

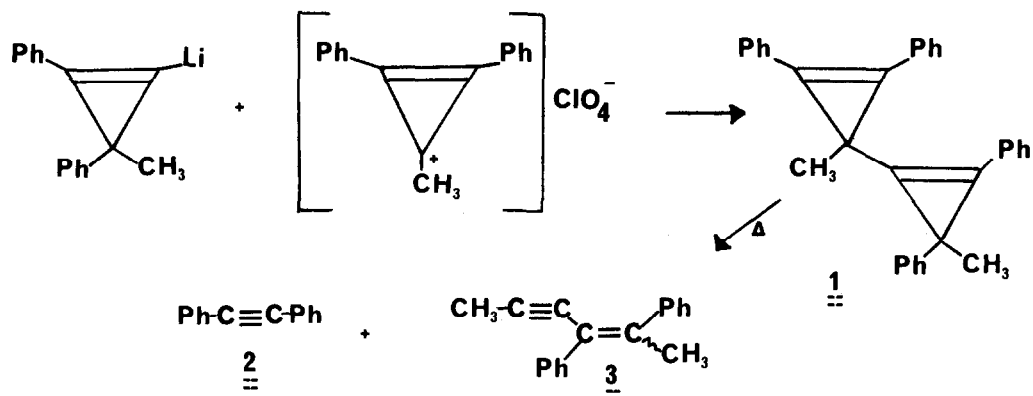
REARRANGEMENT IN THE
1,3'-BICYCLOPROPENYL SERIES

Albert Padwa*, Mitchell J. Pulwer and Robert J. Rosenthal
Department of Chemistry
Emory University
Atlanta, Georgia 30322

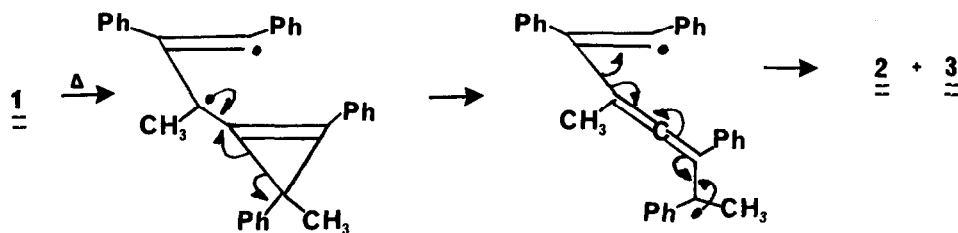
Abstract: The photochemical behavior of a representative 1,3'-bicyclopropene was studied and was found to undergo a novel rearrangement to a naphthalene derivative.

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 diradical⁵ 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.

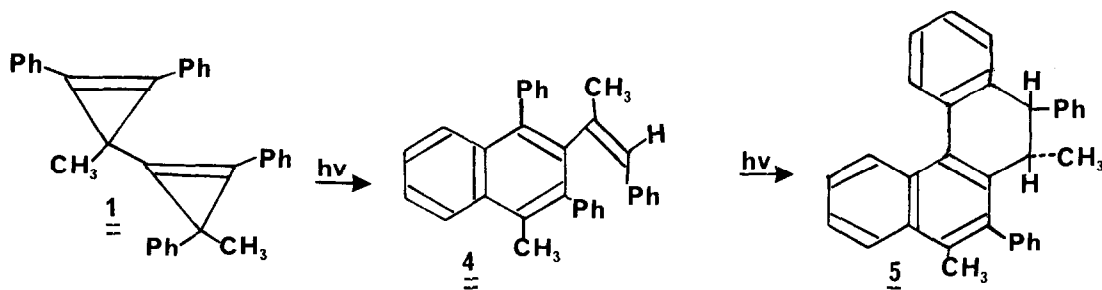
3-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (1) was prepared by treating 1,3-diphenyl-3-methylcyclopropene with methyl lithium followed by addition of the resulting organolithiate⁹ to diphenylmethylcyclopropenyl cation.¹⁰ Thermolysis of a benzene solution of 1 at 120°C produced a mixture of diphenylacetylene (2) and E (46%) and Z-2,3-diphenyl-2-hexen-4-yne (3) (33%). The two isomeric ene-yne 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 $a=10.5252(16)\text{\AA}$, $b=11.1005(19)\text{\AA}$, $c=11.2777(20)\text{\AA}$, $\alpha=63.436(14)^\circ$, $\beta=86.535(13)^\circ$, $\gamma=80.907(13)^\circ$ and two molecules per unit cell. Intensity data were collected with copper radiation using the omega scan method for $3 < 2\theta < 100^\circ$. The struc-

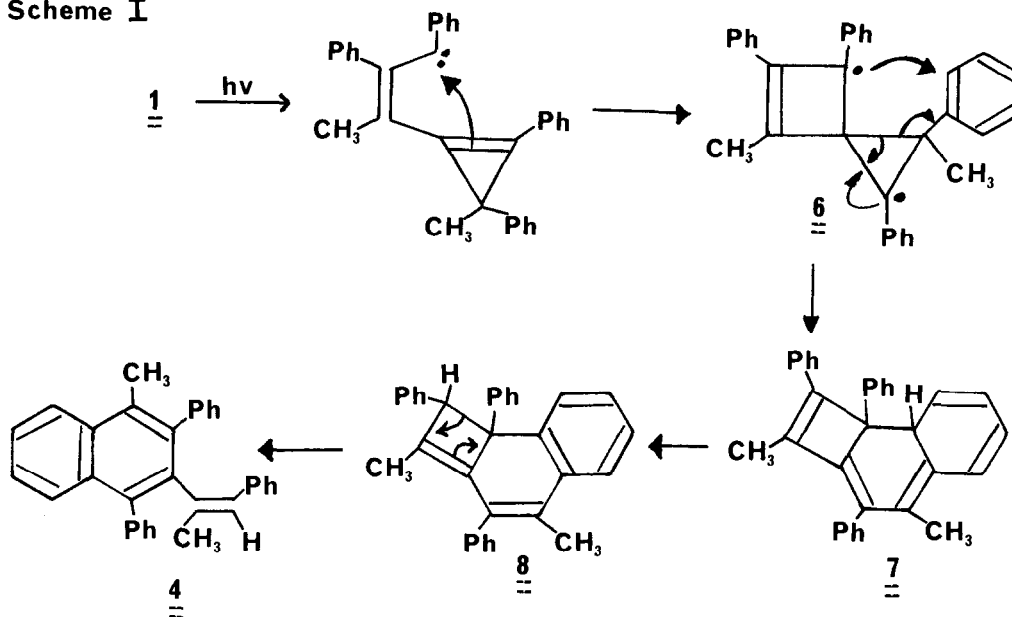


ture was solved by direct methods using the random starting point tangent refinement routines of the SHELXTL software package¹¹ and was refined to $R_1=5.0\%$ and $R_2=6.4\%$ for 2195 independent observed reflections.

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 (CDCl₃, 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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