38. *The Synthesis and Structure of Aromatic Boron Compounds.*

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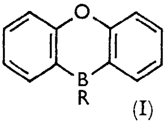
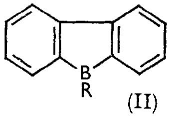
10-Hydroxy-9-oxa-10-bora-anthracene has been prepared and its aromatic character demonstrated by ultraviolet spectroscopy. The mechanism of the reaction of n-butyl metaborate with Grignard and lithio-reagents has been investigated, and the conditions under which organic boronous or boronic acid is the predominant product have been examined. An attempt to prepare 9-diethylamino-9-borafluorene is also described.

OF the known aromatic boron compounds there are few in which the boron atom is included in an aromatic ring, and of these the borazoles constitute by far the largest number. Dewar, Kubba, and Pettit[1] have pointed out that a new series of aromatic compounds may be derived from the known carbocyclic ones by replacement of two atoms in the system severally by boron and by an element which can contribute a lone pair of electrons to the π-electron system in order to retain the requisite sextet structure. Thus the 9-aza-10-bora-phenanthrene and 2-bora-1-azanaphthalene ring systems have been shown to be aromatic.[1,2] There are no aromatic heterocyclic compounds known in which a boron atom is connected directly to two carbon atoms, and the current investigation concerns the boron analogues (I and II) of the xanthenylium cation and the dibenzofulvene ring system. In the latter it was hoped to replace the exocyclic double bond by a back-co-ordinate linkage between the boron atom and an exocyclic atom with a lone pair of electrons, but this system has proved inaccessible by the usual methods. However, 10-hydroxy-9-oxa-10-bora-anthracene (I; R = OH) has been prepared by the action of 2,2′-dilithiobiphenyl ether on n-butyl metaborate or the boron trifluoride–ether complex.


(I)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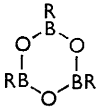
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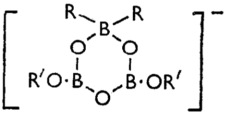
(IV)

Mikhailov and Vaver,[3] and Povlock and Lippincott,[4] recently prepared a number of aromatic boronous acids by the action of an excess of Grignard reagent on an alkyl metaborate (III; R = OAlk). Povlock and Lippincott suggested that nucleophilic substitution produces an intermediate anion of type (IV), and that only two such substitutions can take place while the boron–oxygen ring remains intact. However, phenylmagnesium bromide and 2-biphenylylmagnesium iodide with phenylboronic anhydride (III; R = Ph) yielded respectively diphenylboronous acid and *B*-2-biphenylyl-*B*-phenylboronous acid. It

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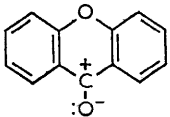
[1] Dewar, Kubba, and Pettit, *J.*, 1958, 3073.
[2] Dewar and Dietz, *J.*, 1959, 2728.
[3] Mikhailov and Vaver, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1956, 441.
[4] Povlock and Lippincott, *J. Amer. Chem. Soc.*, 1958, **80**, 5409.

appears that phenylboronic acid is a likely intermediate in the formation of diphenylboronous acid from alkyl metaborates, arising by simple substitution of the alkoxy-groups by the Grignard reagent, and that, by starting with this "intermediate," unsymmetrical boronous acids should be readily accessible. Replacement of the alkoxy-groups of the alkyl metaborate by bulky aromatic groups with large *ortho*-substituents should then yield a boronic anhydride sterically hindered against further attack by the Grignard reagent. Reaction of 2-biphenylylmagnesium iodide with n-butyl metaborate gave 2-diphenylylboronic acid in 75% yield.

The most frequent difficulty in the preparation of higher aromatic boronic acids is the insolubility of the Grignard reagent, which is often precipitated or crystallises on to the magnesium and prevents formation of the reagent; *e.g.*, Yabroff, Branch, and Bettman [5] obtained only a 5% yield of 2-biphenylylboronic acid from n-butyl orthoborate at —78°.

The present method has been extended by the simultaneous addition of the aromatic halide and n-butyl metaborate in ether to magnesium, whereby the metaborate reacts with the Grignard reagent as it is formed. 9-Bromophenanthrene and 2-iododiphenyl ether normally form Grignard reagents only very slowly [6] but by this method these halides were converted into boronic acids in a very short time. Both 9-phenanthryl and 2-biphenylylboronic acid are unusually resistant to conversion into anhydrides: Thielens [7] noted that 9-phenanthrylboronic acid is unchanged at its melting point (324°).

