69. *Alkyl Bisdialkylaminoboronites and Related Compounds.*

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n-Butyl bisdiethylaminoboronite, $Bu^nO{\cdot}B(NEt_2)_2$, has been prepared by reaction of diethylamine with *n*-butyl dichloroboronite and of butan-1-ol with trisdiethylaminoboron or bisdiethylaminoboron chloride in the presence of triethylamine. It is a stable, monomeric liquid which does not co-ordinate with pyridine, but hydrolyses readily. Diethylamine is displaced by either butan-1-ol or di-*n*-butylamine, in the latter instance to afford *n*-butyl bisdi-*n*-butylaminoboronite, $Bu^nO{\cdot}B(NBu^n_2)_2$, which was also prepared by another route. Hydrogen chloride reacted with *n*-butyl bisdiethylaminoboronite to give di-*n*-butyl chloroboronate, diethylammonium chloride, and a 1 : 1-complex between diethylaminoboron dichloride and hydrogen chloride. Boron halides (F, Cl) afforded *n*-butyl dihalogenoboronite and diethylaminoboron dihalide. Trisdiethylaminoboron, tris-di-*n*-butylaminoboron, bisdiethylaminoboron chloride, and diethylaminoboron difluoride were prepared; for the last two substances, the methods are alternative to those available hitherto for these classes of compounds; all are new. The action of hydrogen chloride on trisdiethylaminoboron and diethylaminoboron dichloride has been studied. The 1 : 1 complex of the latter with hydrogen chloride is regarded as a co-ordination compound, because its electrical conductivity in nitrobenzene is of a similar order to that of triethylamine–boron trichloride.

ALTHOUGH trialkyl borates, $B(OR)_3$, and trisaminoborons, $B(NR'R'')_3$, are well-known and stable compounds, the alkyl diaminoboronites, $RO{\cdot}B(NR'R'')_2$, have not hitherto been prepared.[1] The present paper is concerned mainly with the chemistry of *n*-butyl bisdiethylaminoboronite, $Bu^nO{\cdot}B(NEt_2)_2$, the first member of this class. In connection with certain of its properties a higher homologue was desirable and *n*-butyl bisdi-*n*-butylaminoboronite, $Bu^nO{\cdot}B(NBu^n_2)_2$, was chosen. It was also necessary to prepare trisdiethylaminoboron, $B(NEt_2)_3$, diethylaminoboron difluoride, $Et_2N{\cdot}BF_2$, and bisdiethylaminoboron chloride, $(Et_2N)_2B{\cdot}Cl$, and to study certain properties of diethylaminoboron dichloride.

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[1] Lappert, *Chem. Rev.*, 1956, 959.

n-Butyl bisdiethylaminoboronite was prepared by three methods (1—3), and *n*-butyl bisdi-*n*-butylaminoboronite by a method analogous to (1). Two other attempted preparations [$B(OBu^n)_3 + 2B(NEt_2)_3 \longrightarrow 3Bu^nO{\cdot}B(NEt_2)_2$; $B(OBu^n)_3 + 2Et_2NH \longrightarrow Bu^nO{\cdot}B(NEt_2)_2 + 2Bu^nOH$] failed, the starting materials being recovered.

$$(1) \qquad Bu^nO{\cdot}BCl_2 + 4Et_2NH \xrightarrow{77\%} Bu^nO{\cdot}B(NEt_2)_2 + 2Et_2NH,HCl$$

$$(2) \qquad Bu^nOH + B(NEt_2)_3 \xrightarrow{76\%} Bu^nO{\cdot}B(NEt_2)_2 + Et_2NH$$

$$(3) \qquad Bu^nOH + (Et_2N)_2B{\cdot}Cl + Et_3N \xrightarrow{67\%} Bu^nO{\cdot}B(NEt_2)_2 + Et_3N,HCl$$

n-Butyl bisdiethylaminoboronite was a colourless, mobile liquid, which slowly became brown in light. It was monomeric in *cyclo*hexane.

