269. *New Heteroaromatic Compounds. Part V.*[1] *Some 9,10-Boroxarophenanthrenes.*[2]

By M. J. S. Dewar and R. Dietz.

The syntheses of some substituted 9,10-boroxarophenanthrenes are described. The aromaticity of this system is less pronounced than that of the 9,10-borazarophenanthrenes.

An earlier paper[3] in this series described 9,10-borazarophenanthrene.[2] An analogous system is now described, derived from this by replacement of the annular nitrogen by oxygen.

2-Hydroxybiphenyl reacted readily with an excess of boron trichloride, giving presumably[4] 2-biphenyl chloroboronite. In warm benzene or light petroleum containing aluminium chloride, this evolved nearly one mol. of hydrogen chloride. The product, containing equivalent amounts of boron and chlorine, was readily hydrolysed to an acid, $C_{12}H_9O_2B$, which when heated gave an anhydride, $C_{24}H_{16}O_3B_2$.

Fusion of the acid with potassium hydroxide gave 2-hydroxybiphenyl and oxidation with hydrogen peroxide gave 2,2′-dihydroxybiphenyl. The formation of a monomethyl ester, both by crystallisation of the acid from methanol and by methanolysis of the chloro-compound, showed the acid to be monobasic. The absence of a phenolic hydroxyl group was shown by the infrared spectra of the anhydride and the methyl ester. The ultraviolet spectra of the acid and its anion, reversibly produced in ethanol, were quite unlike that of a substituted biphenyl (Fig. 1). The acid is therefore 9-hydroxy-9,10-boroxarophenanthrene (I; R = OH) and the chloro-compound and methyl ester are 9-chloro- and 9-methoxy-9,10-boroxarophenanthrene (I; R = Cl and OMe respectively).

Treatment of the crude chloro-compound with phenylmagnesium bromide gave 9-phenyl-9,10-boroxarophenanthrene (I; R = Ph), spectrally very similar to 9-phenyl-9,10-borazarophenanthrene (Fig. 2). With two mols. of bromine in glacial acetic acid, 9-hydroxy-9,10-boroxarophenanthrene gave the 1,3-dibromo-derivative (III): an excess of bromine produced 1,3,7-tribromo-9-hydroxy-9,10-boroxarophenanthrene (IV). The

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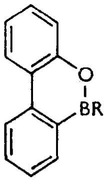
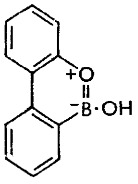
[1] Part IV, Dewar and Kubba, *Tetrahedron*, in the press.
[2] For nomenclature see Dewar and Dietz, *J.*, 1959, 2728.
[3] Dewar, Kubba, and Pettit, *J.*, 1958, 3073.
[4] Colclough, Gerrard, and Lappert, *J.*, 1956, 3006.

orientations of the substituents were proved by syntheses of identical bromo-compounds from 3,5-dibromo- and 3,5,4′-tribromo-2-hydroxybiphenyl. The ultraviolet spectra of the bromo-compounds resembled that of 9-hydroxy-9,10-boroxarophenanthrene, but showed bathochromic shifts.

Although classically a monoester of a boronic acid, 9-hydroxy-9,10-boroxarophenanthrene has considerable stability. Oxidation with potassium permanganate and chromium trioxide was difficult. Prolonged boiling with 10% aqueous potassium hydroxide failed to produce an ultraviolet spectrum different from that of the anion. Recovery was nearly quantitative after 10 hours' boiling with 6N-hydrochloric acid. Deboronation took place in warm concentrated sulphuric acid.



(I)



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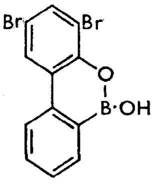

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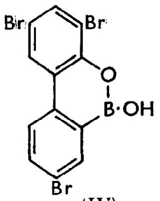


(IV)

The ultraviolet spectrum of 9-phenyl-9,10-boroxarophenanthrene was reproducible in cyclohexane. In 95% ethanol, or in water, 9-phenyl-9,10-boroxarophenanthrene was slowly oxidised and hydrolysed to 9-hydroxy-9,10-boroxarophenanthrene. Ultraviolet spectra measured during the conversion indicated that the boroxarophenanthrene ring remained intact.

FIG. 1. *Ultraviolet spectra of* 9-*hydroxy*-9,10-*boroxarophenanthrene in* 95% *ethanol* (———) *and in* 95% *ethanol with alkali* (. . . . .). *Ultraviolet spectrum of* 2-*hydroxybiphenyl in cyclohexane* (— · — · —).

