762. *The Properties of the Anhydride and Esters of Diphenylboronous Acid.*

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Diphenylboronites, $Ph_2B{\cdot}OR$, are readily hydrolysed, generally by B–O fission, but C–O fission (R = PhMeCH) in formic acid has been noted. Only esters having highly electron-releasing alkyl groups are dealkylated by hydrogen chloride, although hydrogen bromide and the (+)-1-methylheptyl ester did react (S_N2) provided that the concentration of hydrogen bromide was high. *n*-Butyl diphenylboronite gave diphenylboron chloride with boron trichloride, *n*-butyl dichloroboronite, or di-*n*-butyl chloroboronate. Diphenylboron bromide was obtained from an ester and either boron tribromide or phosphorus pentabromide. Diphenylboronous anhydride, $(Ph_2B)_2O$, yielded diphenylboronous acid on hydrolysis, and with boron trihalides (Cl, Br) or phosphorus pentahalides (Cl, Br) afforded the appropriate diphenylboron halide. Diphenylboronous acid $Ph_2B{\cdot}OH$, its anhydride, and several of its esters were examined by infrared spectroscopy. The results are discussed.

THE present paper reports continued investigation of diphenylboronous acid, $Ph_2B{\cdot}OH$, and its derivatives, $Ph_2B{\cdot}Y$ (where Y is a univalent atom or group). We have earlier described the preparation and characteristics of diphenylboron chloride,[1] $Ph_2B{\cdot}Cl$, and diphenylboronous esters,[2] $Ph_2B{\cdot}OR$. We now report reactions of diphenylboronous anhydride, $(Ph_2B)_2O$ [hydrolysis, reaction with boron tribromide and phosphorus pentahalides (Cl, Br)], and of diphenylboronous esters [hydrolysis and reactions with hydrogen, boron, and phosphorus halides (Cl, Br)]. Diphenylboronous anhydride is well known but, apart from its use in analysis,[3] only its reactions with alcohols and phenols (to give esters and water) [2] and with boron trichloride (to give diphenylboron chloride) [1] have been previously established. Reactions of diphenylboronous esters hitherto studied have been with phosphorus pentachloride to give diphenylboron chloride [analogous to reaction (8) [4]] and with alcohols and phenol (to give esters); [2] in addition some observations on the manner of their hydrolysis have been made.[5] In order to obtain information about the

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[1] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.
[2] Abel, Gerrard, and Lappert, *J.*, 1957, 112.
[3] Lappert, *Chem. Rev.*, 1956, **56**, 959.
[4] Mikhailov and Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1956, 375.
[5] Mikhailov and Vaver, *ibid.*, 1956, 508.

steric course of reactions at the 1-carbon atom of the alkyl chain, certain of the reactions of diphenylboronous esters have now been carried out with optically active compounds. The (+)-1-methylheptyl ester [2] was chosen as typical of those generally responsive to S_N2 replacement, and the (+)-1-phenylethyl ester as representative of those having a high degree of electron-release at the 1-carbon atom and hence responsive to S_N1 replacement.

(+)-1-Phenylethyl diphenylboronite was obtained from (—)-1-phenylethanol by reaction (1) (see ref. 2 for discussion of similar reactions):

$$(Ph_2B)_2O + 2ROH \longrightarrow 2Ph_2B{\cdot}OR + H_2O \quad . . . . (1)$$

Diphenylboronous esters were hydrolysed readily by cold water, sodium hydroxide, or aqueous formic acid:

$$Ph_2B{\cdot}OR + H_2O \longrightarrow Ph_2B{\cdot}OH + ROH \quad . . . . . . (2)$$

When three of the butyl (*n*-, *sec.*-, and *tert.*-) diphenylboronites were severally treated with hydrogen chloride, only the *tert.*-butyl ester reacted [reaction (3)]; (+)-1-phenylethyl diphenylboronite gave much racemised 1-chloro-1-phenylethane. Hydrogen bromide was without effect on (—)-1-methylheptyl diphenylboronite when continuously passed through the ester for 4 hr.; however, when the reactants were mixed in the liquid state (—80°), subsequent reaction (3) at 20° under pressure did occur, although benzene and phenylboronic anhydride were isolated instead of diphenylboronous acid [attributed to reaction (4)].