2,2'-Dilithiodiphenyl ether should not suffer steric hindrance to attack by the second lithio-group after initial formation of the boronic anhydride. It is readily prepared by Oita and Gilman's method [8] and with n-butyl metaborate forms 10-hydroxy-9-oxa-10-bora-anthracene (I; R = OH), which may also be obtained by the reaction of the same reagent with the boron trifluoride–ether complex.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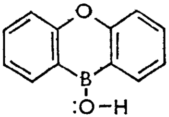
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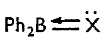
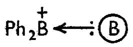

$\mathrm{Ph_2B} \leftleftarrows \ddot{\mathrm{X}}$

(VII)


$\mathrm{Ph_2}\overset{+}{\mathrm{B}} \longleftarrow : Ⓑ$

(VIII)

The structure (VI) has been assigned to this product on the basis of the method of preparation, analysis, molecular weight, and infrared and ultraviolet spectra. In the region 12·0—14·5 μ characteristic of the aromatic C–H out-of-plane deformations, this compound has only a single strong peak at 13·22 μ, assigned to *ortho*-disubstitution [cf. xanthone (V), single strong peak at 13·21 μ]. The O–H stretching frequency at 3·20 μ is very strong; the maximum around 8·1 μ, which has been assigned by Dahlgard and Brewster [9] to the C–O stretching vibration in diphenyl ethers and which occurs at 8·14 μ in *o*-phenoxyphenylboronic acid, is split into a doublet at 8·11 and 8·20 μ. *o*-Phenoxyphenylboronic acid is the most likely impurity from the metalation of diphenyl ether, and as this has very strong absorption at 12·52, 13·14, 13·32, and 14·54 μ the infrared spectrum offers a good test for the purity of 10-hydroxy-9-oxa-10-bora-anthracene.

The ultraviolet spectrum of the product (see Figure) shows in its envelope a striking resemblance to that of xanthone, and is interesting because if the carbonyl bond is polarised as in formula (V) so that the central ring retains only the six π-electrons required for aromatic character, this will be isoelectronic with (VI) in which there is no back-co-ordination from an oxygen lone-pair to the boron atom of the heterocyclic system. It appears, therefore, that 10-hydroxy-9-oxa-10-bora-anthracene is stabilised by the aromatic character

[5] Yabroff, Branch, and Bettman, *J. Amer. Chem. Soc.*, 1934, **56**, 1850.

[6] Kharasch and Reinmuth, " Grignard Reactions of Non-metallic Substances," Constable and Co. Ltd., London; Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363; Cook, *J.*, 1930, 1087.

[7] Thielens, *Naturwiss.*, 1958, **45**, 543.

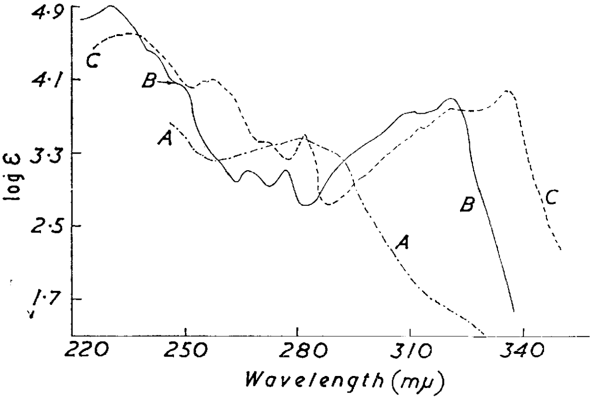
[8] Oita and Gilman, *J. Amer. Chem. Soc.*, 1957, **79**, 339.

[9] Dahlgard and Brewster, *ibid.*, 1958, **80**, 5861.

of the central ring rather than by back-co-ordination. This is in contrast to the more usual aromatic boron compounds.

