995. *Chemistry related to Borazole. Part II.*[1] *The Reaction of Secondary Amines with Boron Trichloride.*

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The interaction of diethyl- and diphenyl-amine with boron trichloride gives the corresponding tetrachloroborate $[R_2NH_2]^+[BCl_4]^-$ and the amino-boron dichloride R_2NBCl_2 ($R = Et$ or Ph). Other secondary amines (R'_2NH where $R' = Me, Pr^n, Pr^i, Bu^n$) afford essentially the 1 : 1 complex, the structures of which are considered.

EARLIER workers [2] have shown that addition of boron trichloride to secondary aliphatic amines results in the stepwise amination of boron with the elimination of hydrogen chloride as the dialkylammonium chloride. Trisdialkylaminoborons have recently been prepared in this way.[3]

It has now been found that the products obtained on addition of the amine to boron trichloride depend upon the nature of the substituents. We have stated [4] that diethylamine yields diethylammonium tetrachloroborate in about 90% yield in both methylene dichloride and benzene, but in n-pentane the yield falls to 50—60%. The other main product is diethylaminoboron dichloride; small amounts of the 1 : 1 complex are also formed. Similarly, diphenylamine forms the diphenylammonium tetrachloroborate, but in smaller amounts (76% yield), and both the 1 : 1 complex [1] and diphenylaminoboron dichloride, whereas previously only the 1 : 1 complex Ph_2NH,BCl_3 was reported.[5] The direct formation of substituted ammonium tetrachloroborates has been observed with primary aliphatic amines [6] and *m*-toluidine.[1]

$$2Et_2NH + 2BCl_3 \longrightarrow [Et_2NH_2]^+[BCl_4]^- + Et_2N\cdot BCl_2 \quad . \; . \; . \; . \; . \; . \quad (1)$$

The formation of the tetrachloroborate cannot be explained by disproportionation of the 1 : 1 complex (2), which is stable. If, however, another molecule of amine reacts with the complex, as in (3), then nucleophilic attack of the chloride ion on the boron trichloride could result in the formation of the dialkylammonium tetrachloroborate in accord with certain observations.[7,8] Halide ions behave as ligands in highly ionising solvents and co-ordinate with boron halides to afford tetrachloroborates and mixed halogenochloroborates,[9] and this would explain the higher yield of diethylammonium tetrachloroborate obtained in methylene dichloride or benzene, in which diethylammonium chloride is soluble, as compared to the poor yield from n-pentane in which it is insoluble. The poorer yields of tetrachloroborates from other secondary amines are difficult to understand.

$$2R_2NH,BCl_3 \longrightarrow [R_2NH_2]^+[BCl_4]^- + R_2N\cdot BCl_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$R_2NH,BCl_3 \xrightarrow[\text{by } R_2NH]{-HCl} R_2N\cdot BCl_2 + [R_2NH_2]^+Cl^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Diethylammonium tetrachloroborate decomposes when heated. At 80° (in boiling benzene) 1 mol. of hydrogen chloride is evolved, with formation of the 1 : 1 complex in high yield. The complex contains an NH group, yet, unlike the alkylaminoboron dichlorides, which decompose [1] in benzene to afford the tri-*B*-chlorotri-*N*-alkylborazole, it does not decompose in benzene. In boiling tolune (110°), however, decomposition (40%)

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[1] Part I, Gerrard and Mooney, *J.*, 1960, 4028.

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

[3] Gerrard, Lappert, and Pearce, *J.*, 1957, 381.

[4] Gerrard, Hudson, and Mooney, *Chem. and Ind.*, 1959, 432.

[5] Becher, *Z. anorg. Chem.*, 1957, **289**, 262.

[6] Gerrard and Mooney, *Chem. and Ind.*, 1958, 1259.

[7] Lappert, *Proc. Chem. Soc.*, 1958, 121.

[8] Kynaston and Turner, *Proc. Chem. Soc.*, 1959, 304.

