

generally give light-induced uphill oxidation of the surface-bound material compared to the behavior of reversible materials derivatized with the same reagents. The formal potential, E° , for ferrocene confined to the surface of a reversible electrode is about the same as for ferrocene in solution. But on n-type Si, the ferrocene can be oxidized in an uphill sense by ~ 0.5 V. Further, for derivatized n-type Si the sequence of events occurs as sketched in Figure 2 where B = ferrocene or N,N,N',N' -tetramethyl-*p*-phenylenediamine in nonaqueous media or $[\text{Fe}(\text{CN})_6]^{4-}$ in aqueous electrolyte solution. Finally, Figure 3 illustrates the remarkable ability of the derivatized electrode to survive as a photoanode compared to the naked electrode; apparently derivatization does not compromise efficiency for electricity generation, but substantial improvement in durability obtains by inhibiting photogenerated hole processes associated with SiO_x formation.

Derivatized semiconductor photoelectrodes offer a way to design photosensitive interfaces for effecting virtually any redox process. Efforts here are really just beginning and will comprise an important part of our continuing research.

Prognosis

Photoelectrochemistry has already provided the most efficient means of transducing solar energy into chemical fuel ($\text{H}_2 + 0.5\text{O}_2$ from H_2O , $\sim 1\%$) or elec-

tricity ($\sim 12\%$) using man-contrived, wet-chemical systems. There is great interest in this area; many new and good researchers are being attracted into the field. Large numbers of research articles are appearing reporting new systems and higher efficiencies. Significant advances are likely to be made in preparation of large area, thin film photoelectrodes and in surface modification for purposes of manipulating charge-transfer kinetics. The race is on to gain sufficient understanding to provide a scientific base for a new, large-scale energy resource option for use in the first half of the twenty-first century.

The research described above has been possible through the efforts of a very talented and energetic set of colleagues associated with M.S.W. during the last several years. Their research is summarized in the individual references to this article. The different aspects of the research have been supported by various Federal agencies, including the National Aeronautics and Space Administration (oxides, direct H_2 and O_2 generation, laser energy conversion), the United States Department of Energy, Office of Basic Energy Sciences (exploratory interfacial photoredox processes for energy storage, derivatized electrodes for improved durability), and the Office of Naval Research (molecular manipulation of surface state energies). M.S.W. acknowledges support as an A. P. Sloan Fellow (1974–1976) and a Dreyfus Teacher-Scholar Grant Recipient (1975–1980) which provided financial flexibility during portions of this work. Support from the M.I.T. Cabot Solar Energy Fund is also gratefully acknowledged.

Excited-State Chemistry of Cyclopropene Derivatives

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Cyclopropene, a molecule first prepared in 1922,¹ is of current interest from both an experimental and a theoretical point of view. The strain energy in cyclopropene is approximately 54.5 kcal/mol² and is primarily due to the strain present in the σ framework. Addition across the double bond in cyclopropene proceeds quite readily since it reduces ring strain by 26 kcal/mol. The relief of ring strain combined with resonance stabilization of the corresponding ring-opened species accounts for the relatively facile ring-opening reaction of this molecule. The work to be reported here originated in the hope that the nature and chemical reactivity of the ring-opened species derived from the irradiation of cyclopropene might be elucidated and that such studies might sharpen our ability to predict or understand the behavior of this transient intermediate when it is generated from other sources.

In this Account we review some of the photochemical reactions of cyclopropene derivatives and attempt, using available evidence, to formulate generalizations concerning structure and reactivity relations for these compounds.

Two intermediates have been given serious consideration to explain the products of ring opening of cyclopropene, a diradical **3** and a vinylcarbene **4**.³ Stretching of the C–C bond in cyclopropene **1**, without rotation of the methylene group, leads to the bisected geometry of the vinylmethylene diradical **2**. Detailed theoretical calculations show that it is the 1,3-diradical singlet state **2** which correlates directly with the ground state and is presumably involved in the thermal cleavage of cyclopropenes.⁴ Allowing the CH_2 group to twist leads to structure **3** with a drop of 4.5 kcal in energy for the singlet state. In reality, the thermal

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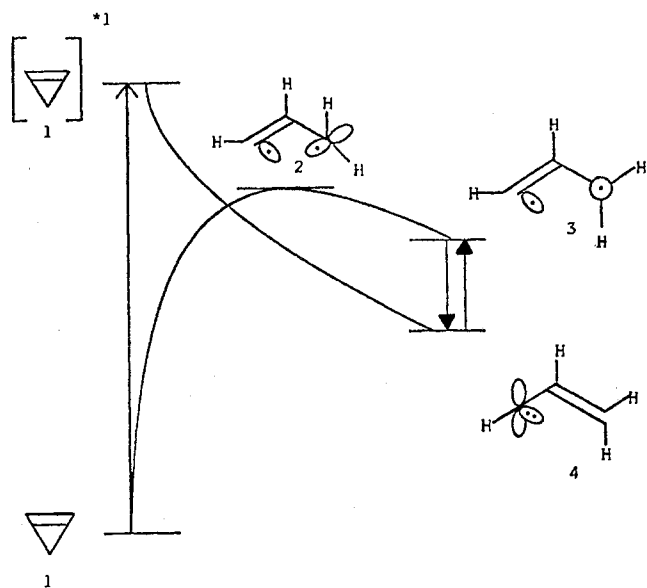
(1) N. Y. Demyanov and M. N. Doyarenko, *Bull. Acad. Sci. Russ.*, **16**, 297 (1922).