$$Ph_2B{\cdot}OR + HX \longrightarrow RX + Ph_2B{\cdot}OH \quad . . . . (3)$$

$$Ph_2B{\cdot}OH \longrightarrow PhH + Ph{\cdot}BO \quad . . . . (4)$$

Boron trichloride reacted with *n*-butyl diphenylboronite according to reaction (5). In order to compare B–Cl reactivity in diphenylboron chloride and in boron trichloride and its mono- and di-alkoxy-derivatives, reactions (6) and (7) were also carried out. The product of reaction (7) was an equilibrium mixture, for only about a 50% yield of diphenylboron chloride was isolated as its water-insoluble pyridine complex.

$$Ph_2B{\cdot}OR + BCl_3 \longrightarrow Ph_2B{\cdot}Cl + RO{\cdot}BCl_2 \quad . . . . (5)$$

$$Ph_2B{\cdot}OR + RO{\cdot}BCl_2 \longrightarrow Ph_2B{\cdot}Cl + (RO)_2B{\cdot}Cl \quad . . . . . . (6)$$

$$Ph_2B{\cdot}OR + (RO)_2B{\cdot}Cl \longrightarrow Ph_2B{\cdot}Cl + (RO)_3B \quad . . . . (7)$$

A reaction analogous to (5) to obtain diphenylboron bromide was demonstrated with *n*-octyl diphenylboronite and boron tribromide; to facilitate separation of products, a trace of ferric chloride was added to ensure that the *n*-octyl dibromoboronite was decomposed ($3RO{\cdot}BBr_2 \longrightarrow 3RBr + BBr_3 + B_2O_3$, by analogy with dichloroboronites [6]).

Phosphorus pentabromide also reacted with diphenylboronites to give diphenylboron bromide [reaction (8)]; the low yield (20%) is attributable to the necessarily high temperature, dissociation of the pentabromide being appreciable ($PBr_5 \longrightarrow PBr_3 + Br_2$).

$$Ph_2B{\cdot}OR + PBr_5 \longrightarrow Ph_2B{\cdot}Br + RBr + POBr_3 \quad . . . . . . (8)$$

Diphenylboronous anhydride afforded the acid on hydrolysis [reaction (9)]. With the boron trihalides (trichloride [1]) [reaction (10)] or analogously phosphorus pentahalides, the diphenylboron halides (Cl, Br) were obtained. With the boron halides this appeared to be a rapid reaction at low temperatures, whereas with phosphorus halides even at high temperatures the yield was again low.

$$(Ph_2B)_2O + H_2O \longrightarrow 2Ph_2B{\cdot}OH \quad . . . . (9)$$

$$(Ph_2B)_2O + BX_3 \longrightarrow 2Ph_2B{\cdot}X + BOX \quad . . . . (10)$$

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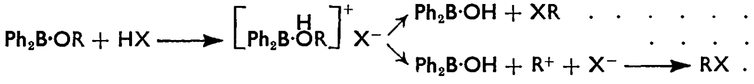
[6] Gerrard and Lappert, *J.*, 1955, 3084.

Discussion.—Esterification of diphenylboronous anhydride with (—)-1-phenylethanol afforded the ester with complete retention of configuration, so reaction (1), with an alcohol having a highly electron-releasing alkyl group, involves B–O and not C–O fission.

Hydrolysis (2) of diphenylboronites also generally involves B–O fission: for there was complete retention of configuration on alkaline hydrolysis of the optically active esters of 1-methylheptanol, 1-phenylethanol, and *neo*pentanol. With (+)-1-phenylethyl diphenylboronite there was some slight loss of activity when the reaction was carried out in aqueous formic acid, conditions which are conducive to pre-ionisation.

