308. *Stability, Solvolysis, and Co-ordination Reactions of Esters of Boronic Acids and their Halogen Derivatives.*

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Esters of *n*-butyl- and phenyl-boronic acid $R\cdot B(OR')_2$ and *n*-butyl *n*-butyl- and phenyl-halogenoboronite $R\cdot BHal\cdot OR'$, and *n*-butyl(and phenyl)-boron dihalides $R\cdot BHal_2$, have been studied in respect of their thermal stability, hydrolysis, alcoholysis, and co-ordination (action of pyridine) reactions. Where evidence is available, mechanisms are suggested and the general resemblance of these three classes to respectively borates, alkoxy-boron halides, and boron trihalides is pointed out.

IN continuation of the study [1, 2] of esters, $R\cdot B(OR')_2$, and halogeno-esters, $R\cdot BHal\cdot OR'$, of alkyl- or aryl-boronic acids and of alkyl- or aryl-boron dihalides, $R\cdot BHal_2$, we have examined the hydrolysis, alcoholysis, thermal stability, and co-ordination reactions of these compounds, wherein R = Bu^n or Ph and Hal = F or Cl.

That esters of boronic acids are hydrolysed to the parent acids [see (1)] is known. Esters of alkylboronic acids are hydrolysed more slowly than those of arylboronic acids and also than esters of boric acid, and this may be utilised in the separation of alkylboronates from trialkyl borates.[1] Such hydrolysis might involve either alkyl–oxygen or boron–oxygen fission. The latter is probably the usual mechanism because di-(+)-2-methylheptyl phenylboronate afforded the (+)-alcohol, without loss of activity, and di*neo*pentyl phenylboronate gave *neo*pentyl, and not a rearranged, alcohol. The configuration and maximum activity of the (+)-2-methylheptyl phenylboronate were calculated on the assumption that its preparation from phenylboron dichloride and (+)-octan-2-ol [see (10)] occurs with complete retention of configuration, as this appears not to involve substitution at the asymmetric carbon atom.

$$R\cdot B(OR')_2 + 2H_2O \longrightarrow 2R\cdot B(OH)_2 + 2R'OH \quad . \; . \; . \; . \; . \quad (1)$$

Alcoholysis of boronates [see (2)] led to exchange of alkoxy-groups when the alcohol used had a higher boiling point than the alcohol of the original ester. This was demonstrated by the high yields of *n*-, *iso*-, and *sec*.-butyl phenylboronate obtained from diethyl phenylboronate. This reaction also probably involved boron–oxygen fission, because (+)-2-methylheptyl phenylboronate was obtained when (+)-octan-2-ol interacted with diethyl phenylboronate.

$$R\cdot B(OR')_2 + 2R''OH \rightleftharpoons R\cdot B(OR'')_2 + 2R'OH \quad . \; . \; . \; . \; . \; . \quad (2)$$

There was no evidence for compound formation between pyridine and *n*-butyl phenyl- or *n*-butyl-boronate, but a stable 1 : 1 complex was obtained with di-(2 : 2 : 2-trichloroethyl) phenylboronate. That the electron-attracting chlorine atoms have increased the availability of boron for co-ordination with nitrogen would be a plausible enough explanation were it not that tri(-2 : 2 : 2-trichloroethyl)borate, like other borates (except trimethyl or triaryl borates [3]), gave no such complex; the explanation would be valid if steric hindrance to approach to the boron atom in the heavily chlorinated borate were responsible for this inactivity.

Hydrolysis, as well as *n*-butyl-alcoholysis, of *n*-butyl *n*-butylchloroboronite afforded di-*n*-butyl *n*-butylboronate [see (3) and (4)]. Whereas addition of *n*-butyl phenylchloroboronite to an excess of pyridine afforded an unstable 1 : 2 complex, which may have an

$$2Bu^n\cdot BCl\cdot OBu^n + 2H_2O \longrightarrow 2HCl + Bu^n\cdot B(OBu^n)_2 + Bu^n\cdot B(OH)_2 \quad . \; . \; . \quad (3)$$

$$Bu^n\cdot BCl\cdot OBu^n + Bu^nOH \longrightarrow HCl + Bu^n\cdot B(OBu^n)_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

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[1] Brindley, Gerrard, and Lappert, *J.*, 1955, 2956.
[2] *Idem, ibid.*, 1956, 824.
[3] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.