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(4) J. H. Davis, W. A. Goddard, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 2427 (1977).

cleavage of cyclopropene 1 undoubtedly involves si-

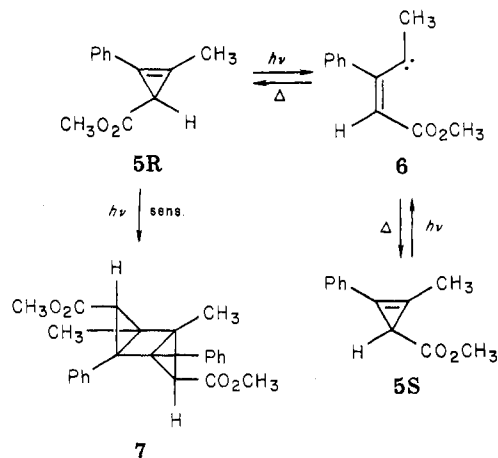


multaneous rotation and bond stretching to give 3 directly. According to the calculations,^{4,5} the electronically excited singlet state of cyclopropene correlates directly with the lower-lying vinylcarbene state 4.⁶⁻⁸ Since the photochemical ring-opening reaction does not occur from the triplet state,⁹⁻¹¹ it seems likely that the initial intermediate produced in the photolytic cleavage is the singlet rather than the more stable triplet vinylcarbene.¹²⁻¹⁵

Multiplicity Effects

One of the characteristic features of the electronically excited singlet state of cyclopropenes is that the quantum efficiency for reaction is quite low.⁷ The low efficiency can be explained by thermal return of the carbene intermediate to the cyclopropene. Such thermal behavior of vinylcarbenes is well-known and is in fact the basis of synthetic procedures used for the preparation of cyclopropenes.¹⁶ Recently, Pincock and Moutsokapas have shown that the photochemical racemization of methyl 1-methyl-2-phenylcyclopropene-3-carboxylate (5) occurs about four times as fast as photorearrangement, thereby indicating there is an intermediate vinylcarbene on the singlet surface.¹⁷ Interestingly, no racemization was observed with the triplet state. Instead, the only product obtained on

triplet sensitization was the tricyclic dimer 7.



The failure of triplet cyclopropenes to undergo ring opening⁹⁻¹¹ is somewhat puzzling and merits discussion. Considering the high strain energy of the cyclopropene, plus the added energy from electronic excitation, it is surprising that the triplet state is long-lived enough as a three-membered ring to react by a bimolecular path. Recent MINDO/3 semiempirical MO calculations by Pincock and Boyd suggest a reason for this behavior.¹⁸ The calculations indicate that the triplet states of cyclopropenes have a large barrier (13 kcal/mol) for ring opening. This is perfectly consistent with the absence of photochemical racemization of the triplet state of cyclopropene 5. The singlet state, on the other hand, can readily undergo ring opening in an unactivated process to give a vinylcarbene. The behavior of the singlet-state surface agrees well with the "funnel theory" of excited-state to ground-state conversions as outlined principally by Michl.¹⁹ Close approach of the two surfaces greatly enhances internal conversion and therefore gives a route for excited singlet cyclopropene to open to vinylcarbene and then return to ground-state cyclopropene. Presumably there is a competition between this process leading to regeneration of the cyclopropene and other processes leading to photoproducts.

Vinylcarbenes as Intermediates in the Direct Irradiation of Cyclopropenes

As was noted above, vinylcarbenes have frequently been proposed as intermediates in the direct irradiation of cyclopropenes. Some of the reactions that these species undergo include insertion into a C-H bond,²⁰ alkyl group migration²¹ and electrocycloaddition.²²⁻²⁵ Interestingly, none of the products previously reported correspond to addition of the carbene to a double bond. When we initiated our studies several years ago, it seemed to us that the intermediate vinylcarbene might undergo cycloaddition, provided an intramolecular trap were available. In order to establish the viability of this route, we studied the photochemistry of a series of

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(19) J. Michl, *J. Mol. Photochem.*, **4**, 243 (1972); **4**, 257 (1972).

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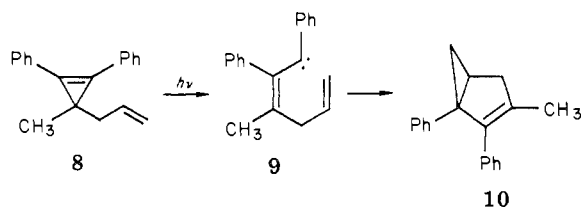
(22) M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967).

(23) H. Durr, *Justus Liebigs Ann. Chem.*, **723**, 102 (1969).

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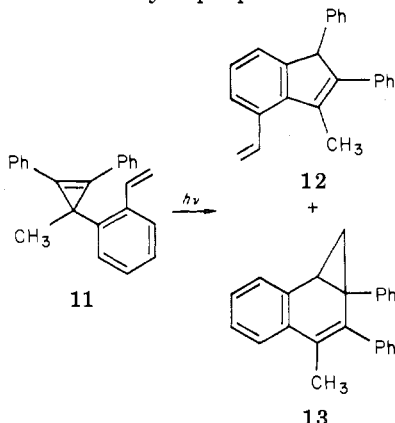
(25) B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Am. Chem. Soc.*, **93**, 2327 (1971).

3-allyl-substituted cyclopropene derivatives.⁸ Irradiation of cyclopropene **8** was found to afford bicyclohexene **10** in high yield. The most reasonable ex-



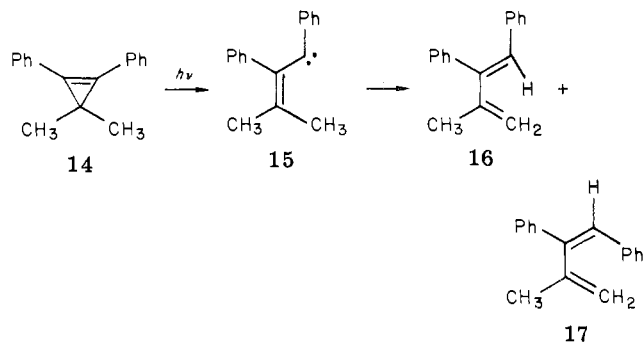
planation to account for the formation of bicyclohexene **10** involves a sequence consisting of ring opening of the electronically excited singlet state to a vinylcarbene intermediate (**9**). Attack of the carbene carbon on the neighboring double bond generates the bicyclo-[3.1.0]hex-2-ene skeleton.