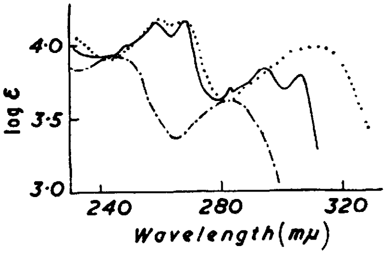
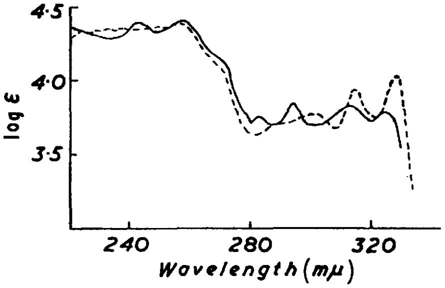


FIG. 2. *Ultraviolet spectra of* 9-*phenyl*-9,10-*boroxarophenanthrene in cyclohexane* (———) *and* 9-*phenyl*-9,10-*borazarophenanthrene in cyclohexane* (- - - -)



We attribute the stability of 9-hydroxy-9,10-boroxarophenanthrene to the contribution of the pseudoaromatic structure (II), which should, however, be less important than the corresponding 9,10-borazarophenanthrene structure, since oxygen is more electronegative than nitrogen. The aromatic character of the 9,10-boroxarophenanthrenes should therefore be less pronounced than that of the 9,10-borazarophenanthrenes. This is clearly reflected in the relative stabilities of the 9-phenyl compounds. Of interest in this connexion is the 9,10-borathiarophenanthrene system, on which work is now in progress.

Letsinger and Nazy [5] showed that tolan-2,2′-diboronic acid was isomerised in alkali to a compound which could be formulated as (V) or (VI) and had unusual properties. They preferred the formulation (V), by analogy with the compound (VII) which Snyder, Reedy, and Lennarz [6] reported to be remarkably stable to hydrolysis. Our work suggests that the

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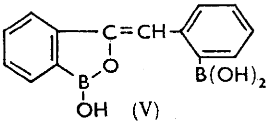
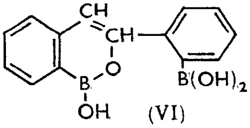
[5] Letsinger and Nazy, *J. Amer. Chem. Soc.*, 1959, **81**, 3013.

[6] Snyder, Reedy, and Lennarz, *J. Amer. Chem. Soc.*, 1958, **80**, 835.

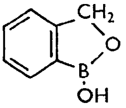
isomerisation product may well have been (VII), owing its stability to the presence of an aromatic boron-containing ring.



(V)



(VI)



(VII)

EXPERIMENTAL

9-*Chloro*-9,10-*borazarophenanthrene*.—2-Hydroxybiphenyl 6·9 g., 0·041 mole) in dry methylene chloride (50 ml.) was added slowly to boron trichloride (9·6 g., 0·082 mole) at −70°. Hydrogen chloride (1·40 g., 93%), absorbed on soda-asbestos, was evolved while the mixture was allowed to warm to 15°. Removal of solvent and excess of boron trichloride at room temperature and 0·1 mm. left a dark viscous oil. Dry light petroleum (b. p. 40—60°; 70 ml.) and aluminium chloride (0·05 g.) were added, and the mixture was refluxed. Hydrogen chloride (1·05 g., 70%), which was evolved in 2 hr., was swept from the apparatus with dry nitrogen and absorbed in water. No boric acid was detected on further titration in the presence of mannitol. The mixture was cooled and filtered under dry nitrogen. Solvent (*ca.* 30 ml.) was removed at 15°/0·1 mm. until a dark red oil separated and solidified. Filtration and evaporation of the filtrate to dryness yielded 9-chloro-9,10-borazarophenanthrene (5·8 g., 66%) (Found, by direct hydrolysis and titration: Cl, 15·8; B, 4·8. $C_{12}H_8OBCl$ requires Cl, 16·6; B, 5·1%). After sublimation at 85°/0·2 mm., this material softened at 72—73° and decomposed at 115—120° without melting.

9-*Hydroxy*-9,10-*boroxarophenanthrene*.—A solution of the crude chloro-compound in light petroleum was diluted with an equal volume of ether and washed with water. Slow removal of solvent resulted in crystallisation of 9-*hydroxy*-9,10-*boroxarophenanthrene* (4·8 g., 60%), m. p. 200—203°. Recrystallisation from benzene raised the m. p. to 205—206·5° (Found: C, 72·6; H, 4·6%; *M*, 179. $C_{12}H_9O_2B$ requires C, 73·5; H, 4·6%; *M*, 196).

