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RING OPENING REACTIONS OF BENZOCYCLOBUTENE AND DERIVATIVES

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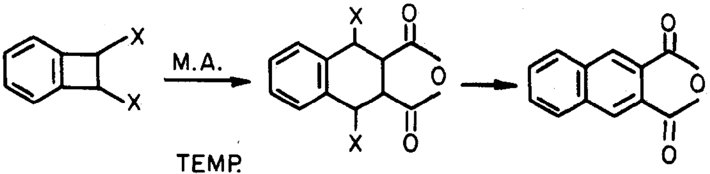
IN an earlier paper[1] it was shown that 1,2-diphenylbenzocyclobutene (I) readily reacts with dienophiles at room temperature. For example, with maleic anhydride, 1,4-diphenylnaphthalene-2,3-dicarboxylic anhydride (II) is obtained in almost quantitative yield. This ring opening reaction has been found to be general for benzocyclobutenes.



	TEMP.		
I, X = C_6H_5	25°	II, X = C_6H_5	V
III, X = Br	100°	IV, X = Br	
VI, X = H	200°	VII, X = H	

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[1] F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.* **80**, 6149 (1958).

Cava and Napier[2] obtained no product upon heating 1,2-dibromobenzocyclobutene (III) with maleic anhydride at 100° for 15 hours. This reaction has been reinvestigated, and after heating a mixture of the two compounds for 5 days at 95-100°, 2,3-naphthalenedicarboxylic anhydride (V) was isolated in 32% yield. The anhydride crystallized from ethyl acetate as colorless prisms and showed m.p. 248.2-249.2° (Lit.,[3] 245°). A reasonable pathway for the reaction involves 1,4-dibromo-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride (IV) as an intermediate. Loss of hydrogen bromide should readily occur from this compound under the reaction conditions.

The corresponding ring opening reaction with maleic anhydride and benzocyclobutene is virtually complete (98% yield) after 10 hours at 200°. The 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride (VI) showed m.p. 186.8-187.8° (Lit.,[4] m.p. 185°) and the diacid showed m.p. 195.6-196.2° (Lit.,[4] m.p. 195°). It has been reported that upon refluxing benzocyclobutene for one hour at 150°, no change in its boiling point or infrared spectrum occurs.[5] In our work, when benzocyclobutene was heated in a sealed flask for five days

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[2] M. P. Cava and D. R. Napier, J. Am. Chem. Soc. **79**, 1701 (1957).

[3] K. Yogi, J. Agr. Chem. Soc., Japan **23**, 43 (1944); C. A. **45**, 5142 (1951).

[4] R. D. Hawarth and F. H. Slinger, J. Chem. Soc. 1321 (1940).

[5] M. P. Cava and D. R. Napier, J. Am. Chem. Soc. **80**, 2255 (1958).

at 200°, 1,2:5,6-dibenzocyclooctadiene (VIII) (m.p., 108-109°; Lit.,[6] 109.4-109.9°) was obtained in 23.6% yield along with other higher molecular weight products. Since this

IX VIII

+OTHER PRODUCTS

reaction reasonably occurs through 5,6-dimethylene-1,3-cyclohexadiene (or the corresponding diradical) as an intermediate, it was expected that the addition of sulfur dioxide to the reaction flask should result in the formation of 1,3-dihydroisothianaphthene-2,2-dioxide (IX). This expectation was realized and the sulfone (IX), m.p. 150.2-150.8°, was obtained in 69.3% yield.

The observation that the presence of both bromo and phenyl groups in the 1,2-positions accelerate the reaction with maleic anhydride supports the view that these reactions occur through ring opening prior to reaction with dienophile. The exact nature of the intermediate in these reactions is as yet unclear.[1]

It had been hoped to include 1,2-dimethylbenzocyclobutene in this series. However, when α,α'-diiodo-*ortho*-diethylbenzene was heated with sodium iodide, the expected *cis*- and

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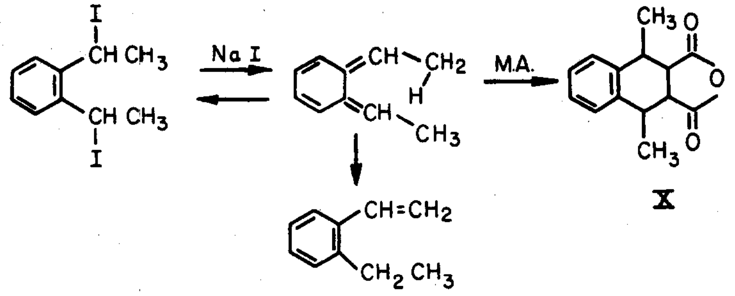
[6] A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.* **73**, 1668 (1951).

trans-1,2-dimethylbenzocyclobutenes were obtained in, at most, trace quantities. The interesting feature concerning this reaction is that *ortho*-ethylstyrene was obtained as a product in about 6% yield. A reasonable pathway for its formation is by a 1,5-hydrogen shift occurring in the intermediate, 5,6-diethenyl-1,3-cyclohexadiene. This type of intermediate has been postulated in similar reactions.[2] Evidence for its formation in this reaction is that the addition of maleic anhydride to the reaction mixture resulted in the formation of an adduct, presumed to be 1,4-dimethyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride (X). It is of interest to note that in



X

order for the 1,5-hydrogen shift to occur, one methyl group must exist in a *cis*-relationship, although this structure should be relatively unstable. A strong driving force for the shift to occur is the formation of the aromatic π system.

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