

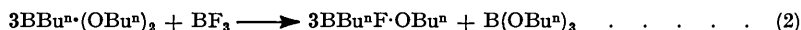
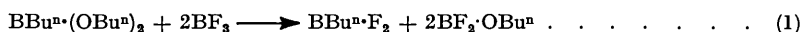
**176. Interaction of Boron and Hydrogen Halides with Esters of Boronic Acids.**

By P. B. BRINDLEY, W. GERRARD, and M. F. LAPPERT.

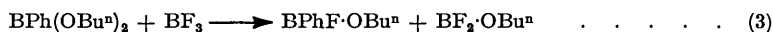
Boron trifluoride and trichloride, interacting in various proportions with di-*n*-butyl *n*-butylboronate (or di-*n*-butyl phenylboronate) afforded either *n*-butyl(or phenyl)boron dihalides, BRHal<sub>2</sub>, or the corresponding halogenoboronites, BRHal·OBu<sup>n</sup>, a novel class of organoboron compounds also obtained from the boronates and either *n*-butyl dihalogenoboronites or phenylboron dichloride. Hydrogen chloride rapidly dealkylated di-*tert*-butyl phenylboronate, but not at all the *n*-, *iso*-, or *sec*-butyl isomer or di-*n*-butyl *n*-butylboronate. Di-*n*-butyl phenylboronate was slowly dealkylated with hydrogen bromide, as was (+)-di-2-methylheptyl phenylboronate, in this case with preponderant inversion. The reactions are compared with analogous ones of trialkyl borates.

CERTAIN alkyl- and aryl-boronates [BR(OR')<sub>2</sub>] have recently been prepared.<sup>1,2</sup> The interactions of boron trifluoride and trichloride, of *n*-butyl difluoro- and dichloro-boronite (BHal<sub>2</sub>·OBu<sup>n</sup>), and of hydrogen chloride and bromide with di-*n*-butyl *n*-butylboronate [BBu<sup>n</sup>(OBu<sup>n</sup>)<sub>2</sub>] and with di-*n*-butyl phenylboronate [BPh(OBu<sup>n</sup>)<sub>2</sub>] and other esters of phenylboronic acid, have been investigated in order to compare these reactions with those of boric esters, and to compare the fluorine with the chlorine systems.

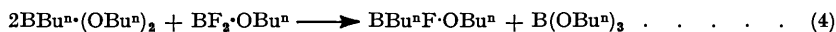
Boron trifluoride reacted readily with di-*n*-butyl *n*-butylboronate at 0°, to give *n*-butylboron difluoride [see (1)] or *n*-butyl *n*-butylfluoroboronite [see (2)] in good yield, depending on the proportion in which the reagents were mixed :



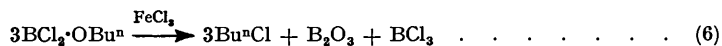
Reaction in equimolecular proportion [see (3)] was demonstrated with di-*n*-butyl phenylboronate :



*n*-Butyl *n*-butylfluoroboronite was also obtained [see (4)] from *n*-butyl difluoroboronite and di-*n*-butyl *n*-butylboronate, and was less stable than the corresponding phenyl compound, disproportionating readily at 20° according to (5) :



Boron trichloride and di-*n*-butyl phenylboronate gave phenylboron dichloride [analogous to (1)]. The difficulty of separation from *n*-butyl dichloroboronite, due to the proximity of boiling points, was overcome either (i) by adding to the mixture a trace of ferric chloride, which causes decomposition of the dichloroboronite at low temperature<sup>3</sup> [see (6)], or (ii) by using diethyl or di-*sec*-butyl phenylboronate as the starting compound.