A related rearrangement was also encountered on direct irradiation of cyclopropene **11**. In this case,



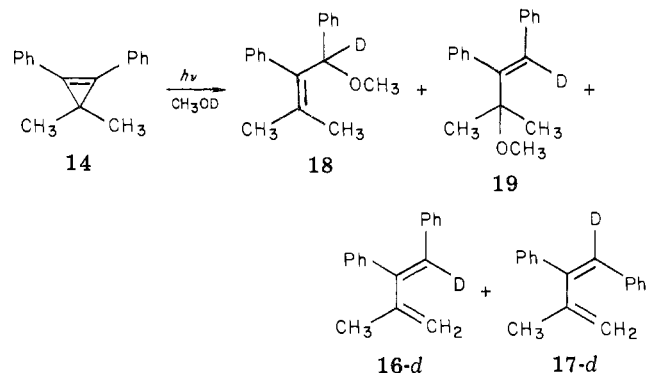
however, the initially formed vinylcarbene undergoes cyclization to an indene (**12**) as well as competitive addition to the adjacent π bond.²⁶

One of the more commonly observed reactions that vinylcarbenes undergo consists of insertion into a C-H bond.⁷ For example, Arnold and co-workers found that irradiation of 1,2-diphenyl-3,3-dimethylcyclopropene (**14**) produced the isomeric dienes **16** and **17** in a 3:1



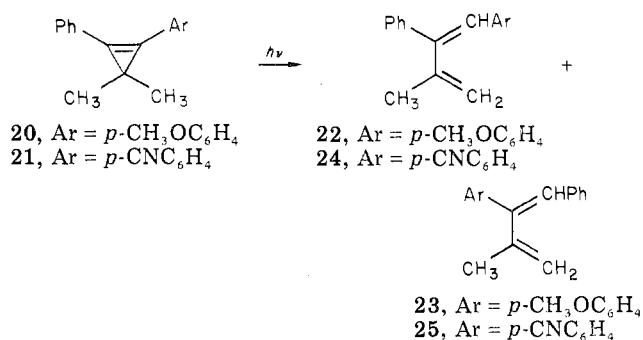
ratio.⁷ The formation of the dienes can readily be accounted for by a sequence consisting of ring opening of the electronically excited state of **14** to a vinylcarbene intermediate **15**. Insertion of the vinylcarbene onto the neighboring methyl group generates the observed products. Photolysis of **14** in a 9:1 methanol-pyridine solution gave 38% 1,2-diphenyl-1-methoxy-3-methyl-2-butene (**18**), 21% *cis*-1,2-diphenyl-3-methoxy-3-methyl-1-butene (**19**), 25% **16**, and 17% **17**. Photolysis

(26) A. Padwa, R. Loza, W. Reicker, and R. Polniaszek, unpublished results.



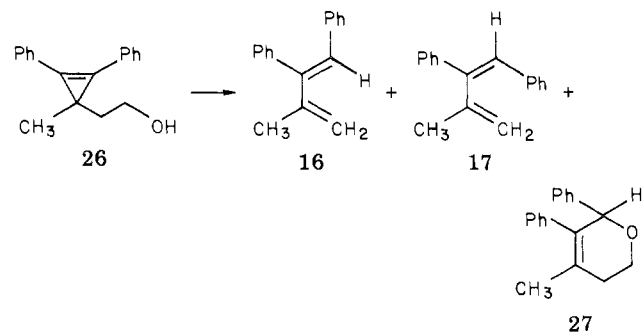
of **14** in CH_3OD gives the same products, but now deuterated. These results are consistent with the intervention of **15**, which can be trapped by protonation to give an allyl cation which subsequently reacts with methanol to give the observed products.

Irradiation of the related *p*-methoxy (**20**) and *p*-cyano (**21**) cyclopropene derivatives was also studied in order



to define the factors which influence the ring-cleavage process.²⁷ The results obtained indicate that there is a marked preference for formation of the dienes which result from cleavage of the cyclopropene bond adjacent to the aryl ring which donates electrons. In the vinylcarbene intermediate, the aryl ring on the carbene carbon would be conjugated with the electron-deficient π system. The observed product distribution then follows the expected stability of the alternative vinylcarbenes; that is, *p*-methoxyphenyl is favored relative to phenyl and phenyl is favored over *p*-cyano-phenyl at the carbene carbon.

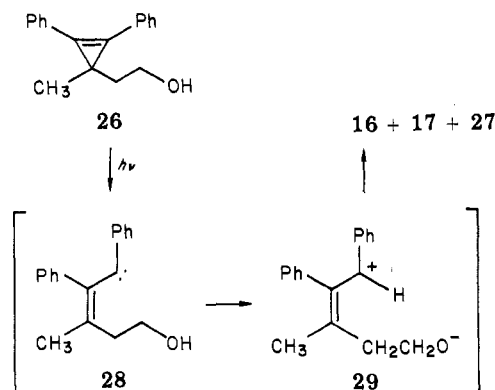
Yet another reaction undoubtedly resulting from a vinylcarbene intermediate is the formation of dienes **16** and **17** and dihydropyran **27** from the irradiation of cyclopropene **26**.²⁶ The formation of **27** is perfectly



consistent with a carbene intermediate (**28**). This reactive species inserts into the neighboring OH bond to give zwitterion **29** which either collapses to dihydro-

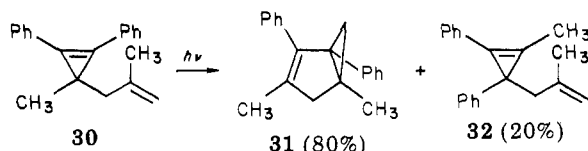
(27) R. M. Morchat and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 743 (1978).

pyran **27** or undergoes loss of formaldehyde and formation of dienes **16** and **17**.

