295. *Interaction of Boron Trichloride with Catechol, Quinol, Resorcinol, and Pyrogallol.*

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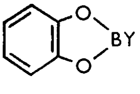
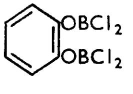
Catechol and boron trihalides readily gave *o*-phenylene halogenoboronates (I; Y = Cl, Br) and tris-*o*-phenylene bisborate (III). From the chloroboronate various derivatives (I; Y = OR, OPh, NR_2, SR, OH) and (IV) were prepared, whilst from catechol two others (I; Y = Ph, Bu^t) were obtained. The chemical properties of these cyclic boron compounds are described. Reactions between resorcinol, quinol, or pyrogallol and boron trichloride gave polymers of variable composition.

In the search for " boron polymers "[1] of satisfactory thermal and hydrolytic stability, reactions of di- and poly-hydric phenols have been examined. With catechol, owing to the proximity of the hydroxyl groups, cyclic boron compounds were formed, whereas with resorcinol, quinol, and pyrogallol the polymers obtained, although satisfactory thermally, were easily hydrolysed, as were all the boron compounds derived from catechol.

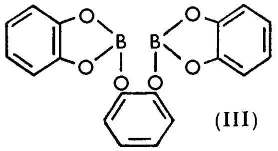
Catechol readily gave *o*-phenylene chloroboronate (I; Y = Cl) with one or more mol. of boron trichloride, thus showing that there is a low probability of forming the bisdichloroborinate (II). The bromoboronate (I; Y = Br) was similarly prepared from boron tribromide. With catechol and boron trichloride in the ratio 3 : 2, the bisborate (III) was readily formed; it was also obtained from catechol and the chloroboronate.



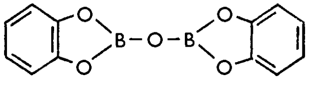
(I)



(II)



(III)



(IV)

The chloroboronate (I; Y = Cl) had exceptional thermal stability, thus resembling ethylene chloroboronate, $(CH_2O)_2B{\cdot}Cl$,[2] but differing from the phenyl analogue, $(PhO)_2B{\cdot}Cl$.[3] Prolonged heating at 220—230° was required in order to demonstrate a clear redistribution into boron trichloride and the bisborate (III). The bromoboronate (I; Y = Br) had comparable stability and this is of interest because earlier[4] attempts to prepare bromoboronates $(RO_2)B{\cdot}Br$ and dibromoborinates $RO{\cdot}BBr_2$ have failed, although one bromoborinate $Ph{\cdot}B(OBu^n)Br$ is known.[5]

Both the *o*-phenylene halogenoboronates reacted with alcohols or phenol to give borates (I; Y = OR or OPh). With a controlled amount of water, the chloroboronate afforded *o*-phenylene hydrogen borate (I; Y = OH). Thiols reacted slowly with the chloroboronate, but prolonged heating gave the thio-esters (I; Y = SBu^n and $S{\cdot}C_8H_{17}$-*n*). Both the halogenoboronates formed stable 1 : 1 complexes with pyridine. With a secondary amine (2 mol.) the chloroboronate (1 mol.) gave an *o*-phenylene dialkylaminoboronate (I; Y = NEt_2 and $NBu^n{}_2$) and dialkylammonium chloride; these dialkylaminoboronates were appreciably more stable than the di-*n*-butyl dialkylaminoboronates,[6] the only other known compounds of this class.

o-Phenylene hydrogen borate (I; Y = OH) is an example of the very rare partially hydrolysed esters[2] of boric acid. When heated it afforded the anhydride (IV), which was

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[1] Gerrard, *Chem. Prod.*, 1957, **20**, 489.

[2] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.

[3] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.

[4] Bujwid, Gerrard, and Lappert, *Chem. and Ind.*, 1957, 1386; Goubeau, Becher, and Griffel, *Z. anorg. Chem.*, 1956, **282**, 86.

[5] Abel, Gerrard, and Lappert, *J.*, 1957, 5051.

[6] Gerrard, Lappert, and Pearce, *Chem. and Ind.*, 1958, 292.

converted into the halogenoboronate with boron trihalide (Cl,Br) and into the chloroboronate with phosphorus pentachloride. With alcohols, the anhydride was converted into the esters (I; Y = OR). The anhydride was also prepared from catechol and boric acid by azeotropic removal of water by use of benzene.

Pyrolysis of methyl *o*-phenylene borate (I; Y = OMe) gave trimethyl borate and the bisborate (III), whereas other *n*-alkyl esters were stable; the *sec.*-butyl ester, however, was almost completely decomposed into but-2-ene and the anhydride (pyroborate; IV).

