Interaction of Boron Trichloride with Chloro-alcohols and with Cyclic Ethers.

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Studies on boron trichloride–alcohol systems have been extended to include examples in which the alkyl group contains chlorine. By interaction in appropriate proportion of the respective alcohols with boron trichloride, tri-2-chloroethyl and tri-4-chlorobutyl borate, di-2-chloroethyl chloroboronate, and 2-chloroethyl and 4-chlorobutyl dichloroboronites were prepared. The alkoxyboron chlorides disproportionate reversibly and form adducts with pyridine. 4-Chlorobutyl dichloroboronite unlike the 2-chloroethoxyboron chlorides, but like other alkoxyboron chlorides, decomposes to form the chloroalkane, boron trichloride, and boron trioxide. Ethylene oxide and boron trichloride gave no 1 : 1 adduct even at −80°, but afforded 2-chloroethyl dichloroboronite. From the tetrahydrofuran–boron trichloride complex, 4-chlorobutyl dichloroboronite (or its decomposition products) was obtained only on heating. Reactions are described which differentiate dichloroboronites from their isomeric 1 : 1 complexes.

Tri-2-chloroethyl borate and tri-4-chlorobutyl borate have been obtained quantitatively by the interaction of boron trichloride (1 mol.) with 2-chloroethanol (3 mols.) and 4-chlorobutan-1-ol (3 mols.) respectively. In the 2-chloroethyl series, the intermediate alkoxyboron chlorides, $RO\cdot BCl_2$ and $(RO)_2BCl$, were prepared by the appropriate reaction (1)—(4):

$$Cl\cdot[CH_2]_2\cdot OH + BCl_3 \longrightarrow Cl\cdot[CH_2]_2\cdot O\cdot BCl_2 + HCl \quad (1)$$

$$2Cl\cdot[CH_2]_2\cdot OH + BCl_3 \longrightarrow (Cl\cdot[CH_2]_2\cdot O)_2BCl + 2HCl \quad (2)$$

$$(Cl\cdot[CH_2]_2\cdot O)_3B + 2BCl_3 \rightleftharpoons 3Cl\cdot[CH_2]_2\cdot O\cdot BCl_2 \quad (3)$$

$$2(Cl\cdot[CH_2]_2\cdot O)_3B + BCl_3 \rightleftharpoons 3(Cl\cdot[CH_2]_2\cdot O)_2BCl \quad (4)$$

Both 2-chloroethyl dichloroboronite and di-2-chloroethyl chloroboronate disproportionate on being heated under reflux at reduced pressure:

$$2Cl\cdot[CH_2]_2\cdot O\cdot BCl_2 \rightleftharpoons BCl_3 + (Cl\cdot[CH_2]_2\cdot O)_2BCl \quad (5)$$

$$2(Cl\cdot[CH_2]_2\cdot O)_2BCl \rightleftharpoons (Cl\cdot[CH_2]_2\cdot O)_3B + Cl\cdot[CH_2]_2\cdot O\cdot BCl_2 \quad (6)$$

and in consequence distillation of these compounds was invariably accompanied by disproportionation.

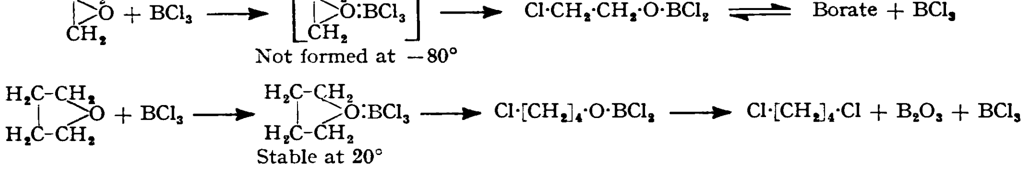
These results differ from those obtained with other alkoxyboron chlorides (Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1, 22, 31; Gerrard and Lappert, *J.*, 1951, 2545), where disproportionation has not been reported, although similar disproportionation was observed in the phenoxyboron chloride systems (Colclough, Gerrard, and Lappert, *J.*, 1955, 907). In contrast to the behaviour of the butoxyboron chlorides (Gerrard and Lappert, *loc. cit.*), alkyl chloride was not obtained from the corresponding 2-chloroethyl compounds.

