1009. *Reactions of the Phenylboron Chlorides and Bromides and the Chemistry of* n-*Butyl Phenylbromoboronite.*

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Diphenylboron halides (Cl, Br) do not react with ethers or sodium. Phenylboron dibromide with *n*-butyl *tert.*-butyl ether gives *n*-butyl phenylbromoboronite, $Ph{\cdot}BBr{\cdot}OBu^n$, and *tert.*- and *iso*-butyl bromide. Reaction of diphenylboron halides with boron halides, hydrogen bromide, or bromine at high temperature and pressure causes cleavage of boron–carbon bonds. The properties of *n*-butyl phenylbromoboronite, the first stable alkoxyboron bromide, are described.

THE present paper extends work on the preparation [1,2,3,4] and properties [5,6,7,8] of phenylboron halides, $PhBX_2$ and Ph_2BX ($X = Cl, Br$) to reactions involving replacement of halogen or phenyl (B–C cleavage).

Phenylboron dibromide, previously prepared in low yield from diphenylmercury and boron tribromide,[8] has now been prepared in good yield from phenylboron oxide and boron tribromide.

Phenylboron bromides, like the chlorides,[2] are readily hydrolysed: $Ph{\cdot}BBr_2 + H_2O \longrightarrow Ph{\cdot}BO + 2HBr$; or $2Ph_2B{\cdot}Br + H_2O \longrightarrow (Ph_2B)_2O + 2HBr$.

Alcoholysis of phenylboron chlorides has previously been reported.[9,10] Phenylboron dibromide with butan-1-ol yielded *n*-butyl phenylbromoboronite ($Ph{\cdot}BBr_2 + Bu^nOH \longrightarrow Ph{\cdot}BBr{\cdot}OBu^n + HBr$) or di-*n*-butyl phenylboronate [$Ph{\cdot}BBr_2 + 2Bu^nOH \longrightarrow Ph{\cdot}B(OBu^n)_2 + 2HBr$]. Diphenylboron bromide with (—)-1-methylheptanol gave (+)-1-methylheptyl, diphenylborate, $Ph_2B{\cdot}OR$ with retention of configuration.[4]

Diphenylboron halides did not react with ethers, whereas phenylboron dibromide cleaved *n*-butyl *tert.*-butyl ether at room temperature, being thus more reactive than phenylboron dichloride: [6]

$$Ph{\cdot}BBr_2 + ROR' \longrightarrow Ph{\cdot}BBr{\cdot}OR' + RBr$$

It appears that for a boron halide to cause C–O fission of an ether it is necessary that it be a tri- or di-halide. Thus boron trihalides and alkyl dichloroboronites [11] $RO{\cdot}BCl_2$ cleave most ethers at $-80°$ or at lower temperatures, phenylboron dichloride [6] reacts at about 150°, and dialkyl chloroboronates [11] $(RO)_2BCl$ and alkyl arylchloroboronites [5] $Ar{\cdot}BCl{\cdot}OR$ are generally unreactive. The products from phenylboron dibromide were *n*-butyl phenylbromoboronite and a mixture of *tert.*- and *iso*-butyl bromide. The direction of fission is in accord with an S_N1 mechanism,[6,12] involving carbonium-ion formation from the more electron-releasing of the two alkyl groups in the ether. This is further supported by the observed molecular rearrangement, although rearrangement of *tert.*-butyl to *iso*butyl compounds is not common.

Diphenylboron halides did not react with metallic sodium, possibly owing to steric hindrance to the formation of the expected tetraphenyldiboron, $(Ph_2B)_2$.

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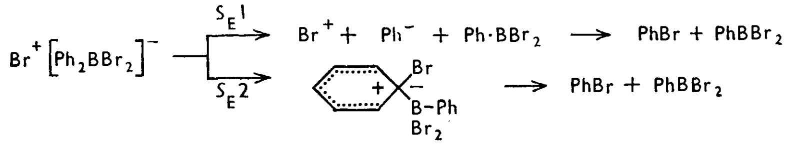
[1] Brindley, Gerrard, and Lappert, *J.*, 1956, 824.
[2] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.
[3] Mikhailov and Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 375.
[4] Abel, Gerrard, and Lappert, *J.*, 1957, 3833.
[5] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.
[6] *Idem*, *J.*, 1957, 2893.
[7] Mikhailov and Fedotov, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk*, 1956, 1511.
[8] Michaelis and Richter, *Annalen*, 1901, **315**, 216.
[9] Brindley, Gerrard, and Lappert, *J.*, 1956, 1540.
[10] Abel, Gerrard, and Lappert, *J.*, 1957, 112.
[11] Lappert, *Chem. Rev.*, 1956, **56**, 959.
[12] Martin, *ibid.*, 1948, **42**, 581.