In the former case, ethyl dichloroboronite was more readily separated, but even here the use of ferric chloride was preferred, and in the latter the *sec*-butyl dichloroboronite initially formed decomposed at room temperature to *sec*-butyl chloride.<sup>3,4</sup>

By mixing boron trichloride with di-*n*-butyl *n*-butylboronate or phenylboronate in equimolecular proportions, *n*-butyl *n*-butylchloroboronite or *n*-butyl chlorophenylboronite

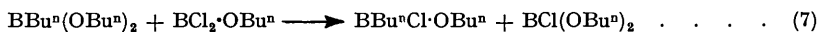
<sup>1</sup> Brindley, Gerrard, and Lappert, *J.*, 1955, 2956.

<sup>2</sup> Torssell, *Acta Chem. Scand.*, 1954, **8**, 1779.

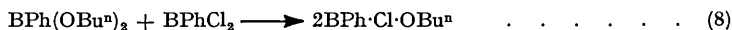
<sup>3</sup> Gerrard and Lappert, *J.*, 1955, 3084.

<sup>4</sup> *Idem*, *J.*, 1951, 2545.

was obtained [analogous to (3)]. These boronites are quite stable. The butylchloroboronite was also obtained by a reaction analogous to (4), and also by the reaction (7).



The most convenient method for preparing *n*-butyl chlorophenylboronite was by mixing phenylboron dichloride with di-*n*-butyl phenylboronate [see (8)], as it was the only product of reaction.

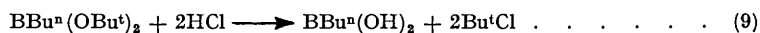


The preparations of *n*-butyl- and phenyl-boron dihalides, mentioned above, have advantages over earlier methods. First, the boronic esters are stable and easy to handle, and, secondly, mild reaction conditions are employed. Earlier methods<sup>5-11</sup> employed either the reaction between organometallic compounds and boron halides, or that between boron alkyls (or aryls, or aminodialkylborons) and boron or hydrogen halides. Methylboron difluoride was prepared from methylboronic anhydride and boron trifluoride.<sup>12</sup>

*n*-Butyl *n*-butyl- and phenyl-halogenoboronite are members of a new class of organoboron compound. They are unimolecular in cyclohexane (owing to its instability the molecular weight of *n*-butyl *n*-butylfluoroboronite was not determined). They are of particular interest as they provide examples of trivalent boron compounds having three unlike groups attached to the boron atom. Their characterising physical constants are shown in the Table.

Compound	B. p./mm.	$n_D^{20}$	$d_4^{20}$
BBu <sup>n</sup> F·OBu <sup>n</sup> .....	Volatile at 0.01 mm.	1.3900	0.888
BBu <sup>n</sup> Cl·OBu <sup>n</sup> .....	50°/1.5	1.4170	0.898
BPhF·OBu <sup>n</sup> .....	27°/0.005	1.4565	0.972
BPhCl·OBu <sup>n</sup> .....	65°/0.4 (m. p. -32°)	1.4996	1.021

Hydrogen chloride did not react, even after 7 hr. at 120°, with di-*n*-butyl *n*-butylboronate or with *n*-, *iso*-, or *sec*-butyl phenylboronate, but with di-*tert*-butyl phenylboronate it produced rapid dealkylation [see (9)] at 20°. Hydrogen bromide produced



partial dealkylation of di-*n*-butyl phenylboronate and of (+)-di-2-methylheptyl phenylboronate at 120°. In the latter case the 2-bromo-octane obtained was preponderantly inverted in configuration. These results may be interpreted as involving an initial protonisation of one oxygen atom to afford a halide ion and a cation (inset). This either yields a carbonium cation if the alkyl group R' is electron-releasing (*e.g.*, Bu<sup>t</sup>), or reacts by an in-line attack of Hal<sup>-</sup> on the carbon atom attached to the protonated oxygen if the alkyl group is of weaker electron-releasing type (*e.g.*, 2-methylheptyl).

