clopentadiene formation leads to complex kinetic arguments which are delayed for our full paper. Also complicating matters in the carbene mechanism is the possibility of cis and trans carbenes.

(9) (a) H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **91**, 5307 (1969); (b) H. E. Zimmerman and G. A. Epling, *ibid.*, **94**, 8749 (1972); (c) H. E. Zimmerman, F. X. Albrecht, and M. J. Haire, *ibid.*, **97**, 3726 (1975).

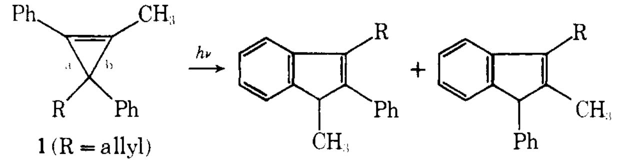
Howard E. Zimmerman,* Steven M. Aasen
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received December 6, 1976

Regioselectivity of Bond Cleavage in the Photochemical Rearrangement of 3-Vinylcyclopropenes[1]

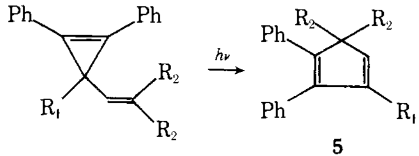
Sir:

Vinylcarbenes have frequently been proposed as intermediates in the thermal and photochemical reactions of cyclopropenes.[2] Extended Huckel calculations carried out on the parent vinylcarbene system suggest a triplet diradical type structure for the ground state of this system.[3] More recent calculations by Davis, Goddard, and Bergman[4] predict that the ring opening reaction of cyclopropene first proceeds to a diradical planar intermediate which subsequently decays to a carbene. As part of a continuing study dealing with the thermal and photochemical reactions of cyclopropenes, we recently encountered an unusual substituent effect on the mode of ring opening of an unsymmetrical diarylcyclopropene.[5] Thus, irradiation of methylcyclopropene **1** afforded a 4:1 mixture of indenes **2** and **3**.[6] It is well known that phenyl substituents stabilize free radicals, and thereby lower carbon-carbon bond energies in saturated three-membered rings.[7] Were this effect to operate in the cyclopropene system, methylphenylcyclopropene **1** should undergo preferential cleavage at bond a. We note, however, that the major indene produced corresponds to cleavage of bond b. In this communication we suggest an explanation to account for this unusual regioselectivity as well as a description of the formation of cyclopentadienes from the irradiation of 3-vinylcyclopropenes.[8]



1 (R = allyl) 2 3

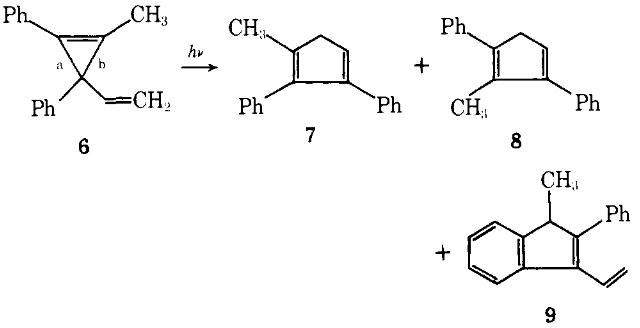
A number of 3-vinyl substituted diarylcyclopropenes were prepared by treating variously substituted cyclopropenyl cations with vinyl Grignard reagents and separating the mixture of isomers formed by column chromatography. Although indenes are generally formed from the irradiation of 3-aryl substituted cyclopropenes,[2b,d,e] the photolysis of **4a** resulted in the exclusive formation of cyclopentadiene **5a**. Similar rearrangements were also found to occur with cyclopropenes **4b-d**.[9]



4 5

a, R_1 = Ph; R_2 = H
b, R_1 = R_2 = H
c, R_1 = CH_3; R_2 = H
d, R_1 = R_2 = CH_3

Subjection of cyclopropene **6** to similar photolysis conditions gave a mixture of 1-methyl-2,3-diphenyl (**7**) and 2-methyl-1,3-diphenyl-1,3-cyclopentadiene (**8**) as well as 1-vinyl-2-phenyl-3-methylindene (**9**) in good yield. With this system the formation of the isomeric 1-vinyl-2-methyl-3-phenylindene was not observed. The structures of these compounds were based on their spectroscopic and analytical properties and were further confirmed by the Diels-Alder reactions of **7** and **8** with dimethyl acetylenedicarboxylate. The major products obtained correspond to the preferential cleavage of bond b (ratio **7**/**8** = 2.5/1).