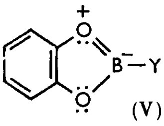
Boron trichloride and the *n*-butyl ester (I; Y = OBu^n) readily gave *o*-phenylene chloroboronate and *n*-butyl dichloroborinate, $Bu^nO{\cdot}BCl_2$.[7] The bromoboronate, together with methyl bromide, was similarly obtained from methyl *o*-phenylene borate and boron tribromide. Alkyl, as well as phenyl, *o*-phenylene borates formed stable 1 : 1-complexes with pyridine; this is of interest because trialkyl borates do not as a rule form amine complexes, whereas triaryl borates do owing to decreased back-co-ordination, $(C_6H_5\text{—}\overset{\curvearrowleft}{\ddot{O}}\text{—}B\langle)$.[3,8] The alkyl *o*-phenylene borates may be regarded as mixed alkyl aryl borates, and evidently the boron atom in them is sufficiently electrophilic to permit co-ordination to take place.

n-Butyl *o*-phenylene borate was also prepared from catechol and either tri-*n*-butyl borate or butan-1-ol and boric acid.

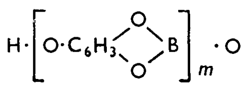
The *S*-alkyl *o*-phenylene thioborates (I; Y = SR) were readily hydrolysed by cold water affording the thiol, catechol, and boric acid. Butan-1-ol was not displaced by octanethiol by heating *n*-butyl *o*-phenylene borate with octanethiol, but the *n*-butylthio-group in *S*-*n*-butyl *o*-phenylene thioborate was replaced by the *n*-octyloxy-group by reaction with octanol. A substituted amino-group attached to a boron atom is replaceable by an alkoxy-group but not the reverse;[9] it is now evident that a thiol group attached to boron is replaceable by an alkoxy-group, and again not conversely. The *S*-alkyl *o*-phenylene thioborates are the first reported examples of monothio-boric esters.

o-Phenylene phenylboronate[10,11] (I; Y = Ph) was obtained by azeotropic removal of water from a mixture of phenylboronic anhydride $(PhBO)_3$ and catechol, and *o*-phenylene *tert.*-butylboronate (I; Y = Bu^t) was prepared by treating *tert.*-butylboron dichloride with catechol.

Compounds of type (I) possess considerable thermal stability and this is greater than in corresponding acyclic compounds of type $(RO)_2B{\cdot}Y$. This may be attributed to stabilisation by cyclisation (cf. ref. 2), but may in part also be due to the fact that the boron-containing ring can exhibit 6π-electron resonance, giving rise to canonical structures of the type (V). Evidence for this view has recently been obtained from ultraviolet spectra of *o*-phenylene phenylboronate.[11]


(V)

$$HO{\cdot}C_6H_4{\cdot}O{\cdot}[BCl{\cdot}O{\cdot}C_6H_4{\cdot}O]_n{\cdot}H$$
(VI)


(VII)

With resorcinol, quinol, and pyrogallol no volatile materials or bisdichloroborinates were obtained. With an excess of boron trichloride, resorcinol afforded a trinuclear compound $[Cl_2B{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}B(Cl){\cdot}O]_2C_6H_4$. All other products were polymeric and appeared to correspond to (VI) for the dihydric phenols and to (VII) for pyrogallol. The chlorine-containing polymers lost boron trichloride when heated, presumably forming polymeric

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[7] Gerrard and Lappert, *J.*, 1951, 2545; 1955, 3084.

[8] Colclough, Gerrard, and Lappert, *J.*, 1956, 3006; Abel, Gerrard, Lappert, and Shafferman, *J.*, 1958, 2895.

[9] Gerrard, Lappert, and Pearce, *J.*, 1957, 381.

[10] Kuivila, Keough, and Soboczenski, *J. Org. Chem.*, 1954, **19**, 780.

[11] Dewar, Kubba, and Pettit, *J.*, 1958, 3076.

cross-linked borates. Hydrolysis of all products invariably afforded the parent polyhydric phenol and boric acid. The polymers were generally insoluble in non-polar solvents.