Of the trisdialkylaminoborons, the methyl homologue, $B(NMe_2)_3$, had been prepared from boron trichloride and dimethylamine.[2, 3] By use of a similar method (4), trisdiethylaminoboron, and trisdi-*n*-butylaminoboron have now been prepared. An attempt to use a method [$B(OH)_3 + 3Et_2NH \longrightarrow B(NEt_2)_3 + 3H_2O$], analogous to a well-known one [1] for trialkyl borates, was unsuccessful.

$$(4) \qquad 6R_2NH + BCl_3 \longrightarrow B(NR_2)_3 + 3R_2NH,HCl$$

In contrast to trisdimethylaminoboron, which formed a 1 : 3-complex with hydrogen chloride,[2] we found that trisdiethylaminoboron (1 mol.) reacts with 5 mols. of hydrogen chloride [scheme (5)].

$$(5) \qquad B(NEt_2)_3 + 5HCl \longrightarrow Et_2N{\cdot}BCl_2,HCl + 2Et_2NH,HCl$$

Of the bisdialkylaminoboron chlorides the methyl homologue had been prepared by action of dimethylamine on boron trichloride,[2] or dimethylaminoboron dichloride in presence of triethylamine.[3] We have now prepared bisdiethylaminoboron chloride by an alternative method (6).

$$(6) \qquad 2B(NEt_2)_3 + BCl_3 \longrightarrow 3(Et_2N)_2BCl$$

Diethylaminoboron dichloride had previously been reported.[4, 5, 6] It is known [5] to form a 1 : 1 complex [cf. scheme (5)] with hydrogen chloride, an observation that has now been confirmed. This complex (and a corresponding dimethylamino-complex [7]) had been regarded as ionic (I),[5, 6] but it is now shown that it hydrolyses only slowly in water and that its electrical conductivity in nitrobenzene is low and of the same order as that of the 1 : 1 co-ordination compound between boron trichloride and triethylamine, which is a new compound and was obtained by scheme (7); we therefore consider structure (II) more probable (see also ref. 6).

$$(7) \qquad Et_3N + BCl_3 \longrightarrow Et_3N,BCl_3$$

$$\text{(I)} \quad [Et_2NH{\cdot}BCl_2]^+Cl^- \qquad\qquad Cl_2B \longleftarrow :NEt_2H \quad \text{(II)}$$

Dimethylaminoboron difluoride was the only previously known dialkylaminoboron difluoride.[8, 9] We have now prepared the ethyl homologue by a method (8), which we believe to be superior to those used for the methyl compound.

$$(8) \qquad B(NEt_2)_3 + 2BF_3 \longrightarrow 3Et_2N{\cdot}BF_2$$

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[2] Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 77.

[3] Skinner and Smith, *J.*, 1954, 2324.

[4] Michaelis and Luxembourg, *Ber.*, 1896, **29**, 715.

[5] Osthoff and C. A. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 2378.

[6] Goubeau, Rahtz, and Becher, *Z. anorg. Chem.*, 1954, **275**, 161.

[7] C. A. Brown and Osthoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2340.

[8] J. F. Brown, *ibid.*, p. 1219.

[9] Burg and Banus, *ibid.*, 1954, **76**, 3903.

The preparation and properties of these organic compounds of boron had to be studied in order to have evidence for the existence of *n*-butyl bisdiethylaminoboronite and to describe its properties in detail.