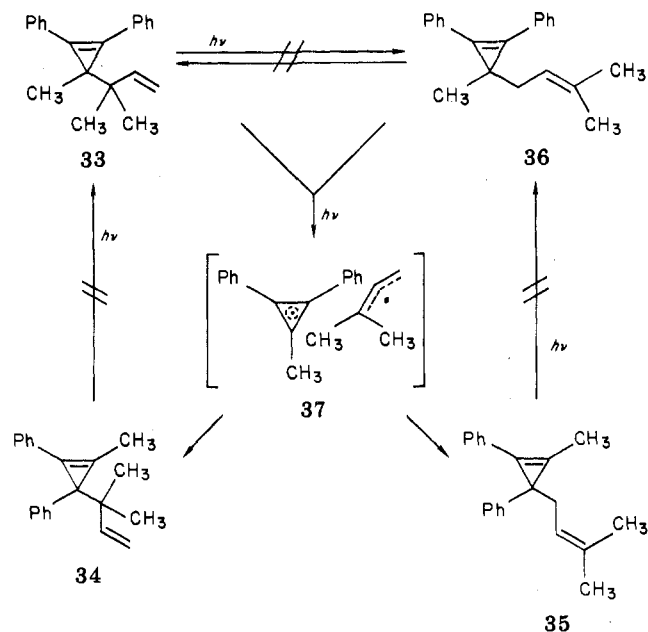


Side-Chain Cleavage

A more detailed investigation of the photochemistry of 3-allyl-substituted cyclopropenes has shown that the direct irradiation of these compounds can also lead to products which retain the three-membered ring.²⁸ We have recently observed that the irradiation of cyclopropene **30** gives products derived from both cyclopropenyl ring opening and from side-chain cleavage. Rupture of the cyclopropene σ bond leads to bicyclohexene **31** (80%) while α cleavage affords the isomeric cyclopropene **32** in 20% yield.



Successive introduction of methyl groups on the α or γ carbon was found to dramatically enhance the importance of side-chain cleavage relative to ring opening.²⁸ Thus, irradiation of cyclopropene **33** afforded a 1:1 mixture of the isomeric cyclopropenes **34** and **35** as the exclusive photoproducts. Similar results were



encountered with cyclopropene **36**, although in this case

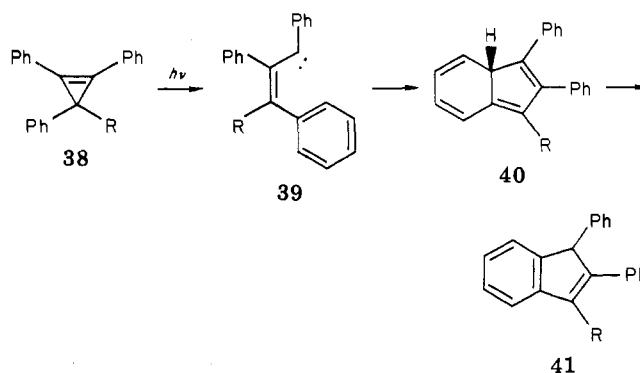
(28) A. Padwa, T. J. Blacklock, and R. Loza, *Tetrahedron Lett.*, 219 (1979).

the ratio of **34** to **35** was 1:3. Control experiments showed that **33** and **36** were not interconverted under the photolytic conditions. The formation of **34** and **35** from the radical pair **37** is to be expected since the transition state prefers to localize the odd electron on the phenylated carbon.²⁹ Further irradiation of **34** and **35** did not afford **33** and **36**, but instead gave indenenes derived from a vinylcarbene intermediate.

A mechanism analogous to that accepted for the type I cleavage reaction of ketones can readily account for the formation of the rearranged cyclopropenes. Introduction of methyl groups on the α or γ position of the allyl side chain will stabilize the radical-pair intermediate **37** enough to allow fragmentation to compete efficiently with ring cleavage. Cyclopropene **24**, without this stabilization, yields only ring-opened products. This same reasoning can explain the behavior of **33** (or **36**) where disubstitution prevents ring cleavage from competing with side-chain fragmentation.

Ring-Expansion Reactions

One of the more frequently encountered photochemical reactions of 3-aryl-substituted cyclopropenes involves rearrangement to indenenes.^{24,25} Formally analogous to the vinylcyclopropane-cyclopentene isomerization, this rearrangement can also be effected by acid,³⁰ transition metals,³¹⁻³³ or heat.²² The reaction has been proposed to proceed via an isoindene intermediate, **40**, which subsequently undergoes a thermally allowed sigmatropic shift to give the aromatic indene **41**.²²



The photochemistry of a number of unsymmetrically substituted aryl- and vinyl-substituted cyclopropenes has recently been studied in our laboratory³⁴⁻³⁶ and independently by Zimmerman.³⁷ The results obtained revealed the existence of an unusual substituent effect on the mode of ring opening of a series of unsymmetrically substituted cyclopropenes. Thus, the major product obtained from the irradiation of cyclopropene **42** was derived from the preferential cleavage of the cyclopropene single bond which is methyl rather than

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(30) R. Breslow, *Mol. Rearrangements*, 1, 257 (1963).

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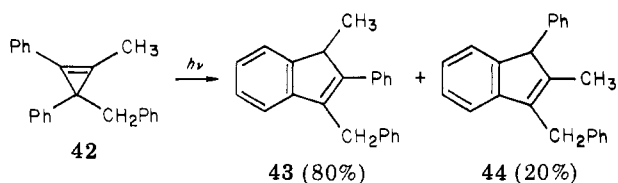
(34) A. Padwa, T. Blacklock, D. Getman, and N. Hatanaka, *J. Am. Chem. Soc.*, 99, 2344 (1977).

(35) A. Padwa, R. Loza, and D. Getman, *Tetrahedron Lett.*, 2847 (1977).