EXPERIMENTAL.

o-*Phenylene Halogenoboronates.*—Catechol (3·76 g., 1 mol.) was added in suspension in methylene chloride to boron trichloride (4·67 g., 1·17 mol.) at −80°. As the system warmed to 15°, hydrogen chloride (2·27 g., 91%) and boron trichloride (0·66 g.) were absorbed by potassium hydroxide, and the residue (5·1 g., after being kept at 20°/15 mm.) gave o-*phenylene chloroboronate* (4·88 g., 92%), b. p. 64°/10 mm., m. p. 57° (Found: C, 47·0; H, 2·5; Cl, 22·4; B, 6·9; $C_6H_4O_2$, 69·4. $C_6H_4O_2ClB$ requires C, 46·7; H, 2·6; Cl, 23·0; B, 7·0; $C_6H_4O_2$, 70·0%). Similarly o-*phenylene bromoboronate* (6·24 g., 90%), b. p. 76°/9 mm., m. p. 47° (Found: Br, 39·9; B, 5·4. $C_6H_4O_2BrB$ requires Br, 40·2; B, 5·4%), and hydrogen bromide (5·45 g., 97%) were obtained from boron tribromide and catechol.

The chloroboronate (3·25 g.) was recovered in 96·4% yield after it had been heated at 55—60°/15 mm. for 12 hr., the remaining material being accounted for as boron trichloride (0·035 g.) and an undistilled residue (Found: B, 6·5%). Similarly the bromoboronate was recovered in 75·6% yield, the remainder having given boron tribromide and a residue (Found: B, 6·5%). At 220—230° (23·25 hr.), the chloroboronate (8·4 g.) gave boron trichloride (0·28 g.), and tris-*o*-phenylene bisborate (1·03 g.), b. p. 180°/0·02 mm., m. p. 102° (Found: B, 6·2; Cl, 0. Calc. for $C_{18}H_{12}O_6B_2$: B, 6·26; Cl, 0%), and was partly recovered (6·4 g., 76%), b. p. 57°/5 mm. (Found: Cl, 22·4; B, 7·0%).

The chloroboronate (7·4 g., 1 mol.) was shaken with a suspension of water (2·6 g., 3 mol.) in ether (40 c.c.), and immediately at 20°/15 mm. hydrogen chloride (1·74 g., 99%) was evolved. The solid residue (8·2 g.) was separated by benzene into boric acid (2·9 g., 98%) and catechol (5·1 g., 97%), b. p. 120°/10 mm., m. p. 103—104°. Hydrogen bromide (0·85 g., 95%), boric acid (0·69 g., 100%), and catechol (1·22 g., 100%), m. p. and mixed m. p. 103—104°, were similarly obtained from the bromoboronate (2·21 g.).

When only 1 mol. of water was used with the chloroboronate (7·6 g., 1 mol.), there was no precipitation from the ether. On removal of solvent, hydrogen chloride (1·77 g., 99%) was evolved, and the residue of o-*phenylene hydrogen borate* (6·7 g., 100%), m. p. 70—75° (Found: C, 52·4; H, 3·7; B, 8·0. $C_6H_5O_3B$ requires C, 52·9; H, 3·7; B, 8·0%), afforded water (in 80% yield) and *di*-o-*phenylene pyroborate* (96%) (see also ref. 13), b. p. 160°/0·1 mm. (Found: C, 56·0; H, 3·2; B, 8·5. $C_{12}H_8O_5B_2$ requires C, 56·8; H, 3·2; B, 8·5%). Acidic hydrogen was absent. This anhydride (45·4 g., 89%), b. p. 160°/0·1 mm. (Found: B, 8·3; $C_6H_4O_2$, 84·9. Calc. for $C_{12}H_8O_5B_2$: B, 8·5; $C_6H_4O_2$, 85·2%), together with an undistilled residue (2·8 g.) (Found: B, 7·2%), was also obtained by the azeotropic (benzene, 50 c.c.) removal of water from a mixture of catechol (44·0 g., 1 mol.) and boric acid (24·7 g., 1 mol.).

Di-o-*phenylene Pyroborate.*—The pyroborate (3·4 g., 1 mol.) shaken with water (1·2 g., 5 mol.) in benzene (25 c.c.) immediately afforded boric acid (1·66 g., 100%), isolated by filtration, and catechol (2·8 g., 95%), m. p. 102—103°, obtained from the filtrate by removal of solvent at 20°/0·1 mm. After being heated for 12 hr. at 290°, the pyroborate (Found: B, 8·6%) was recovered in 89% yield, and there was a black residue. Boron trifluoride in methylene chloride was without determined action, the anhydride (Found: B, 8·4%) being recovered in 91% yield, whereas the anhydride (5·63 g., 1 mol.) and boron trichloride (3·37 g., 1·3 mol.) in methylene chloride (10 c.c.) gave at 20° (48 hr.) boron trichloride (1·57 g.), removed at 20°/15 mm., *o*-phenylene chloroboronate (5·4 g., 79%), b. p. 67°/10 mm., m. p. 56° (Found: Cl, 22·5; B, 7·1%), the anhydride (0·92 g.), and a residue (0·75 g.) (Found: B, 2·6%). Corresponding results with the anhydride (6·06 g., 1 mol.) and boron tribromide (6·0 g., 1 mol.) were: tribromide recovery (1·55 g.), *o*-phenylene bromoboronate (6·5 g., 68%), b. p. 78°/10 mm., m. p. 48° (Found: Br, 40·1; B, 5·4%), anhydride recovery (1·2 g.), and a residue (1·1 g.) (Found: B, 16·0%).

