Tetrahedron Letters No. 3, pp 219 - 222. 0040-4039/79/0115-0219$02.00/0

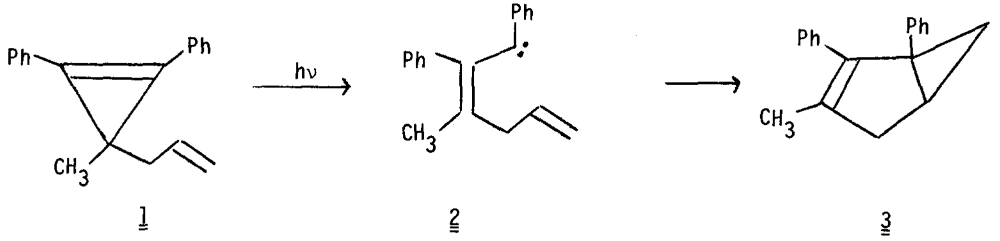
NORRISH TYPE I BEHAVIOR IN THE PHOTOCHEMISTRY OF CYCLOPROPENE DERIVATIVES

Albert Padwa,* Thomas J. Blacklock and Roman Loza
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

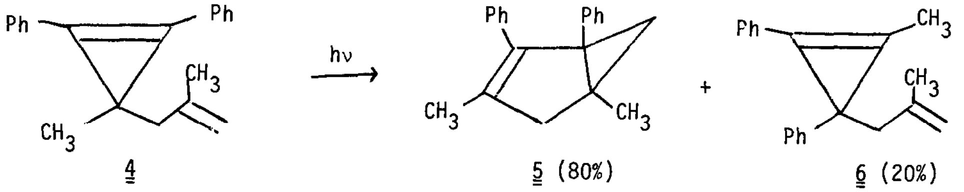
During the last few years the photochemistry of cyclopropene derivatives has attracted considerable interest.[1] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes,[2,3] while triplet states, generated by sensitization techniques, give 2+2 dimers[4] or cycloadducts.[5,6] Recent MO calculations suggest that the singlet excited state of cyclopropenes can readily open in an unactivated process to relieve the strain energy present in the ring.[7] Triplet states, on the other hand, have a barrier to ring opening and are therefore long-lived enough to encounter another ground state molecule leading to dimerization. We now wish to report the first example of a singlet state reaction of a cyclopropene in which the three-membered ring has been retained.

We had previously found that the direct irradiation of 3-allyl-3-methyl-1,2-diphenylcyclopropene (1) afforded 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-2-ene (3) as the exclusive photoproduct.[8] The most reasonable explanation to account for the formation of 3 involves ring opening of the electronically excited singlet state of 1 to a vinylcarbene intermediate (2). The formation of the vinylcarbene can be viewed as the result of an initial heterolytic cleavage and rotation of the disubstituted carbon atom.[9] Both electrons occupy an in-plane σ-orbital with only two electrons in the conjugated π-orbital. Extended Hückel calculations carried out on the parent system show that the vinylcarbene correlates with the excited singlet state but not the ground state.[10] Attack of the carbene carbon on the neighboring double bond generates the bicyclo[3.1.0]hexene skeleton.

Irradiation of the related cyclopropene 4 yields products derived from both cyclopropenyl ring opening and from α-cleavage. Rupture of the cyclopropene σ-bond leads to bicyclohexene 5 (80%) while α-cleavage affords the isomeric cyclopropene 6 in 20% yield.