The *anhydride*, of identical m. p., was formed on 2 hours' heating at 140°/0·1 mm. (Found: C, 76·5; H, 4·3; B, 5·4. $C_{24}H_{16}O_3B_2$ requires C, 76·6; H, 4·3; B, 5·8%). The neutralisation equivalent, found by potentiometric titration in aqueous ethanol, was 184 ($C_{24}H_{16}O_3B_2$ requires equiv., 187).

9-*Methoxy*-9,10-*boroxarophenanthrene*.—(*a*) The *methyl ester*, m. p. 63·5—64·5, was formed quantitatively by crystallisation of 9-hydroxy-9,10-boroxarophenanthrene from methanol (Found: C, 74·3; H, 5·3%; *M*, 197. $C_{13}H_{11}O_2B$ requires C, 74·3; H, 5·3%; *M*, 210). Hydrolysis to the hydroxy-compound took place overnight in air.

(*b*) Excess of dry methanol in methylene chloride (10 ml.) was added slowly at −70° to 9-chloro-9,10-boroxarophenanthrene (0·83 g.) in dry methylene chloride (10 ml.). After removal of all matter volatile at 20°/0·1 mm., the methyl ester remained (0·81 g., 98%), having m. p. and mixed m. p. 63—64·5°.

9-*Phenyl*-9,10-*boroxarophenanthrene*.—9-Chloro-9,10-boroxarophenanthrene was prepared from 2-hydroxybiphenyl (6 g., 0·035 mole), cyclisation being effected in dry benzene at 60°. The mixture was cooled and phenylmagnesium bromide, from bromobenzene (5·6 g., 0·036 mole) and magnesium (0·9 g.) was added dropwise in ether at room temperature under nitrogen. After 2 hours' refluxing and then cooling, the mixture was hydrolysed by brief shaking with dilute hydrochloric acid. The organic layer was separated, dried, and evaporated under nitrogen. Crystallisation from light petroleum under nitrogen yielded 9-*phenyl*-9,10-*boroxarophenanthrene* (4·6 g., 51%), m. p. 82—83° (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).

1,3-*Dibromo*-9-*hydroxy*-9,10-*boroxarophenanthrene*.—(*a*) Bromine (3·2 g., 0·02 mole) in glacial acetic acid (10 ml.) was added to 9-hydroxy-9,10-boroxarophenanthrene (2 g., 0·01 mole) in glacial acetic acid (50 ml.) at 50°. After 2 hr. at 80°, water was added to precipitate the crude *dibromo-compound* (3·0 g., 84%), m. p. 274—277°. Crystallisation from aqueous acetic acid raised the m. p. to 279—280·5° (Found: C, 40·6; H, 1·8; Br, 45·3%; *M*, 342. $C_{12}H_7O_2Br_2B$ requires C, 40·7; H, 2·0; Br, 45·2%; *M*, 354).

(*b*) 3,5-Dibromo-2-hydroxybiphenyl [7] (0·6 g., 0·002 mole) was treated successively with boron

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[7] Auwers and Wittig, *J. prakt. Chem.*, 1924, **108**, 99.

trichloride and aluminium chloride as described for 2-hydroxybiphenyl, to give the preceding dibromo-compound (0·33 g., 50%).

1,3,7-*Tribromo*-9-*ethoxy*-9,10-*boroxarophenanthrene*.—(*a*) Bromine (6 g., 0·038 mole) in acetic acid (15 ml.) was added to 9-hydroxy-9,10-boroxarophenanthrene (2 g., 0·01 mole) in acetic acid (40 ml.) at 50°. The solution was heated at 100° until no further hydrogen bromide was evolved (3 hr.). Water was added to precipitate the crude tribromo-compound (4·0 g., 91%), m. p. $>310°$. Crystallisation from ethanol yielded the *ethyl ester*, m. p. 141—142° (Found: C, 36·2; H, 2·0; Br, 52·7. $C_{14}H_{10}O_2Br_3B$ requires C, 36·5; H, 2·2; Br, 52·1%).

(*b*) 3,5,4′-Tribromo-2-hydroxybiphenyl[7] (5 g., 0·012 mole) was treated successively with boron trichloride and aluminium chloride. Crystallisation from benzene gave the tribromo-compound (1·2 g., 23%), m. p. $>310°$. The infrared spectrum of this compound was identical with that of the product of the preceding reaction. On potentiometric titration in aqueous ethanol, the compound behaved as a monobasic *acid* of neutralisation equivalent 420 ($C_{12}H_6Br_3O_2B$ requires equiv., 433).

We are grateful to the University of London for a grant for the purchase of apparatus and for the award of the William Lincoln Shelley Research Studentship (to R. D.).

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[*Received, October* 12*th*, 1959.]