Hydrogen chloride reacted with *n*-butyl bisdiethylaminoboronite according to scheme (9). This distinguished the aminoboronite from a mixture of tri-*n*-butyl borate (1 mol.)

$$2Bu^nO\cdot B(NEt_2)_2 + 7HCl \longrightarrow (Bu^nO)_2B\cdot Cl + Et_2N\cdot BCl_2,HCl + 3Et_2NH,HCl \tag{9}$$

and trisdiethylaminoboron (2 mols.), the possible products of disproportionation. Such a mixture reacted according to scheme (5), the tri-*n*-butyl borate being recovered. *n*-Butyl bisdiethylaminoboronite was stable at 145—155° for 12 hr. Absence of disproportionation was confirmed by subjecting the pyrolysed specimen to the action of hydrogen chloride, whereupon reaction (9) occurred.

n-Butyl bisdiethylaminoboronite was readily hydrolysed by cold water [scheme (10)], whereas with butan-1-ol the diethylamine was displaced [scheme (11)]. Diethylamine was also displaced by di-*n*-butylamine [scheme (12)], but the *n*-butoxy-group was not replaceable by an amino-group. This was confirmed by demonstrating absence of reaction between di-*n*-butylamine and tri-*n*-butyl borate $[B(OBu^n)_3 + 3Bu^n{}_2NH \longrightarrow B(NBu^n{}_2)_3 + 3Bu^nOH]$, despite the lower boiling point of butan-1-ol than of di-*n*-butylamine. Likewise, there was no reaction between tri-*n*-butyl borate and diethylamine.

$$Bu^nO\cdot B(NEt_2)_2 + 3H_2O \longrightarrow B(OH)_3 + 2Et_2NH + Bu^nOH \tag{10}$$

$$Bu^nO\cdot B(NEt_2)_2 + 2Bu^nOH \longrightarrow B(OBu^n)_3 + 2Et_2NH \tag{11}$$

$$Bu^nO\cdot B(NEt_2)_2 + 2Bu^n{}_2NH \longrightarrow Bu^nO\cdot B(NBu^n{}_2)_2 + 2Et_2NH \tag{12}$$

Like trialkyl borates,[10a] *n*-butyl bisdiethylaminoboronite failed to co-ordinate with pyridine. This was confirmed by cryoscopic examination of an equimolar mixture of pyridine and the aminoboronite. Failure to co-ordinate is due to the lowering of the electrophilic character of the boron atom in the aminoboronite, by the back-co-ordination from the adjacent nitrogen and oxygen atoms.

n-Butyl bisdiethylaminoboronite reacted with boron trichloride at −80° according to scheme (13). Separation of the products by distillation proved difficult, owing to the

$$Bu^nO\cdot B(NEt_2)_2 + 2BCl_3 \longrightarrow Bu^nO\cdot BCl_2 + 2Et_2N\cdot BCl_2 \tag{13}$$

proximity of boiling points. Reaction (13) was however established by passage of hydrogen chloride through the product and isolation of *n*-butyl dichloroboronite and the hydrochloride of diethylaminoboron dichloride and also by addition of a trace of ferric chloride (which is known to cause decomposition of the dichloroboronite [10b]) and isolation of diethylaminoboron dichloride.

Boron trifluoride reacted with *n*-butyl bisdiethylaminoboronite by a scheme analogous to (13). Separation of the two fluorides again proved difficult, but the reaction was established by infrared spectroscopy.

EXPERIMENTAL

Preparation and Techniques.—*n*-Butyl dichloroboronite was prepared from tri-*n*-butyl borate by Gerrard and Lappert's method; [10b] tri-*n*-butyl borate was obtained by Johnson and Tompkins's procedure; [11] and *n*-butyl difluoroboronite by Lappert's method.[13]

Molecular weights were determined cryoscopically in *cyclo*hexane, in an apparatus adapted for anhydrous operation.[14] Nitrogen was determined by the Kjeldahl method, boron by Thomas's method,[15] and chlorine by Volhard titration.

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[10] (*a*) Colclough, Gerrard, and Lappert, *J.*, 1955, 907; (*b*) Gerrard and Lappert, *ibid.*, p. 3084.

[11] Johnson and Tompkins, *Org. Synth.*, 1933, **13**, 16.

[12] Gerrard and Lappert, *J.*, 1951, 2545.

