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REARRANGEMENT IN THE 1,3'-BICYCLOPROPENYL SERIES

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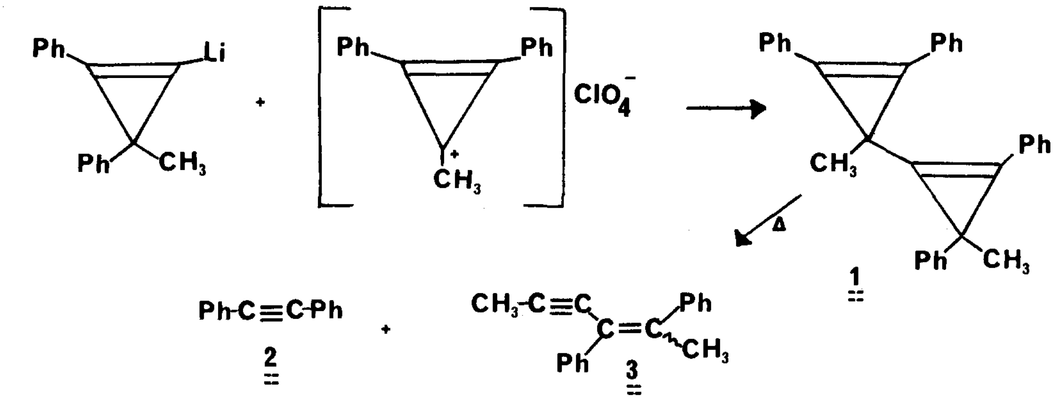
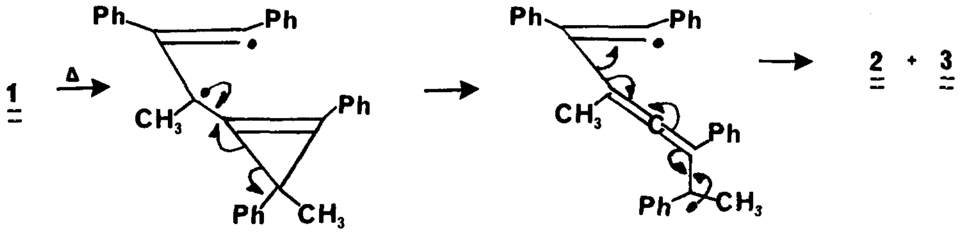
Abstract: The photochemical behavior of a representative 1,3'-bicyclopropene was studied and was found to undergo a novel rearrangement to a naphthalene derivative.

Studies dealing with the chemical reactions of unsaturated three-ring systems have played an important role in the development of our understanding of the mechanism by which carbon-carbon bonds may be broken and reformed.[1] The rearrangement of 3,3'-bicyclopropenyls to benzene derivatives represents one of the more fascinating unimolecular isomerizations known.[2-8] Its mechanism has been a source of controversy over the years. At various times the rearrangement has been postulated to proceed through Dewar benzene,[3] benzvalene,[8] prismane,[2] diradical[5] and ionic pathways.[3] The most recent data are consistent with a path involving homolytic cleavage of one of the cyclopropene rings followed by expansion of the other ring, closure to a Dewar benzene, and finally opening of the Dewar intermediate to form aromatic products.[6,7] So far as we know, there are no reports in the literature involving rearrangement of the closely related 1,3'-bicyclopropenyl system. In this communication we wish to describe some novel reactions which occur when a representative 1,3'-bicyclopropene is subjected to thermal and photochemical excitation.

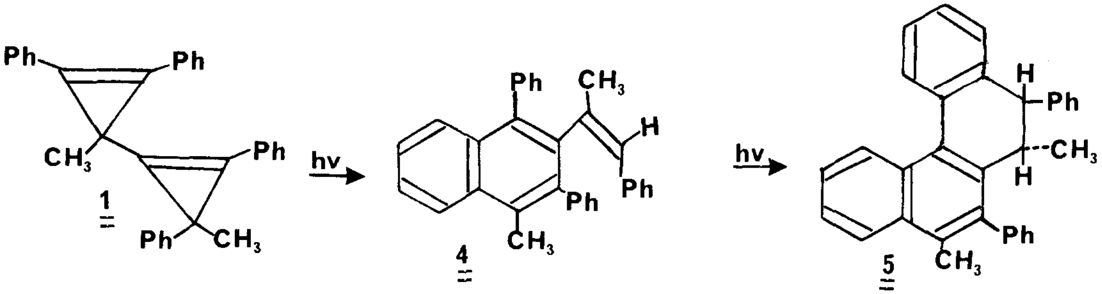
3-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (**1**) was prepared by treating 1,3-diphenyl-3-methylcyclopropene with methyl lithium followed by addition of the resulting organolithiate[9] to diphenylmethylcyclopropenyl cation.[10] Thermolysis of a benzene solution of **1** at 120°C produced a mixture of diphenylacetylene (**2**) and *E* (46%) and *Z*-2,3-diphenyl-2-hexen-4-yne (**3**) (33%). The two isomeric ene-ynes could be readily interconverted on photolysis or on heating in benzene with a trace of iodine. The assignment of structure **3** was further verified by an independent synthesis. The Grignard reagent derived from 1-propyne was allowed to react with 1,2-diphenylpropan-1-one and the resulting alcohol was dehydrated to give **3** in high yield. A reasonable