Reaction (2) is an equilibrium (the reverse reaction has been demonstrated [2]), for we obtained identical infrared spectra from equimolar mixtures of ester and water, and acid and alcohol. The spectra also show that the equilibrium is virtually completely in favour of acid and alcohol; thus all of the alcohol bands can be identified in the spectrum of an equimolar mixture between ester and water. Further, no bands attributable to water occur in the 3 μ and the 6 μ region. Bands due to diphenylboronous acid can also be readily identified in the mixture, and in particular the diphenylboronous acid band at 880 cm.$^{-1}$ occurs clearly in a region where both alcohol and ester are transparent. Our conclusions differ from those of Mikhailov and Vaver,[5] who considered that alkyl diphenylboronites are not hydrolysed in water, and in alkali only on warming, a result which they interpreted as evidence for the formation of a stable complex between esters and water, $[Ph_2B{\cdot}OH(OR)]^-H^+$. Infrared spectra of a water–ester mixture are not consistent with the formation of such a complex and acid and alcohol may be separated merely by application of a vacuum, the most volatile component, the alcohol–water azeotrope, being removed.

The reactions of diphenylboronites with the hydrogen halides indicate both S_N1 and S_N2 mechanism, depending on the nature of the alkyl group:



$$\mathrm{Ph_2B{\cdot}OR + HX \longrightarrow \left[Ph_2B{\cdot}\overset{H}{O}R\right]^+ X^-} \begin{array}{ll} \nearrow \mathrm{Ph_2B{\cdot}OH + XR} & (S_N2) \\ & (11) \\ \searrow \mathrm{Ph_2B{\cdot}OH + R^+ + X^- \longrightarrow RX} & (S_N1) \end{array}$$

The evidence for the S_N2 mechanism for those esters having alkyl groups responsive to " in-line " replacements rests on: (1) the effect of increasing hydrogen bromide concentration in the 1-methylheptyl case; (2) the greater reactivity of hydrogen bromide than of hydrogen chloride; and (3) the observed high degree of Walden inversion in the (+)-1-methylheptyl–hydrogen bromide reaction. The evidence of the S_N1 mechanism rests on: (1) the high degree of reactivity with hydrogen chloride only with those esters having powerfully electron-releasing alkyl groups; and (2) the preponderant racemisation observed in the (+)-1-phenylethyl–hydrogen chloride system.

Reactions (5)—(7) indicate that the ease of B–Cl fission in diphenylboron chloride is of the same order as in chloroboronates, but lower than in dichloroboronites and boron trichloride.

To the good methods hitherto available for the preparation of diphenylboron chloride (*i.e.*, ester–PCl_5,[4] anhydride–BCl_3[1]) are now added reactions (5) and (10). All these are sound provided the starting materials are available; the boron trichloride reactions require far less vigorous reaction conditions than those with phosphorus pentachloride. Analogous methods (5, 8, 9, and 10) are now available for the preparation of diphenylboron bromide. This compound has only been reported once before,[7] being prepared in poor yield from boron tribromide and diphenylmercury.

The infrared spectra of diphenylboronous acid and anhydride and the alkyl diphenylboronites have been observed in the range 650—5000 cm.$^{-1}$. In all diphenylboron compounds we have observed a splitting of the out-of-plane C–H vibration at levels of the phenyl group by about 20 cm.$^{-1}$. This suggests a coupling of the modes, and may be

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[7] Michaelis and Richter, *Annalen*, 1901, **315**, 26.

through the boron atom, or it may be caused by the close approach of the hydrogen atoms *ortho* to the boron.

The B–O stretching modes occur in diphenylboronous acid and its esters in the region 1325 ± 2 cm.$^{-1}$; this is similar to the value obtained in phenylboronic compounds by Dandegaonker, Gerrard, and Lappert.[8] In the case of diphenylboronous anhydride, however, two bands attributable to B–O stretching modes occur, at 1262 cm.$^{-1}$ and 1378 cm.$^{-1}$. These are undoubtedly the expected in-phase and out-of-phase modes of the B–O–B grouping.