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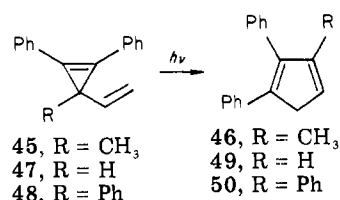
(37) H. E. Zimmerman and S. M. Aasen, *J. Am. Chem. Soc.*, 99, 2342 (1977); *J. Org. Chem.*, 43, 1493 (1978).

phenyl substituted.³⁶ Interestingly, the thermolysis of **42** gave indene **44** as the exclusive product. These



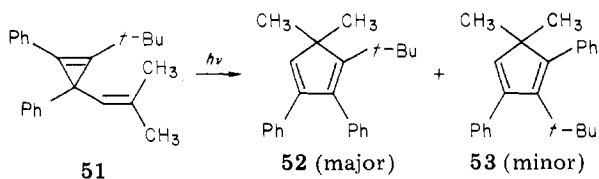
results clearly indicate that the excited-state and ground-state behavior of this small-ring system are quite distinct.

A number of 3-vinyl-substituted diarylcyclopropenes were also found to undergo rearrangement on direct irradiation. The photolysis of 1,2-diphenyl-3-methyl-3-vinylcyclopropene (**45**) resulted in the exclusive formation of 1,2-diphenyl-3-methyl-1,3-cyclopentadiene (**46**). Similar rearrangements were also found to occur



with cyclopropenes **47** and **48**. It is interesting to note that while indenenes are generally formed from the irradiation of 3-aryl-substituted cyclopropenes, the photolysis of **48** resulted in the exclusive formation of 1,2,3-triphenyl-1,3-cyclopentadiene (**50**). The photolysis of these systems was sufficiently free of byproducts that the reaction can be considered to be of general synthetic utility for the construction of substituted 1,3-cyclopentadienes.

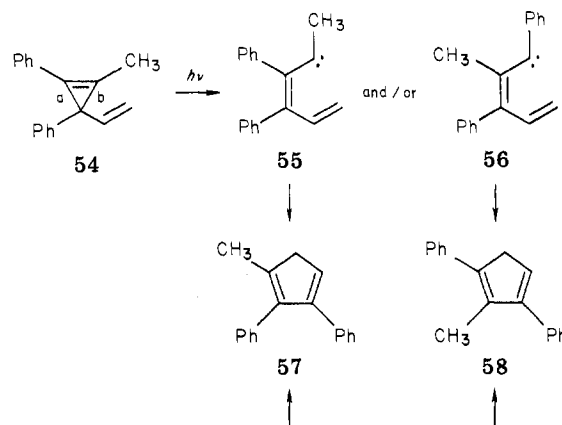
The photochemical rearrangement of a series of unsymmetrically 3-vinyl-substituted cyclopropenes was also studied by our research group. The reaction was found to be regioselective and to parallel the behavior encountered with the 3-aryl-substituted systems. Similar findings were made in related systems. For example, Zimmerman and Aasen reported that **52** is the major cyclopentadiene produced from the direct irradiation of cyclopropene **51**.³⁷



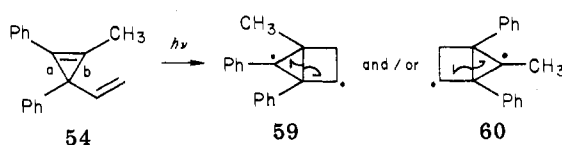
The two fundamentally different mechanisms which have been suggested to rationalize the above rearrangements are presented in Scheme I. Path A involves cyclopropene ring opening to give a butadienylcarbene, followed by electrocyclic ring closure. In the case of the 3-aryl-substituted cyclopropene system (**38**), the initially formed isoindene (i.e., **40**) would be expected to undergo a rapid 1,5-hydrogen shift to give an indene derivative (i.e., **41**). The alternate path (B) involves π - π bridging of the excited cyclopropene to give a diradical intermediate which subsequently cleaves to produce either the isoindene or 1,3-cyclopentadiene ring system. The bridging and cleavage steps are related to the first two formal steps of a di- π -methane rearrangement.³⁸ The two mechanistic

Scheme I

path A

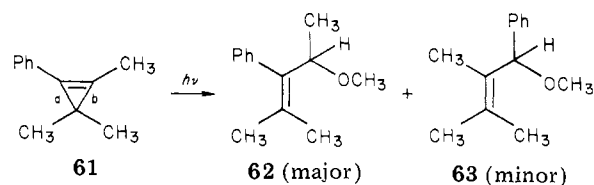


path B



possibilities illustrated in Scheme I make use of the unsymmetrical 3-vinyl-substituted cyclopropene ring system **54**. Analogous pathways can also be drawn for indene formation from the irradiation of the 3-aryl-substituted cyclopropenes.

Although path B seems to be a very reasonable mechanistic possibility, the bulk of the data is more compatible with the vinylcarbene route (path A). Thus, the complete suppression of indene formation when the irradiation is carried out in methanol can only be rationalized by a vinylcarbene intermediate which is trapped by protonation in methanol. Additional support for path A was obtained from the irradiation of 1-phenyl-2,3,3-trimethylcyclopropene (**61**). The only



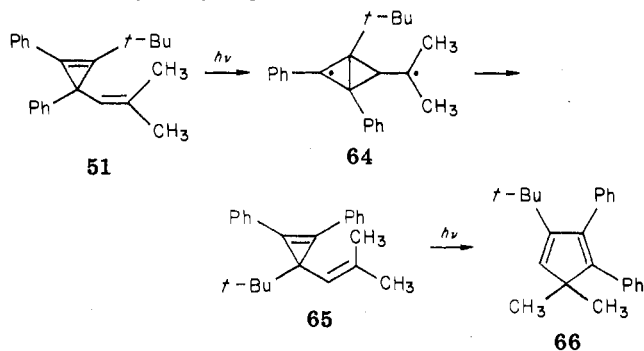
products obtained from the irradiation of **61** in methanol are methoxy ethers **62** (78%) and **63** (9%).³⁵ It is particularly worthy to note that the distribution of the methoxy ethers obtained corresponds to preferential bond b cleavage (78%) and is closely related to the results encountered with the 3-aryl- and vinyl-substituted cyclopropenes. In all of these cases, the major product is derived from cleavage of the cyclopropene bond attached to the methyl group. Even though cyclopropene **61** does not contain a π bond at the 3-position, it still prefers to undergo bond b fragmentation.