[13] Lappert, *J.*, 1955, 784.

[14] Brindley, Gerrard, and Lappert, *J.*, 1956, 824.

[15] Thomas, *ibid.*, 1946, 820.

Preparation of n-*Butyl Bisdiethylaminoboronite.*—*Reaction* (1). *n*-Butyl dichloroboronite (18·4 g., 1 mol.) in *n*-pentane (25 ml.) was added dropwise to a solution of diethylamine (34·70 g., 4 mols.) in *n*-pentane (250 ml.) at −10°. The mixture was set aside for 48 hr. at 20°, whereafter the white precipitate (29·0 g.) Calc. for $C_4H_{12}NCl$, 26·0 g.), mainly diethylammonium chloride (Found: N, 12·1; Cl, 29·1. Calc. for $C_4H_{12}NCl$: N, 12·8; Cl, 32·4%), was filtered off and washed with *n*-pentane. The combined filtrate and washings were freed from *n*-pentane by evacuation. Distillation of the remainder gave n-*butyl bisdiethylaminoboronite* (20·86 g., 77%), b. p. 68—68·5°/0·3 mm., n_D^{20} 1·4348, d_4^{20} 0·8419 (Found: C, 63·0; H, 12·7; N, 12·4; B, 4·7%; *M*, 210. $C_{12}H_{29}ON_2B$ requires C, 63·1; H, 12·8; N, 12·3; B, 4·75%; *M*, 228).

Reaction (2). Butan-1-ol (1·03 g., 1 mol.), added to trisdiethylaminoboron (3·03 g., 1 mol.) at −20°, afforded diethylamine (0·63 g., 62%), b. p. 54°, n_D^{20} 1·3865, and *n*-butyl bisdiethylaminoboronite (2·31 g., 76%), b. p. 57—62°/0·4 mm., n_D^{20} 1·4358 (Found: N, 12·3; B, 4·76%).

Reaction (3). Bisdiethylaminoboron chloride (3·65 g., 1 mol.) in *n*-pentane (25 ml.) was added dropwise to butan-1-ol (1·42 g., 1 mol.) and triethylamine (1·92 g., 1 mol.) in *n*-pentane (100 ml.) at 18°. The white precipitate of impure triethylammonium chloride (2·92 g. Calc. for $C_6H_{16}NCl$, 2·64 g.), m. p. 214—245°, was filtered off and the filtrate was freed from *n*-pentane at low pressure. The residue afforded *n*-butyl bisdiethylaminoboronite (2·94 g., 67%), b. p. 52—55°/0·3 mm., n_D^{20} 1·4345 (Found: N, 12·1; B, 4·69%).

Preparation of n-*Butyl Bisdi*-n-*butylaminoboronite.*—*n*-Butyl dichloroboronite (5·25 g., 1 mol.) in *n*-pentane (25 ml.) was added dropwise to di-*n*-butylamine (17·48 g., 4 mols.) in *n*-pentane (150 ml.) at −2°. A precipitate, mainly di-*n*-butylammonium chloride (12·73 g. Calc. for $C_8H_{20}NCl$, 11·23 g.) (Found: Cl, 19·7. Calc. for $C_8H_{20}NCl$: Cl, 21·4%), was filtered off and washed with pentane, and the combined filtrate and washings were freed from solvent at low pressure. Distillation of the residue afforded foreruns consisting mainly of crude *n*-butyl bisdi-*n*-butylaminoboronite: (1) 1·46 g., b. p. 116—118°/0·1 mm., n_D^{20} 1·4406 (Found: N, 6·6%); (2) 2·49 g., b. p. 118—123°/0·1 mm., n_D^{20} 1·4446 (Found: N, 7·5%); and (3) pure n-*butyl bisdi*-n-*butylaminoboronite* (2·90 g., 25%), b. p. 124—131°/0·1 mm., n_D^{20} 1·4470 (Found: C, 70·6; H, 13·3; N, 8·1; B, 3·2. $C_{20}H_{45}ON_2B$ requires C, 70·6; H, 13·3; N, 8·2; B, 3·2%).