In these reactions of boronates a broad similarity to those of borates may be discerned. Thus boron trifluoride reacts with tri-*n*-butyl borate to give *n*-butyl difluoroboronite,<sup>13</sup> although di-*n*-butyl fluoroboronate does not exist; hence reactions analogous to (2), (3), and (4) are not found in the boron trifluoride-borate systems. Boron trichloride does react with trialkyl borates to give alkoxyboron chlorides<sup>3, 4, 14, 15</sup> [analogous to (1), (2), (3), and (8)]; and alkyl dichloroboronites also react with trialkyl borates<sup>15</sup> [analogous to (4)] to give dialkyl chloroboronates. The readier dealkylation of tri-*tert*-butyl borate than of its *n*-, *iso*-, and *sec*-isomers is also similar,<sup>4</sup> whilst the preponderant inversion of

<sup>5</sup> Krause and Nitzsche, *Ber.*, 1922, **55**, 1261; Krause, D.R.-P., 371,467/1924.

<sup>6</sup> Wiberg and Buchheit as quoted by Goubeau, F.I.A.T. Review of German Science (1939-46), Inorganic Chemistry, Vol. I, pp. 215-238.

<sup>7</sup> Michaelis *et al.*, *Ber.*, 1880, **13**, 58; 1882, **15**, 180; 1894, **27**, 244; *Annalen*, 1901, **315**, 19.

<sup>8</sup> Borisov, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1951, 402.

<sup>9</sup> Burg and Banus, *J. Amer. Chem. Soc.*, 1954, **76**, 2537.

<sup>10</sup> Becher, *Z. anorg. Chem.*, 1953, **271**, 243.

<sup>11</sup> Booth and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1415.

<sup>12</sup> Burg, *ibid.*, 1940, **62**, 2228.

<sup>13</sup> Lappert, *J.*, 1955, 784.

<sup>14</sup> Wiberg and Smedsrud, *Z. anorg. Chem.*, 1935, **225**, 204.

<sup>15</sup> Lappert, *J.*, 1956, in the press.

the 2-bromo-octane obtained from (+)-tri-2-methylheptyl borate and hydrogen bromide<sup>16</sup> shows also the general resemblance of the two systems.

#### EXPERIMENTAL

*Preparations and Techniques.*—Boron trifluoride was prepared by Booth and Willson's method;<sup>17</sup> the trichloride was the commercial product purified by redistillation. Hydrogen chloride was prepared by action of concentrated sulphuric acid on anhydrous ammonium chloride and hydrogen bromide by Gerrard's method.<sup>18</sup> Both gases were dried by passage through a phosphoric oxide tower. The boronates were prepared by the method of Brindley, Gerrard, and Lappert.<sup>1</sup> Determination of boron in phenylboronates and derivatives was by hydrolysis to phenylboronic acid, which was estimated as a weak monobasic acid, after neutralisation, in the presence of mannitol. With *n*-butyl boronates and its derivatives a similar method was not practicable, owing to the weakness of *n*-butylboronic acid, and hence, following Snyder, Kuck, and Johnson,<sup>19</sup> the acid was oxidised and hydrolysed to boric acid by the addition of hydrogen peroxide (30%; 15 minutes' standing). Chlorine and fluorine were estimated (acidimetrically) as hydrogen halide formed on hydrolysis; some results were checked by the Volhard method (Cl) and for fluoride by gravimetric analysis (as CaF<sub>2</sub>). The molecular weights were determined by freezing-point depressions in cyclohexane under nitrogen.

*Interaction of Boron Trifluoride with Boronates.*—(a) *With di-n-butyl n-butylboronate.* Boron trifluoride was bubbled through the boronate (16.00 g., 1 mol.) at 0° until the solution was saturated, the increase in weight being 10.25 g. [Calc. for BF<sub>3</sub> (2 mols.): 10.30 g.]. *n*-Butylboron difluoride (6.70 g., 81%), a violently fuming liquid, was withdrawn at 20°/17 mm., condensed at -80°, and distilled; it had b. p. 34—36°/760 mm.,  $n_D^{20}$  1.3300 (Found: F, 33.8; B, 9.7. C<sub>4</sub>H<sub>9</sub>BF<sub>2</sub> requires F, 35.8; B, 10.2%). The non-volatile residue afforded on distillation *n*-butyl difluoroboronite (16.10 g., 85%), b. p. 50—53°/23 mm.,  $n_D^{23}$  1.3840 (Found: C, 39.8; H, 7.7. Calc. for C<sub>4</sub>H<sub>9</sub>OBF<sub>2</sub>: C, 39.4; H, 7.5%), and a residue (1.82 g.). The yields are based on scheme (1).

