68. *Interaction of Boron Trichloride with Alkyl Chloroalkyl Ethers.*

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Chloromethyl methyl, 2-chloroethyl methyl, 2-chloroethyl ethyl, di-2-chloroethyl, and di-*n*-butyl ether each formed 1 : 1 complexes with boron trichloride, unlike bischloromethyl ether which did not react. There was evidence for such a complex with *n*-butyl *iso*butyl, but not with ethyl 1-methylheptyl ether. The chloromethyl methyl ether complex afforded bischloromethyl ether, methyl chloride, and boron trioxide when heated in the presence of chloromethyl methyl ether, whereas the other alkyl chloroalkyl ethers gave the alkyl chloride and chloroalkyl dichloroboronite, $RO\cdot BCl_2$, on pyrolysis. The relative stability of the alkyl 2-chloroethyl ether complexes was determined. The complexes afforded the free ethers when treated with either pyridine or butan-1-ol. The results are discussed.

EARLIER work [1,2,3] on the interaction of boron trichloride with mixed ethers revealed that ether fission (1) occurred at low temperature and that the alkyl chloride was produced exclusively from the more electron-releasing (R′) of the two groups:

$$(1)\quad ROR' + BCl_3 \longrightarrow RO\cdot BCl_2 + R'Cl$$

The present investigation concerns mainly the reactions of certain 2-chloroethyl and chloromethyl ethers. Intermediate, unstable 1 : 1 complexes have previously been isolated in the dimethyl and diethyl ether systems [4] and certain allylic systems; [3] their properties have not received much attention. The only ether which has hitherto proved unreactive is diphenyl ether.[5]

1 : 1 Boron trichloride complexes have now been isolated with the following ethers: chloromethyl methyl, 2-chloroethyl methyl, 2-chloroethyl ethyl, di-2-chloroethyl, and di-*n*-butyl; and there was evidence for the formation of such a complex with *n*-butyl *iso*butyl ether, whereas no such evidence could be obtained with ethyl 1-methylheptyl ether. Bischloromethyl ether was shown not to react with boron trichloride.

These complexes, with the exception of that obtained from chloromethyl methyl ether, decomposed when heated, in accordance with scheme (1). The direction of fission of the *n*-butyl *iso*butyl [2] and ethyl 1-methylheptyl [1] ether complexes was as previously described. The 2-chloroethyl methyl, 2-chloroethyl ethyl, and di-2-chloroethyl ether complexes each afforded 2-chloroethyl dichloroboronite in yields of 100%, 92%, and 25%, respectively, and as well methyl chloride (64%), ethyl chloride (78%), and 1 : 2-dichloroethane (31%) respectively.

The yields in the di-2-chloroethyl ether system were low because the decomposition was accompanied by reversible dissociation (56%) of the complex. In view of its known disproportionation into boron trichloride and successively di-2-chloroethyl chloroboronate, $(RO)_2BCl$, and tri-2-chloroethyl borate, $B(OR)_3$, the dichloroboronite was not isolated as such. The yields indicated above were estimated from the borate obtained by 2-chloroethanolysis of the pyrolysis products with the appropriate amount (based on analysis) of alcohol.

Preliminary experiments on the pyrolysis of the chloromethyl methyl ether–boron trichloride complex indicated decomposition according to scheme (2), and in view of the

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[1] Gerrard and Lappert, *J.*, 1951, 1020.
[2] *Idem, J.*, 1952, 1486.
[3] Gerrard, Lappert, and Silver, *J.*, 1956, 4987.
[4] Ramser and Wiberg, *Ber.*, 1930, **63**, 1136.
[5] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.

difficulty of separating the products, the pyrolysis was subsequently carried out in presence of the ether [see scheme (3)], thus avoiding the formation of boron trichloride.

$$(2)\quad 6Cl{\cdot}CH_2{\cdot}OMe,BCl_3 \longrightarrow 6MeCl + 3(Cl{\cdot}CH_2)_2O + 4BCl_3 + B_2O_3$$

$$(3)\quad 2Cl{\cdot}CH_2OMe,BCl_3 + 4Cl{\cdot}CH_2{\cdot}OMe \longrightarrow 6MeCl + 3(Cl{\cdot}CH_2)_2O + B_2O_3$$

The relative ease of decomposition of the alkyl 2-chloroethyl ether complexes was ethyl > methyl ≫ 2-chloroethyl (see Table 2).

The action of pyridine on the ether (2-chloroethyl methyl and di-2-chloroethyl) complexes was to displace the boron trichloride [see scheme (4)].

$$(4)\quad ROR',BCl_3 + C_5H_5N \longrightarrow C_5H_5N,BCl_3 + ROR'$$

When the 2-chloroethyl methyl ether complex was treated with butan-1-ol the reaction proceeded according to scheme (5).

$$(5)\quad ROR',BCl_3 + 3Bu^nOH \longrightarrow B(OBu^n)_3 + 3HCl + ROR'$$

Discussion.—The lack of reaction between di-2-chloromethyl ether and boron trichloride is attributed to the $-I$ effect of the two chlorine atoms in the ether which lowers the electron density on the oxygen atom.