Phosphorus pentachloride (6·6 g.) was heated with the anhydride (6·7 g.) at 120—140° for 4 hr. A liquid trapped at −80° contained boron trichloride (0·9 g.) (pyridine complex, m. p. 110° [14]). The residue gave phosphorus oxychloride (2·8 g., 69%), b. p. 106—108° (Found:

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[12] Thomas, *J.*, 1946, 820, 823.

[13] Schäfer and Braun, *Naturwiss.*, 1952, **39**, 280.

[14] Gerrard and Lappert, *J.*, 1951, 1020.

Cl, 68·4. Calc. for $POCl_3$: Cl, 69·4%), *o*-phenylene chloroboronate (4·9 g., 60%), b. p. 66°/10 mm., m. p. 57° (Found: Cl, 22·7; B, 6·9%), and a non-volatile residue (1·2 g.).

Alkyl o-*Phenylene Borates.*—Butan-1-ol (4·2 g., 1 mol.) in methylene chloride (5 c.c.) was added to *o*-phenylene chloroboronate (8·6 g., 1 mol.) in methylene chloride (15 c.c.) at 15°. Hydrogen chloride (1·84 g., 91%) was evolved, and n-*butyl* o-*phenylene borate* (9·5 g., 89%), b. p. 106°/5 mm., n_D^{20} 1·4891, d_4^{20} 1·0707, $[R_L]_D$ 51·74 (Calc. 51·62) (Found: C, 62·4; H, 7·1; B, 5·7; $C_6H_4O_2$, 55·6. $C_{10}H_{13}O_3B$ requires C, 62·5; H, 6·8; B, 5·6; $C_6H_4O_2$, 56·3%), and a residue (1·0 g.) (Found: B, 6·2%) were obtained. Similarly other esters were prepared; the essential details are shown in the Table. Hydrogen chloride determined varied from 91 to 97%.

Phenyl *o*-phenylene borate, m. p. 44° (Found: C, 67·2; H, 4·4; B, 5·2. Calc. for $C_{12}H_9O_3B$: C, 68·0; H, 4·3; B, 5·1%), previously prepared [12] by the azeotropic technique, was similarly obtained.

The *n*-butyl ester (45·2 g., 86%), b. p. 106°/6 mm. (Found: B, 5·6%), was also prepared by heating catechol (30 g., 1 mol.) with tri-*n*-butyl borate (62·8 g., 1 mol.) under a Vigreux column, butan-1-ol (38·2 g., 97%) being distilled off; the ester was prepared (85% yield) from *o*-phenylene bromoboronate and butan-1-ol, hydrogen bromide (95%) being collected. A fourth method of preparing the *n*-butyl ester (33·2 g., 86%), b. p. 106°/5 mm. (Found: B, 5·6%), comprised the azeotropic separation of water (10·9 c.c., 100%) from a mixture of catechol (22·0 g., 1 mol.), boric acid (12·4 g., 1 mol.), and butan-1-ol in excess. There was an undistilled residue (2·0 g.) (Found: B, 6·3%).

The *sec.*-butyl ester (9·4 g., 69%), b. p. 97°/5 mm. (Found: B, 5·6%), was also obtained by heating (2 hr.) a mixture of *o*-phenylene pyroborate (9·0 g.) and the alcohol (20 c.c. excess) under reflux, followed by distillation.