Preparation of Trisdiethylaminoboron. Reaction (4).—Boron trichloride (4·85 g., 1 mol.) at −40°, in *n*-pentane (25 ml.), was added dropwise to diethylamine (18·60 g., 6 mols.) in *n*-pentane (100 ml.) at −80°. The white precipitate (13·82 g. Calc. for $C_4H_{12}NCl$, 13·60 g.) consisting mainly of diethylammonium chloride (Found: N, 12·4; Cl, 30·5%) was filtered off and washed with *n*-pentane, and the combined filtrate and washings were freed from solvent at low pressure. Distillation of the residue afforded colourless *trisdiethylaminoboron* (3·59 g., 38%), b. p. 50—53°/0·4 mm., n_D^{20} 1·4450, d_4^{20} 0·826 (Found: C, 63·4; H, 13·1; N, 18·0; B, 5·1. $C_{12}H_{30}N_3B$ requires C, 63·5; H, 13·2; N, 18·5; B, 4·8%). Owing to repeated fractionation the yield was low; the crude product (6·65 g., 71%) had n_D^{20} 1·4448 (Found: N, 17·9; B, 4·98%).

Trisdiethylaminoboron was not obtained when a mixture of diethylamine (25·48 g., 7 mols.), boric acid (3·1 g., 1 mol.), and toluene (50 ml.) was carefully fractionated. Diethylamine (20·50 g.), b. p. 55—56°, was recovered.

Preparation of Trisdi-n-*butylaminoboron. Reaction* (4).—Boron trichloride (4·83 g., 1 mol.) at −40° in *n*-pentane (20 ml.) was added dropwise to di-*n*-butylamine (31·8 g., 6 mols.) in *n*-pentane (100 ml.) at −4°. The white precipitate, mainly di-*n*-butylammonium chloride (23·89 g. Calc. for $C_8H_{20}NCl$, 20·4 g.) (Found: Cl, 18·2. Calc. for $C_8H_{20}NCl$: Cl, 21·4%), was filtered off and the filtrate, freed from pentane, gave *trisdi*-n-*butylaminoboron* (10·00 g., 62%), b. p. 136—142°/0·1 mm., n_D^{22} 1·4578, d_4^{20} 0·8399 (Found: C, 73·0; H, 13·8; N, 10·6. $C_{24}H_{54}N_3B$ requires C, 72·9; H, 13·8; N, 10·6%).

Action of Hydrogen Chloride on Trisdiethylaminoboron. Reaction (5).—Hydrogen chloride was passed into a solution of trisdiethylaminoboron (1·33 g.) in *n*-pentane (50 ml.) at 20° for 40 min. The white precipitate (2·55 g.; *i.e.*, HCl absorbed, 5·7 mols.) appeared to be a 2 : 1 mixture of diethylammonium chloride and the 1 : 1 complex of diethylaminoboron dichloride and hydrogen chloride (Found: N, 10·5; Cl, 41·6. Calc. for $C_4H_{11}NCl_3B + 2C_4H_{12}NCl$: N, 10·3; Cl, 43·5%). A portion (0·65 g.) was extracted with ether (3 × 25 ml.) at 30°, leaving an ether-insoluble residue (0·34 g., 98%) of diethylammonium chloride, m. p. 219—221° (Found: N, 12·9; Cl, 33·5%), whereas the ethereal solution afforded solid diethylaminoboron dichloride hydrochloride (0·28 g., 93%), m. p. 125—129° (Found: N, 6·6; Cl, 54·0. Calc. for $C_4H_{11}NCl_3B$: N, 7·35; Cl, 56·0%).