According to the carbene mechanism for cyclopentadiene or indene formation (path A, Scheme I), preferential formation of the more stabilized carbene **56** (phenyl-substituted) might be expected. This is indeed the case when cyclopropene **42** is thermolyzed. The excited-state behavior of these systems, however,

(38) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

is substantially different. A reasonable explanation which can account for this difference assumes close approach of the excited singlet surface of cyclopropene **54** with the ground-state surfaces of vinylcarbenes **55** and **56**. The preferential cleavage of the cyclopropene bond attached to the methyl group agrees well with the "funnel theory" of excited-state to ground-state conversions.¹⁹ Close approach of the two surfaces greatly enhances internal conversion and therefore gives a route for excited singlet cyclopropene to open to vinylcarbene and then either return to ground-state cyclopropene or rearrange to the 1,3-cyclopentadiene or indene. Since the carbene derived from bond b cleavage (i.e., **55**) is higher lying than that derived from bond a cleavage (i.e., **56**), it could be more easily funneled into from the excited singlet surface of the cyclopropene.

One additional point of interest concerns the photochemistry of cyclopropene **51**.³⁷ Irradiation of this



compound afforded 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene (**66**) in addition to the expected cyclopentadienes **52** and **53**. The formation of this unusual product has been rationalized as arising from an incipient di- π -methane rearrangement to give diradical **64** which affords isomeric cyclopropene **65**.³⁷ This cyclopropene then should proceed onward to give **66**. NMR monitoring of the reaction did not reveal the presence of **65**, and thus it appears to be consumed as rapidly as it is formed.

Photodimerization Reactions

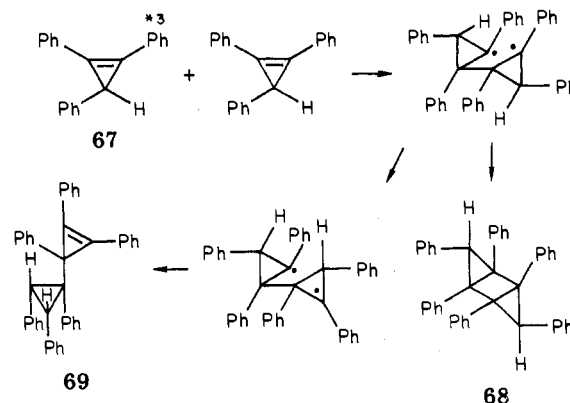
As discussed earlier, singlet states of cyclopropenes generally react by σ -bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes, while triplet states, generated by sensitization techniques, give high yields of cyclopropene dimers.³⁹⁻⁴¹ The photosensitized irradiation of 1,2,3-triphenylcyclopropene (**67**) has been reported to give a tricyclohexane dimer (i.e., **68**) as the major product as well as cyclopropylcyclopropene **69** as the minor dimer. Photophysical studies including quantum yield measurements and isotope effects are consistent with the interpretation that the dimerization of **67** occurs in a stepwise fashion via a diradical intermediate.⁴² Further observations by DeBoer⁹ indicate that there are severe steric constraints on the cyclopropene dimerization reaction. Thus, 1,2-diphenylcyclopropenes where both 3-positions are substituted with groups larger than a hydrogen atom do not dimerize as a consequence of severe steric factors.

(39) H. H. Stechl, *Chem. Ber.*, **97**, 2681 (1964).

(40) C. DeBoer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967).

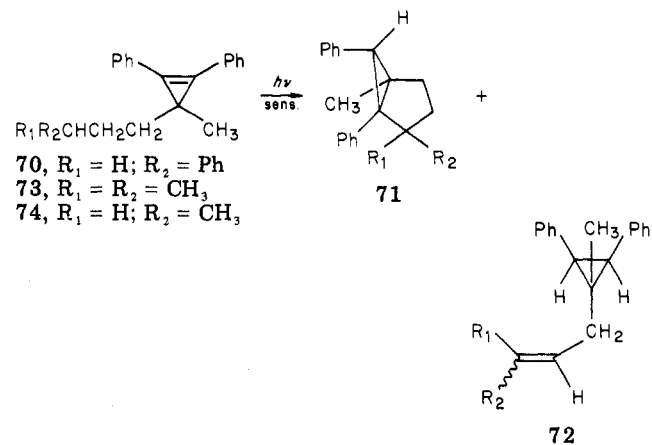
(41) H. Durr, *Tetrahedron Lett.*, 1649 (1967).

(42) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).



Hydrogen Atom Transfer Reactions

Recent work in our laboratory has shown that tetrasubstituted cyclopropenes which possess γ hydrogens on the 3-alkyl side chain undergo an intramolecular hydrogen atom transfer reaction when photolyzed in the presence of a triplet sensitizer.⁴³ Thus, irradiation of cyclopropene **70** in the presence of thioxanthone produced a mixture of *endo*- and *exo*-5-methyl-1,2,6-triphenylbicyclo[3.1.0]hexane (**71**) as well as *cis*-1,2-di-



phenyl-*cis*-3-methyl-3-(3-phenyl-2-propenyl)cyclopropene (**72**) as a mixture of isomers. The triplet-sensitized rearrangement was remarkably efficient, with a quantum yield of 0.57. A similar set of reactions was encountered with cyclopropenes **73** and **74**.⁴³

A mechanism analogous to that accepted for the type II reaction of ketones can readily account for the formation of **71** and **72**.⁴³ The excited triplet state of the cyclopropene abstracts a hydrogen from the benzylic carbon, via a six-membered transition state, to produce a 1,5-biradical which either couples or disproportionates. There are a number of reports in the literature that indicate that hydrogen transfer reactions occur in the photochemistry of alkenes,⁴⁴⁻⁴⁶ thereby providing good analogy for the above reaction. Further studies with the structurally related cyclopropene **75** have shown that the triplet state of this system affords bicyclohexane **76** and cyclopropane **77** as the exclusive photoproducts.⁴⁷ Thus, the reaction is completely regioselective and involves hydrogen atom transfer from

