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1,2-DIMETHYLENEBENZOCYCLOBUTENE

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RECENTLY we have described[1] a synthesis of the stable 1,2-dicarbomethoxymethylenebenzocyclobutene (I). We wish to report now the synthesis and some properties of the parent 1,2-dimethylenebenzocyclobutene (II), an isomer of naphthalene which has been calculated to have a delocalization energy of 3.15 β.[2]

Reaction of benzocyclobutadienoquinone (III)[3] with methyl magnesium bromide gave a mixture of cis-1,2-dimethylbenzocyclobutene-1,2-diol (IV), m.p. 157°, and the corresponding trans-isomer (V), m.p. 122-123°.[4,5] Acetylation of diol IV with refluxing acetic anhydride-pyridine mixture gave the cis-diacetate (VI), m.p. 94.5-95.0°. Pyrolysis of VI at 300° on Stercha-mol fire-brick afforded hydrocarbon II in 27 per cent yield.

1,2-Dimethylenebenzocyclobutene is a colorless low-melting solid (m.p. 15-16°) which polymerizes to a thick gum at room temperature after a few hours. Its ease of polymerization is therefore similar to that of the recently reported related hydrocarbon 3,4-dimethylenecyclobutene (VII).[6]

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1 M.P. Cava and R.J. Pohl, J. Amer. Chem. Soc. 82, 5242 (1960).

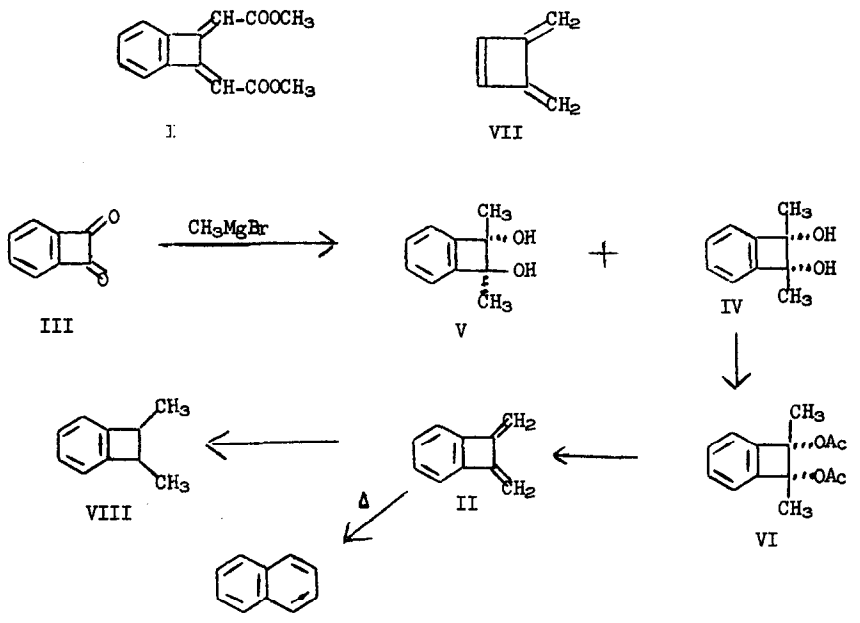
2 S.L. Manatt and J.D. Roberts, J. Org. Chem. 24, 1336 (1959).

3 M.P. Cava and D.R. Napier, J. Amer. Chem. Soc. 79, 3606 (1957).

4 All new compounds gave satisfactory analyses.

5 The structure proof of diols (IV) and (V), including stereochemistry, will be discussed in the full paper.

6 A.T. Blomquist and P.M. Maitlis, Proc. Chem. Soc. 332 (1961).



Like compound VII, the benzo analog (II) gave only complex products with tetracyanoethylene.

Catalytic reduction of II in the presence of palladium gave a single 1,2-dimethylbenzocyclobutene, presumably the cis-isomer (VIII). Pyrolysis of II in the gas phase over a Nichrome wire at 700° afforded naphthalene.

The methylene groups of II absorb strongly in the infrared at 11.42 μ and as a doublet at 5.92 and 5.95 μ. The ultraviolet spectrum of II is complex: λ_{max}^{EtOH} 230 mμ (log ε = 4.82), 273 (3.32), 304 (3.66), 314 (3.95), 319.5 (3.72) and 3.29 (4.15).

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