Alkyl o-*phenylene borates.*

Ester	Yield (%)	Found (%) Calc. (%) C	H	B	B. p. (°/mm.)	n_D^{20}	d_4^{20}	Molar refractivity Found	Calc.†
Me	82	56·2	4·8	7·2	81°/10	1·5059	1·1890	37·45	37·68
		56·1	4·7	7·2					
Et	89	58·1	5·8	6·6	91/10	1·4960	1·1316	42·30	42·33
		58·6	5·5	6·6					
Pr^n	91	60·8	6·4	6·1	105/10	1·4900	1·0937	47·03	46·98
		60·7	6·2	6·1					
Bu^n	88	62·4	7·1	5·7	104/5	1·4891	1·0707	51·74	51·62
		62·5	6·8	5·6					
Bu^i	77	62·5	6·7	5·6	100/5	1·4846	1·0558	52·08	51·62
Bu^s	88	62·9	7·1	5·7	97/5	1·4853	1·0704	51·43	51·62
n-C_5H_{11}	94	65·1 *	7·4	5·2	116/5	1·4891	1·0578	56·22	56·27
		64·1	7·3	5·3					
n-C_8H_{17}	92	67·7	8·4	4·4	124/0·05	1·4856	1·0158	70·09	70·21
		67·7	8·5	4·4					

* Repeated.

† Calculations based on Vogel's values (*J.*, 1943, 638; 1946, 133; 1948, 616, 654), the value 2·28 being assigned to boron.

After methyl *o*-phenylene borate (5·2 g.) had been heated at 240° for 16·5 hr., trimethyl borate (1·1 g., 92%), b. p. 68° (Found: B, 10·4. Calc. for $C_3H_9O_3B$: B, 10·4%), and tri-*o*-phenylene bisborate (3·4 g., 85%), b. p. 168°/0·01 mm., m. p. 100—102° (Found: B, 6·3%), were obtained. Octyl *o*-phenylene borate (6·2 g.), however, was recovered (5·7 g.), b. p. 115°/0·01 mm. (Found: B, 4·4%), after being refluxed at 350° for 12 hr.

Similarly the *n*-butyl ester (7·9 g.) was recovered in 96% yield (Found: B, 5·6%) after being heated at 280° for 24 hr. The *sec.*-butyl ester (6·9 g.), however, at 330° (12 hr.) gave but-2-ene (1·81 g., 90%) (2 : 3-dibromobutane, b. p. 157°, $n_D^{20·5}$ 1·5109), and *o*-phenylene pyroborate (4·2 g., 92%), b. p. 155°/0·05 mm. (Found: B, 8·4%).

Addition of the butyl ester (8·0 g., 1 mol.) to boron trichloride (4·9 g., 1 mol.) at −80°, followed by warming to 15°, gave at 20°/0·1 mm. *n*-butyl dichloroborinate (6·2 g., 96%), b. p. 39—43°/18—20 mm. (Found: Cl, 45·9; B, 7·0. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%) (first collected at −80°), and a residue of *o*-phenylene chloroboronate (6·1 g., 95%), m. p. 54° (Found: Cl, 22·0; B, 7·1%).

The methyl ester (6·6 g., 1 mol.) added to boron tribromide (11·0 g., 1 mol.) at 15° afforded at 60° methyl bromide (3·8 g., 91%) (Found: Br, 85·0. Calc. for CH_3Br: Br, 84·2%) (collected at $-80°$), followed at 60°/20 mm. by boron tribromide (3·1 g., 85%), b. p. 91°, pyridine complex, m. p. 125° (Found: Br, 71·0; B, 3·3; C_5H_5N, 24·2. Calc. for $C_5H_5NBr_3B$: Br, 72·7; B, 3·3; C_5H_5N, 24·0%), and at higher temperature by *o*-phenylene bromoboronate (7·0 g., 80%), b. p. 79°/10 mm., m. p. 47° (Found: Br, 39·8; B, 5·5%), leaving a residue (2·0 g.) (Found: Br, 14·8; B, 14·6%).

The *n*-butyl ester (4·6 g., 1 mol.) was shaken with water (1·3 g., 3 mol.) and benzene (30 c.c.). Boric acid (1·46 g., 99%) was immediately formed and filtered off, and catechol (2·4 g., 91%) was obtained from the filtrate.

Similarly, the octyl ester (7·6 g., 1 mol.) gave boric acid (1·84 g., 97%); catechol (2·9 g., 86%), m. p. and mixed m. p. 105°, was obtained by evaporation of the solvent and addition of *n*-pentane.