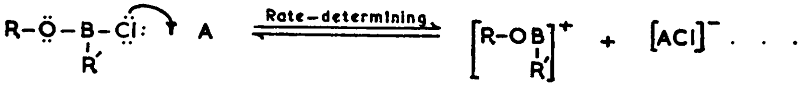
ionic structure, $(Ph{\cdot}B{\cdot}OBu^n,2py)^+Cl^-$, the addition of pyridine (1 mol.) to *n*-butyl *n*-butylchloroboronite (2 mols.) led to disproportionation [see (5)].

$$2Bu^n{\cdot}BCl{\cdot}OBu^n + py \longrightarrow Bu^n{\cdot}BCl_2,py + Bu^n{\cdot}B(OBu^n)_2 \quad . \; . \; . \; . \; . \quad (5)$$

Both *n*-butyl phenylchloroboronite and *n*-butyl *n*-butylchloroboronite were stable for 3 hr. at 100° but decomposed slowly at 200°, the former compound being the more stable. In both cases traces of anhydrous ferric chloride catalysed the decomposition, and a rapid reaction at 20° [see (6)] was then observed. Similar decomposition of (+)-2-methylheptyl

$$R{\cdot}BCl{\cdot}OBu^n \longrightarrow R{\cdot}BO + Bu^nCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

phenylchloroboronite afforded (—)-2-chloro-octane, with little loss of activity. The decomposition of these compounds probably involves a rate-determining B–Cl heterolysis which is catalysed by Lewis acids [designated " A " in (7)], subsequent alkyl halide formation then taking place by an in-line S_N2 mechanism (8).



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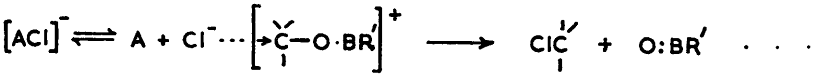

. . . (8)

n-Butyl phenyl- and *n*-butyl-fluoroboronite underwent hydrolysis in an excess of water to the boronic acid and hydrogen fluoride, as indicated by acidimetric estimation for boron and fluorine. Addition of pyridine to the esters effected disproportionation [analogous to (5)]. When *n*-butyl *n*-butylfluoroboronite was heated at 80° for 5 hours complete disproportionation [see (9)] occurred (see also ref. 2).

$$2Bu^n{\cdot}BF{\cdot}OBu^n \longrightarrow Bu^n{\cdot}BF_2 + Bu^n{\cdot}B(OBu^n)_2 \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

It has previously been demonstrated in a few isolated examples that alkyl- or arylboron dichlorides on alcoholysis give alkyl- or aryl-boronic esters.[4] It is now shown that this is a step-wise reaction [see (10) and (11)], involving the alkyl alkyl(or aryl)chloroboronite as an intermediate, and the product isolated is determined by the relative proportion of reagents used. Further, the influence of branching in the alcohol must be considered. Thus, whereas each of *n*-, *iso*-, and *sec*.-butyl alcohol and octan-2-ol (2 mols.) with phenylboron dichloride (1 mol.) gave high yields of the respective ester, *tert*.-butyl alcohol gave a

$$Ph{\cdot}BCl_2 + ROH \longrightarrow HCl + Ph{\cdot}BCl{\cdot}OR \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

$$Ph{\cdot}BCl{\cdot}OR + ROH \longrightarrow HCl + Ph{\cdot}B(OR)_2 \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

$$Ph{\cdot}BCl_2 + 2Bu^tOH \longrightarrow 2Bu^tCl + Ph{\cdot}B(OH)_2 \quad . \; . \; . \; . \; . \; . \quad (12)$$