[9] Waddington and Klanberg, *Naturwiss.*, 1959, **46**, 578.

occurs, with formation of diethylaminoboron dichloride and hydrogen chloride. This behaviour could be explained by the existence of two forms of the 1 : 1 complex, the covalent form [3,11] (I) obtained from the toluene solution being more stable than the ionic form [10] (II). Infrared examination of the 1 : 1 complex obtained from benzene solution shows it to be a mixture of covalent and ionic forms, while that obtained from toluene solution is of the covalent form (I).

$$\underset{(R = Me\ or\ Et)}{R_2N{\cdot}BCl_2} \xrightarrow{HCl} \underset{(I)}{R_2NH,BCl_3} \text{ or } \underset{(II)}{[R_2NH{\cdot}BCl_2]^+Cl^-}$$

Triethylamine has been used [12] as a dehydrohalogenating agent for the preparation of tri-*B*-chloroborazole derivatives from monoalkylammonium tetrachloroborates; its application to the conversion of diethylammonium tetrachloroborate into diethylaminoboron dichloride leads to difficultly separable products. Diethylaminoboron dichloride could not be quantitatively recovered even on heating at 90°/0·1 mm., indicating a possible association between the dichloride and the triethylammonium chloride produced. Similarly, the separation of diethylaminoboron dichloride and diethylamine–boron trichloride (formed as a by-product in the reaction of diethylamine and boron trichloride) proved difficult, and again association is indicated.

Structure of Secondary Amine Complexes.—Two forms of the diethylamine–boron trichloride complex have been identified, but only the covalent form (I; R = Et) has been isolated pure, and shows the normal NH stretching band at 3165 cm.$^{-1}$ and weak NH deformation band at 1595 cm.$^{-1}$; in addition, there are three maxima (at 782, 740, 717 cm.$^{-1}$) of the B–Cl stretching modes which form an overall strong absorption band commencing at 820 cm.$^{-1}$, which we believe to be diagnostic of the partially tetrahedral BCl_3 group in co-ordination complexes. Di-n-propylamine and di-n-butylamine with boron trichloride afford covalent complexes (I; R = Pr^n or Bu^n) which have similar spectral features: NH stretching band at 3165 cm.$^{-1}$, weak NH deformation band at 1575 for Pr^n and 1585 cm.$^{-1}$ for Bu^n, and similar absorption envelopes commencing at 815 cm.$^{-1}$ with maxima at 787, 754, and 725 for Pr^n, and 786, 749, and 717 cm.$^{-1}$ for Bu^n.

Dimethylamine afforded an ionic complex (II; R = Me) with a series of bands at 2755, 2600, and 2463 cm.$^{-1}$, which are characteristic of the NH^+ stretching bands as found in tertiary amine hydrochlorides, and a band at 905 cm.$^{-1}$ which is characteristic of the BCl_2 group.[13] The band does not occur at lower frequency, as found in the alkylaminoboron dichlorides,[1] because the nitrogen cannot increase the electron density of the boron atom, for the lone-pair of nitrogen is utilised in the formation of the ionic complex. However, the second type of complex showed both covalent and ionic NH stretching bands, and a similar observation was made for the complex from di-isopropylamine; recrystallisation did not affect the nature of the complexes. Both showed bands (Me, 893 cm.$^{-1}$, Pr^i, 943 cm.$^{-1}$) which suggested the presence of a BCl_2 group, and absorption envelopes which are characteristic of the tetrahedral tetrachloroborate ion. These facts conform with structure (III).

$$\underset{(III)}{[(R_2NH)_2BCl_2]^+[BCl_4]^-} \qquad \underset{(IV)}{[(H_3N)_2BH_2]^+[BH_4]^-}$$

A similar structure has been suggested for the pyridine–boron trichloride complex,[14] and there is formal resemblance with the suggested structure of diammonia–diborane (IV).[15]

Infrared Spectra of Disubstituted Ammonium Tetrachloroborates.—The infrared spectra of diethylammonium tetrachloroborate prepared by direct interaction of the amine and

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[10] Brown and Osthoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2340.

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

[12] Gerrard and Mooney, unpublished work.

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

[14] Greenwood and Wade, *J.*, 1958, 1663; 1960, 1134.