2-Chloroethyl dichloroboronite formed a 1 : 1 complex with pyridine, and there was some evidence to support the formation of a 1 : 2 complex, $Cl{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl_2,2py$. By the interaction of pyridine (1 mol.) with the chloroboronate (1 mol.) a small amount of borate was isolated, the main product being a mixture of addition compounds of the chloroboronate and dichloroboronite with pyridine, in which the 1 : 1 pyridine–chloroboronate complex preponderated.

Martin and Mako (*J. Amer. Chem. Soc.*, 1951, **73**, 2674) by reaction of boron trichloride (1 mol.) and 2-chloroethanol (1 mol.) obtained hydrogen chloride, boron trichloride, the chloroboronate (15%), and the borate (38%) on distillation, but no dichloroboronite. These results are now understandable in view of the ready disproportionation of the dichloroboronite. Tri-2-chloroethyl borate has previously been prepared (90%) by Jones, Thomas, Pritchard, and Bowden (*J.*, 1946, 825) from boron trioxide and 2-chloroethanol.

4-Chlorobutyl dichloroboronite was prepared by reactions analogous to (1) and (3), but in contrast to the 2-chloroethyl compound it decomposed when heated to 1 : 4-dichlorobutane, boron trichloride, and boron trioxide: $3Cl{\cdot}[CH_2]_4{\cdot}O{\cdot}BCl_2 \longrightarrow 3Cl{\cdot}[CH_2]_4{\cdot}Cl + BCl_3 + B_2O_3$. There was also some disproportionation during distillation. A 1 : 1 pyridine–dichloroboronite complex was formed.

The dichloroboronites (2-chloroethyl and 4-chlorobutyl) were also obtained by the reaction of boron trichloride with ethylene oxide or tetrahydrofuran (for reaction of boron trichloride with dialkyl ethers, see Ramser and Wiberg, *Ber.*, 1930, **63**, 1136, and Gerrard and Lappert, *J.*, 1952, 1486) but a difference was noted between the two systems. Ethylene oxide (1 mol.) and boron trichloride (1 mol.) at —80° afforded the ester, as was evident from the identity of its properties with early specimens. Successive addition of ethylene oxide (1 mol.) and 2-chloroethanol (2 mols.) to boron trichloride (1 mol.) at —80° gave only tri-2-chloroethyl borate and hydrogen chloride, indicating that even at this temperature no 1 : 1 ethylene oxide–boron trichloride complex was formed. Tetrahydrofuran on the other hand gave a solid 1 : 1 complex stable at 20°, which only on heating gave the isomeric dichloroboronite or its decomposition products depending on the conditions of experiment. The evidence for the existence of the 1 : 1 tetrahydrofuran complex was its hydrolysis and alcoholysis (*n*-butanol) to yield tetrahydrofuran, hydrogen chloride, and boric acid (or tri-*n*-butyl borate). Moreover all the chlorine was available as hydrogen chloride after hydrolysis with cold water, indicating the presence of three boron–chlorine bonds.



These conclusions differ from those of Grimley and Holliday (*J.*, 1954, 1212) who considered that both ethers formed 1 : 1-complexes, which differed only in that the ethylene oxide complex was said to dissociate reversibly [$(CH_2)_2O,BCl_3 \rightleftharpoons (CH_2)_2O + BCl_3$; shown by a saturated vapour-pressure–temperature curve], whereas the tetrahydrofuran complex dissociated irreversibly. We are of the opinion that their vapour-pressure measurements in the ethylene oxide system represented the reversible disproportionation of

2-chloroethyl dichloroboronite. In addition, since aqueous hydrolysis of the latter gives two-thirds and alkaline hydrolysis all of its chlorine as chloride ion, their use of sodium hydroxide for chlorine estimation would not have distinguished between a 1 : 1 complex and the isomeric dichloroboronite. In the tetrahydrofuran system hydrogen chloride was stated to be one of the products, but we could not confirm this.

EXPERIMENTAL

Chlorine attached to boron was hydrolysed (except in the case of monopyridine–boron trichloride) by cold water (e.h. Cl hereafter). Chlorine attached to carbon was hydrolysed in boiling aqueous or alcoholic alkaline solution (total chlorine is designated Cl hereafter).