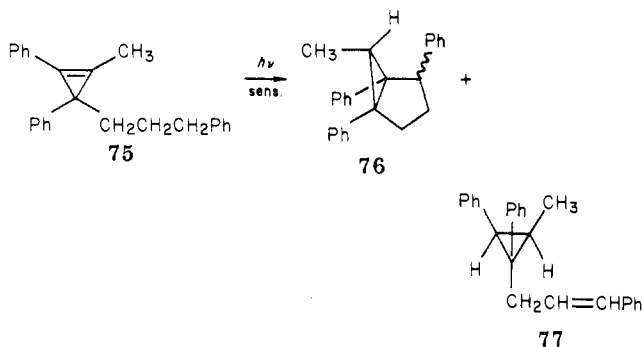
(43) A. Padwa, U. Chiacchio, and N. Hatanaka, *J. Am. Chem. Soc.*, **100**, 3928 (1978).

(44) H. M. Rosenberg and P. Serve, *J. Am. Chem. Soc.*, **92**, 4746 (1970).

(45) J. M. Hornback, *J. Am. Chem. Soc.*, **96**, 6772 (1974); *Tetrahedron Lett.*, 3389 (1976).

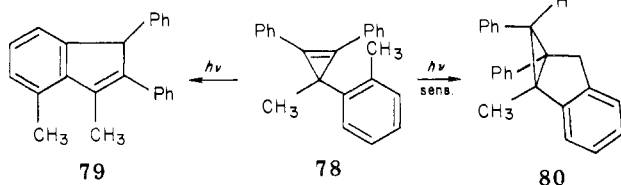
(46) F. Scully and H. Morrison, *J. Chem. Soc., Chem. Commun.*, 529 (1973).

(47) A. Padwa and S. Chou, unpublished results.



the carbon bearing methyl group. This is undoubtedly related to the fact that the diradical produced on hydrogen transfer to the methyl-bearing carbon allows maximum delocalization of the radical centers in the resulting diradical intermediate.

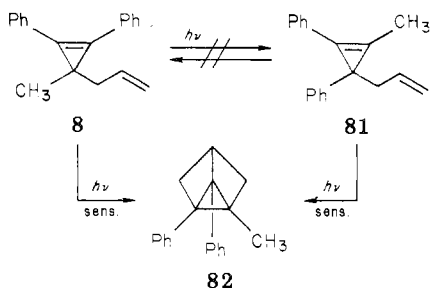
The irradiation of 1,2-diphenyl-3-methyl-3-*o*-tolylcyclopropene (78) provides another example of a system in which the products of the direct and triplet-sensitized photolysis are completely different. Direct irradiation of 78 afforded indene 79 in quantitative yield. The



sensitized photolysis of 78 followed an entirely different course and produced benzobicyclo[3.1.0]hexane 80 in high yield.⁴³ A mechanism similar to that suggested for 70 readily rationalizes the formation of 80.

Intramolecular 2 + 2 Cycloadditions

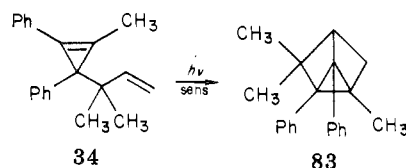
Previous work has shown that trisubstituted cyclopropenes dimerize on triplet sensitization to give tricyclo[3.1.0.0^{2,4}]hexanes.⁹ Attempts to obtain cross-adducts with other π bonds are usually unsuccessful, since the rate of reaction of the excited triplet cyclopropene with cyclopropene ground state is so rapid that observable cross-adduct formation is precluded.⁹ By retaining the π bond within the same molecule, we reasoned that it should be possible to observe intramolecular cycloaddition, especially if tetrasubstituted cyclopropenes are used. In fact, work in our laboratory has shown that 3-allyl-substituted cyclopropenes undergo smooth intramolecular 2 + 2 cycloaddition on triplet sensitization.⁸ Thus, irradiation of either 8 or 81 with thioxanthone produced 1,2-diphenyl-6-methyltricyclo[2.2.0.0^{2,6}]hexane (82) as the exclusive photoproduct.⁸



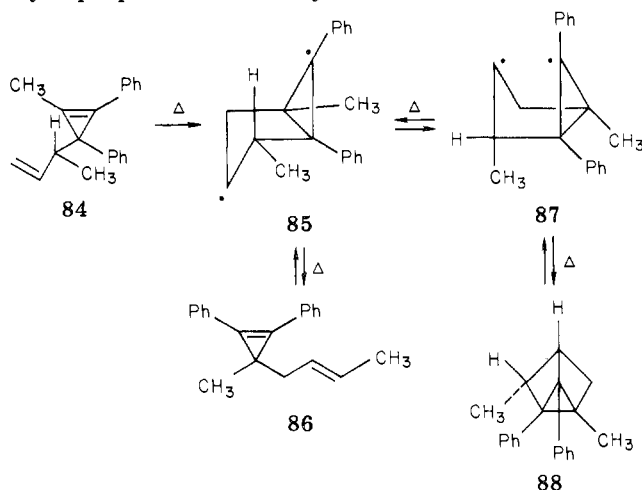
Although cyclopropenes 8 and 81 are thermally equilibrated upon heating in xylene,⁴⁵ control experi-

ments showed that they were not interconverted by a Cope reaction under the sensitized photolytic conditions.⁸ Similar 2 + 2 cycloadditions were encountered with a related series of cyclopropenes. The regioselectivity observed with cyclopropene 34 indicates that the initial bond-forming step occurs on the cyclopropene carbon bearing the methyl group. This parallels the behavior exhibited by cyclopropene 75 in the intramolecular hydrogen-transfer reaction.