[15] Parry *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 1—24.

boron trichloride and from diethylammonium chloride and boron trichloride were essentially similar; the di-isopropylammonium tetrachloroborate was also prepared from di-isopropylammonium chloride. Both these tetrachloroborates showed similar spectra, an NH stretching band (Et, 3155; Pr^i, 3145 cm.$^{-1}$) and stretching and deformation bands due to the NH_2^+ group were also present (Et, 2762, 2457, 2326, 1567; Pr^i, 2740, 2469, 2370, 1575 cm.$^{-1}$), and both showed the characteristic absorption envelope commencing at 780 cm.$^{-1}$; these envelopes show usually two or three absorption maxima (Et, 762, 738, 676; Pr^i, 755, 735, 645 cm.$^{-1}$). The diphenylammonium tetrachloroborate does not show a distinct NH stretching band, but only a shoulder at 3135 cm.$^{-1}$, due to overlap with the CH aromatic stretching vibrations; but there are a series of bands at 2667, 2469, 2353, and 2309 cm.$^{-1}$ characteristic of the NH_2^+ stretching frequencies, and a band (1563 cm.$^{-1}$) characteristic of the NH_2^+ deformation mode. The BCl_4 absorption envelope also commences at 781 cm.$^{-1}$, showing two maxima at 735 and 690 cm.$^{-1}$.

The NH stretching bands which have been observed in the disubstituted ammonium ions ($R_2NH_2^+$; R = Et, Pr^i, Ph) occur at higher frequency than in the corresponding disubstituted ammonium chlorides. Similar occurrences of NH stretching bands at higher frequency have been observed[8] in the mono- and tri-methylammonium tetrachloroborates.

Infrared Spectra of Dialkylaminoboron Dichlorides.—Assignments have previously been made for the B–N bond in aminoboron dichlorides (R = Me, 1526 cm.$^{-1}$; R = Et, 1505 cm.$^{-1}$; R = Ph, 1378 cm.$^{-1}$; refs. 11, 16, and 5 respectively), and the assignments for the dichlorides (R = Et, 1499 cm.$^{-1}$; R = Ph, 1383 cm.$^{-1}$) have been confirmed; the assignment for the isopropyl compound (1486 cm.$^{-1}$) has now been made, which supports the expected correlation of increasing B=N character with the increasing electron-releasing propensity of the substituent alkyl groups (Me < Et < Pr^i) and is further supported by the considerable double-bonded character of the B–N bond with the *B*-phenyl substituent. The following assignments have also been made for the B–Cl stretching modes: R = Et, 888 cm.$^{-1}$; R = Pr^i, 896 cm.$^{-1}$; R = Ph, 969 cm.$^{-1}$.

EXPERIMENTAL

General Procedures.—Chloride analyses were carried out potentiometrically; except where designated Cl*, chlorine was easily hydrolysed. Amine was added dropwise in a solvent to the boron trichloride in the same solvent (total volume stated) at −80°, stirring or shaking being maintained. The mixture was filtered at room temperature, the filtrate being evaporated under reduced pressure to afford a residue; meanwhile volatile matter was trapped at −80°. In the Table, results for the amine–boron trichloride systems are given.

Decomposition of Diethylammonium Tetrachloroborate.—The compound (8·4 g., 1·0 mol.) was heated (46·5 hr.) in boiling benzene (100 ml.), evolution of hydrogen chloride (1:0 mol.) then having ceased. An insoluble residue (0·1 g.) was filtered off, and the solution afforded pale brown, crystalline diethylamine–boron trichloride (6·1 g., 86% yield) (Found: B, 5·9; Cl, 54·1*; N, 7·4. Calc. for $C_4H_{11}BCl_3N$: B, 5·7; Cl, 55·9; N, 7·4%).

Similarly, the tetrachloroborate (46·4 g., 1·0 mol.) was heated (79 hr.) in toluene under reflux, and hydrogen chloride (0·72 mol.) was evolved. On cooling, crystalline diethylamine–boron trichloride (9·6 g., 0·25 mol.), m. p. 139° (Found: B, 5·7; Cl, 55·6*; N, 7·4%), was filtered off. The filtrate afforded a crystalline residue (15·1 g.) of diethylamine–boron trichloride (0·36 mol.) and diethylaminoboron dichloride (0·05 mol.) (Found: B, 5·9; Cl, 55·3*; N, 7·7%). The residue (11·4 g.) was heated (5 hr.) at 110—120°/1 mm. to afford diethylaminoboron dichloride (4·6 g.) (Found: B, 7·1; Cl, 45·8; N, 8·9%), a crystalline sublimate (0·8 g.) (Found: B, 5·9%), and a dark brown residue (4·8 g.) (Found: B, 5·1%). The trap contents (−80°) gave toluene and mixtures of toluene and diethylaminoboron dichloride: (i) b. p. 112—113° (26·1 g.) (Found: Cl, 2·9%); (ii) b. p. 113—118° (10·6 g.) (Found: Cl, 5·7%); (iii) b. p. 118—144° (7·5 g.) (Found: Cl, 18·5%); (iv) a brown solid residue (1·4 g.) (Found: Cl, 41·7%).