low yield of ester and a side-reaction (12) produced *tert*.-butyl chloride. This difference may be due to attack of the hydrogen chloride formed on di-*tert*.-butyl phenylboronate,[2] to low stability of *tert*.-butyl phenylchloroboronite (5), or to the ease with which *tert*.-butyl alcohol reacts with hydrogen chloride. The side-reaction (12) was avoided when the reaction was carried out in presence of pyridine (see also ref. 1) : $Ph{\cdot}BCl_2 + 2ROH + 2py \longrightarrow Ph{\cdot}B(OR)_2 + 2py,HCl$. This reaction does not involve a pyridine–phenylboron dichloride complex as an intermediate, because the above reaction is instantaneous at −70°, whereas reaction of such a 1 : 1 complex with alcohol and pyridine is slow even at

$$Ph{\cdot}BCl_2,py + 2Bu^nOH + py \longrightarrow Ph{\cdot}B(OBu^n)_2 + 2py,HCl \quad . \; . \; . \; . \quad (13)$$

20°. Easters can be prepared from the complex, however, as shown in scheme (13) if the reagents are heated in chloroform for 6 hr.

Pyridine with phenylboron dichloride afforded a stable, solid 1 : 1 complex. Neither

[4] Michaelis and Becker, *Ber.*, 1880, **13**, 58; 1882, **15**, 180.

this complex nor its *n*-butyl analogue was soluble, or hydrolysed, in cold water. *n*-Butylboron difluoride gave with pyridine a liquid 1 : 1 complex.

Phenylboron dichloride and *n*-butylboron difluoride are colourless liquids which fume in air, being apparently hydrolysed quantitatively to hydrogen halide and the boronic acid, as was indicated by acidimetric estimations for halogen and boron.

The general similarity [2] of boronates and borates is further demonstrated by the present experiments. Similarities between the halogen derivatives of these esters are also observed. Thus hydrolysis of borates normally involves boron–oxygen fission.[5,6] Alcoholysis of borates causes alkoxy-exchange. Hydrolysis and alcoholysis of dichloroboronites, $Cl_2B{\cdot}OR$, and chloroboronates, $ClB(OR)_2$, result in evolution of hydrogen chloride and hydroxylation or alkoxylation respectively, of the boron atom.[7,8] These esters with pyridine give stable (usually 1 : 1) complexes,[3,9,10] and are thermally decomposed to alkyl chloride; this decomposition is catalysed by traces of Lewis acids such as ferric chloride.[4,7,8] *n*-Butyl difluoroboronite does not give a complex with pyridine, but disproportionation is observed, which also takes place when the compound is heated alone.[11] The nature of the product obtained on alcoholysis of boron trichloride depends on the branching in the alcohol. Those with powerfully electron-releasing groups (*e.g.*, *tert.*-butyl or 1-phenylethyl) give largely the alkyl chloride, whereas others afford hydrogen chloride and alkoxylation of the boron atom.[5,12] When pyridine is used, only alkoxylation is observed,[5,9] but the reaction does not proceed through a pyridine–boron trichloride complex [9] although the use of such a complex for the preparation of borates is general.[13] It thus appears that considerable resemblances in properties exist between (*a*) boronates and borates, (*b*) alkyl alkyl(or aryl)halogenoboronites, alkyl dihalogenoboronites, and dialkyl chloroboronates, and (*c*) alkyl(or aryl)boron dihalides and boron trihalides.

EXPERIMENTAL

General Procedures.—Boronic esters were prepared by the methods described previously.[1] Pyridine was estimated by steam-distillation from sodium hydroxide solution and titration of the distillate with sulphuric acid (bromophenol-blue). Other analytical procedures and the preparations of *n*-butyl *n*-butylhalogenoboronites, *n*-butyl phenylhalogenoboronites, *n*-butylboron difluoride, and phenylboron dichloride were as described elsewhere.[2] Rotatory powers are recorded for $l = 10$ cm.