It should be noted that the thermolysis of these 3-allyl-substituted cyclopropenes results in both a Cope rearrangement and tricyclo[2.2.0.0^{2,6}]hexane forma-



tion.⁴⁶ For example, heating a sample of 84 afforded cyclopropene 86 and tricyclohexane 88. The mecha-

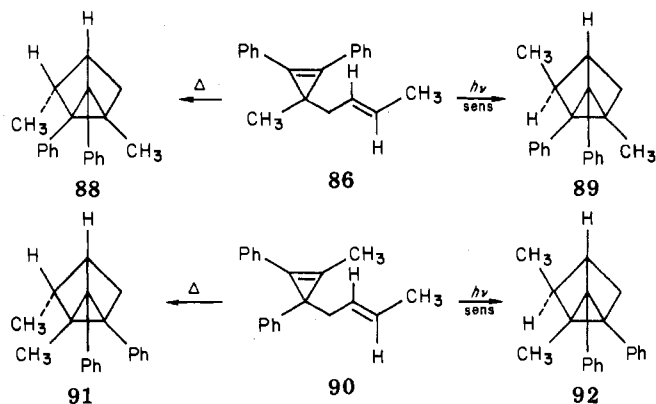


nism which has been proposed to account for the stereochemical results encountered on thermolysis of 84 involves the initial formation of a biradical intermediate (85) in a conformation which is analogous to the chair conformation of cyclohexane. Subsequent fragmentation of this species affords the Cope rearrangement product 86. Ring inversion of the initially formed chair intermediate 85 generates the boat biradical 87 which cyclizes to the tricyclo[2.2.0.0^{2,6}]hexane ring system. Tricyclohexane 88 was also formed from the thermolysis of cyclopropene 86 via intermediates 85 and 87. The overall inversion of stereochemistry in the thermal 2 + 2 cycloaddition reaction of 86 can be attributed to that fact that the thermal reaction proceeds through a four-center, chairlike conformation. The ring flip of the initially formed chair intermediate 85 to the boat diradical 87 is the major factor responsible for the overall inversion of stereochemistry of the thermal cycloaddition.

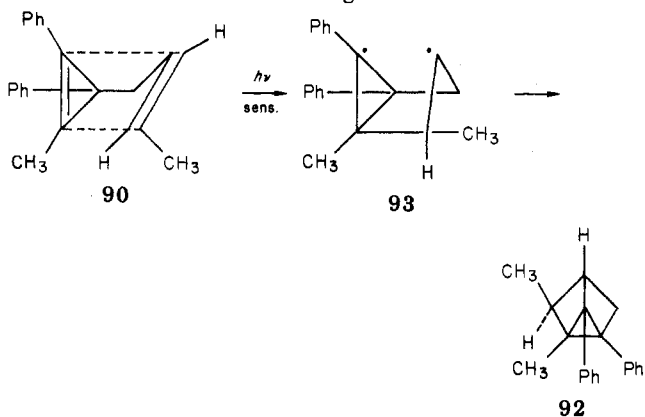
In marked contrast to the thermal results, we have found that the triplet-sensitized cycloaddition reaction of 86 produces tricyclo[2.2.0.0^{2,6}]hexane (89) in which retention of stereochemistry has occurred.⁴⁹ Similar results were encountered with cyclopropene 90. The above results indicate that there is a major difference in the stereochemical course of the thermal and trip-

(48) A. Padwa and T. J. Blacklock, *J. Am. Chem. Soc.*, **100**, 1321 (1978).

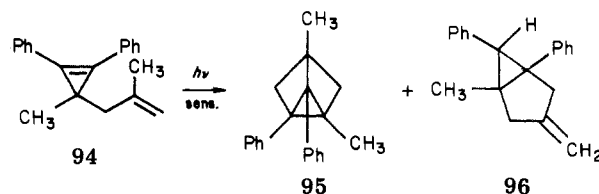
(49) A. Padwa, T. J. Blacklock, and R. Loza, unpublished results.



let-induced 2 + 2 cycloaddition reactions of these allyl-substituted cyclopropenes. It is tempting to suggest that the triplet-induced cycloaddition reactions of these systems proceed through a six-center, boatlike conformation. The secondary overlap of the frontier orbitals involved in the 2 + 2 cycloaddition reaction should favor the boatlike arrangement in the excited state and disfavor it in the ground state.



That these triplet-induced cycloaddition reactions are not concerted processes was demonstrated by the finding that cyclopropene **94** gave rise to a 2 + 2 adduct (**95**) and a bicyclohexane (**96**) on triplet sensitization.



The formation of **96** proceeds via an intramolecular hydrogen-transfer reaction. Both products were equally quenched with added triplet quenchers, thereby indicating that they are both derived from a common triplet state.

Conclusion

Cyclopropene derivatives have been found to undergo a wide array of novel photochemistry. The photobehavior encountered is markedly dependent on the substituent groups present and the multiplicity of the excited state. Significant progress has been made toward understanding the factors which determine the photochemical behavior in a given system. Further work will be needed to clarify the mechanistic features of some of the systems.

It is a pleasure to acknowledge the vital contribution of my collaborators, whose names are to be found in the references. Our studies have been generously supported by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

Inductive Enhancement of Neighboring Group Participation

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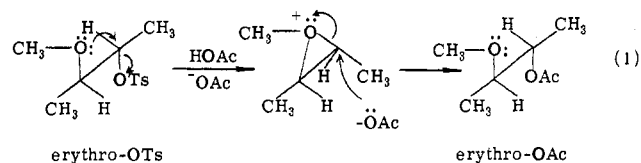
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The nucleophilic displacement reaction (S_N) is particularly rapid when the nucleophile and the leaving group are in the same molecule (1). Such intramolecular

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displacement, which has been termed anchimeric assistance or neighboring group participation, occurs not only in appropriate organic systems but also in many biochemical processes. Among the internal nucleophiles believed to be able to carry out such displacements are those possessing nonbonding electrons (halogen, oxygen, nitrogen, sulfur), those containing a π bond (double and