Preparation of Bisdiethylaminoboron Chloride. Reaction (6).—Boron trichloride (2·54 g., 1 mol.) at $-80°$ was added to trisdiethylaminoboron (9·85 g., 2 mols.) at $-80°$. Repeated distillation of the mixture afforded *bisdiethylaminoboron chloride* (4·47 g., 36%), b. p. 83—87°/16 mm., n_D^{20} 1·4549 (Found: N, 14·7; Cl, 19·4. $C_8H_{20}N_2ClB$ requires N, 14·7; Cl, 18·7%). The yield of pure compound was low because of losses in purification.

Preparation of Triethylamine–Boron Trichloride. Reaction (7).—Boron trichloride (7·76 g., 1 mol.), in *n*-pentane (25 ml.) at $-40°$, was added dropwise to triethylamine (6·68 g., 1 mol.) in *n*-pentane (100 ml.) at $-80°$, and the mixture was allowed to warm to 20°. The white precipitate (14·16 g., 99%), m. p. 81—88°, was filtered off, freed from solvent, and washed three times with cold water. Recrystallisation of the remaining precipitate from dilute ethanol afforded pure *triethylamine–boron trichloride*, m. p. 92—93·5° (Found: C, 33·4; H, 7·01; N, 6·8; Cl, 48·1. $C_6H_{15}NCl_3B$ requires C, 33·0; H, 6·91; N, 6·4; Cl, 48·8%).

Electrical Conductivities of Complexes.—Electrical conductivities were determined by using a dip-cell with platinum electrodes, with dilute (0·4%) solutions in nitrobenzene of the triethylamine–boron trichloride complex and the 1 : 1-complex of diethylaminoboron dichloride and hydrogen chloride. The molar conductivities [λ_M (18·5°), ohm^{-1} cm.$^{-2}$] were 0·196 for the triethylamine complex and 0·332 for the diethylamine complex.

Preparation of Diethylaminoboron Difluoride. Reaction (8).—Boron trifluoride was passed into trisdiethylaminoboron (4·61 g.) at 28°, until saturated, heat being evolved. The increase in weight was 2·66 g. (1·93 mols.). The product was *diethylaminoboron difluoride*, m. p. 65·5° (Found: C, 39·2; H, 9·0; N, 11·3. $C_4H_{10}NF_2B$ requires C, 39·7; H, 9·3; N, 11·6%). The resublimed material was used for spectroscopic examination.

Action of Hydrogen Chloride on n-*Butyl Bisdiethylaminoboronite. Reaction* (10).—Dry hydrogen chloride was passed into a solution of *n*-butyl bisdiethylaminoboronite (1·35 g.) in *n*-pentane (50 ml.) at 20° for 25 min. The white precipitate (1·57 g.) was filtered off, washed with *n*-pentane, and freed from solvent at low pressure. It had m. p. 170—200° (Found: N, 10·4; Cl, 39·4; B, 2·1. Calc. for $C_4H_{11}NCl_3B + 3C_4H_{12}NCl$: N, 10·8; Cl, 41·0; B, 2·0%). A portion (0·25 g.) of the precipitate was extracted with ether (3 × 30 ml.) at 30°; the ether-insoluble residue (0·15 g., 95%) was diethylammonium chloride, m. p. 220—224° (Found: Cl, 32·8%). The ethereal solution gave diethylaminoboron dichloride hydrochloride (0·05 g., 55%), m. p. 109° (Found: Cl, 54·6%), which on recrystallisation from chloroform had m. p. 132—136°. The combined *n*-pentane filtrate and washings were freed from solvent at low pressure, to afford di-*n*-butyl chloroboronate (0·55 g.), n_D^{21} 1·4132 (Found: Cl, 17·7; B, 5·9. Calc. for $C_8H_{18}O_2ClB$: Cl, 18·4; B, 5·6%).