Hydrolysis of Boronic Esters.—(a) *Dineopentyl phenylboronate. neo*Pentyl alcohol [4·1 g., 77% based on (1)], b. p. 111°, m. p. 58°, was steam-distilled from a mixture of the ester (8·0 g.) and an aqueous solution of sodium hydroxide, the steam-distillate being extracted with ether, and the extract dried ($MgSO_4$) and fractionally distilled.

(b) *Di-(+)-2-methylheptyl phenylboronate.* When the ester (1·08 g.) was shaken with water (10 c.c.) and *n*-pentane (10 c.c.) for 1 hr., only slight hydrolysis took place, but after the ester (1·31 g.; α_D^{20} +15·08°) had been heated under reflux with 20% aqueous potassium hydroxide (10 c.c.) for 1 hr., extraction with *n*-pentane afforded (+)-octan-2-ol [0·74 g., 98% based on (1)], b. p. 80°/13 mm., n_D^{20} 1·4259, α_D^{20} +7·58°.

Alcoholysis of Diethyl Phenylboronate.—The ester (1 mol., 0·02—0·05 molar scale) was heated with the appropriate alcohol (2·1 mols.). The lower fractions of ethanol and any unchanged alcohol were removed at 1 atm. and subsequent fractional distillation at reduced pressure afforded the new *boronate*. The results are shown in Table 1.

In the experiment with octan-2-ol, the alcohol had α_D^{20} +7·58° and the ester α_D^{20} +15·08°.

Interaction of Pyridine and Boronic Esters.—That pyridine and neither di-*n*-butyl *n*-butylboronate nor di-*n*-butyl phenylboronate formed a complex at 20° was demonstrated by adding

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[5] Scattergood, Miller, and Gammon, *J. Amer. Chem. Soc.*, 1945, **67**, 2150.
[6] Gerrard and Lappert, *J.*, 1951, 1020.
[7] *Idem, J.*, 1955, 3084.
[8] Lappert, *J.*, 1956, in the press.
[9] *Idem, J.*, 1953, 667.
[10] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.
[11] Lappert, *J.*, 1955, 784.
[12] Gerrard and Lappert, *J.*, 1951, 2545.
[13] *Idem, Chem. and Ind.*, 1952, 53.

pyridine (0·025 mole) to the ester (0·025 mole) at −70° to −40°. All the pyridine was withdrawn at 20°/0·2 mm. That pyridine and tri-(2 : 2 : 2-trichloroethyl) borate formed no complex was demonstrated in like manner. The *borate* (Found: Cl, 69·7; B, 2·3. $C_6H_6O_3Cl_9B$ requires Cl, 70·0; B, 2·4%), m. p. 97—98°, b. p. 112°/0·05 mm., was obtained in 64% yield from 2 : 2 : 2-trichloroethanol (23 g., 3 mols.) and boron trichloride (6·0 g., 1 mol.).

TABLE 1.

Alcohol	Yield (%) of ester [based on (2)]	B. p./mm.	n_D^{20}	Found : B (%)	Calc. : B (%)
Bu^nOH	83	96°/0·08	1·4748	4·7	4·6
Bu^iOH	85	75°/0·005	1·4719	4·7	4·6
Bu^sOH	87	71°/0·05	1·4675	4·75	4·6
Octan-2-ol	82	142—148°/0·1	1·4668	3·2	3·1

Pyridine (5·17 g., 3 mols.) was added to molten di-(2 : 2 : 2-trichloroethyl) phenylboronate (8·37 g., 1 mol.) at 60°. On cooling to 20°, a viscous liquid was obtained, which crystallised in 3 days. Unchanged pyridine was removed at 20°/0·2 mm. and after 8 hr. no further loss in weight occurred. The residue (9·93 g., 99%) was the 1 : 1 *compound* between pyridine and the boronate, m. p. 111—116° (Found: Cl, 45·3; C_5H_5N, 16·7. $C_{15}H_{14}O_2NCl_6B$ requires Cl, 45·9; C_5H_5N, 17·1%). The recovered pyridine had b. p. 115°, n_D^{20} 1·5073.