Interaction of Boron Trichloride (1 *Mol.*) *and 2-Chloroethanol* (1, 2, *and* 3 *Mols., severally*).—(*a*) The alcohol (80·1 g., 3 mols.) was added slowly to the trichloride (47·1 g., 1 mol.) at −80° and the whole kept overnight at −80°. Hydrogen chloride was then removed at the pump. The residue (98·7 g.) gave on distillation tri-2-chloroethyl borate [93·6 g., 93·6% based on : $3ROH + BCl_3 \longrightarrow (RO)_3B + 3HCl$], b. p. 70°/0·1 mm. (Found: B, 4·39. Calc. for $C_6H_{12}O_3Cl_3B$: B, 4·33%).

(*b*) The alcohol (4·05 g., 1 mol.) was added to the trichloride (5·85 g., 1 mol.) at −80°. After 20 min. at −80°, the mixture was allowed to warm to 20°, whereupon hydrogen chloride (1·69 g., 93% based on : $ROH + BCl_3 \longrightarrow RO{\cdot}BCl_2 + HCl$) was evolved. At 20°/0·5 mm., *2-chloroethyl dichloroboronite* (5·20 g.), n_D^{20} 1·4429, d^{18} 1·358 (Found : e.h. Cl, 43·9; Cl, 66·2; B, 6·7. $C_2H_4OCl_3B$ requires e.h. Cl, 44·0; Cl, 66·0; B, 6·7%), distilled, leaving a residue (1·95 g.), n_D^{20} 1·4560 (Found : e.h. Cl, 15·6; Cl, 51·0; B, 5·3%). Some material was lost during distillation (probably boron trichloride by disproportionation of the dichloroboronite).

(*c*) The alcohol (6·80 g., 2 mols.) was added slowly to the trichloride (4·90 g., 1 mol.) at −80°. Volatile material was removed (15°/15 mm.), leaving di-2-chloroethyl chloroboronate [8·45 g., 98·7% based on : $2ROH + BCl_3 \longrightarrow (RO)_2BCl + 2HCl$] (Found : e.h. Cl, 16·9; B, 5·4. Calc. for $C_4H_8O_2Cl_3B$: e.h. Cl, 17·3; B, 5·3%). Distillation of this material led to disproportionation.

Interaction of Boron Trichloride and Tri-2-chloroethyl Borate.—(*a*) The trichloride (4·05 g., 2 mols.) at −39° was added to the borate (4·30 g., 1 mol.) at −5°. At 20°/0·5—1 mm., 2-chloroethyl dichloroboronite (6·10 g.), n_D^{20} 1·4433, d_4^{17} 1·361 (Found : e.h. Cl, 44·8; B, 6·8%), distilled from the product and condensed at −80°, leaving a residue (1·55 g.) (Found : e.h. Cl, 20·0; B, 5·6%). The loss in weight (0·70 g.) is attributed to boron trichloride.

(*b*) The borate (6·38 g., 2 mols.), dissolved in *n*-pentane (10 ml.), was added to boron trichloride (1·50 g., 1 mol.) at −80°. The pentane was removed (20°/10 mm.), leaving a residue (7·75 g.) of di-2-chloroethyl chloroboronate, n_D^{20} 1·4551, d_4^{18} 1·320 (Found : e.h. Cl, 16·8; Cl, 51·6; B, 5·3. Calc. for $C_4H_8O_2Cl_3B$: e.h. Cl, 17·3; Cl, 51·9; B, 5·3%).