*Tri-*o*-phenylene Bisborate.*—Whereas catechol (3·2 g., 1 mol.) suspended in methylene chloride (15 c.c.) and boron trichloride (6·8 g., 2 mol.) afforded boron trichloride (3·14 g., 0·92 mol.) and *o*-phenylene chloroboronate (4·2 g., 93%), b. p. 62°/10 mm., m. p. 57° (Found: Cl, 22·6; B, 7·2%), instead of the bisdichloroborinate, the use of 3 mol. of catechol (7·4 g.) and 2 mol. of boron trichloride (5·2 g.), mixed at $-80°$ and allowed to warm to 20°, afforded hydrogen chloride (4·8 g., 98%) and tri-*o*-phenylene bisborate (7·6 g., 98%), b. p. 170—175°/0·03 mm. (Found: B, 6·3%). Similarly, from 3 mol. of catechol (9·6 g.) and 1 mol. of boron trichloride (3·4 g.), catechol (3·7 g.), b. p. 120°/10 mm., m. p. 101—104°, and the bisborate (4·0 g.), b. p. 175—180°/0·03 mm., m. p. 104° (Found: B, 6·1%), were obtained. The bisborate (3·1 g., 95%), b. p. 175—180°/0·03 mm., m. p. 105° (Found: C, 62·5; H, 4·9; B, 6·2. Calc. for $C_{18}H_{12}O_6B_2$: C, 62·5; H, 3·5; B, 6·3%), was obtained from the chloroboronate (2·9 g., 2 mol.) and catechol (1·0 g., 1 mol.), mixed in methylene chloride (10 c.c.) at $-80°$, and warmed to 20°

On being shaken with water (0·6 g., 6 mol.), the bisborate (1·9 g., 1 mol.) in benzene (25 c.c. immediately gave a precipitate of boric acid (0·68 g., 100%), and catechol (1·8 g., 99%), m. p. 102—104°, was obtained from the solvent.

After the bisborate (3·8 g.) had been heated at 290° for 12 hr., 82% was recovered, b. p. 175—180°/0·03 mm., m. p. 104° (Found: B, 6·2%), there being a black residue (0·6 g.).

Pyridine Complexes.—Pyridine–methyl o*-phenylene borate* (7·8 g., 93%), m. p. 161—163°, after being washed with pentane, stable at 20°/0·01 mm. (5 hr.) (Found: B, 4·8; C_5H_5N, 34·6. $C_{12}H_{12}O_3NB$ requires B, 4·7; C_5H_5N, 34·7%), was obtained from the base (2·9 g., 1 mol.) and the borate (5·5 g., 1 mol.) mixed at $-80°$ and warmed to 20°. *Pyridine–ethyl* o*-phenylene borate* (5·7 g., 94%), m. p. 130—140° (Found: B, 4·5; C_5H_5N, 33·0. $C_{13}H_{14}O_3NB$ requires B, 4·45; C_5H_5N, 32·6%), was precipitated on mixing the ester (4·1 g.) and base (1·98 g.) in *n*-pentane. It lost 1·3% of its weight in 5 hr. at 20°/0·005 mm.

Similarly *pyridine–*n*-propyl* o*-phenylene borate* (95%), m. p. 148—151° (Found: B, 4·2; C_5H_5N, 31·0. $C_{14}H_{16}O_3NB$ requires B, 4·2; C_5H_5N, 30·8%), was obtained, but the initial oil had to be heated in the mixture to obtain the solid complex before filtration. This was also necessary for *pyridine–*n*-butyl* o*-phenylene borate* (73%), m. p. 160—165° (Found: B, 4·0; C_5H_5N, 30·2. $C_{15}H_{18}O_3NB$ requires B, 4·0; C_5H_5N, 29·2%), which lost 0·7% of its weight in 5 hr. at 20°/0·001 mm. *Pyridine–phenyl* o*-phenylene borate* (95% yield), m. p. 135—138°, stable at 20°/0·02 mm. (5 hr.) (Found: B, 3·9; C_5H_5N, 26·6. $C_{17}H_{14}O_3NB$ requires B, 3·7; C_5H_5N, 27·2%), was similarly prepared, a mixture of *n*-pentane (5 vol.) and methylene chloride (1 vol.) being used as a medium. In this way, too, *pyridine–*o*-phenylene chloroboronate* (97% yield), m. p. 80—90°, stable at 20°/0·01 mm. (3 hr.) (Found: B, 4·6; C_5H_5N, 33·8. $C_{11}H_9O_2NClB$ requires B, 4·6; C_5H_5N, 33·9%), and *pyridine* o*-phenylene bromoboronate* (100%), m. p. 80—85°, stable at 20°/0·005 mm. (3 hr.) (Found: B, 3·8; C_5H_5N, 28·4. $C_{11}H_9O_2NBrB$ requires B, 3·9; C_5H_5N, 28·5%), were obtained from the halogenoboronates. The complexes were easily hydrolysed.