Hydrolysis of n-*Butyl* n-*Butylchloroboronite*.—To the ester (8·5 g., 1 mol.) at 0°, water (10·90 g., 1 mol.) was added during 1 hr. at 0°. A vigorous reaction occurred with evolution of hydrogen chloride and formation of a white precipitate. The mixture was shaken (2 hr.) whilst dry nitrogen was bubbled through it. Hydrogen chloride (1·8 g., 100%) was evolved and was absorbed in potassium hydroxide. On distillation a forerun (0·75 g.) of aqueous *n*-butanol, b. p. 35—40°/11 mm., was followed by di-*n*-butyl *n*-butylboronate (5·0 g., 100%), b. p. 109—111°/11 mm., which on redistillation had b. p. 103°/8 mm., n_D^7 1·4205, d_4^{20} 0·8308 (Found: B, 4·9. Calc. for $C_{12}H_{27}O_2B$: B, 5·1%). A higher-boiling fraction (0·70 g.) b. p. 115—119°/11 mm., slowly deposited a white solid (identified, after crystallisation from water, as boric acid). Yields are based on scheme (3).

n-*Butyl-alcoholysis of* n-*Butyl* n-*Butylchloroboronite*.—*n*-Butanol (1·26 g., 1 mol.) was added with shaking to the ester (3·00 g., 1 mol.) at 20°. Hydrogen chloride (0·60 g., 100%) was absorbed in potassium hydroxide. Distillation afforded di-*n*-butyl *n*-butylboronate (3·2 g., 88%), b. p. 112—115°/17 mm. (Found: B, 4·9%). Yields are based on scheme (4).

Interaction of Pyridine and n-*Butyl Phenylchloroboronite*.—The ester (6·75 g., 1 mol.) was added dropwise to pyridine (8·15 g., 3 mols.) at −10°. A white solid was formed and became molten at 0°. This was repeatedly extracted with *n*-pentane and then diethyl ether. A deliquescent solid (4·1 g.) (Found: Cl, 9·4; C_5H_5N, 37·2; B, 3·3%) remained. The pentane extract afforded pyridine (2·40 g., 0·9 mols.), b. p. 112°, n_D^{20} 1·5031 (Found: C_5H_5N, 97·8%), and an undistillable residue (0·5 g.). The ether extract, after removal of volatile matter (at 15°/0·3 mm. for 8 hr.), afforded the 1 : 2 *compound* between *n*-butyl phenylchloroboronite and pyridine (6·0 g., 49%) (Found: Cl, 10·05; C_5H_5N, 44·7. $C_{20}H_{24}ON_2ClB$ requires Cl, 10·0; C_5H_5N, 44·6%), which slowly (several days) lost pyridine at 15°/0·02 mm.

Interaction of n-*Butyl* n-*Butylchloroboronite and Pyridine*.—To the boronite (5·10 g., 2 mols.) at −70° was added pyridine (1·14 g., 1 mol.). The resulting oil solidified when kept at −70° for 7 days. This was thoroughly washed with *n*-pentane and filtered. The white, crystalline 1 : 1-*complex* between pyridine and *n*-butylboron dichloride (3·00 g., 96%), m. p. 77—81° (Found: Cl, 31·9; C_5H_5N, 38·3. $C_9H_{14}NCl_2B$ requires Cl, 33·2; C_5H_5N, 37·8%), was thus obtained. The pentane filtrate afforded di-*n*-butyl *n*-butylboronate (2·85 g., 93%), b. p. 104°/11 mm., n_D^{20} 1·4102 (Found: B, 4·6%). The yields are based on scheme (5).