EXPERIMENTAL

Preparations and Techniques.—Hydrogen chloride was prepared by the action of concentrated sulphuric acid on dry ammonium chloride, and hydrogen bromide was prepared by Gerrard's method[9] and condensed at −80°. Both gases were dried by passage through phosphoric oxide. Diphenylboronous anhydride and its esters were prepared and analysed as described previously.[2] Amines were estimated by steam-distillation in the presence of sodium hydroxide, and subsequent titration against sulphuric acid. Infrared spectra were observed on a Grubb-Parsons double-beam spectrometer. *n*-Butyl dichloroboronite and di-*n*-butyl chloroboronate were prepared by known methods.[6, 10] Rotatory powers are recorded for $l = 10$ cm.

1-*Phenylethyl Diphenylboronite. Reaction* (1).—The *ester* (93%), b. p. 140°/0·1 mm., d_4^{20} 1·0489, n_D^{20} 1·5805, α_D^{20} +2·81° (Found: C, 83·4; H, 6·7; B, 3·84. $C_{20}H_{19}OB$ requires C, 83·9; H, 6·6; B, 3·78%), was prepared from diphenylboronous anhydride and excess of 1-phenylethanol (α_D^{20} −11·78°) by azeotropic distillation.[2]

Alkaline Hydrolysis of Alkyl Diphenylboronites. Reaction (2).—The ester was shaken for 2 hr. with aqueous potassium hydroxide (20%). After extraction with *n*-pentane and drying ($MgSO_4$, 3 days), careful fractionation yielded *n*-pentane, and the alcohol (Table 1).

TABLE 1.

R in $Ph_2B{\cdot}OR$	ROH recovered (%)	B. p./mm.	n_D^{20}	α_D^{20}
*neo*Pentyl	77	110°/760	(M. p. 48°)	—
1-Methylheptyl, α_D^{20} −4·20° (from ROH, α_D^{20} +7·28°)	93	78°/10	1·4263	+ 7·26°
1-Phenylethyl, α_D^{20} +2·81° (from ROH, α_D^{20} −11·78°)	81	100°/20	1·5271	−11·56

Acid Hydrolysis of Alkyl Diphenylboronites. Reaction (2).—The ester was shaken for 48 hr. with 40% formic acid, then the mixture rendered alkaline and steam-distilled. The distillate was extracted with ether, and the extract dried ($MgSO_4$, 3 days). Fractionation yielded ether and the recovered alcohol (Table 2).

TABLE 2.

R in $Ph_2B{\cdot}OR$	ROH recovered (%)	B. p./mm.	n_D^{20}	α_D^{20}
1-Methylheptyl, α_D^{20} −3·91° (from ROH, α_D^{20} +6·20°)	83	78°/10	1·4266	+ 6·16°
1-Phenylethyl, α_D^{20} +1·73° (from ROH, α_D^{20} −7·72°)...	58	65°/0·2	1·5251	−6·66 *

* Found: C, 78·2; H, 8·4. Calc. for $C_8H_{10}O$: C, 78·7; H, 8·2%.

Neutral Hydrolysis of sec.-*Butyl Diphenylboronite. Reaction* (2).—The ester (11·47 g.) was shaken for 5 hr. with water (50 c.c.), volatile matter being continuously removed at 20 mm. and trapped at −80°. The trapped azeotrope was extracted with ether, and the extract dried ($MgSO_4$, 30 hr.). Fractionation yielded ether and *sec.*-butanol (2·37 g., 65%), b. p. 97—100°, n_D^{20} 1·3957. Ether-extraction of the residue and removal of ether at 10 mm. produced diphenyl-

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[8] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.

[9] Gerrard, *Research*, 1954, **7**, s20.