Reactions of 2-Chloroethyl Dichloroboronite.—(a) *Disproportionation.* The dichloroboronite (4·10 g.) was heated under reflux at 70°/14 mm. In series with the condenser were, first, a trap at −80° and then a trap containing pyridine. After 2·33 hr. a condensate had collected in the cold trap, and a white deposit had accumulated at the mouth of the pyridine trap. A residue (2·50 g.) remained in the reaction flask. On warming to 20°/760 mm. the contents of the cold trap largely distilled into the pyridine trap, leaving a remainder (0·25 g.) (Found : e.h. Cl, 34·9; Cl, 62·0; B, 6·7%). The contents of the pyridine trap were dissolved in methylene dichloride, concentrated, and treated with *n*-pentane, whereupon a white solid, monopyridine–boron trichloride complex (1·84 g.) (Gerrard and Lappert, *Chem. and Ind.*, 1952, 53), insoluble in water, m. p. 115° (Found : Cl, 54·3; B, 5·49; py, 41·1. Calc. for $C_5H_5NCl_3B$: Cl, 54·2; B, 5·50; py, 40·2%), was deposited. The residue from the reaction flask afforded on distillation : (1) (0·80 g.), b. p. up to 70°/0·2—0·1 mm., n_D^{20} 1·4500 (Found : e.h. Cl, 11·0; Cl, 49·7; B, 4·9%); (2) tri-2-chloroethyl borate (0·60 g.), b. p. 70°/0·1 mm., n_D^{20} 1·4550 (Found : Cl, 43·2; B, 4·35%); and the dichloroboronite (0·80 g.), n_D^{20} 1·4468 (Found : e.h. Cl, 39·0; Cl, 63·9; B, 6·4%), condensed at −80°.

(b) *Reaction with pyridine* (1 : 1). Pyridine (2·50 g., 1 mol.), in methylene dichloride (30 ml.), was added to the dichloroboronite (5·15 g., 1 mol.) at −80°. The solvent was removed (20°/15 mm.) and the oily product thrice washed with *n*-pentane, solvent traces being removed under reduced pressure. The residue (7·65 g., 100%) was the *monopyridine–2-chloroethyl dichloroboronite complex* (Found : e.h. Cl, 29·2; Cl, 42·7; B, 4·3; C_5H_5N, 32·4. $C_7H_9ONCl_3B$ requires e.h. Cl, 29·5; Cl, 44·3; B, 4·5; C_5H_5N, 32·9%).

(c) *Reaction with pyridine* (1 : 2). To the dichloroboronite (4·00 g., 1 mol.) in pentane (20 ml.) pyridine (4·20 g., 2 mols.) was added. A sticky solid precipitate formed which after filtration and repeated washing with *n*-pentane weighed 7·57 g. This appeared to be a dipyridine–2-chloroethyl dichloroboronite complex (Found: e.h. Cl, 21·1; C_5H_5N, 45·6. Calc. for $C_{12}H_{14}ON_2Cl_3B$: e.h. Cl, 22·2; C_5H_5N, 49·5%). It was hydrolysed in water.

Reactions of Di-2-chloroethyl Chloroboronate.—(a) *Disproportionation.* The chloroboronate (5·10 g.) was heated (7·8 hr.) under reflux at 100—120°/1·0 mm. The reflux condenser was connected to a trap at −80° in which a condensate of crude dichloroboronite (1·10 g.), n_D^{20} 1·4450 (Found: e.h. Cl, 40·0; Cl, 63·0; B, 6·7%), recondensed at 20°/1 mm. (n_D^{20} 1·4430) (Found: e.h. Cl, 44·1; Cl, 65·5; B, 6·5%), had collected. The residue (3·60 g.) in the reaction vessel was the impure borate, n_D^{20} 1·4545 (Found: e.h. Cl, 2·25; Cl, 43·6; B, 4·4%). A portion (3·25 g.) afforded on distillation: (1) a forerun (0·5 g.), b. p. 52—71°/0·1 mm., n_D^{20} 1·4556 (Found: e.h. Cl, 4·65; Cl, 45·5; B, 4·7%); (2) pure tri-2-chloroethyl borate (2·55 g.), b. p. 71°/0·1 mm., n_D^{20} 1·4547 (Found: Cl, 42·8; B, 4·35%); and a residue (0·15 g.).

(b) *Reaction with pyridine.* The chloroboronate (2·00 g., 1 mol.) in *n*-pentane (10 ml.) was added to pyridine (0·77 g., 1 mol.) in pentane (10 ml.) cooled to −10°. A white solid was precipitated which at 20° became a faintly yellow oil. The solvent was decanted off and the oil washed with *n*-pentane (10 ml.). Traces of solvent were removed (20°/10 mm.), leaving a residue (2·34 g.) which was probably substantially a monopyridine–di-2-chloroethyl chloroboronate complex (Found: e.h. Cl, 13·7; Cl, 35·9; C_5H_5N, 29·7. Calc. for $C_9H_{13}O_2NCl_3B$: e.h. Cl, 12·5; Cl, 37·5; C_5H_5N, 27·8%). Concentration of the pentane washings left a residue (0·32 g.) of tri-2-chloroethyl borate (Found: e.h. Cl, none; Cl, 41·6; B, 4·5%).