Thermal Stability of n-*Butyl Phenylchloroboronite*.—To the ester (2·56 g.), anhydrous ferric chloride (0·0187 g.) was added at 20°. Within 10 min., the mixture set solid and became hot. After 1 hr. at 20°, volatile matter was removed at 10 mm. A condensate of *n*-butyl chloride (1·14 g., 95%), b. p. 76—79°/760 mm., n_D^{20} 1·4027, was collected and a white solid (1·48 g. Calc. for Ph·BO, 1·28 g.) remained. Yields are based on scheme (6).

The stability of the ester in the absence of a catalyst was determined by heating weighed samples in sealed tubes and analysing acidimetrically the mixture after arbitrary time intervals by hydrolysis with cold water (the chloroboronite, unlike *n*-butyl chloride, has chlorine which is readily hydrolysed by cold water). Results are shown in Table 2.

Thermal Stability of n-*Butyl* n-*Butylchloroboronite.*—When ferric chloride (0·0535 g.) was added to the ester (2·94 g.) at 20° an immediate heat of reaction was observed. After 10 min. at 20° volatile matter was removed at 10 mm., and *n*-butyl chloride (1·54 g., 100%), b. p. 77—79°/760 mm., n_D^{20} 1·4023, was collected at −80°. Ferric chloride was removed from the residue (1·52 g.) by filtration and washing with ether. The filtrate afforded *n*-butylboron oxide (1·17 g., 84%), b. p. 130°/13 mm., n_D^{20} 1·4208 (Found: B, 12·8. Calc. for C_4H_9OB: B, 12·9%). Yields are based on scheme (6).

TABLE 2.

Ester	Temp.	Time (hr.)	Decompn. (%)	Ester	Temp.	Time (hr.)	Decompn. (%)
Ph·BCl·OBu^n	100°	3	0	Bu^n·BCl·OBu^n	100°	1	0
,,	200	1	0	,,	200	1	4·5
,,	200	2½	4	,,	200	2½	23
,,	200	5	10	,,	200	5	43
,,	200	34	75	,,	200	24	92

The stability of the ester in the absence of a catalyst was determined by the method described above. Results are shown in Table 2.

Catalytic Decomposition of 2-*Methylheptyl Phenylchloroboronite.*—To the chloroboronite (1·84 g.; α_D^{20} +30·0°), ferric chloride (0·05 g.) was added at 20°. The mixture was set aside for 12 hr., whereupon it set solid. Distillation afforded 2-chloro-octane (0·93 g., 94%), b. p. 60°/12 mm., α_D^{20} −10·5°, n_D^{20} 1·4272, and phenylboron oxide (0·84 g., 95%) was obtained from the solid residue. Yields are based on scheme (6).

Interaction of Pyridine and n-*Butyl Phenylfluoroboronite.*—Pyridine (1·45 g., 1·3 mols.) in *n*-pentane (20 c.c.) was added dropwise to the ester (2·60 g., 1 mol.) in *n*-pentane (10 c.c.) at 0°. The white precipitate which was instantly formed was filtered off and identified as the 1 : 1 *compound* between phenylboron difluoride and pyridine [1·50 g., 100% based on scheme (6)], m. p. 100—102° (Found: B, 5·7; C_5H_5N, 39·9. $C_{11}H_{10}NF_2B$ requires B, 5·3; C_5H_5N, 38·6%).

Interaction of Pyridine and n-*Butyl* n-*Butylfluoroboronite.*—To the boronite (4·35 g., 2 mols.) at −80° was added pyridine (1·08 g., 1 mol.). After 1 hr. at 20° there was a separation into two layers. The upper was di-*n*-butyl *n*-butylboronate (2·90 g., 99%), b. p. 90°/4 mm., n_D^{20} 1·4169 (Found: B, 5·0%), whilst the lower on distillation afforded the 1 : 1 *compound* between *n*-butylboron difluoride and pyridine (1·81 g., 72%), b. p. 74—76°/0·01 mm., n_D^{20} 1·4655 (Found: C_5H_5N, 42·1. $C_9H_{14}NBF_2$ requires C_5H_5N, 42·6%). Yields are based on a scheme analogous to (5).