The reaction sequences involved in (2) and (3) are probably as shown in (6) and (7):

$$(6)\quad 6Cl{\cdot}CH_2{\cdot}OMe,BCl_3 \longrightarrow 6MeCl + 6Cl{\cdot}CH_2{\cdot}O{\cdot}BCl_2 \xrightarrow{-4BCl_3} 2B(O{\cdot}CH_2Cl)_3 \longrightarrow B_2O_3 + 3(Cl{\cdot}CH_2)_2O$$

$$(7)\quad 2Cl{\cdot}CH_2{\cdot}OMe,BCl_3 \longrightarrow 2MeCl + 2Cl{\cdot}CH_2{\cdot}O{\cdot}BCl_2 \xrightarrow{2Cl\cdot CH_2\cdot OMe} 2MeCl + 2(Cl{\cdot}CH_2{\cdot}O)_2B{\cdot}Cl$$

$$\xrightarrow{2Cl\cdot CH_2\cdot OMe} 2MeCl + 2B(O{\cdot}CH_2Cl)_3 \longrightarrow B_2O_3 + 3(Cl{\cdot}CH_2)_2O$$

In these postulated sequences, the direction of fission is in accord with the fact that the methyl group is more electron-releasing than chloromethyl; disproportionation of alkyloxyboron chlorides is a known property;[6,7,8] and the final step of decomposition of trischloromethyl borate into the ether and boron trioxide receives plausibility from the known decomposition in that manner of tri-(1 : 2-dichloroethyl) borate.[9]

The direction of fission of the alkyl 2-chloroethyl ether complexes is in accord with the relative electron-release of the alkyl groups concerned and supports the view that the mechanism of ether fission is of the S_N1 type, involving a rate-determining C–O heterolysis. This view is confirmed by data on the relative ease of decomposition of the complexes, which show that the ease of fission is greater the greater the electron density on the ethereal oxygen atom. The dissociation of the di-2-chloroethyl ether complex into the ether and boron trichloride, which accompanies the fission reaction, points to the same conclusion.

The reactions with pyridine (4) and butan-1-ol (5) indicate that the complexes have the structure (I) and not (II).

$$(\text{I})\quad RR'O{:}BCl_3 \qquad\qquad R'^{+}[RO{\cdot}BCl_3]^{-}\quad(\text{II})$$

EXPERIMENTAL

Preparations and Analytical Methods.—2-Chloroethyl ethyl ether was obtained by Ames and Bowman's method,[10] and chloromethyl methyl ether by Marvel and Porter's procedure.[11] 2-Chloroethyl methyl ether (50·6 g., 74%), b. p. 90—91°, was prepared by the addition of thionyl chloride (107 g., 1·2 mols.) to a cooled (−20°) mixture of 2-methoxyethanol (57·5 g., 1 mol.) and pyridine (59·7 g., 1 mol.), whereafter the mixture was heated (4·75 hr.) under reflux,

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[6] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.

[7] Gerrard and Lappert, *J.*, 1955, 3084.

[8] Lappert, *J.*, 1956, 1768.

[9] Frazer, Gerrard, and Lappert, *J.*, 1957, in the press.

[10] Ames and Bowman, *J.*, 1950, 407.

[11] Marvel and Porter, *Org. Synth.*, Coll. Vol. I, 1947, p. 377.

then cooled and treated with concentrated hydrochloric acid (100 c.c.), and extracted with ether; the extract was washed with dilute aqueous sodium hydroxide, dried ($MgSO_4$), and distilled.

Estimations of easily hydrolysable chlorine (called e.h. Cl hereafter) and boron have been described before.[6] Methyl and ethyl chloride and boron trichloride were severally analysed by employing weighed samples in sealed tubes which were hydrolysed in closed systems.

Interaction of Ethers (1 *Mol.*) *and Boron Trichloride* (1 *Mol.*).—The ether (1 mol.) in *n*-pentane (5 c.c. per g. of ether) was added to the trichloride (1 mol.) in *n*-pentane (5 c.c. per g.) at −80°. In all cases except the di-2-chloroethyl ether system, a white solid, the 1 : 1 *ether–boron trichloride complex*, separated, which was filtered off while still cold and was washed with cold *n*-pentane. During the earlier stages in the filtration, the filter funnel was surrounded by a cooling jacket (−66°); this was removed towards the end so that the last traces of solvent might be removed. The di-2-chloroethyl ether complex was an *n*-pentane-immiscible liquid at 20°, and in order to ensure complete removal of the ether, it was prepared by employing a 0·2-molar excess of the trichloride. This complex was isolated by removal of matter volatile at 20°/20 mm. The results are shown in Table 1.