S-*Alkyl* o*-Phenylene Thioborates.*—*n*-Butanethiol (6·2 g., 2·2 mol.) and *o*-phenylene chloroboronate (4·8 g., 1 mol.) were heated at 150—160° for 4 hr., and hydrogen chloride (1·07 g., 94%), *n*-butanethiol (3·4 g., excess of 1 mol.), and S-n-*butyl* o*-phenylene thioborate* (5·1 g., 79%), b. p. 80—84°/0·1 mm., n_D^{20} 1·5334 (Found: S, 15·9; B, 5·2. $C_{10}H_{13}O_2SB$ requires S, 15·4; B, 5·2%) were obtained. Evolution of hydrogen chloride was slow at 20° (23·2% after 4·5 hr.), but within ½ hr. at 150—160° a further 58% of gas was liberated.

Similarly, S-*octyl* o*-phenylene thioborate* (11·3 g., 93%), b. p. 142°/0·05 mm., n_D^{20} 1·5198

(Found: C, 64·2; H, 8·0; B, 4·1. $C_{14}H_{21}O_2SB$ requires C, 63·6; H, 8·0; B, 4·1%), was obtained at 200—220°.

With water (1·2 g., 3 mol.) the *n*-butyl thio-ester (4·65 g.) readily afforded *n*-butanethiol (2·0 g., 99%), b. p. 98°, n_D^{20} 1·4420, boric acid (1·3 g., 94%), and catechol (2·25 g., 92%), m. p. 102—103°, mixed m. p. 103°.

No reaction was observed when a mixture of *n*-butyl *o*-phenylene borate (1 mol.) and octanethiol (1 mol .)was heated at 200° for 1 hr., the reagents being recovered upon distillation. Similarly, no reaction was apparent between *n*-butanethiol and ethyl *o*-phenylene borate. By contrast, from octanol (2·60 g., 1 mol.) and *S*-*n*-butyl *o*-phenylene thioborate (4·10 g., 1 mol.), *n*-butanethiol (1·70 g., 96%), b. p. 98°, n_D^{20} 1·4435, and octyl *o*-phenylene borate (4·60 g., 93%), b. p. 126°/0·05 mm., n_D^{20} 1·4854 (Found: B, 4·3%), were obtained.

o-*Phenylene Dialkylaminoboronates.*—Diethylamine (18·0 g., 2 mol.) in *n*-pentane (50 c.c.) was added to *o*-phenylene chloroboronate (19·0 g., 1 mol.) in *n*-pentane (100 c.c.) at −80°. The mixture was warmed to 20° and set aside for 18 hr. The white precipitate of diethylammonium chloride (13·6 g., 100%) (Found: Cl, 31·7. Calc. for $C_4H_{12}NCl$: Cl, 32·3%) was filtered off and washed with *n*-pentane. The filtrate afforded o-*phenylene diethylaminoboronate* (18·6 g., 79%), b. p. 72°/0·1 mm., n_D^{20} 1·5061 (Found: C, 62·5; H, 7·5; N, 7·4; B, 5·6. $C_{10}H_{14}O_2NB$ requires C, 62·9; H, 7·3; N, 7·3; B, 5·7%), and a non-volatile residue (0·50 g.) (Found: B, 4·4%).

Similarly, from di-*n*-butylamine (29·3 g.) and the chloroboronate (17·5 g.) there were obtained di-*n*-butylammonium chloride (18·6 g., 96%) (Found: Cl, 21·5. Calc. for $C_8H_{20}NCl$: Cl, 21·4%) and o-*phenylene di*-n-*butylaminoboronate* (23·0 g., 82%), b. p. 108°/0·005 mm., n_D^{20} 1·4971 (Found: C, 67·6; H, 8·7; N, 5·6; B, 4·4. $C_{14}H_{22}O_2NB$ requires C, 68·1; H, 8·9; N, 5·7; B, 4·4%).

o-*Phenylene Alkyl*(*and Aryl*)*boronates.*—A mixture of benzene (30 c.c.), phenylboronic anhydride [15] (6·11 g., 1 mol.), and catechol (6·50 g., 1 mol.) was heated under a Vigreux column fitted with a Dean and Stark head. Water (1·00 g., 94%) was separated from the first fraction, which was the water–benzene azeotrope. The residue (11·55 g.), after removal of benzene, afforded *o*-phenylene phenylboronate (10·73 g., 93%), m. p. 111°, b. p. 124°/0·4 mm. (Found: C, 73·9; H, 4·6. Calc. for $C_{12}H_9O_2B$: C, 73·5; H, 4·6%).