The gas was passed into the boronate (24.68 g., 3 mols.) at 0° until 1 mol. of the gas (2.62 g.) was absorbed. The mixture was set aside for 2 hr. at 20° and then volatile matter was removed, with shaking, and after 6 hr. *n*-butyl *n*-butylfluoroboronite (16.21 g., 88%),  $n_D^{20}$  1.3892 (Found: F, 11.3; B, 6.4. C<sub>8</sub>H<sub>18</sub>OBF requires F, 11.8; B, 6.8%), had collected in a trap at -80°. The residue afforded on distillation a fore-run (2.13 g.), b. p. 26—69°/0.2 mm.,  $n_D^{20}$  1.4078, and tri-*n*-butyl borate (8.70 g., 98%), b. p. 70°/0.2 mm.,  $n_D^{20}$  1.4116 (Found: B, 4.7. Calc. for C<sub>12</sub>H<sub>27</sub>O<sub>3</sub>B: B, 4.7%). Yields are based on scheme (2).

(b) *With di-n-butyl phenylboronate.* The gas was passed into the boronate (22.2 g., 1 mol.) at 0° until 1 mol. (6.8 g.) had been absorbed (about 2 hr.). On evacuation (25°/0.05 mm.) a condensate was collected at -70°. The residue afforded *n*-butyl fluorophenylboronite (12.3 g., 72%) on distillation, b. p. 40—42°/0.04 mm.,  $n_D^{20}$  1.4532 (Found: F, 9.2; B, 5.9%), and a residue (1.0 g.). The impure ester had b. p. 27°/0.005 mm.,  $n_D^{20}$  1.4605 (Found: C, 65.2; H, 8.3; F, 10.2; B, 5.7%; *M*, 198. Calc. for C<sub>10</sub>H<sub>14</sub>OBF: C, 66.7; H, 7.8; F, 10.6; B, 6.0%; *M*, 180), on redistillation, and was a fuming liquid. The combined condensates (10.55 g. Calc. for BF<sub>2</sub>·OBu<sup>n</sup>: 11.6 g.) consisted of crude *n*-butyl difluoroboronite, b. p. 46°/15 mm.,  $n_D^{20}$  1.3900. The yields are based on scheme (3).

*Interaction of n-Butyl Difluoroboronite with Di-n-butyl n-Butylboronate.*—The difluoroboronite<sup>13</sup> (4.42 g., 1 mol.) and the boronate (15.52 g., 2 mols.) were mixed at 23°. The reaction was endothermic, a temperature drop of 7° being noted. The mixture was kept at 0.01 mm. whilst shaken for 6 hr. A condensate of *n*-butyl *n*-butylfluoroboronite (10.8 g., 93%),  $n_D^{20}$  1.3922,  $d_4^{20}$  0.888 (Found: F, 11.6; B, 6.3%), was collected in a trap at -80°, and the major product isolated from the non-volatile residue was tri-*n*-butyl borate (8.10 g., 97%), b. p. 117°/16 mm.,  $n_D^{20}$  1.4110 (Found: B, 4.7%). The yields are based on scheme (4).

*Disproportionation of n-Butyl n-Butylfluoroboronite at 25°.*—The freshly prepared boronite (6.60 g.) was kept in a desiccator at 25° for 5 days. At 20 mm., a condensate of *n*-butylboron difluoride (0.88 g., 39.2%), b. p. 35°/760 mm.,  $n_D^{20}$  1.3285 (Found: F, 35.1; B, 10.0%), was collected. The remainder, at 0.005 mm., afforded unchanged *n*-butyl *n*-butylfluoroboronite

<sup>16</sup> Gerrard and Lappert, *J.*, 1951, 1020.