[10] Lappert, *J.*, 1956, 1768.

boronous acid (7·01 g., 88%), n_D^{20} 1·5973 (Found: B, 5·8. Calc. for $C_{12}H_{11}OB$: B, 5·9%), as a brown oil.

Interaction of Hydrogen Chloride and Alkyl Diphenylboronites. Reaction (3).—(a) n- *and* sec.-*Butyl.* There was no observed reaction after 10 hr. at 20°. After removal of dissolved gas at 10 mm. no change in weight was observed, and distillation afforded the esters in nearly quantitative yield.

(b) tert.-*Butyl.* The gas was bubbled through the ester (1·88 g.) at 20°, the reaction vessel being connected to a trap at −80°. Within 5 min. a white precipitate had formed. Bubbling was continued for 15 min., then volatile matter (0·64 g.) was condensed at −80°/20 mm. To the condensate was added lead carbonate (0·5 g.) and then anhydrous magnesium sulphate (0·5 g.). From the trap *tert.*-butyl chloride (0·58 g., 72%), n_D^{20} 1·3847 (Found: Cl, 38·1. Calc. for C_4H_9Cl: Cl, 38·4%), was recondensed at 10 mm. The residue in the reaction flask, after being rapidly washed by decantation with *n*-pentane (5 c.c.), was dried in a vacuum-desiccator, to give diphenylboronous anhydride (1·34 g., 98%), m. p. 112° (Found: B, 6·2. Calc. for $C_{24}H_{20}OB_2$: B, 6·3%).

(c) 1-*Phenylethyl.* The gas was bubbled into the ester (4·09 g.) (α_D^{20} +2·81°; from ROH, α_D^{20} −11·78°) in *n*-pentane (20 c.c.) at 0°. After 30 min. a turbidity developed, and later a thick white crystalline precipitate. Passage of gas was stopped after 3 hr., and after removal of unchanged hydrogen chloride at 30 mm. there was a weight increase of 0·61 g. (required for complete reaction, 0·52 g.). Distillation gave 1-chloro-1-phenylethane (1·83 g., 91%), b. p. 74°/10 mm., n_D^{20} 1·5321, α_D^{20} −1·56° (Found: Cl, 24·6. Calc. for C_8H_9Cl: Cl, 25·2%). The residue was diphenylboronous anhydride (2·37 g., 96%) (Found: B, 6·5%). Benzene (0·18 g.), n_D^{20} 1·4983, was condensed at −80° during the distillation.

Interaction of Hydrogen Bromide and 1-*Methylheptyl Diphenylboronite. Reaction* (3).—(a) *Gaseous hydrogen bromide.* The dry gas was bubled into the ester (4·73 g.) for 4 hr. at 20°; no observable change took place, but there was an increase in weight (0·35 g.) due to dissolved gas. This gas was removed at 20°/20 mm., leaving unchanged ester (4·68 g.), purified by distillation (4·36 g., 92%), b. p. 143°/0·01 mm., n_D^{20} 1·5183 (Found: B, 3·6. Calc. for $C_{20}H_{27}OB$: B, 3·7%). A solid residue (0·23 g.) remained.

(b) *Liquid hydrogen bromide. Reactions* (3) *and* (4).—The ester (7·50 g., 1 mol.) (α_D^{20} −3·96°; from ROH, α_D^{20} +6·90°) and liquid hydrogen bromide (2·09 g., 1·01 mol.) were sealed in a heavy-walled glass tube at −80°, and then allowed to warm to room temperature. After 25 days the tube was cooled to −80° and the contents were distilled. (−)-2-Bromo-octane (4·22 g., 86%), b. p. 71°/15 mm., n_D^{20} 1·4485, α_D^{20} −24·70° (Found: Br, 41·4. Calc. for $C_8H_{17}Br$: Br, 41·4%), was obtained. The residue was phenylboronic anhydride (2·47 g., 93%) (Found: B, 10·5%). Trapped at −80° was benzene (1·81 g., 91%), b. p. 80°, n_D^{20} 1·498. After recrystallization from hot water and dehydration (120° for 10 hr.), the anhydride had m. p. 215°.