The derivatives of diphenylboronous acid, of type (VII), scarcely resemble the analogous carbonium ions or even benzophenone in their ultraviolet absorption (cf. Table). They do, however, resemble styrene and 1,1-diphenylethylene for which Jones[10] noted almost identical absorption, presumably because the rings are not coplanar in 1,1-diphenylethylene, which then, for the purposes of spectroscopy, reduces to the styrene chromophore. Diphenylboronous acid derivatives absorb at almost the same wavelength as styrene and 1,1-diphenylethylene, and this offers qualitative evidence that the rings in this series of compounds are non-coplanar, and that back-co-ordination plays an important part in their stabilisation. When back-co-ordination is not possible, as in the diphenylboronium cation (VIII),[11] both rings appear to take part in the conjugation, as in the diphenylcarbonium ion. Diethylaminodiphenylboron shows this type of spectrum in concentrated sulphuric acid, where it appears that the molecule takes up a proton with loss of back-co-ordination. The resulting solution is yellow and quite stable, but is decolorised on addition of about 15% of water (cf. reaction 1).

Ultraviolet absorption of (A) o-*phenoxyphenylboronic acid, (B) 10-hydroxy-9-oxa-10-bora-anthracene, and (C) xanthone.*



Ultraviolet absorption maxima (in mμ).

Compound	Solvent	Wavelengths	log ε
$(Ph_2B)_2O$	Cyclohexane	270, 240	3·15, 4·34
$Ph_2B{\cdot}O{\cdot}[CH_2]_2{\cdot}NH_2$	,,	233	3·98
$Ph_2B{\cdot}NEt_2$	,,	240	4·17
,,	98% H_2SO_4	435, 362, 272, 265, 259	1·26, 1·44, 3·42, 3·47, 3·36
Ph·CH:CHPh [12]	EtOH	245	4·01
$Ph_2C{:}CH_2$ [12]	,,	248	4·05
o-$PhO{\cdot}C_6H_4{\cdot}BO{\cdot}OH$	$CHCl_3$	281	3·452
Xanthone	Cyclohexane	336, 322, 282, 271, 257, 255, 237	3·979, 3·783, 3·502, 3·421, 4·098, 4·078, 4·606
(VI)	,,	321, 311, 277, 267, 250, 231	3·895, 3·747, 3·114, 3·104, 4·013 (sh), 4·893

2-Biphenylylboronic acid has been considered as a precursor of the 9-borafluorene ring system if the cyclisation of a suitable derivative could be effected. 2-Biphenylylboron dichloride is not a suitable compound, as the chlorine atom in 9-chloro-9-borafluorene could react with the aluminium chloride used as a catalyst; so an attempt was made to

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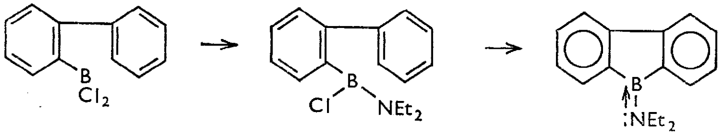
[10] Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1818.

[11] Davidson and French, *J.*, 1958, 114.

prepare 9-diethylamino-9-borafluorene (II; R = NEt_2) according to reaction 2. Diethylamino-2-biphenylylboron chloride was not isolated and attempted cyclisation of the crude product yielded tars.

The reaction between 2,2′-dilithiobiphenyl and n-butyl metaborate offers a route to 9-hydroxy-9-borafluorene, (II; R = OH), and it was hoped to isolate this compound as

$$\overset{\longleftarrow}{\mathrm{Ph_2B\ddot{N}Et_2}} + \mathrm{H^+} \longrightarrow \left[\mathrm{Ph_2B \leftarrow NHEt_2}\right]^+ \quad \cdots\cdots\cdots (1)$$



·······(2)

a stable 2-aminoethyl ester (II; R = $O{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$) (cf. Letsinger and Skoog[12]). After hydrolysis of the mixture and esterification with ethanolamine, the only product isolated was di-(2-aminoethyl) 2-biphenylylboronate, indicating that, if any of the required product had been formed, it had been hydrolysed to 2-biphenylylboronic acid. This is not surprising when it is considered that the ring system, by analogy with the fluorenyl cation, will have an unfilled bonding molecular orbital and should be very sensitive to nucleophilic attack. Wittig and Herwig[13] prepared lithium bis-(2,2′-biphenylylene) borate, which, on acid hydrolysis, likewise yielded 2-biphenylylboronic acid.