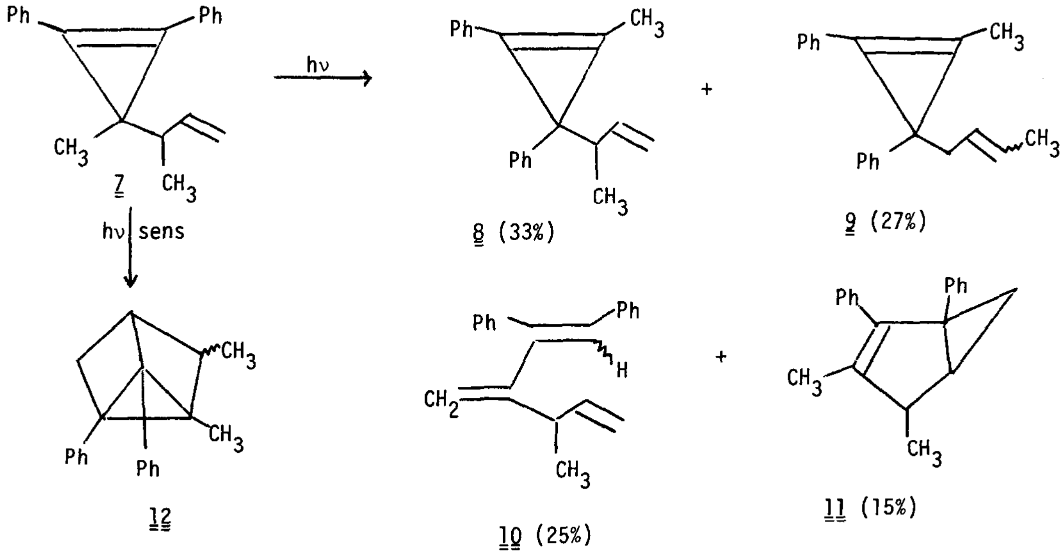


1 2 3



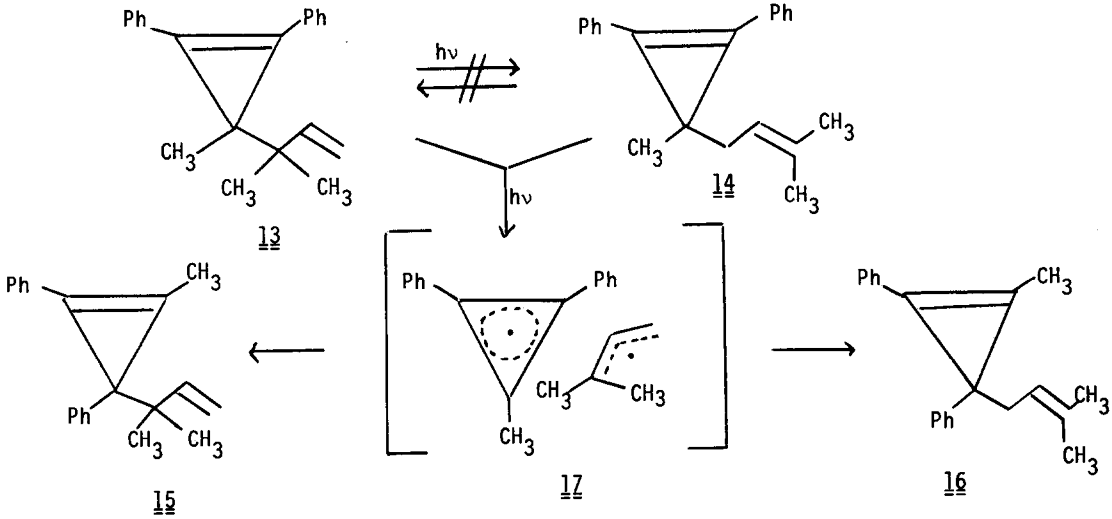
4 5 (80%) 6 (20%)

The photochemistry of cyclopropene 7 was found to proceed differently from 4 in that the major products (8 and 9) are now derived from α-cleavage (60% overall). The two minor components (40% overall) in the reaction mixture (10 and 11) can be considered to be formed from a transient vinylcarbene intermediate which either inserts into the methyl group[3] or undergoes addition to the neighboring π-system. The photochemical reactions encountered on direct irradiation of 7 proceed through the singlet manifold since sensitization with thioxanthone gave tricyclo[2.2.0.0^{2,6}]hexane 12 as the exclusive photoproduct.[11]



7 8 (33%) 9 (27%) 12 10 (25%) 11 (15%)

We have found that the successive introduction of methyl groups on the α-carbon dramatically increases the importance of α-cleavage relative to ring opening. Thus, irradiation of cyclopropene 13 afforded a 1:1 mixture of the isomeric cyclopropenes 15 and 16 as the exclusive photoproducts. Similar results were encountered with cyclopropene 14; although in this case, the ratio of 15:16 was 1:3. Control experiments showed that 13 and 14 were not interconverted under the photolytic conditions. The formation of 15 and 16 from the radical pair 17 is to be expected since the transition state prefers to localize the odd electron on a phenylated carbon.[12] Further irradiation of 15 and 16 did not afford 13 or 14 but instead gave indenes derived from a vinylcarbene intermediate.[13]



We propose a mechanism analogous to that accepted for the type I reaction of ketones to 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 17 enough to allow fragmentation to compete efficiently with ring cleavage. Cyclopropene 1, without this stabilization, yields only ring opened products. This same reasoning can explain the behavior of 13 (or 14), where disubstitution prevents ring cleavage from competing with side chain fragmentation.

The above results allow the following generalizations to be made regarding the photochemistry of allyl-substituted cyclopropene derivatives: (1) Excited cyclopropene singlets give products consistent with σ-bond cleavage to vinyl carbenes whereas triplet states undergo intramolecular 2+2 cycloadditions; (2) Cyclopropene singlets have very inefficient intersystem crossing efficiencies which accounts for the absence of tricyclo[2.2.0.$0^{2,6}$]-hexanes from direct irradiation experiments; (3) Side chain fragmentation can compete with ring cleavage as a primary process when stable radicals are produced.

Acknowledgement: We gratefully acknowledge the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

References

1. For some leading references see A. Padwa, T. J. Blacklock, D. Getman, N. Hatanaka and R. Loza, J. Org. Chem., 43, 1481 (1978).
2. G. E. Palmer, J. R. Botton and D. R. Arnold, J. Am. Chem. Soc., 96, 3708 (1974).
3. D. R. Arnold, J. A. Pincock and R. Morchat, J. Am. Chem. Soc., 95, 7536 (1973).
4. C. D. DeBoer, D. H. Wadsworth and W. C. Perkins, J. Am. Chem. Soc., 95, 861 (1973).
5. D. R. Arnold and R. M. Morchat, Can. J. Chem., 55, 393 (1977).
6. K. A. Brown-Wensley, S. L. Mattes and S. Farid, J. Am. Chem. Soc., 100, 4162 (1978).
7. J. A. Pincock and R. J. Boyd, Can. J. Chem., 55, 2482 (1977).
8. A. Padwa and T. J. Blacklock, J. Am. Chem. Soc., 99, 2345 (1977).
9. R. M. Morchat and D. R. Arnold, Chem. Commun., 743 (1978).
10. J. H. Davis, W. A. Goddard III and R. G. Bergman, J. Am. Chem. Soc., 98, 4015 (1976); 99, 2427 (1977).
11. Actually, a 1:1 epimeric mixture of isomers were obtained. Complete spectroscopic and degradative details will be given in our full publication.
12. For related observations see R. W. Johnson, T. Widlanski and R. Breslow, Tetrahedron Lett., 4685 (1976).
13. A. Padwa, T. Blacklock, D. Getman and N. Hatanaka, J. Am. Chem. Soc., 99, 2344 (1977).