mechanism to account for the formation of these products involves opening of the diphenyl substituted cyclopropene ring followed by a subsequent fragmentation of the adjacent three-ring system and elimination of the acetylene moiety.



In marked contrast to the thermal results, the photolysis of 1 gave rise to an isomer (4, 70%), mp 220-221°C, whose structure was assigned as 4-methyl-1,3-diphenyl-2-(1-methyl-2-phenylethenyl)naphthalene (4) on the basis of its spectral data: NMR ($CDCl_3$,90 MHz) δ 1.37 (3H, d, J=1.4 Hz), 2.52 (s, 3H), 6.11 (q, 1H, J=1.4 Hz), 6.65 (m, 2H), 7.0-7.6 (m, 16H) and 8.15 (m, 1H). The UV spectrum of this material was very characteristic of a substituted naphthalene with maxima at 308 (ϵ 5600), 286 (13000), 267 (18400) and 235 (ϵ 60100). Unequivocal proof of this assignment derives from a single crystal X-ray structure analysis. The compound crystallizes in the triclinic space group P1 with a=10.5252(16)A°, b=11.1005(19)A°, c=11.2777(20)A°, α=63.436(14)°, β=86.535(13)°, α=80.907(13)° and two molecules per unit cell. Intensity data were collected with copper radiation using the omega scan method for $3<2\theta<100°$. The struc-



1

4

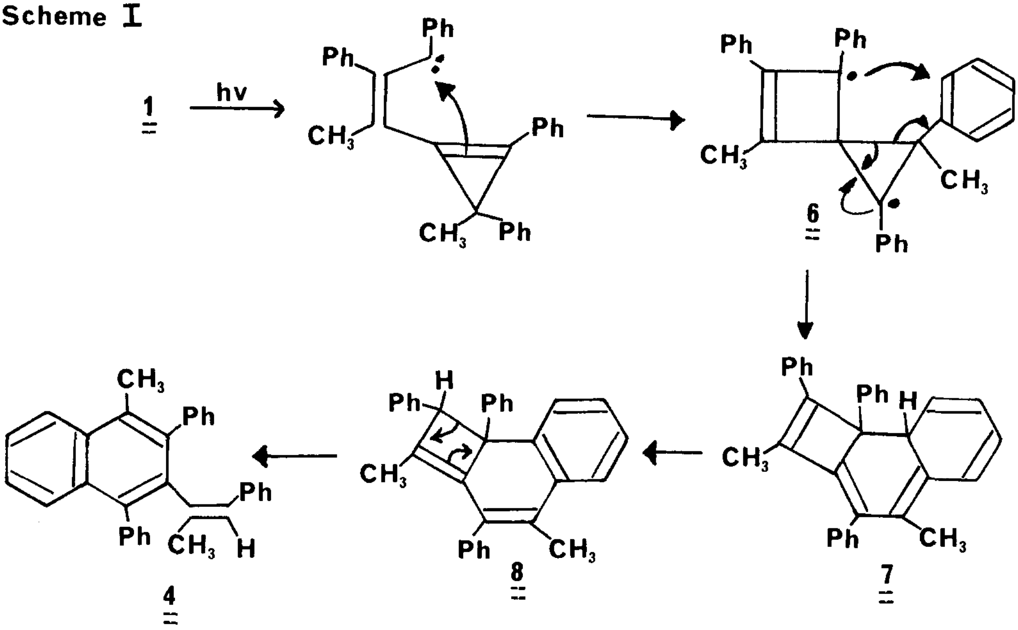
5

ture was solved by direct methods using the random starting point tangent refinement routines of the SHELXTL software package[11] and was refined to R_1=5.0% and R_2=6.4% for 2195 independent observed reflections.

