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SYNTHESIS OF A BOREPIN

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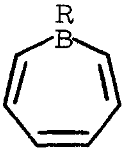
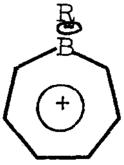
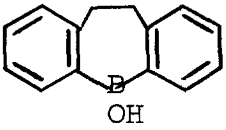
Theoretical considerations[1] permit the conclusion that borepin (1-boro-2.4.6-cycloheptatriene) (Ia-Ib), in which neutral trivalent

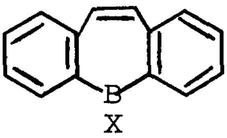

Ia


Ib

boron is incorporated into a cyclic molecular orbital of six electrons, should possess aromatic stability. We provide herein the first example of this heterocyclic system.

The anhydride of the borinic acid II, prepared by reaction of


II


III

o, o'-dilithiobibenzyl and tributyl borate according to the method of

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[1] E. Hückel, Grundzüge der Theorie ungesättigter und aromatischer Verbindungen, Verlag Chemie, Berlin, 1938, pp. 71-85.

Letsinger and Skoog,[2] was converted by means of N-bromosuccinimide to an intermediate bromo substitution product, which without purification was dehydrohalogenated with methanolic sodium methoxide. The resulting dibenzoborepin III (**X** = OH) was isolated as the ethanolamine derivative (IIIa), m.p. 222-226° (Calcd: C, 77.1; H, 6.4; N, 4.4. Found: C, 77.1; H, 6.6; H, 4.3. λ_{max}^{EtOH} 227, 298 mμ ϵ = 16,000, 8,230, resp.). The structure of III was established through degradation to *cis*-stilbene by means of ammoniacal silver nitrate,[3] which reagent transforms the starting dihydro compound II to bibenzyl. Lithium aluminum hydride converts[4] IIIa to a product--isolated as the low-melting, unstable pyridine complex--regarded as the parent borane (III, **X** = H), on the basis of (i) its BH absorption at 4.32 microns, and (ii) the acid-promoted hydrolytic oxidation to the starting borinic acid (III, **X** = OH), isolated and identified as IIIa.

Aromatization by means of N-bromosuccinimide, and protection of intermediates as borinic acids, are being applied in this Laboratory to the preparation of simpler members of the borepin family.

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[2] R. Letsinger and I. Skoog, *J. Am. Chem. Soc.* **77**, 5175 (1955).

[3] A. Michaelis and M. Behrens, *Ber.* **27**, 244 (1894).

[4] M. F. Hawthorne, *J. Am. Chem. Soc.* **80**, 4293 (1958).