Interaction of n-*Butyl Diphenylboronite and Boron Trichloride. Reaction* (5).—The diphenylboronite (4·54 g., 1 mol.) was added to boron trichloride (2·23 g., 1 mol.) at −80°. After the mixture had attained room temperature, the volatile *n*-butyl dichloroboronite (2·75 g., 93%), n_D^{20} 1·4151 (Found: Cl, 45·4; B, 6·98. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·02%), was removed at 0·3 mm. and trapped at −80°. The residual liquid afforded diphenylboron chloride (3·04 g., 80%), b. p. 105°/0·7 mm., n_D^{20} 1·6091 (Found: Cl, 17·5; B, 5·37. Calc. for $C_{12}H_{10}ClB$: Cl, 17·7; B, 5·39%).

Interaction of n-*Butyl Diphenylboronite and* n-*Butyl Dichloroboronite. Reaction* (6).—The diphenylboronite (4·31 g., 1 mol.) was added to *n*-butyl dichloroboronite (2·80 g., 1 mol.) at −80°. After the mixture had attained room temperature, it was distilled to afford: (*a*) di-*n*-butyl chloroboronate (2·96 g., 85%), b. p. 41°/0·1 mm., n_D^{20} 1·4148 (Found: Cl, 18·8; B, 5·7. Calc. for $C_8H_{18}O_2ClB$: Cl, 18·5; B, 5·6%); (*b*) *n*-butyl borate (0·33 g.), b. p. 78—81°/0·1 mm., n_D^{20} 1·4129; and (*c*) diphenylboron chloride (3·28 g., 98%), b. p. 98°/0·1 mm., n_D^{20} 1·6043 (Found: Cl, 17·4; B, 5·5%). *n*-Butyl dichloroboronite (0·26 g.), n_D^{20} 1·4158 (Found: Cl, 45·5; B, 7·1%), was trapped at −80° during the distillation.

Interaction of n-*Butyl Diphenylboronite and Di*-n-*butyl Chloroboronate. Reactions* (7) *and* (8).—The diphenylboronite (3·36 g., 1 mol.) in ether (10 c.c.) was added to di-*n*-butyl chloroboronate (2·72 g., 1 mol.) in ether (10 c.c.). After 1 hr. pyridine (10 g.) in ether (20 c.c.) was added. A white precipitate was immediately formed. This was filtered off and washed with ether (10 c.c.). The precipitate (3·32 g.) was then washed with water (2 × 50 c.c.), and placed in a vacuum-desiccator over phosphoric oxide for 48 hr. The remaining precipitate (1·69 g., corresponding to a 43% yield of diphenylboron chloride) was the 1 : 1 *pyridine–diphenylboron chloride complex* (Found: C_5H_5N, 27·3; Cl, 12·3. $C_{12}H_{10}ClB,C_5H_5N$ requires C_5H_5N, 28·2; Cl, 12·8%).

Interaction of n-*Octyl Diphenylboronite and Boron Tribromide. Analogous to Reaction* (5).—The ester (8·25 g., 1 mol.) in *n*-pentane (20 c.c.) was added (10 min.) to boron tribromide (7·02 g., 1 mol.) in *n*-pentane (20 c.c.) at −60°. Ferric chloride (0·01 g.) was added at 20°, whereafter the mixture was set aside for 24 hr. Solvent was then removed at 10 mm., and boron tribromide (2·15 g., 91%) was trapped in potassium hydroxide solution. Distillation then yielded 1-bromo-octane (5·31 g., 96%), b. p. 44°/0·01 mm., n_D^{20} 1·4509 (Found: Br, 41·2. Calc. for $C_8H_{17}Br$: Br, 41·5%), and *diphenylboron bromide* (5·33 g., 79%), b. p. 110°/0·01 mm., n_D^{20} 1·631 (Found: Br, 32·0; B, 4·4. $C_{12}H_{10}BrB$ requires Br, 32·7; B, 4·5%). A residue (1·57 g.) contained boron, equivalent to boric oxide (0·71 g., 110%), presumably containing a little undistilled diphenylboron bromide.

