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AROMATIC BORON-OXYGEN HETEROCYCLES

M.J.S. Dewar and R. Dietz

Department of Chemistry, Queen Mary College, Mile End Road, London

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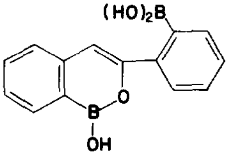
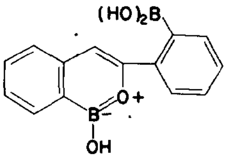
LETSINGER and NAZY[1] recently reported the isomerization of 2:2'-tolandiboronic acid to a compound of doubtful structure. We favour the formation I.



I



II

Its unusual properties are then attributable to the contribution of the pseudoaromatic structure II. The recently proposed[2] system of nomenclature

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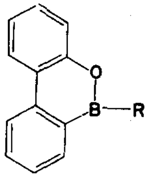
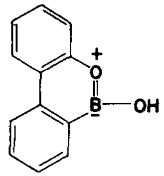
[1] Letsinger and Nazy, J. Amer. Chem. Soc. 81, 3013 (1959).

[2] Dewar and Dietz, J. Chem. Soc. In press.

would accommodate this as a derivative of 1:2-boroxaronaphthalene. This representation is supported by our synthesis of an analogous heteroaromatic system.



III



IV

Successive reaction of 2-hydroxydiphenyl with boron trichloride at -70°, and aluminium chloride in benzene at 60° gave 10-chloro-10:9-horoxarophenanthrene (III, R=Cl) (Found: Cl, 15.8; B, 4.8%. $C_{12}H_8OBCl$ requires Cl, 16.6; B, 5.1%). Hydrolysis was rapid and gave 10-hydroxy-10:9-boroxarophenanthrene (III, R=OH), characterized as the anhydride, m.p. 205-206.5°. (Found: C, 76.5; H, 4.3; B, 5.4%, neutralization equivalent 184. $C_{24}O_{16}O_3B_2$ requires: C, 76.6; H, 4.3; B, 5.8%, neutralization equivalent 187). Crystallization from methanol gave the methyl ester (III, R=OMe), m.p. 63.5-64.5 (Found: C, 74.3; H, 5.3%. M, 197. $C_{13}H_{11}O_2B$ requires C, 74.3; H, 5.3; M, 210), and reaction of the chloro-compound with phenyl magnesium bromide gave 10-phenyl-10:9-boroxarophenanthrene (III, R=Ph), m.p. 82-3° (Found: C, 84.3; H, 5.1; B, 3.9%, M, 249. $C_{18}H_{13}OB$ requires

C, 84.4; H, 5.1; B, 4.3%, M, 256). Some bromo derivatives have also been prepared.

Evidence for these structures include the methods of preparation, and the ultra-violet spectra, which are quite different from those of substituted diphenyls, rather resembling those of the corresponding 10:9-borazarophenanthrenes.[3]

10-Hydroxy-10:9-boroxarophenanthrene, although classically an internal ester of 1-(1-hydroxyphenyl)-phenyl boronic acid (III, R=OH), has considerable stability to aqueous acid and alkali, in which the ultra-violet spectrum is unchanged, and to oxidation. We attribute this stability to its aromatic nature, emphasized by IV.

Full details of this work will appear shortly.

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[3] Dewar, Kubba and Pettit, J. Chem. Soc. 3073 (1958).