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[16] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 3561.

Amine (1 *mol.*) *added to boron trichloride* (1 *mol.*), *or* (2 *mol.*) *where indicated.*†

				Precipitate				Residue from filtrate				
		R_2NH			Found (%)				Found (%)			
Solvent	(c.c.)	R	(g.)	(g.)	B	Cl	N	(g.)	B	Cl	N	Note
CH_2Cl_2	(45)	Me	13·0	20·8 [1]	6·2	67·0 *	8·0	10·6 [2]	6·6	63·1 *	8·3	[3]
CH_2Cl_2	(100)	Et	34·3	49·1 [4]	4·8	62·0	6·2	19·3 [5]	5·8	50·9 *	8·2	[6]
C_6H_6	(70) [7]	Et	20·6	28·2	4·8	62·3	6·1	6·3	5·9	50·8 *	7·5	[8]
n-C_5H_{12}	(100)	Et	32·3 [9]	32·2	4·8	62·2	6·3	24·5 [10]	4·7	49·0 *	8·8	[11]
CH_2Cl_2	(50)	Pr^n	14·3	4·1 [12]	4·2	55·5 *	5·4	24·7 [13]	4·9	48·6 *	6·3	[14]
CH_2Cl_2	(50)	Pr^i	9·7	—	—	—	—	18·8 [15]	4·8	50·5 *	6·2	
CH_2Cl_2	(50)	Bu^n	16·9	—	—	—	—	32·1	4·3	42·2 *	5·5 [16]	
CH_2Cl_2	(50)	Ph	27·1	19·7	3·5	43·7	4·3 [17]	22·3	4·1	29·1 *	5·2 [18]	
CH_2Cl_2	(60)	Et †	23·9	—	—	—	—	22·0	1·0	34·4	11·8 [19]	[20]
n-C_5H_{12}	(100)	Et †	65·0	69·5	2·6	46·2	9·6	39·5	—	31·4	— [21]	