Interaction of Ethylene Oxide (1 *Mol.*) *with Boron Trichloride* (1 *Mol.*).—(*a*) Ethylene oxide (2·75 g., 1 mol.), cooled to −40°, was added slowly with continuous shaking to the trichloride (7·50 g., 1 mol.) at −75°. The crude product (10·1 g.) was 2-chloroethyl dichloroboronite, n_D^{20} 1·4455, d_4^{23} 1·380 (Found: e.h. Cl, 46·0; Cl, 68·2; B, 6·8%). Distillation (20°/2 mm.) gave a purer specimen of the dichloroboronite, n_D^{20} 1·4443, d_4^{19} 1·365 (Found: e.h. Cl, 45·0; Cl, 66·6; B, 6·7%), and a residue, largely di-2-chloroethyl chloroboronate, indicating disproportionation as already shown.

(*b*) Ethylene oxide (1·88 g., 1 mol.) in methylene dichloride (25 ml.), cooled to −39°, was added to boron trichloride (5·00 g., 1 mol.) in methylene dichloride (10 ml.) at −80°. 2-Chloroethanol (6·86 g., 2 mols.) was added to this cooled mixture. On removal of solvent (at 20°/15 mm.), a residue of tri-2-chloroethyl borate (10·6 g., 100%) (Found: Cl, 42·5; B, 4·2%) remained which was distilled, affording the pure borate (9·95 g., 93%), b. p. 96—97·5°/0·8 mm., n_D^{20} 1·4555 (Found: Cl, 42·8; B, 4·3%). The yield is based on: $RO{\cdot}BCl_2 + 2ROH \longrightarrow (RO)_3B + 2HCl$.

Interaction of 4-*Chlorobutanol with Boron Trichloride.*—(*a*) The alcohol (9·9 g., 3 mols.) in *n*-pentane (5 ml.) was added to the trichloride (3·55 g., 1 mol.) at −80°. At 20°/10 mm., hydrogen chloride and *n*-pentane were removed, leaving a residue [10·25 g., 100% based on: $3ROH + BCl_3 \longrightarrow (RO)_3B + 3HCl$] which on distillation afforded: (1) a forerun (0·8 g.), b. p. up to 136°/0·1 mm., n_D^{20} 1·4590 (Found: Cl, 30·3; B, 2·9%); (2) *tri-4-chlorobutyl borate* (9·0 g.), b. p. 136—140°/0·1 mm., n_D^{21} 1·4618, d_4^{20} 1·350 (Found: Cl, 32·0; B, 3·2. $C_{12}H_{24}O_3Cl_3B$ requires Cl, 32·0; B, 3·2%); and a residue (0·20 g.).

(*b*) The alcohol (2·90 g., 1 mol.) was added to the trichloride (3·15 g., 1 mol.) at −80°. Hydrogen chloride was evolved on warming and was trapped in potassium hydroxide (chloride ion, 0·367 g., 97·4% based on: $BCl_3 + ROH \longrightarrow RO{\cdot}BCl_2 + HCl$). The residue (5·00 g., 98·6%) was *4-chlorobutyl dichloroboronite*, n_D^{20} 1·4522, d_4^{20} 1·254 (Found: e.h. Cl, 36·5; Cl, 55·9; B, 5·65. $C_4H_8OCl_3B$ requires e.h. Cl, 37·5; Cl, 56·3; B, 5·7%). Distillation of a portion (4·3 g.) under reduced pressure apparently led to disproportionation, giving: (1) (0·88 g.), b. p. up to 68°/1·0 mm., n_D^{20} 1·4541 (Found: e.h. Cl, 30·1; Cl, 52·5; B, 5·1%); (2) (0·35 g.), b. p. 68—74°/1·0 mm., n_D^{20} 1·4615 (Found: e.h. Cl, 23·0; B, 5·2%); and a residue (1·70 g.), n_D^{20} 1·4630 (Found: e.h. Cl, 7·72; Cl, 36·4; B, 3·9%). A condensate (0·35 g.), collected in a trap at —80°, had n_D^{20} 1·4499 (Found: e.h. Cl, 13·37; Cl, 53·9; B, 2·0%). Some material (1·10 g.), probably boron trichloride, was lost during distillation.