<sup>17</sup> Booth and Willson, *Inorg. Synth.*, 1939, 1, 21.

<sup>18</sup> Gerrard, *Research*, 1954, 7, S20.

<sup>19</sup> Snyder, Kuck, and Johnson, *J. Amer. Chem. Soc.*, 1938, 60, 105.

(3.90 g.; 59%),  $n_D^{20}$  1.3896 (Found : F, 11.3; B, 6.5%), as a further condensate, whilst the non-volatile residue was di-*n*-butyl *n*-butylboronate (1.64 g., 37.2%), b. p. 113—115°/14 mm.,  $n_D^{20}$  1.4175 (Found : B, 5.03. Calc. for  $C_{12}H_{22}O_2B$  : B, 5.1%). The yields are based on scheme (5).

*Interaction of Boron Trichloride with Boronates.*—(a) *With di-n-butyl n-butylboronate.* The boronate (15.3 g., 1 mol.) was added (1.6 hr.) dropwise with shaking to boron trichloride (8.4 g., 1 mol.) at  $-70^\circ$ . On evacuation (20°/1 mm.) crude *n*-butyl dichloroboronite (9.7 g., 93%) was collected as a condensate at  $-80^\circ$ , which was purified by four distillations (Found : Cl, 46.2; B, 6.4. Calc. for  $C_4H_9OCl_2B$  : Cl, 45.8; B, 7.0%). The non-volatile residue afforded *n*-butyl *n*-butylchloroboronite (8.1 g., 64%), b. p. 48—52°/2 mm.,  $n_D^{23}$  1.4170,  $d_4^{20}$  0.898 (Found : C, 54.5; H, 8.7; Cl, 21.0; B, 6.1%; *M*, 175.  $C_8H_{18}OCIB$  requires C, 54.5; H, 10.2; Cl, 20.1; B, 6.1%; *M*, 177), as a fuming, colourless liquid. Yields are based on :  $BBu^a(OBu^a)_2 \xrightarrow{+BCl_3} BBu^aClOBu^a + BCl_2OBu^a$ .

(b) *With phenylboronates* (2 : 1). Preliminary experiments showed that mixing boron trichloride (2 mols., or more) with either the ethyl or the *n*-butyl ester (1 mol.) of phenylboronic acid led to difficulty in separation of pure phenylboron dichloride, the chlorine content of the product being invariably low; hence we report below only those experiments, with these two esters, wherein ferric chloride was added to the mixture.

Di-*n*-butyl phenylboronate (20.5 g., 1 mol.) was added to boron trichloride (20.5 g., 2 mols.) and ferric chloride (0.21 g.) at  $-80^\circ$ . The mixture was kept at 20° for 20 min., whereupon volatile matter was removed at 20 mm. A solid cake remained, which was extracted with methylene dichloride (3 × 25 c.c.). The residue, after removal of solvent from this extract, was crude phenylboron dichloride (10.8 g., 81%), b. p. 62°/18 mm.,  $n_D^{19}$  1.4392,  $d_4^{20}$  1.194 (Found : Cl, 44.0; B, 6.8. Calc. for  $C_6H_5Cl_2B$  : Cl, 44.6; B, 6.8%).

Diethyl phenylboronate (6.0 g., 1 mol.) with boron trichloride (7.9 g., 2 mols.) and ferric chloride (0.01 g.) similarly (violent reaction) afforded the dichloride (4.6 g., 80%), b. p. 57°/8 mm.,  $n_D^{20}$  1.4385 (Found : Cl, 44.3; B, 6.9%).