Diphenylboron halides underwent mutual replacement with boron trihalides at 200° under pressure: $Ph_2B{\cdot}X + BX_3 \longrightarrow 2Ph{\cdot}BX_2$.

Diphenylboron bromide with hydrogen bromide at 100° under pressure gave benzene and boron tribromide (isolated as its pyridine complex[12]). The boron–carbon bonds in diphenylboron bromide were also cleaved by bromine at 200° under pressure, yielding bromobenzene and boron tribromide, with small amounts of polybromobenzenes (formed by bromination of bromobenzene or of diphenylboron bromide).

We interpret the last three reactions as involving initial nucleophilic attachment of the appropriate reagent to the diphenylboron halide to form complexes, $H^+[Ph_2BBr_2]^-$, $Br^+[Ph_2BBr_2]^-$, and $[BX_2]^+[Ph_2BX_2]^-$. Subsequent transformation may then involve either of two mechanisms, exemplified as follows:



n-*Butyl Phenylbromoboronite.*—This compound (prepared as above) is the first bromoboronite, R·BBr·OR′ (R and R′ = alkyl or aryl) to be prepared: corresponding fluoro- and chloro-compounds are known.[1, 9, 13] It is also the first alkoxyboron bromide: dialkyl bromoboronates $(RO)_2B{\cdot}Br$ and alkyl dibromoboronites $RO{\cdot}BBr_2$ are unknown;[11] recent attempts to prepare the methyl homologues have failed.[14]

n-Butyl phenylbromoboronite is a colourless liquid at room temperature, but crystalline at −80°. It fumes in air with evolution of hydrogen bromide and reacts with *n*-butanol: $Ph{\cdot}BBr{\cdot}OBu^n + Bu^nOH \longrightarrow Ph{\cdot}B(OBu^n)_2 + HBr$. Thermally it is fairly stable; after 8 hr. at 100° only 10% of decomposition (to phenylboron oxide and butyl bromide) had occurred, but this was complete after 2 hr. at 200°. Its chloro-analogue underwent negligible decomposition under these conditions.[9] This is to be expected from the mechanism, involving rate-determining boron–halogen fission, proposed for decomposition of phenylchloroboronites.[9] *n*-Butyl phenylbromoboronite, like its chloro-analogue,[9] was catalytically and exothermally decomposed at 20° (as above) by a trace of anhydrous ferric chloride.

EXPERIMENTAL

General Procedures.—Dry hydrogen bromide was prepared by Gerrard's method [15] and condensed at −80°. Diphenylboron chloride was obtained by the method of Abel, Dandegaonker, Gerrard, and Lappert [2] and diphenylboron bromide as described by us previously.[4] Analytical methods were those used in earlier investigations.[4, 6]

Interaction of Boron Tribromide and Phenylboronic Anhydride.—The tribromide (24·1 g.) was added to the anhydride (10·0 g.) in methylene dichloride (100 c.c.) at −80°. After 25 hr. at 20° volatile matter and solvent were removed (20°/15 mm.) to afford phenylboron dibromide (12·7 g., 53·6%), b. p. 80°/8 mm. (Found: B, 4·5; Br, 64·7. Calc. for $C_6H_5BBr_2$: B, 4·4; Br, 64·5%). Ether-extraction of the residue gave phenylboronic anhydride (3·82 g.) (Found: B, 10·1. Calc. for C_6H_5OB: B, 10·4%). A sample after recrystallisation (as phenylboronic acid from water, and subsequent dehydration) had m. p. 216°. After allowance for recovered anhydride the yield of dibromide was 85%.

Hydrolysis of Phenylboron Dibromide.—Water (0·135 g.) in *n*-pentane (30 c.c.) was added to phenylboron dibromide (1·86 g.) in *n*-pentane (20 c.c.). Hydrogen bromide (97%) was trapped in potassium hydroxide. Removal of solvent at 0·2 mm. left phenylboronic anhydride (0·75 g., 95%) (Found: B, 10·4%), which after recrystallization, as phenylboronic acid from hot water, and dehydration (120°/5 hr.) had m. p. 218°.