EXPERIMENTAL

Ultraviolet spectra were determined by means of a Unicam S.P.500 spectrophotometer. Boron analyses were carried out by direct titration in the presence of mannitol or by Fowler and Kraus's method.[14] Molecular weights were determined in naphthalene and camphor.

Diphenylboronous Acid.—To phenylmagnesium bromide [from bromobenzene (15·7 g.) in ether (50 ml.)] phenylboronic anhydride (10 g.) in benzene (75 ml.) was added dropwise with stirring, under reflux. After refluxing for a further 30 min. the mixture was hydrolysed with 15% hydrochloric acid (200 ml.) and solvents were removed from the dried solution. To the residual mixed oil and solid was added light petroleum (20 ml.). Filtration then afforded recovered phenylboronic anhydride (3·5 g., 33·6%), m. p. 214°. Removal of the solvent from the filtrate gave crude diphenylboronous acid (11·5 g., 65·0%), n_D^{20} 1·5907 (lit.,[15] 1·5913), which with ethanolamine formed 2-aminoethyl diphenylboronite, m. p. 187° (lit.,[12] 187°).

2-Biphenylylphenylboronous acid was prepared similarly from phenylboronic anhydride (7·5 g.) and ethereal 2-biphenylylmagnesium iodide (1 mol.). After hydrolysis, ethanolamine (4·4 g.) was added to the dried ethereal solution; 2-*aminoethyl* 2-*biphenylylphenylboronite* slowly crystallised. After recrystallisation from ethanol it (10·2 g., 46·5%) had m. p. 175° (Found: C, 79·2; H, 6·2; N, 4·4; B, 3·3. $C_{14}H_{16}ONB$ requires C, 79·7; H, 6·6; N, 4·65; B, 3·65%). This ester (3·0 g.) was shaken with ether (30 ml.) and 10% hydrochloric acid (30 ml.) until dissolved. The ether layer was then separated, dried, and evaporated, to leave 2-*biphenylylphenylboronous acid* as a very viscous colourless oil (2·55 g., 98%) (Found: B, 4·3. $C_{18}H_{15}OB$ requires B, 4·3%). The acid decomposed on storage, and with phosphorus pentachloride yielded tars.

o-*Phenoxyphenylboronic Acid.*—Magnesium (0·7 g.) reacted readily with 2-iododiphenyl ether (7·5 g.) and n-butyl metaborate (3·0 g.) in ether (60 ml.). After addition of iodine, the spontaneous refluxing (10 min.) was followed by heating for 30 min. The mixture was hydrolysed with 15% hydrochloric acid (100 ml.), and acid products were extracted with 5% sodium hydroxide solution. This yielded, on acidification, o-*phenoxyphenylboronic acid* which formed white crystals, m. p. 114° from benzene–cyclohexane (1·5 g., 27·6%) (Found: C, 67·8; H,

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[12] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 2491.

[13] Wittig and Herwig, *Chem. Ber.*, 1955, **88**, 962.

[14] Fowler and Kraus, *J. Amer. Chem. Soc.*, 1940, **62**, 1143.

[15] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

5·2; B, 5·1. $C_{12}H_{11}O_3B$ requires C, 67·2; H, 5·1; B, 5·0%), unchanged after storage over concentrated sulphuric acid at 0·1 mm. for 10 days.

9-Phenanthrylboronic acid was prepared from 9-bromophenanthrene (5 g., 1 mol.) and n-butyl metaborate (2·5 g., 1·1 mol.) as for *o*-phenoxyphenylboronic acid, and after recrystallisation from hot water (yield, 2·45 g., 57%), had m. p. 324° (lit., 324°) (Found: B, 5·05. Calc. for $C_{14}H_{11}O_2B$: B, 4·95%).