*Action of Hydrogen Chloride on a Mixture of Tri-*n*-butyl Borate and Trisdiethylaminoboron.*—Tri-*n*-butyl borate (0·81 g.) and trisdiethylaminoboron (0·69 g.) were dissolved in *n*-pentane (30 ml.), and hydrogen chloride was passed into the solution for 20 min. The white precipitate (1·23 g.) (Found: Cl, 41·4. Calc. for $C_4H_{11}NCl_3B + 2C_4H_{12}NCl$: Cl, 43·4%) was filtered off and washed with *n*-pentane, and the combined filtrate and washings were freed from solvent at low pressure, to afford tri-*n*-butyl borate (0·795 g., 98%), n_D^{20} 1·4100 (Found: B, 4·79. Calc. for $C_{12}H_{27}O_3B$: B, 4·71%).

Pyrolysis of n-*Butyl Bisdiethylaminoboronite.*—*n*-Butyl bisdiethylaminoboronite was heated at 145—155° for 12·25 hr. Samples, taken at 0, 7·5, and 12·25 hr. intervals, were dissolved in *n*-pentane. Hydrogen chloride was passed into each solution, the white precipitate was filtered off, the filtrate freed from solvent at low pressure and the residue was analysed for chlorine. The results are shown in the Table (Calc. for $C_8H_{18}O_2ClB$: Cl, 18·4%; n_D^{20} 1·4132 [12]). They indicate that no significant disproportionation had occurred.

Time (hr.) at 145—155°	0	7·5	12·25
Cl (%) in pentane-free filtrate	17·7	18·8	17·4
n_D^{20} of pentane-free filtrate	1·4130	1·4150	1·4150

Properties of n-*Butyl Bisdiethylaminoboronite.*—*Hydrolysis* [*Reaction* (10)]. Water (0·27 g., 3 mols.) was added to a solution of *n*-butyl bisdiethylaminoboronite (1·15 g., 1 mol.) in *n*-pentane (50 ml.), and the mixture was shaken. The precipitate of impure boric acid (0·32 g.) (Found: B, 13·0; N, 6·3. Calc. for H_3O_3B: B, 17·5%) was filtered off and washed with pentane. Dry hydrogen chloride was passed into the combined filtrate and washings, precipitating the diethylamine present as the hydrochloride (0·94 g., 85%), m. p. 224° (Found: Cl, 31·0%), which was filtered off and washed with pentane. The combined filtrate and washings were freed from solvent at low pressure, leaving butan-1-ol (0·21 g., 68%), $n_D^{22.5}$ 1·4070.

Alcoholysis [*Reaction* (11)]. Butan-1-ol (4·22 g., 2 mols.) was added to *n*-butyl bisdiethylaminoboronite (6·46 g., 1 mol.), some heat of mixing being observed. On distillation, diethylamine (3·62 g., 87%), b. p. 55°, n_{D}^{20} 1·3861 (Found : N, 19·0. Calc. for $C_4H_{11}N$: N, 19·2%), and tri-*n*-butyl borate (6·04 g., 92·5%), b. p. 99°/8 mm., $n_{\mathrm{D}}^{25\cdot5}$ 1·4073 (Found : B, 4·69. Calc. for $C_{12}H_{27}O_3B$: B, 4·71%), were obtained.

Aminolysis [*Reaction* (12)]. Di-*n*-butylamine (2·84 g., 2 mols.) was added to *n*-butyl bisdiethylaminoboronite (2·45 g., 1 mol.) at 20°. Distillation of the mixture afforded diethylamine (0·73 g., 47%) and a fraction (2·65 g.), b. p. 90—122°/0·1 mm., which, on redistillation to eliminate the more volatile materials, left an undistilled residue of *n*-butyl bisdi-*n*-butylaminoboronite (1·36 g., 37%), n_{D}^{20} 1·4455 (Found : N, 8·25; B, 3·43%). The low yields are mainly due to necessity for repeated fractionation.