The same products were obtained when the order of addition of the reagents was reversed.

Thermal Stability of n-*Butyl* n-*Butylfluoroboronite.*—When the freshly prepared ester (8·74 g.) was heated (5 hr.) under reflux at 80°/20 mm., *n*-butylboron difluoride (2·84 g., 98%), b. p. 34°/760 mm., n_D^{20} 1·3272 (Found: F, 35·3; B, 10·1. Calc. for $C_4H_9F_2B$: F, 35·8; B, 10·2%), was collected at −70°. The residue gave a forerun (0·85 g.), b. p. 68—110°/15 mm., n_D^{20} 1·3985, and di-*n*-butyl *n*-butylboronate (4·35 g., 74%), b. p. 110—112°/13 mm., n_D^{20} 1·4164 (Found: B, 5·0%). Yields are based on scheme (9).

Alcoholysis of Phenylboron Dichloride.—(a) *With* n-*butanol* (1 : 1). To the dichloride (4·45 g., 1 mol.) at 0° was added *n*-butanol (2·10 g., 1 mol.). The mixture was allowed to warm to 20° whilst through it a current of nitrogen was passed. Hydrogen chloride (0·98 g., 99%) was evolved and absorbed in potassium hydroxide. Distillation afforded *n*-butyl phenylchloroboronite (5·26 g., 96%) and a residue (0·20 g.). Yields are based on scheme (10).

(b) *With octan-2-ol* (1 : 1). The alcohol (1·66 g., 1 mol.; α_D^{20} + 5·62°) was added to the dichloride (2·03 g., 1 mol.) at −80°. Distillation afforded (+)-2-*methylheptyl phenylchloroboronite* (2·27 g., 70%), b. p. 94°/0·1 mm., α_D^{20} +29·5°, n_D^{20} 1·4865, d_4^{20} 0·965 (Found: Cl, 13·9; B, 4·4. $C_{14}H_{22}OClB$ requires Cl, 14·0; B, 4·3%).

(c) *With* tert.-*butanol* (1 : 2). The dichloride (3·60 g., 1 mol.) was added slowly to the alcohol (3·36 g., 2 mols.) at −80°, and the mixture was kept at −80° for ½ hr., whereupon a solid was formed; at 20°/6 mm., a condensate of *tert.*-butyl chloride [1·36 g., 33% based on scheme (13)], b. p. 50—51°/760 mm., n_D^{20} 1·3873, was collected and there was a pasty white residue (4·24 g.). This was washed with *n*-pentane and filtered off. The filtrate afforded di-*tert.*-butyl phenylboronate [2·62 g., 51% based on schemes (10) and (11)], b. p. 58—65°/0·5 mm., n_D^{20} 1·4650 (Found: B, 5·3%), and a solid remained.

(d) *With other alcohols* (1 : 2). The chosen alcohol (2 mols., usually on 0·05 molar scale) was added slowly to phenylboron dichloride (1 mol.) at −80°. The loss in weight at 20 mm. corresponded to hydrogen chloride. Results are shown in Table 3.

TABLE 3. [Yields based on schemes (10) and (11)].

R in ROH	Yield (%) of HCl	Yield (%)	B. p./mm.	n_D^{20}	Found : B (%)	Calc. : B (%)
Bu^n	100	94	96°/0·02	1·4740	4·6	4·6
Bu^i	98	94	70°/0·02	1·4710	4·7	4·6
Bu^s	99	90	64°/0·02	1·4671	4·7	4·6
2-Methylheptyl (α_D^{20} + 5·62°)	98 (α_D^{20} +11·28°)	89	128°/0·2	1·4665	3·25	3·1