Hydrolysis of Diphenylboron Bromide.—Water (0·0397 g.) in ether (10 c.c.) was added to

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[13] Mikhailov and Kostroma, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk*, 1956, 376.

[14] Goubeau, Becher, and Griffel, *Z. anorg. Chem.*, 1956, **282**, 86.

[15] Gerrard, *Research*, 1954, **7**, S20.

diphenylboron bromide (1·08 g.). Hydrogen bromide (96%) was trapped in potassium hydroxide. Removal of solvent at 10 mm. left crystalline diphenylboronous anhydride (0·74 g., 97%), m. p. 115° (Found: B, 6·3. Calc. for $C_{24}H_{20}OB_2$: B, 6·3%).

*Interaction of Phenylboron Dibromide and Butan-*1-*ol.*—Butan-1-ol (1·19 g., 1 mol.) in *n*-pentane (10 c.c.) was added to phenylboron dibromide (4·00 g., 1 mol.) in *n*-pentane (15 c.c.). Hydrogen bromide (1·19 g., 91%) was trapped in potassium hydroxide. After removal of solvent at 10 mm., distillation yielded n-*butyl phenylbromoboronite* (3·69 g., 95%), b. p. 67°/0·15 mm., d_4^{20} 1·233, n_D^{20} 1·5166 (Found: C, 50·3; H, 5·8; Br, 33·4; B, 4·6. $C_{10}H_{14}OBrB$ requires C, 49·8; H, 5·8; Br, 33·4; B, 4·5%).

Use of two mols. of butanol gave hydrogen bromide (91%) and di-*n*-butyl phenylboronate (2·72 g., 84%), b. p. 87°/0·01 mm., n_D^{20} 1·4748 (Found: B, 4·5. Calc. for $C_{14}H_{23}O_2B$: B, 4·6%).

Alcoholysis of Diphenylboron Bromide.—(−)-Octan-2-ol (2·05 g.; α_D^{20} −6·96°) in *n*-pentane (10 c.c.) was added to diphenylboron bromide (3·86 g.) in *n*-pentane (20 c.c.) at −80°, whereafter the mixture was warmed to 20°. Hydrogen bromide (1·26 g., 96%) was trapped in sodium hydroxide. Solvent was removed at 10 mm., to give (+)-1-methylheptyl diphenylboronite (4·43 g., 96%), n_D^{20} 1·5196, α_D^{20} +4·06° (Found: B, 3·7. Calc. for $C_{20}H_{27}OB$: B, 3·7%).

Interaction of Phenylboron Dibromide and n-*Butyl* tert.-*Butyl Ether.*—The ether (1·46 g.) was added to the dibromide (2·74 g.); heat was evolved. After 50 hr. at 20°, volatile matter (1·47 g.) was removed at 0·2 mm. and trapped at −80°. A gas-phase chromatogram of the condensate showed the presence of *tert.*- (60%), *iso*- (32%), and *n*-butyl bromide (4%) and *n*-butyl *tert.*-butyl ether (4%). The liquid residue afforded *n*-butyl phenylbromoboronite (2·24 g., 82%), b. p. 74°/0·6 mm., n_D^{20} 1·5173 (Found: Br, 33·7; B, 4·5%).

Interaction of Diphenylboron Halide and Boron Trihalide.—Diphenylboron chloride (9·56 g.) and boron trichloride (5·60 g.) were heated in a heavy-walled glass tube at 200° for 75 hr. Phenylboron dichloride (13·65 g., 90%), b. p. 58°/9 mm., n_D^{20} 1·5440 (Found: Cl, 44·4; B, 7·0. Calc. for $C_6H_5Cl_2B$: Cl, 44·6; B, 6·9%), and diphenylboron chloride (0·47 g.) (Found: Cl, 17·2; B, 5·5. Calc. for $C_{12}H_{10}ClB$: Cl, 17·7; B, 5·4%) were obtained. Boron trichloride (0·35 g.) was trapped in potassium hydroxide during the distillation.