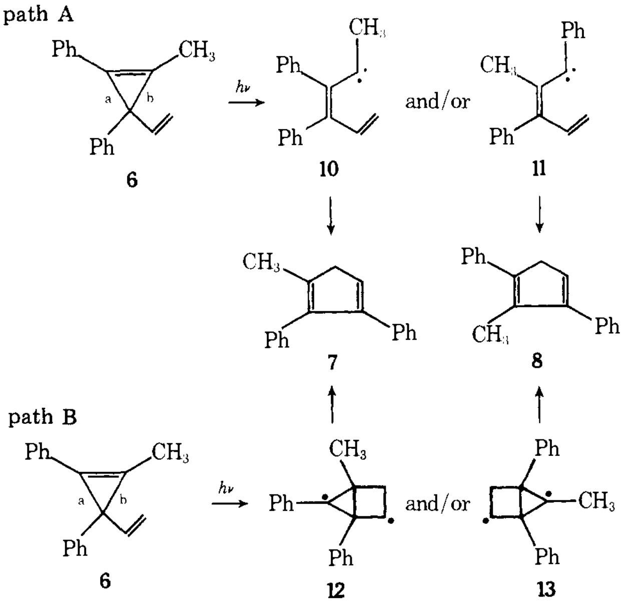
6 7 8 9

The mechanism by which these 3-vinyl substituted cyclopropenes undergo rearrangement and the identification of the excited state responsible for the reaction are of considerable interest. Two fundamentally different mechanisms seem possible and are presented in Scheme I. Path A involves cyclopropene ring opening to give a butadienyl carbene followed by electrocyclic ring closure. This route bears a strong similarity to mechanisms previously suggested to rationalize the products derived from substituted cyclopropenes on electronic excitation.[2,5] The alternate path (B) involves π-π bridging of the excited cyclopropene to give a diradical intermediate which subsequently cleaves to produce the 1,3-cyclopentadiene ring system. The bridging and cleavage steps are related to the first two formal steps of a di-π-methane rearrangement.[10]

The excited state responsible for photoreaction of the 3-vinyl substitued cyclopropenes is a π-π^* singlet, since sensitization with thioxanthone led to no reaction with cyclopropenes **4a** and **4c** and gave a 2 + 2 dimer with **4b**. This is consistent with DeBoer's earlier observation that the intersystem crossing efficiencies of diphenylcyclopropenes are close to zero.[11]

Mention should be made here of the unusual effect of sub-

Scheme I



6 10 11 7 8 6 12 13

stitution on the mode of ring opening of cyclopropene **6**. The distribution of the 1,3-cyclopentadienes obtained corresponds to preferential bond b cleavage and is closely related to the results encountered with cyclopropene **1**. In both of these cases, the major product (indene or cyclopentadiene) formed is derived from cleavage of the cyclopropene bond attached to the methyl group. This result can be understood in terms of the mechanisms outlined in Scheme I. If the carbene mechanism (path A) were correct, preferential formation of the more stabilized carbene **11** (phenyl substituted) might be expected. This is not the case. It should be pointed out, however, that theory predicts[4] that it is the 1,3-diradical singlet state rather than the methylene like singlet which results on opening of the cyclopropene ring. The initially produced 1,3-diradical state may then decay to the carbene which could undergo subsequent reactions characteristic of a singlet vinylcarbene. Thus, the preference for bond b cleavage could conceivably be attributed to inductive destabilization of the initially generated vinyl radical by the attached phenyl group. In support of this explanation, Battiste and co-workers[2b] have found that tetraphenylcyclopropene rearranges to 1,2,3-triphenylindene with an activation energy 7 kcal more than that required for the racemization of optically active 1,3-diethylcyclopropene.[2i] This rather large difference clearly implies that phenyl groups affect the C–C single bond energies in cyclopropenes in a striking unprecedented manner. Alternatively, the predominant scission of bond b may stem from the occurrence of path B. According to this mechanism, π–π bridging would be expected to give the most stable diradical (**12**) and thus lead to the preferential formation of the 2-phenyl substituted 1,3-cyclopentadiene **7**. A similar explanation would also account for the regioselectivity observed for indene formation with cyclopropenes **1** and **6**.