Structure 4 was found to undergo rearrangement on further irradiation. Thus, photolysis of a benzene solution of 4 through a Pyrex filter for 90 min produced 5,6-dihydro-6,8-dimethyl-5,7-diphenylbenzo[*c*]phenanthrene (5) as the exclusive photoproduct: NMR ($CDCl_3$,90 MHz) δ 0.77 (*d*, 3H, J=7.0 Hz), 2.34 (*s*, 3H), 2.90 (*qd*, 1H, J=7.0 and 4.0 Hz), 4.33 (*d*, 1H, J=4.0 Hz), 7.0-7.6 (*m*, 15H), 7.9-8.2 (*m*, 2H) and 8.5-8.7 (*m*, 1H). The formation of 5 may be conveniently viewed as proceeding by a mechanism which involves an initial stilbene-phenanthrene type cyclization followed by a 1,5-sigmatropic hydrogen shift. Related nonoxidative photocyclizations are known in the literature and provide good analogy for the above transformation.[12-14]

We consider that the most economical explanation for the formation of naphthalene 4 is that illustrated in Scheme I. Photolysis of 1,2-diaryl substituted cyclopropenes generally results in σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes.[15] Thus, the initially generated vinyl carbene can add across the cyclopropenyl double bond to produce spiro diradical 6. This transient species is rapidly converted 8 via a cyclopropyl ring opening followed by a 1,7-sigmatropic hydrogen shift. Finally, retrocyclization of 8 results in the formation of 4. It should be pointed out that the carbene mechanism outlined in Scheme I may well be a "vinyl-diradical like" process. It is also possible that the actual reaction mechanism may involve diradical bridging of the excited state of the diphenyl substituted cyclopropene to the adjacent cyclopropene π-bond prior to ring opening. This mechanism differs from the carbene pathway only in the chronology of bond breaking and formation. Intermediate gradations between these extremes is also possible.[16]

Scheme I



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References

*John Simon Guggenheim Memorial Fellow, 1981-1982.
(1) J. F. Liebman and A. Greenberg, Chem. Rev., 76, 311 (1976).
(2) R. Breslow, P. Gal, H. W. Chang, L. J. Altman, J. Am. Chem. Soc., 87, 5139 (1965).
(3) R. Weiss, H. P. Kempeke, Tetrahedron Lett., 155 (1974); R. Weiss, S. Andrae, Angew. Chem., 85, 145, 147 (1973).
(4) W. H. DeWolf, W. Stol, I. J. Landheer, F. Bickelhaupt, Recl. Trav. Chim. Pays-Bas., 90, 405 (1971); W. H. DeWolf, I. J. Landheer, F. Bickelhaupt, Tetrahedron Lett., 179 (1975).
(5) R. Weiss and H. Kobl, J. Am. Chem. Soc., 97, 3222, 3224 (1975).
(6) J. H. Davis, K. Shea and R. G. Bergman, Angew. Chem. Int. Ed. Engl., 15, 232 (1976); J. Am. Chem. Soc., 99, 1499 (1977).
(7) N. J. Turro, G. B. Schuster, R. G. Berman, K. J. Shea, J. H. Davis, J. Am. Chem. Soc., 97, 4758 (1975).
(8) I. J. Landheer, W. H. DeWolf and F. Bickelhaupt, Tetrahedron Lett., 349 (1975); 2813 (1974).
(9) G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 85, 99 (1963).
(10) R. Breslow, H. Hover and H. W. Chang, J. Am. Chem. Soc., 84, 3168 (1962).
(11) We wish to thank Dr. Charles F. Campana, Nicolet Corp., for the single X-ray structure determination of naphthalene 4. Details will be reported elsewhere.
(12) A. Padwa, C. Doubleday and A. Mazzu, J. Org. Chem., 42, 3271 (1977).
(13) W. H. Laarhoven and T. J. Cuppen, Tetrahedron Lett., 163 (1971).
(14) J. S. Swenton, T. J. Ikeler and G. L. Smyser, J. Org. Chem., 38, 1157 (1973).
(15) A. Padwa, Org. Photochem., 4, 261 (1979).
(16) H. E. Zimmerman and M. C. Hovey, J. Org. Chem., 44, 2331 (1979).

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