Diphenylboron bromide (14·24 g.) and boron tribromide (14·65 g.) were similarly heated at 200° for 10 hr. Crystalline phenylboron dibromide (18·18 g., 69%), b. p. 59°/0·5 mm. (Found: Br, 64·1; B, 4·5%), was obtained, leaving a semisolid residue (4·32 g.). Boron tribromide (5·60 g.), n_D^{20} 1·5207 (Found: Br, 95·0; B, 4·2. Calc. for BBr_3: Br, 95·7; B, 4·3%), was trapped at −80°.

Interaction of Diphenylboron Bromide and Hydrogen Bromide.—Diphenylboron bromide (2·11 g.) and liquid hydrogen bromide (1·40 g.) were sealed in a heavy-walled glass tube at −80° and then heated at 100° for 30 hr. The tube was opened at −80°; the contents were condensed from 20°/10 mm. into a trap at −80°. To the condensate pyridine (0·68 g.) was added in 15 min. Benzene (1·30 g., 96%), n_D^{20} 1·5010, b. p. 79°, was removed at 20°/15 mm. and trapped at −80°. The crystalline residue was washed with *n*-pentane and water, and dried to constant weight at 20°/0·05 mm. Boron tribromide–pyridine (3·56 g., 85%) (Found: Py, 23·4; Br, 72·7. Calc. for BBr_3,C_5H_5N: C_5H_5N, 23·9; Br, 72·9%), m. p. 125—128°, was obtained.

Interaction of Diphenylboron Bromide and Bromine.—Diphenylboron bromide (8·65 g.) and bromine (11·32 g.) were heated at 200° for 15 hr. under pressure. Boron tribromide (8·08 g., 91%), b. p. 88°, n_D^{20} 1·5235 (Found: Br, 94·9; B, 4·2%), was removed at 20°/15 mm. and trapped at −80°. The remaining liquid yielded bromobenzene (8·03 g., 72%), b. p. 54°/16 mm., n_D^{20} 1·5613 (identified also by its infrared spectrum). A residue (3·43 g.) gave pale yellow crystals (probably a mixture of polybromobenzenes) on recrystallization from alcohol.

Alcoholysis of n-*Butyl Phenylbromoboronite.*—Butan-1-ol (1·14 g.) in *n*-pentane (10 c.c.) was added to the boronite (3·73 g.) in *n*-pentane (10 c.c.). Hydrogen bromide (1·18 g., 95%) was trapped in sodium hydroxide. After removal of solvent at 0·3 mm., di-*n*-butyl phenylboronate (3·38 g., 93%), b. p. 94°/0·4 mm., n_D^{20} 1·4743 (Found: B, 4·6%), was obtained.

Catalytic Decomposition of n-*Butyl Phenylbromoboronite.*—Ferric chloride (0·01 g.) was added to *n*-butyl phenylbromoboronite (1·65 g.) at −80°. Warming to 20° caused an exothermal reaction. *n*-Butyl bromide (0·92 g., 97%), n_D^{20} 1·4394 (Found: Br, 57·6. Calc. for C_4H_9Br: Br, 58·4%), was removed at 10 mm. and trapped at −80°. Phenylboronic anhydride (0·73 g. Required, 0·71 g.) (Found: B, 10·4%) remained. A sample of the anhydride after recrystallization, as phenylboronic acid from hot water, and subsequent dehydration had m. p. 216°.

Thermal Stability of n-*Butyl Phenylbromoboronite.*—The stability of the ester was determined by heating small samples in sealed tubes, and analysing acidimetrically the contents after stated times, by hydrolysis in cold water. Extent of reaction is indicated by the lowering of ratio of easily hydrolysed bromine to boron. Results are tabulated.

Temp.	100°	100°	100°	200°	200°	200°	200°
Time (hr.)	1	5	8	0·25	0·5	1	2
Decompn. (%)	2·7	6·4	10	11·2	30·2	65·5	97

Addition of Ethers to Diphenylboron Bromide and Chloride.—Diphenylboron bromide and chloride were recovered quantitatively after an equimolecular mixture of each halide severally and diethyl ether had been at 20° for 2 hr. Recovery was the same in each case after admixture with allyl phenyl ether.

Addition of Diphenylboron Bromide and Chloride to Sodium.—The halide (about 5 g.) in *n*-pentane (20 c.c.) was added to sodium wire (10 g.) in *n*-pentane (50 c.c.). After 50 hr. at 20° the sodium was filtered off; removal of solvent left diphenylboron halide, which on distillation left only a small solid residue.

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