Lack of Reaction with Pyridine.—Pyridine (0·116 g., 1 mol.) was added to butyl bisdiethylaminoboronite (0·329 g., 1 mol.) at 20° and the depression of freezing point of a solution of this mixture in *cyclo*hexane was determined (Found : *M*, 150. Calc. for mixture $C_5H_5N + C_{12}H_{29}ON_2B$ with no molecular association : *M*, 153).

Reaction (13) *with Boron Trichloride.*—Boron trichloride (3·91 g., 2·05 mols.) at −80° was added to *n*-butyl bisdiethylaminoboronite (3·70 g., 1 mol.) at −80° and the mixture was allowed to warm to 18°. The excess of boron trichloride was removed by evacuation. The liquid residue was divided into two portions. One portion (2·39 g.) was dissolved in *n*-pentane (100 ml.), and hydrogen chloride was passed into it for 30 min. The white precipitate of diethylaminoboron dichloride hydrochloride (1·91 g., 97%), m. p. 132—134° (m. p. after recrystallisation from chloroform 140°) (Found : C, 25·5; H, 5·8; N, 7·3; Cl, 55·9; B, 6·1. Calc. for $C_4H_{11}NCl_3B$: C, 25·2; H, 5·8; N, 7·4; Cl, 56·0; B, 5·7%), was filtered off and washed with pentane, and the combined filtrate and washings were freed from solvent by evacuation, leaving impure *n*-butyl dichloroboronite (0·44 g., 82%), n_{D}^{20} 1·4153 (Found : Cl, 41·6; B, 7·1. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%).

To the second portion (4·85 g.) of the reaction product, anhydrous ferric chloride (0·12 g.) was added and the mixture was set aside for 4 hr. On distillation of the resulting mixture diethylaminoboron dichloride (2·18 g., 68%) was collected, n_{D}^{25} 1·4350 (Found : Cl, 45·2; N, 8·6; B, 7·1. Calc. for $C_4H_{10}Cl_2NB$: Cl, 46·1; N, 9·1; B, 7·0%).

Reaction with Boron Trifluoride.—Boron trifluoride was bubbled into *n*-butyl bisdiethylaminoboronite (2·23 g.), with evolution of heat, until no more gas was absorbed. The increase in weight was 1·38 g. (Calc. for BF_3, 2 mols. : 1·33 g.). The excess of boron trifluoride was removed under a vacuum, the remainder (3·48 g.) was dissolved in *n*-pentane, and the composition of the mixture determined spectroscopically, by using also solutions of authentic specimens of *n*-butyl difluoroboronite and diethylaminoboron difluoride in *n*-pentane at various concentrations and measuring the intensity of the infrared absorption band at 9·85 μ. The results indicated that the mixture comprised diethylaminoboron difluoride 62·6% (Calc., 66·5%) and *n*-butyl difluoroboronite 37·4% (Calc. 33·5%).

Lack of Reaction between Amines and Tri-n-*butyl Borate.*—*Diethylamine.* Diethylamine (2·89 g., 2 mols.) and tri-*n*-butyl borate (4·51 g., 1 mol.) were mixed at 20° and the mixture was distilled. Unchanged diethylamine (2·71 g., 94%), b. p. 55°, n_{D}^{21} 1·3862, and tri-*n*-butyl borate (3·9 g., 86%), b. p. 111—113°/15 mm., n_{D}^{21} 1·4098 (Found : B, 4·66%), were recovered.

Di-n-*butylamine.* The butylamine (9·55 g., 3·01 mols.) was added to tri-*n*-butyl borate (5·66 g., 1 mol.) at 20° and the mixture was distilled. Di-*n*-butylamine (8·78 g., 92%), b. p. 150—162°, $n_{\mathrm{D}}^{22\cdot5}$ 1·4179, and tri-*n*-butyl borate (3·77 g., 67%), b. p. 110—113°/15 mm., $n_{\mathrm{D}}^{22\cdot5}$ 1·4093 (Found : B, 4·62%), were recovered.

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