[1] A white crystalline mixture of dimethylamine–boron trichloride (1 : 1) complex (13·0 g.) and dimethylammonium tetrachloroborate (7·8 g.); recrystallisation from the same solvent gave the 1 : 1 complex (8·2 g.) (Found: B, 6·5; Cl, 64·9; N, 8·5. Calc. for $C_2H_7BCl_3N$: B, 6·7; Cl, 65·6*; N, 8·6%) which showed both covalent NH and ionic NH^+ bands. [2] The 1 : 1 complex. [3] Condensate (−80°) of $Me_2N{\cdot}BCl_2$ (1·15 g.) (Found: Cl, 56·3. Calc. for $C_2H_6BCl_2N$: Cl, 56·4%). [4] *Diethylammonium tetrachloroborate* ($C_4H_{12}BCl_4N$ requires B, 4·8; Cl, 62·5; N, 6·2%). [5] A mixture of diethylamine–boron trichloride and diethylaminoboron dichloride, which (13·3 g.) at 110—120°/3 mm. (4 hr.) gave the latter (3·5 g.) (Found: B, 7·1; Cl, 45·4; N, 9·1. Calc. for $C_4H_{10}BCl_2N$: B, 7·0; Cl, 46·1; N, 9·1%), condensed at −80°, and a sublimate (3·2 g.) of a mixture of this and the former (Found: B, 6·5; Cl, 51·6% *) together with a brown solid (4·2 g.) (B, 6·0%) from which no identified compounds could be extracted by benzene or methylene dichloride. [6] Condensate (−80°) gives $Et_2N{\cdot}BCl_2$ (17·4 g.), b. p. 143—147° (Found: B, 6·9; Cl, 45·4; N, 9·0%), and a semi-solid (4·7 g.) which on heating under reduced pressure gave more dichloride (2·9 g.), b. p. 48—49°/18 mm. (Found: B, 6·8; Cl, 46·1; N, 8·9%). [7] Reagents mixed at 0°. [8] The condensate (−80°) of $Et_2N{\cdot}BCl_2$ could not be entirely freed from solvent; best fraction (7·12 g.) had b. p. 144—148° (Found: B, 6·6; Cl, 44·7; N, 8·7%). [9] First precipitate weighed 59·3 g. Data refer to residue after extraction with methylene dichloride. [10] Brown solid from methylene dichloride. [11] The n-pentane filtrate gave $Et_2N{\cdot}BCl_2$, b. p. 140—147° (11·4 g.); it was difficult to separate n-pentane from the dichloride; best fraction had b. p. 144—147° (Found: B, 6·8; Cl, 45·2; N, 8·9%). [12] *Di-n-propylammonium tetrachloroborate,* m. p. 72—80° (decomp.) ($C_6H_{16}BCl_4N$ requires B, 4·3; Cl, 55·7; N, 5·5%). [13] *Di-n-propylamine–boron trichloride* (I; R = Pr^n) ($C_6H_{15}BCl_3N$ requires B, 5·0; Cl, 48·7 *; N, 6·4%), shown to be covalent. The infrared spectrum remained the same after recrystallisation from methylene dichloride. [14] $Pr_2N{\cdot}BCl_2$ (1·5 g.) (Found: B, 5·5; Cl, 40·6; N, 7·2. Calc. for $C_6H_{14}BCl_2N$: B, 6·0; Cl, 39·0; N, 7·7%), obtained in cold trap by drying filtrate residue at low pressure. [15] There was no precipitate at 15°. Evaporation of solvent gave *di-isopropylamine–boron trichloride* (III; R = Pr^i) recrystallised from the solvent (Found: B, 5·1; Cl, 48·2 *; N, 6·4). [16] *Di-n-butylamine–boron trichloride* (I; R = Bu^n) ($C_8H_{19}BCl_3N$ requires B, 4·4; Cl, 43·2 *; N, 5·7%). [17] *Diphenylammonium tetrachloroborate* ($C_{12}H_{12}BCl_4N$ requires B, 3·4; Cl, 43·9; N, 4·3%). Filtrate later afforded 2·3 g. more. [18] This residue (20·9 g.) was heated in benzene (50 c.c.) until evolution of hydrogen chloride ceased (15 hr.); the new filtrate residue (19·2 g.) (Found: Cl, 26·3%) could not be improved by recrystallisation from methylene chloride or n-pentane; but distillation afforded diphenylaminoboron dichloride (6·6 g.) (Found: B, 4·4; Cl, 28·2; N, 5·4. Calc. for $C_{12}H_{10}BCl_2N$: B, 4·3; Cl, 28·4; N, 5·6%), b. p. 172°/18 mm., m. p. 65—68°, as yellow crystals, a more aminated product (1·25 g.), b. p. >170°/0·8 mm. (Found: B, 4·1; Cl, 18·6 *; N, 6·3%), and a brittle solid (1·8 g.) (Found: B, 4·0; Cl, 2·2 *; N, 6·6%). [19] No precipitate from solvent; residue was a mixture of diethylamine–boron trichloride (20%) and diethylammonium chloride (80%), which on two crystallisations from methylene chloride gave the latter (13·5 g.) (Found: Cl, 31·3; N, 12·2%), from which (12·9 g.) a crop of the chloride (3·0 g.), m. p. 228—233° (Found: Cl, 32·0; N, 12·3. Calc. for $C_4H_{12}ClN$: Cl, 32·4; N, 12·8%), was obtained by heating under reflux with the solvent. [20] The condensate (−80°) (14·8 g.) contained $Et_2N{\cdot}BCl_2$, b. p. 130—140° (Found: B, 6·9; Cl, 44·6; N, 8·8%), and gave the dichloride (9·8 g.), b. p. 144—145° (Found: Cl, 46·1; N, 9·1%), and a brown residue (2·8 g.) (Found: B, 6·2; Cl, 43·4 *; N, 10·1%). [21] A yellow liquid mixture of diethylaminoboron dichloride, bis(diethylamino)boron chloride, and tris(diethylamino)boron, which defined attempts at separation.

Again the difficulty of separating diethylaminoboron dichloride from solvents is clearly demonstrated.