Interaction of Boron Trichloride (2 *Mols.*) *with* 4-*Chlorobutyl Borate* (1 *Mol.*).—The borate (4·4 g., 1 mol.) in methylene dichloride (10 ml.) was added to the trichloride (3·1 g., 2 mols.) at −80°. After 1 hr. at −80° the mixture was allowed to warm to 20° and volatile matter was removed (20 min. at 17 mm.). The residue (7·31 g., 97·4%) was 4-chloroethyl dichloroboronite (Found: e.h. Cl, 34·4; Cl, 54·9; B, 5·55%).

Reactions of 4-*Chlorobutyl Dichloroboronite.*—(a) *Pyrolysis.* The dichloroboronite (5·40 g.) was heated for 5 hr. in a sealed tube at 100°. The tube was cooled to −80° and opened, and the clear liquid contents were allowed to warm, the outlet being attached to water absorption-bottles.

No appreciable evolution of gas was observed, but, on heating, boron trichloride (80%) was evolved and a white precipitate formed simultaneously. Distillation of the residue afforded a liquid (3·5 g.) and a white solid (0·8 g.) which was largely boron trioxide (0·7 g. of boron trioxide required for the reaction : $3RO{\cdot}BCl_2 \longrightarrow B_2O_3 + BCl_3 + 3RCl$). The distillate was dissolved in ether, washed free from traces of boron trichloride, dried ($CaCl_2$), and distilled, giving 1 : 4-dichlorobutane (2·9 g., 80%), b. p. 150—152°/760 mm., n_D^{20} 1·4537 (Found : Cl, 54·3. Calc. for $C_4H_8Cl_2$: Cl, 55·7%).

In separate experiments the rate of decomposition was estimated by heating individual samples in sealed tubes at 100°. These were broken under water in a stoppered flask and the equivalence ratio of e.h. Cl to boron was determined, being initially 2 : 1 and finally 1 : 1.

e.h. Cl : B	1·94	1·91	1·76	1·59	1·44	1·37	1·28	1·15	1·13	1·05	1·01
Time (min.) ...	10	20	30	40	50	60	70	80	90	110	145

(b) *Reaction with pyridine.* The borate (1·70 g., 1 mol.) in *n*-pentane (10 ml.) was added to the trichloride (1·20 g., 2 mols.) at −80°. After 20 min. at 20°, the solution, cooled to −15°, was treated with pyridine (1·21 g., 3 mols.) in *n*-pentane (10 ml.). A pale yellow oil and some white solid were precipitated. The pentane was removed (20°/10 mm.) and the residue (4·10 g.) was washed twice with pentane. Washing with water left the insoluble monopyridine–boron trichloride complex (0·22 g.), m. p. 115°. The water-soluble portion (3·75 g.) was substantially a *monopyridine–4-chlorobutyl dichloroboronite complex* (Found : e.h. Cl, 24·5; Cl, 37·7; B, 4·1; C_5H_5N, 29·0. $C_9H_{13}ONCl_3B$ requires e.h. Cl, 26·4; Cl, 39·7; B, 4·0; C_5H_5N, 29·4%).

Interaction of Tetrahydrofuran (1 *Mol.*) *with Boron Trichloride* (1 *Mol.*).—Tetrahydrofuran (3·35 g., 1 mol.) in *n*-pentane (10 ml.) was added to the trichloride (5·45 g., 1 mol.) in pentane (20 ml.) at −80°. The reaction afforded the white solid, monotetrahydrofuran–boron trichloride complex (8·3 g., 94%), m. p. 88—95° (decomp.) (Found : e.h. Cl, 55·3; B, 5·85. Calc. for $C_4H_8OCl_3B$: e.h. Cl, 56·3; B, 5·7%).