In order to help elucidate the correct pathway, the photochemistry of cyclopropenes **4b** and **4c** was carried out in methanol. These experiments, which were designed to trap a carbene intermediate, were unsuccessful and the only products isolated were 1,3-cyclopentadienes **5b** and **5c**. Failure to trap a carbene intermediate on irradiation in methanol does not necessarily eliminate this species as a reaction intermediate. The absence of methanol insertion products may be due to the facile intramolecular cyclization path available to the butadienyl carbene. Alternatively, a carbene intermediate may not be required if the photoreaction of **4b** proceeds through path B. Further studies on the scope and mechanism of this reaction are in progress and will be reported in due course.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant No. CHE76-02791).

References and Notes

(1) Photochemical Transformations of Small Ring Compounds. 86. For part 85, see A, Padwa, T. Brookhart, D. Dehm, G. West, and G. Wubbels, *J. Am. Chem. Soc.*, **99**, 2347 (1977).

(2) (a) H. Kristinnson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966); (b) M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967); (c) R. D. Streeper and P. D. Gardner, *Tetrahedron Lett.*, 767 (1973); (d) H. Durr, *Justus Liebigs Ann. Chem.*, (e) B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Am. Chem. Soc.*, **93**, 2327 (1971); (f) G. E. Palmer, J. R. Bolton, and D. R. Arnold, *ibid.*, **96**, 3708 (1974); (g) D. R. Arnold, J. A. Pincock, and R. Morchant, *ibid.*, **95**, 7536 (1973); (h) D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, *ibid.*, **98**, 6225 (1976); (i) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *ibid.*, **94**, 2882 (1972); *ibid.*, **95**, 5680 (1973).

(3) (a) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968); (b) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968); (c) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(4) J. H. Davis, W. A. Goddard, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 4015 (1976).

(5) A. Padwa and T. J. Blacklock, *J. Am. Chem. Soc.*, **99**, 2345 (1977).

(6) The formation of indenes from 3-arylcyclopropenes has been previously reported in the literature.[2b,d,e]

(7) (a) L. B. Rodewald and C. H. Depuy, *Tetrahedron Lett.*, 2951 (1964); (b) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

(8) H. E. Zimmerman and S. M. Aasen have informed us of their similar results and we thank them for communicating their results to us, *J. Am. Chem. Soc.*, preceding paper in this issue.

(9) Full experimental details will be given in our full paper.

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

(11) C. D. DeBoer, O. H. Wadsworth, and W. C. Perkins, *J. Am. Chem. Soc.*, **92**, 5541 (1970).

Albert Padwa,* Thomas J. Blacklock
Daniel Getman, Naoto Hatanaka
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received January 24, 1977

Photochemical Transformations of 3-Allyl Substituted Cyclopropenes[1]

Sir:

Studies of the thermal and photochemical reactions of cyclopropenes have played an important role in the development of our understanding of the mechanism by which carbon–carbon bonds may be broken and re-formed.[2] Recent calculations predict that the ring opening of cyclopropene should proceed to a diradical planar intermediate which may subsequently decay to a vinyl carbene.[3] This species can rotate back to the diradical state[2q,3] or undergo reactions characteristic of a singlet or triplet methylene. These include intramolecular hydrogen abstraction,[2m,q] insertion into a C–H bond,[2f] alkyl migration,[2f,o] and cyclization.[2c,g-i] Interestingly, none of the products reported correspond to addition of the carbene to a double bond.[4] It seemed to us that the intermediate vinyl carbene might undergo cycloaddition, provided an intramolecular trap were available. In this communication we describe the occurence of such a process and thus provide additional support for the intermediacy of a vinyl carbene in the photolysis of substituted cyclopropenes.

1,2-Diphenyl-3-allylcyclopropene[5] (**1**) was prepared in high yield by treating diphenylcyclopropenyl cation with allylmagnesium bromide according to the general procedure of Breslow and Dowd.[6] Irradiation of **1** in benzene or hexane with Pyrex filtered light[7] resulted in dimerization[8] and produced tricyclohexane **2**, mp 191–192 °C, in high yield. The assignment of structure **2** rests on its characteristic NMR, IR, and mass spectra,[5] its elemental analysis, and chemical behavior. Thus, photodimer **2** undergoes thermal rearrangement above 190 °C to an isomeric cyclohexadiene, **3**, mp 211–212 °C. Similar thermal rearrangements of related tricyclohexanes have been reported in the literature[8] and provide reasonable chemical analogy for this [2 + 2] retrogression reaction. Sensitization of **1** with benzophenone gave only **2**, in agreement