Similarly, the tetrachloroborate (33·8 g., 1·0 mol.) was heated (5 hr.) in chloroform under reflux. A small amount of hydrogen chloride (0·1 g.) was evolved, and filtration gave a high recovery of the insoluble tetrachloroborate (31·4 g.) (Found: Cl, 62·6%). The filtrate afforded essentially diethylamine-boron trichloride (2·0 g.) (Found: Cl, 51·8%*).

Decomposition of Diphenylammonium Tetrachloroborate in Benzene.—The compound (15·1 g., 1·0 mol.) was heated in benzene under reflux, and after evolution of hydrogen chloride had ceased (1·93 mol. in 15·75 hr.), the solution was filtered from a trace of insoluble matter. The filtrate afforded impure diphenylaminoboron dichloride (12·1 g.) (Found: B, 4·0; Cl, 22·1;

N, 5·5%), of which 9·9 g. gave the dichloride (5·5 g., 58% yield), b. p. 109—112°/0·1 mm. (Found: B, 4·3; Cl, 28·1; N, 5·5%).

Preparation of Diethylammonium Tetrachloroborate from Diethylammonium Chloride.—Boron trichloride (6·6 g., 1·5 mol.) in dry methylene dichloride (25 ml.) at −80° was added (5 min.) to a suspension of diethylammonium chloride (4·5 g., 1·0 mol.) in the same solvent (25 ml.) also at −80°. The mixture was filtered at 15° to afford the white, insoluble diethylammonium tetrachloroborate (8·7 g., 93% yield) (Found: C, 22·8; H, 5·5; B, 5·0; Cl, 61·6; N, 6·2. Calc. for $C_4H_{12}BNCl_4$: C, 21·2; H, 5·3; B, 4·8; Cl, 62·5; N, 6·2%).

Preparation of Di-isopropylammonium Tetrachloroborate from Di-isopropylammonium Chloride.—Boron trichloride (7·0 g., 1·4 mol.) in dry methylene dichloride (10 ml.) was added at −80° to a suspension of di-isopropylammonium chloride (5·8 g., 1·0 mol.) in the same solvent (25 ml.) at −80°. At 15° a clear solution resulted which, on removal of excess of boron trichloride and solvent, gave white, crystalline *di-isopropylammonium tetrachloroborate* (10·4 g., 97% yield) (Found: C, 29·8; H, 6·6; B, 4·4; Cl, 55·6; N, 5·5. $C_6H_{16}BCl_4N$ requires C, 28·3; H, 6·3; B, 4·3; Cl, 55·7; N, 5·5%).

Reaction between Diethylammonium Tetrachloroborate and Triethylamine.—Triethylamine (31·7 g., 2·0 mol.) in benzene (100 ml.), added to diethylammonium tetrachloroborate (35·5 g., 1·0 mol.) suspended in the same solvent (100 ml.), afforded the insoluble triethylammonium chloride (34·1 g., 81% yield) (Found: Cl, 26·2; N, 10·6. Calc. for $C_6H_{16}ClN$: Cl, 25·8; N, 10·2%). Separation of diethylaminoboron dichloride from the benzene filtrate was again not achieved; a fraction (6·3 g.) was obtained which was a mixture of the dichloride (88%) and benzene (12%) (Found: B, 6·2; Cl, 39·6; N, 8·0%).

Preparation of Di-isopropylaminoboron Dichloride.—Di-isopropylamine (19·5 g., 1·0 mol.) in methylene dichloride (25 ml.) was added to boron trichloride (25·0 g., 1·10 mol.) in the same solvent (25 ml.) at −80°. Solvent and excess of boron trichloride were removed; triethylamine (19·8 g., 1·02 mol.), added to the residue dissolved in benzene (50 ml.), gave the insoluble triethylammonium chloride (26·0 g., 0·98 mol.) (Found: Cl, 25·7. Calc. for $C_6H_{16}ClN$: Cl, 25·8%) which was filtered off. Distillation of the filtrate afforded *di-isopropylaminoboron dichloride* (12·8 g., 36·5% yield) (Found: B, 5·8; Cl, 38·8; N, 7·8. $C_6H_{14}BCl_2N$ requires B, 6·0; Cl, 39·0; N, 7·7%), b. p. 61—63°/13 mm., n_D^{20} 1·4492, as a strongly fuming liquid which slowly darkened.

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