropane derivative **99** leads to competitive fragmentation (yielding **100**) and methylenecyclopropane rearrangement (yielding **101**; eq 49).[116]



(49)

A study of the photochemistry of the stereoisomeric monocyclic alkylidenecyclopropanes **102** has been reported by Baum et al., who attempted to determine the regiochemistry of the photochemical methylenecyclopropane rearrangement and the stereochemistry of the fragmentation process (eqs 50 and 51).[112] The study included an investigation of the thermolysis of the two compounds and INDO/S-CI calculations on the ground



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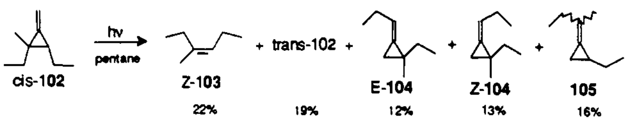
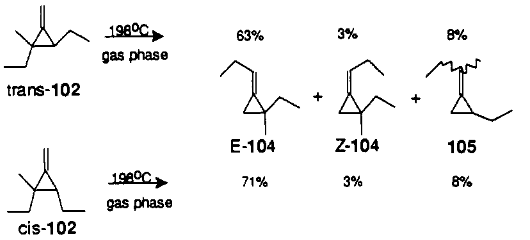


(51)

and excited states of **6** and trimethylenemethane. In both cases, photolysis (185 + 254 nm) leads to stereospecific fragmentation, cis ⇌ trans isomerization, and methylenecyclopropane rearrangement. Fragmentation occurs stereospecifically in both cases, suggesting that the process involves concerted, two-bond fragmentation (the other product is acetylene). This contrasts the behavior of simple cyclopropane derivatives, which undergo two-bond photofragmentation with only partial stereoselectivity (consistent with a stepwise mechanism in which the weakest bond cleaves first).[117] Another significant difference between the photobehavior of **102** and simple cyclopropanes is the interconversion between cis and trans isomers of **102**; cis ⇌ trans photoisomerization is unprecedented in alkylcyclopropane photochemistry.[5]

Cis ⇌ trans photoisomerization and methylenecyclopropane rearrangement presumably occur through the intermediacy of trimethylenemethane biradicals. Interestingly, the distribution of structural isomers (**104** and **105**) formed by methylenecyclopropane rearrangement is almost identical from *cis*- and *trans*-**102**, and there is an almost complete lack of regioselectivity in their formation. Comparison of these results to those of thermolysis of the two isomers (eq 52) suggests that



(52)

photolysis of **102** involves excited states of trimethylenemethane which are not accessible in the thermal reaction. The formation of nearly statistical distributions of all the possible structural isomers of **102** in the photolyses suggests the involvement of planar trimethylenemethane excited states.

C. Theory

INDO/S-CI calculations for **6** predict that three low-lying excited states should be accessible with 185-nm radiation. These are the π,π^* (6.68 eV), σ,π^* (6.85 eV), and π,σ^* (6.90 eV) states. The σ,π^* and/or π,σ^* states, although they have low oscillator strengths, are predicted to be responsible for fragmentation of methylenecyclopropane derivatives on the basis of their electronic characters. The π,π^* state is the one predicted to be responsible for trimethylenemethane formation. The calculations further show that at least one (perhaps two) planar excited state(s) of trimethylenemethane (the ${}^1A'_1$ state and possibly the $2^1E'$ state) should be accessible from the methylenecyclopropane π,π^* state upon ring opening. The authors proposed that ring opening of **102** initially occurs along a potential energy surface of C_2 (conrotatory) or C_s (disrotatory) symmetry and then mixes with the lower lying ${}^1A'_1$ surface to form excited (planar) trimethylenemethane which then recloses to yield all possible methylenecyclopropane rearrangement products in roughly equivalent yields.

VII. Summary and Prospects

Far-UV photochemical techniques provide an invaluable tool for the study of small molecules in solution. The use of these techniques affords the opportunity for correlations between experiment and theory at unprecedented levels of sophistication and reliability. They also allow the study of the photochemistry of systems (e.g. cyclobutene) in which conjugating substituents drastically alter the behavior of the chromophore of primary interest. The field has grown rapidly over the past 20 years and the special techniques required are now refined and as easily mastered as more conventional wet photochemical techniques.

It should be clear from the foregoing that theory is still a good deal behind experiment in unraveling the "mysteries"—and refuting the dogma—that is associated with many fundamental organic photoreactions. The challenge for the experimentalist is to maintain this edge and provide the groundwork for better theoretical understanding of photochemical reactions and processes.

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