By the same technique, but in absence of ferric chloride, di-*sec*-butyl phenylboronate (20.2 g., 1 mol.) and boron trichloride (20.2 g., 2 mols.) afforded the dichloride (10.4 g., 76%), b. p. 62°/18 mm.,  $n_D^{20}$  1.4387 (Found : Cl, 43.7; B, 6.8%). In these experiments yields are based on :  $BPh(OR)_2 + 2BCl_3 \longrightarrow BPhCl_2 + 2BCl_2OR$  (decomp.).

(c) *With di-n-butyl phenylboronate* (1 : 1). To the trichloride (12.5 g., 1 mol.) at  $-70^\circ$ , the boronate (25.0 g., 1 mol.) was added (1 hr.) with shaking. The mixture set solid, but melted at 15°. A condensate (16.6 g.) was collected in a trap at  $-80^\circ$ , when the mixture was shaken for 4 hr. at 40°/10 mm. and 15 hr. at 20°/0.4 mm.; this was largely *n*-butyl dichloroboronite, contaminated with *n*-butyl chloride. The dichloroboronite (12.3 g., 70%) was isolated from this condensate by distillation (b. p. 28°/11 mm.) (Found : Cl, 45.3; B, 7.1%). The non-volatile residue afforded *n*-butyl chlorophenylboronite (10.0 g., 48%), b. p. 70—71°/0.5 mm.,  $n_D^{20}$  1.4760 (Found : Cl, 18.1; B, 5.5%; *M*, 191.  $C_{10}H_{14}OCIB$  requires Cl, 18.1; B, 5.5%; *M*, 196), as a fuming, colourless liquid; and a white, solid residue (10.7 g.), on extraction with dry *n*-pentane, was identified as phenylboron oxide, m. p. 212—213° (Found : B, 10.0. Calc. for  $C_6H_5OB$  : B, 10.4%). The yields are based on :  $BPh(OBu^a)_2 + BCl_3 \longrightarrow BPhClOBu^a + BCl_2OBu^a$ .

*Interaction of n-Butyl Dichloroboronite with Di-n-butyl n-Butylboronate.*—To the dichloroboronite<sup>4</sup> (11.4 g., 1 mol.) at  $-70^\circ$ , the boronate (15.7 g., 1 mol.) was added during  $\frac{1}{2}$  hr. with shaking. After 13 hr. at 20° and passage of dry nitrogen through the mixture, two distillations afforded *n*-butyl *n*-butylchloroboronite (10.0 g., 77%), b. p. 36—40°/1 mm.,  $n_D^{20}$  1.4152 (Found : Cl, 20.3; B, 5.9%). Other fractions were difficult to purify. The yield is based on scheme (7).

To the purified dichloroboronite (11.7 g., 1 mol.) at  $-70^\circ$  was added (0.3 hr.) dropwise with shaking the boronate (31.8 g., 2 mols.). The mixture was set aside for 3 days at  $-70^\circ$  whereupon it partially crystallised. Distillation afforded pure *n*-butyl *n*-butylchloroboronite (20.1 g., 76%), b. p. 66—70°/10 mm.,  $n_D^{20}$  1.4157 (Found : Cl, 20.5; B, 6.4%). The higher-boiling fraction, from which it was difficult to remove traces of the chloro-ester, was tri-*n*-butyl borate, b. p. 104°/12 mm.,  $n_D^{20}$  1.4110 (Found : B, 4.6%). The yield is based on :  $2BBu^a(OBu^a)_2 + BCl_2OBu^a \longrightarrow 2BBu^aClOBu^a + B(OBu^a)_3$ .

*Interaction of Phenylboron Dichloride and Di-n-butyl Phenylboronate.*—The dichloride (1.62 g., 1 mol.) and the boronate (2.38 g., 1 mol.) were mixed at 10°. There was some heat of reaction. Distillation afforded *n*-butyl chlorophenylboronite (3.86 g., 97%), b. p. 58°/0.2 mm.,  $n_D^{19}$  1.4980,  $d_4^{20}$  1.021 (Found : Cl, 17.7; B, 5.5%), and a solid residue (0.15 g.).