Interaction of Phosphorus Pentabromide and sec.-*Butyl Diphenylboronite. Reaction* (8).—The pentabromide (18·93 g., 1 mol.) and the ester (10·49 g., 1 mol.) were heated together for 3 hr. at 90°. Distillation yielded a fraction (12·46 g.), b. p. 20—114°/0·05 mm., and diphenylboron bromide (2·02 g., 19%), b. p. 115°/0·05 mm., n_D^{20} 1·6325 Found: Br, 32·3; B, 4·3%). A residue (6·80 g.) remained, and a condensate (7·31 g.) was collected at −80° during distillation.

Hydrolysis of Diphenylboronous Anhydride. Reaction (9).—Water (0·77 g., 1 mol.) in ether (10 c.c.) was shaken with the anhydride (14·76 g., 1 mol.) for 1 hr., a clear yellow solution being formed. Removal of solvent at 20 mm. gave diphenylboronous acid (15·52 g., 100%), n_D^{20} 1·5930 (Found: B, 5·9%), as a viscous yellow oil.

Interaction of Diphenylboronous Anhydride and Boron Tribromide. Reaction (10).—The anhydride (10·7 g., 1 mol.) in methylene dichloride (50 c.c.) was added during 10 min. to boron tribromide (7·74 g., 1 mol.) in methylene dichloride (20 c.c.) at −60°. Solvent was removed at 20°/15 mm. The resulting mixture yielded diphenylboron bromide (10·9 g., 79%), b. p. 132°/0·4 mm., d_4^{20} 1·364, n_D^{20} 1·635 (Found: C, 57·7; H, 4·08; Br, 33·3; B, 4·42. $C_{12}H_{10}BBr$ requires C, 58·0; H, 4·0; Br, 32·7; B, 4·46%). A residue (4·60 g.) contained both boron and easily ionized bromine. This was undistilled diphenylboron bromide and boric oxide.

Interaction of Diphenylboronous Anhydride and Phosphorus Pentachloride. Reaction (13).—The pentachloride (4·53 g., 1 mol.) and the anhydride (7·53 g., 1 mol.) were heated together at 140° for 3 hr. Thereafter, distillation produced a forerun (0·80 g.), b. p. 20—97°/0·05 mm., and diphenylboron chloride (6·54 g., 75%), b. p. 97°/0·05 mm., n_D^{20} 1·6093 (Found: Cl, 18·0; B, 5·5%). Phosphorus oxychloride (3·07 g., 92%), n_D^{20} 1·467 (Found: Cl, 69·2. Calc. for $POCl_3$: Cl, 69·5%), was condensed as white crystals at −80° during the distillation. A residue (0·97 g.) remained.

Interaction of Diphenylboronous Anhydride and Phosphorus Pentabromide.—The pentabromide (9·57 g., 1·1 mol.) and the anhydride (7·01 g., 1 mol.) were heated together at 90° for 3 hr. Distillation yielded a low-boiling fraction (6·74 g.), b. p. 26—116°/0·05 mm., and diphenylboron bromide (4·00 g., 40%), b. p. 116°/0·05 mm., n_D^{20} 1·6346 (Found: Br, 32·8; B, 4·4%). A residue (3·00 g.) remained. This was extracted with ether (30 c.c.) and the extract washed with water (2 × 20 c.c.). Removal of solvent and then dehydration at 0·005 mm. yielded diphenylboronous anhydride (2·58 g.) (Found: B, 6·7%). A condensate (3·07 g.) was trapped at −80° during the distillation. The overall yield of diphenylboron bromide based on diphenylboronous anhydride used was 64%. This reaction was repeated in refluxing carbon tetrachloride, but diphenylboronous anhydride was recovered substantially unchanged.

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