10-*Hydroxy*-9-*oxa*-10-*bora-anthracene*.—To 2,2′-dilithiodiphenyl ether [10] in ether (156 ml.)) was added n-butyl metaborate (6·7 g.) in ether (25 ml.) during 10 min. The solution was then refluxed for 2 hr. and hydrolysed with 10% hydrochloric acid (100 ml.). Evaporating the dried ethereal solution gave 10-*hydroxy*-9-*oxa*-10-*bora-anthracene*. Recrystallisation from benzene afforded 5·9 g. (42·0%) of fairly pure material, but repeated recrystallisations from benzene and from cyclohexane were required to produce a specimen (m. p. 285°) in which *o*-phenoxyphenylboronic acid could not be detected by infrared analysis (Found: C, 72·5; H, 4·6; B, 5·4%; *M*, 195. $C_{12}H_9O_2B$ requires C, 73·4; H, 4·6; B, 5·6%; *M*, 196).

600 ml. of the same solution of 2,2′-dilithiodiphenyl ether and an ethereal solution (200 ml.) of the boron trifluoride–ether complex (37 g.) were simultaneously added to stirred ether (100 ml.) under nitrogen during 45 min. The whole was refluxed for 1 hr., then worked up as in the previous experiment, yielding 10-hydroxy-9-oxa-10-bora-anthracene (11·1 g., 23%), m. p. and mixed m. p. 285°.

2-*Biphenylylboronic Acid*.—To 2-biphenylylmagnesium iodide (from 10 g. of 2-iodobiphenyl) in warm ether (50 ml.) was added n-butyl metaborate (3·5 g.) in ether (15 ml.) as rapidly as possible. When the reaction subsided the solution was refluxed for 30 min., after which 2-biphenylylboronic acid was recovered by the method used for *o*-phenoxyphenylboronic acid. After recrystallisation from hot water, it (5 g., 72·2%) had m. p. 121—123° (lit., 129°), with resolidification to the anhydride, m. p. 195° (lit., 195°).[5]

This acid (3·9 g.) was esterified with ethanol by azeotropic distillation, affording the *diethyl ester* (3·4 g., 62%), b. p. 136—138°/4·0 mm., n_D^{20} 1·5444 (Found: C, 75·7; H, 7·3; B, 3·8. $C_{16}H_{19}O_2B$ requires C, 75·5; H, 7·5; B, 4·3%).

Di-n-butyl 2-*biphenylylboronate* was prepared by direct esterification of the Grignard reaction mixture after hydrolysis. 26·5 g. of 2-iodobiphenyl and 8·8 g. of n-butyl metaborate afforded 13·3 g. (45·5% overall) of ester, b. p. 149—151°/0·6 mm., n_D^{20} 1·5310 (Found: C, 77·6; H, 8·8; B, 3·5. $C_{20}H_{27}O_2B$ requires C, 77·5; H, 8·7; B, 3·55%).

Di-n-butyl 2-biphenylylboronate (7·5 g.) was heated with phosphorus pentachloride (11 g.) for 18 hr. at 140°; evaporation and distillation then yielded 2-*biphenylylboron dichloride* (4·35 g., 76·6%), b. p. 95—96°/0·25 mm., n_D^{20} 1·5661 (Found: C, 62·0; H, 4·0; B, 4·6; Cl, 30·8. $C_{12}H_9Cl_2B$ requires C, 61·4; H, 3·8; B, 4·6; Cl, 30·3%).

Attempted Preparation of 9-2′-*Aminoethoxy*-9-*borafluorene*.—2,2′-Dilithiobiphenyl [13] in ether solution (60 ml.) (from 2,2′-di-iododiphenyl, 4 g.) was slowly treated with n-butyl metaborate (0·9 g.) in ether (15 ml.) with stirring under dry nitrogen, after which the solution was refluxed for 15 min. and hydrolysed with dilute ammonium chloride solution. The dried ethereal solution was evaporated and then azeotropically distilled with ethanolamine and toluene. On cooling, the residue slowly deposited *bis*-2-*aminoethyl* 2-*biphenylylboronate* (1·3 g., 59%), m. p. 134° (from benzene) (Found: C, 67·4; H, 7·5; N, 9·95; B, 3·9%; *M*, 264. $C_{16}H_{21}O_2N_2B$ requires C, 67·5; H, 7·4; N, 9·8; B, 3·8%; *M*, 284). A sample was hydrolysed with dilute hydrochloric acid to the acid, which was dried to form the anhydride and then recrystallised from cyclohexane; this product had m. p. 206° (Found: C, 80·1; H, 5·2; B, 6·1. Calc. for $C_{12}H_9OB$: C, 80·0; H, 5·0; B, 6·0%).

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