Catechol (4·00 g., 1 mol.) in suspension in methylene dichloride (35 c.c.) was added to *tert.*-butylboron dichloride [16] (5·02 g., 1 mol.) at 20°; the reaction was endothermic and hydrogen chloride was evolved. Matter volatile at 20°/0·5 mm. was removed and the residue (6·07 g.) afforded o-*phenylene* tert.-*butylboronate* (5·89 g., 92%), b. p. 40—41°/0·4 mm., n_D^{20} 1·4924, d_4^{30} 1·016 (Found: C, 67·7; H, 7·4. $C_{10}H_{13}O_2B$ requires C, 68·2; H, 7·45%).

Interaction of Resorcinol and Boron Trichloride.—Resorcinol (2·82 g., 1 mol.) suspended in methylene chloride (50 c.c.) was added to boron trichloride (6·0 g., 2 mol.) at −80°, and after 1 hr. the mixture was warmed to 25°. Boron trichloride (2·06 g., 0·69 mol.) and hydrogen chloride (1·82 g., 1·95 mol.) were removed at 25°/3 mm., leaving the solid $[Cl_2B{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}B(Cl){\cdot}O]_2C_6H_4$ (4·81 g., 0·323 mol.) (Found: Cl, 34·6; B, 7·45. Calc. for $C_{18}H_{12}O_6Cl_6B_4$: Cl, 36·6; B, 7·45%). Yields are based on: $C_6H_4(OH)_2 + 2BCl_3 \longrightarrow 2HCl + [C_6H_4(OBCl_2)_2] \longrightarrow \frac{1}{3}[Cl_2B{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}B(Cl){\cdot}O]_2C_6H_4 + \frac{2}{3}BCl_3$.

Similarly (6·5 g., 1 mol.) of resorcinol and 1 mol. of the trichloride gave hydrogen chloride (4·3 g., 2 mol.) and a solid at 20°/0·05 mm. (9·35 g.), probably a polymer of type (VI) [Found: Cl, 21·2; B, 6·91%; Cl : B = 1 : 1·06. Calc. for (VI; n = 9): Cl, 21·4; B, 6·50%; Cl : B = 1 : 1·00], which was soluble in acetone, but insoluble in ether, chloroform, benzene, and pentane. When this product (5·42 g.) was heated at 300°/0·3 mm. (5 hr.), boron trichloride (0·955 g.) was evolved, leaving a glass (4·17 g.) (Found: Cl, 7·5; B, 5·8%), of which 1·62 g. readily afforded boric acid (0·47 g., 88%) and resorcinol (1·3 g., 91%) when shaken with water (0·47 g., 3 mol. for 1 g. atom of boron) and ether (20 c.c.).

Interaction of Quinol and Boron Trichloride.—Quinol (10·6 g., 3 mol.), suspended in methylene chloride (50 c.c.), was added to boron trichloride (7·6 g., 2 mol.) at −80°, and the mixture was warmed to 20°. At 20°/15 mm. hydrogen chloride (4·3 g., 3·7 mol.) was removed and there was a solid residue (13·5 g.), probably a polymer (VI) [Found: Cl, 18·4; B, 5·2%; Cl : B = 1 : 1·04. Calc. for (VI; n = 3): Cl, 18·6; B, 5·6%]. With water (0·53 g.) suspended in ether (10 c.c.), a portion (2·01 g.) immediately gave hydrogen chloride (0·35 g.), boric acid (0·56 g.), and quinol (1·47 g., 94%), m. p. and mixed m. p. 168°.

[15] Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415.

[16] McCusker, Ashby, and Makowski, *ibid.*, 1957, **79**, 5182.

Interaction of Pyrogallol and Boron Trichloride.—Pyrogallol (6·3 g., 1 mol.) suspended in methylene chloride (40 c.c.) was added to boron trichloride (5·9 g., 1 mol.) at $-80°$. The reaction constituents were then separated at 30°/0·07 mm. into hydrogen chloride (5·1 g., 93%) and a white solid (7·2 g.) (Found: B, 7·2%), considerable difficulty being experienced in removing last traces of solvent, accomplished at 100°/0·01 mm. (1 hr.) [Found: B, 8·0%; *M*, ~700 (ebullioscopic in $CHCl_3$). Calc. for (VII; $m = 5$): B, 7·9%; *M*, 698]. This white solid lost 6·5% of its weight at 300°/0·01 mm. (1 hr.) becoming deep red and extremely hard and tough [Found: B, 8·4%; *M*, *ca.* 500 (ebullioscopic in $CHCl_3$)]. Both solids were quantitatively hydrolysed to boric acid on being shaken (1 hr.) with water suspended in ether.

One of us (B. A. M.) thanks the D.S.I.R. for a personal grant.

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[*Received, August 26th,* 1958.]