*Interaction of Hydrogen Chloride and Boronates.*—(a) *With di-n-, iso-, and -sec-butyl phenylboronate and di-n-butyl n-butylboronate, severally.* In none of these cases was reaction observed.

The dry gas was bubbled through the ester (about 5 g.), both at 15° (30 hr.) and at 120° (7 hr.). After evacuation (20 mm.) no change in weight was observed [except in the case of  $\text{BPh}(\text{O}i\text{Bu})_2$ ] and distillation gave a high yield of unchanged ester, characterised by b. p.,  $n_D^{20}$ , and analysis for boron. In the di-*sec.*-butyl phenylboronate experiment the amount of boronate recovered was only 65%, there being a high-boiling residue.

(b) *With di-tert.-butyl phenylboronate.* The gas was bubbled through a vessel containing the ester (1.95 g.) at 20°, connected to a trap at -80°. Within 5 min., a precipitate formed and the mixture set solid. Xylene (5 c.c.) was added and the gas was passed through the mixture for a further 30 min. A condensate of *tert.*-butyl chloride (1.26 g., 82%) saturated with hydrogen chloride was collected in the trap. After addition of lead carbonate (to remove hydrogen chloride), this condensate was distilled; it had b. p. 50—51°/760 mm.,  $n_D^{17}$  1.3873 (Found: Cl, 37.8. Calc. for  $\text{C}_4\text{H}_9\text{Cl}$ : Cl, 38.4%). Xylene was removed from the residue at 0.001 mm., and phenylboronic acid (1.05 g. Calc.: 1.02 g.) (Found: B, 9.6. Calc. for  $\text{C}_6\text{H}_5\text{O}_2\text{B}$ : B, 9.1%) remained as a white solid. Yields are based on scheme (9).

*Interaction of Hydrogen Bromide and Boronates.*—(a) *With di-n-butyl phenylboronate.* The dry gas was bubbled through the boronate (5.1 g.) at 20° for 14 hr. Distillation afforded the unchanged ester (4.0 g., 79%), b. p. 84°/0.4 mm. (Found: B, 4.6%), and a solid residue (0.55 g.). A condensate (0.45 g., 7.8%) was crude *n*-butyl bromide, b. p. 84—86°,  $n_D^{20}$  1.4300.

When the gas was passed through the ester (2.80 g.) at 120° for 7 hr., the mixture set solid. At 20°/0.05 mm., *n*-butyl bromide (1.90 g., 58%) was collected at -70°. After being washed and dried ( $\text{MgSO}_4$ ), this had b. p. 97°/760 mm.,  $n_D^{21}$  1.4352. The non-volatile residue afforded unchanged boronate (0.80 g., 28.6%), b. p. 60—68°/0.3 mm. The residue (1.08 g., 74%) was phenylboronic acid, m. p. 213—216° (from water), which was converted into the anhydride (Found: B, 10.2%).

(b) *With (+)-2-methylheptyl phenylboronate.* The gas was passed through the ester (2.24 g.,  $\alpha_D^{20} + 15.08^\circ$ , from ROH having  $\alpha_D^{20} + 7.53^\circ$ ; in each case  $l = 1$ ) for 7 hr. at 120°. On cooling, the mixture set solid. Excess of gas was removed by suction at 20 mm. The increase in weight was 1.04 g. (Calc.: 1.047 g. for complete reaction). Distillation afforded (-)-2-bromo-octane (1.60 g., 67%), b. p. 74°/10 mm.,  $n_D^{20}$  1.4504,  $\alpha_D^{20} - 28.4^\circ$  ( $l = 1$ ), and a residue of crude phenylboronic acid (0.89 g.), m. p. 212—216° (from water). Yields in these experiments are based on:  $\text{BPh}(\text{OR})_2 + 2\text{HBr} \longrightarrow 2\text{RBr} + \text{BPh}(\text{OH})_2$ .

The authors thank Dr. G. R. Primavesi, of the Distillers Co., Ltd., for advice regarding the molecular-weight determinations.