(e) *With* n-*butanol in presence of pyridine.* To the alcohol (5·90 g., 2 mols.) and pyridine (6·20 g., 2 mols.) in chloroform (25 c.c.) at −70° was added dropwise, with shaking, phenylboron dichloride (6·20 g., 1 mol.) in chloroform (20 c.c.). The mixture was set aside for 12 hr. at 20°, whereafter the volatile matter was withdrawn at 15°/10 mm. *n*-Pentane was added and pyridinium chloride (8·00 g., 90%) (Found: Cl, 30·3; C_5H_5N, 66·6. Calc. for C_5H_6NCl: Cl, 30·7; C_5H_5N, 68·5%) was filtered off. The filtrate afforded di-*n*-butyl *n*-phenylboronate (9·00 g., 99%) which on redistillation had b. p. 72°/0·1 mm., n_D^{20} 1·4747, d_4^{20} 0·9245 (Found: B, 4·6%).

Interaction of the 1 : 1 *Complex between Phenylboron Dichloride* (1 *mol.*) *and Pyridine* (1 *mol.*) *with* n-*Butanol* (2 *mols.*).—(a) *At room temperature.* The complex (1·76 g., 1 mol.) was allowed to react with pyridine (0·583 g., 1 mol.) and *n*-butanol (1·094 g., 2 mols.) in chloroform (10 c.c.) at 20° for 12 hr., whereafter the solvent was removed at 20°/20 mm., *n*-pentane added and the mixture filtered. The filtrate, after evaporation at 20°/20 mm., left no residue.

(b) *In boiling chloroform.* The complex (1·92 g., 1 mol.), the alcohol (1·28 g., 2 mols.), and pyridine (0·635 g., 1 mol.) were heated under reflux in chloroform (15 c.c.) for 16 hr. The solvent was removed in a vacuum (20 mm.); *n*-pentane was added to separate pyridinium chloride (1·853 g., 98%) (Found: Cl, 30·4; C_5H_5N, 68·0%) which was precipitated, and di-*n*-butyl phenylboronate (1·54 g., 83%), b. p. 92°/0·3 mm., n_D^{20} 1·4750 (Found: B, 4·6%). Yields are based on scheme (13).

Interaction of n-*Butylboron Difluoride and Pyridine.*—Pyridine (2·88 g., 1 mol.) in *n*-pentane (10 c.c.) was added to the difluoride (3·88 g., 1 mol.) at −80°. The reaction was very vigorous and a white precipitate was formed instantly. After 1 hr. at 20°, the precipitate dissolved and two layers had separated. The pentane was removed at 0·1 mm. and the residue, a viscous, coloured oil, was the 1 : 1 *complex* (6·70 g., 99%), n_D^{20} 1·4651 (Found: C_5H_5N, 44·0%). This was distilled, then having b. p. 78°/0·01 mm., n_D^{20} 1·4665, d_4^{20} 1·075 (Found: C, 57·7; H, 7·7; C_5H_5N, 42·3. $C_9H_{14}NF_2B$ requires C, 58·4; H, 7·6; C_5H_5N, 42·6%).

In a separate experiment, the addition of the difluoride (1·26 g., 1 mol.) in *n*-pentane (10 c.c.) to pyridine (1·88 g., 2 mols.) at −80°, also afforded the 1 : 1 complex (1·82 g., 83%), b. p. 76—77°/0·01 mm., n_D^{20} 1·4670 (Found: C_5H_5N, 42·8%).

Interaction of Phenylboron Dichloride and Pyridine.—Pyridine (0·82 g., 1 mol.) in *n*-pentane (10 c.c.) was added to the dichloride (1·63 g., 1 mol.) in the same solvent (20 c.c.) at −80°. The white solid, which was instantly formed, was filtered off, washed with *n*-pentane, and freed from solvent at 15 mm. The 1 : 1 *complex* (2·45 g., 100%), m. p. 64° (opaque) (Found: Cl, 30·0; C_5H_5N, 34·1; B, 4·5. $C_{11}H_{10}NCl_2B$ requires Cl, 29·8; C_5H_5N, 33·2; B, 4·5%), was thus obtained

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[*Received, November* 29*th*, 1955.]