Reactions of the Monotetrahydrofuran–Boron Trichloride Complex.—(a) *With* n-*butanol.* The complex (13·25 g., 1 mol.) was treated with *n*-butanol (15·55 g., 3 mol.) at 20°. Hydrogen chloride was vigorously evolved. After 20 hr. at 20°, material (3·30 g.) volatile at 20°/15 mm. was collected in a trap at −80°. This, after treatment first with lead carbonate and subsequently with anhydrous magnesium sulphate, yielded on distillation tetrahydrofuran (3·10 g., 62%), b. p. 64·5—66°/760 mm., n_D^{20} 1·4063, d_4^{20} 0·885. The remainder yielded tri-*n*-butyl borate (13·00 g., 79%), b. p. 113°/13 mm., n_D^{20} 1·4090 (Found : B, 4·70. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%), on distillation [yields are based on : $C_4H_8O,BCl_3 + 3Bu^nOH \longrightarrow (Bu^nO)_3B + 3HCl + C_4H_8O$].

(b) *Hydrolysis.* The complex (8·00 g.) was treated with water (25 ml., large excess). Tetrahydrofuran (1·55 g., 51·0%), b. p. 64°/760 mm., n_D^{20} 1·4058, d_4^{21} 0·902, was distilled from the reaction mixture.

(c) *Pyrolysis.* The complex (6.00 g.) was heated (0·33 hr. at 100°, and a further 3·25 hr. at 120—135°) at atmospheric pressure. Volatile material was collected in a trap (−80°) connected in series with a potassium hydroxide absorption tube. Boron trichloride (1·02 g., 82·3%) collected in the cooled trap (Found : e.h. Cl, 90·8; B, 9·2. Calc. for Cl_3B : e.h. Cl, 90·8; B, 9·2%). There was a negligible amount of chloride in the potassium hydroxide absorption tube. The residue from the pyrolysis was extracted with hot *n*-pentane (2 × 25 ml.), leaving a dark solid (1·13 g.) (Found : e.h. Cl, 11·0; B, 22·0, equiv. to 70% of the total boron in the system) which may have contained much boron trioxide. From the pentane extract, 1 : 4-dichlorobutane (3·15 g., 78%), b. p. 150°/760 mm., n_D^{20} 1·4532, d_4^{20} 1·132 (Found : Cl, 53·5%), and a small residue (0·22 g.) were obtained [yields are based on : $3C_4H_8O,BCl_3 \longrightarrow 3Cl(CH_2)_4Cl + BCl_3 + B_2O_3$].

In a further experiment a sample of the complex was heated (4·3 hr.) in a sealed tube at 100°. The tube was broken under water in a stoppered flask and the e.h. chlorine and boron estimated. The e.h. chlorine had dropped to one-third of that in the starting material and the equivalence ratio of e.h. chlorine to boron was exactly 1 : 1, as required by the above equation.

(d) *Pyrolysis at reduced pressure.* The complex (6·45 g.) was heated for 2 hr. at 100—120°/1—2 mm., during which a condensate (3·20 g.), n_D^{20} 1·4520 (Found : e.h. Cl, 26·8; B, 4·02%; equivalence ratio of e.h. Cl : B, 2 : 1), believed to be a mixture of 1 : 4-dichlorobutane and 4-chlorobutyl dichloroboronite, had collected at −80°. To a sample (2·80 g.) in methylene dichloride (20 ml.), 4-chlorobutanol (2·30 g., 2 mol. per mol. of boron in condensate) was added at −80°. The solvent and hydrogen chloride were removed (15°/17 mm.) and the residue distilled, affording tri-4-chlorobutyl borate (2·75 g., 79% based on conversion of boron in condensate into borate), b. p. 140°/0·3 mm., n_D^{20} 1·4620, d_4^{20} 1·370 (Found : Cl, 32·3; B, 3·2%), and a residue (0·20 g.). A condensate at −80° (0·70 g.) from this distillation afforded on further distillation 1 : 4-dichlorobutane (0·55 g.), b. p. 150°/760 mm., n_D^{20} 1·4530 (Found : Cl, 55·0%). The yield of borate indicates conclusively the presence of the dichloroboronite in the condensate.

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