TABLE 1. *Ether complexes.*

			Found (%)			Required (%)		
ROR′ in ROR′,BCl_3	Yield (%)	M. p.	e.h. Cl	Cl	B	e.h. Cl	Cl	B
MeO·CH_2Cl	95	<20°	—	71·3	5·6	—	71·8	5·5
MeO·CH_2·CH_2Cl	98	35—36	49·8	—	5·4	50·3	—	5·1
EtO·CH_2·CH_2Cl	99	<20	46·3	62·2	4·9	47·2	62·9	4·8
$(Cl·CH_2·CH_2)_2O$	96	42—49	39·7	68·3	4·2	40·9	68·2	4·1
$(n\text{-}C_4H_9)_2O$	100	<20	42·2	—	4·4	43·1	—	4·4

When bischloromethyl ether (6·67 g.) was added to boron trichloride (6·70 g.) at −80°, no sign of reaction was observed. The mixture was heated under reflux; boron trichloride (6·55 g., 98%) was evolved and collected as a condensate at −80°. The residue (6·85 g.) afforded on distillation the unchanged ether (6·55 g., 98%), b. p. 100°, n_D^{20} 1·4439, d_4^{16} 1·360 (Found: Cl, 61·6. Calc. for $C_2H_4OCl_2$: Cl, 61·7%).

The addition of *n*-butyl *iso*butyl ether (2·80 g.) in *n*-pentane (20 c.c.) to boron trichloride (2·50 g., 1 mol.) in *n*-pentane at −80° produced a white solid which was shown to contain e.h. Cl : B in the ratio 3 : 1, indicating its identity as the ether complex. Hydrolysis afforded the same ether, b. p. 128—129°.

When ethyl 1-methylheptyl ether (3·30 g.) in *n*-pentane (25 c.c.) was added to boron trichloride (2·45 g., 1 mol.) in *n*-pentane (25 c.c.) at −80°, there was observed a separation into two layers. However, the addition of further *n*-pentane at −80° produced a homogeneous solution. The ratio e.h. Cl : B in this solution was 2 : 1 indicating that ether fission had occurred.

Pyrolysis of Ether Complexes.—(a) *Chloromethyl methyl.* This complex melted below room temperature, but not with decomposition. It sublimed unchanged at 20°/15 mm. Preliminary experiments indicated that decomposition afforded methyl chloride and di-2-chloromethyl ether, but the procedure was simplified when the pyrolysis was carried out in the presence of the unchanged ether. Thus, chloromethyl methyl ether (2·90 g., >2 mols.) was added to the complex (2·75 g., 1 mol.), and the solution thus produced was introduced into a test-tube, which was then sealed and kept at 100° for about 85 hr. The tube was cooled to −80° and opened. Methyl chloride [1·70 g., 77% based on (3)] (Found: Cl, 70·2. Calc. for CH_3Cl: Cl, 70·3%) was collected in a trap at −80° when the tube was allowed to stand at 20°/760 mm., whereafter matter volatile at 20°/15 mm. was collected in a second trap, leaving a solid residue (0·60 g., containing 92% of the boron in the system). The condensate was an impure specimen of di-2-chloromethyl ether, which was purified by two distillations, then having b. p. 94—100°, n_D^{20} 1·4423 (Found: Cl, 61·2%).

(b) 2-*Chloroethyl methyl.* The complex (5·90 g.) was heated (0·75 hr.) under reflux at 100°/760 mm., the condenser being connected to a cold (−80°) trap. A mixture (1·85 g.) of methyl chloride and boron trichloride was collected and was separated by removing the trichloride as its pyridine complex by recondensation of the vapour through a wash-bottle containing pyridine. In this way, methyl chloride (0·90 g., 64%) (Found: Cl, 70·1%) and pyridine–boron trichloride (0·40 g.), m. p. 113—114° (Found: Cl, 53·0; B, 5·63. Calc. for $C_5H_5NCl_3B$: Cl, 54·2; B, 5·5%), were finally isolated. The non-volatile residue (4·05 g.), n_D^{20}

1·4440 (Found : e.h. Cl, 35·6; Cl, 60·4; B, 6·5%), in the reaction flask was a mixture of 2-chloroethyl dichloroboronite and di-2-chloroethyl chloroboronate. This was confirmed by a quantitative 2-chloroethanolysis into tri-2-chloroethyl borate. Thus, a portion (3·55 g.) of this residue in methylene dichloride (10 c.c.) at −80° was treated with 2-chloroethanol (2·86 g., equiv. to e.h. Cl in mixture) in the same solvent (10 c.c.), whereupon hydrogen chloride was evolved. Removal of matter volatile at 20°/20 mm. afforded impure tri-2-chloroethyl borate [5·10 g., 100% based on $(RO)_xBCl_{3-x} + (3 - x)ROH \longrightarrow (RO)_3B$], n_D^{20} 1·4542 (Found : e.h. Cl, 0; Cl, 41·8; B, 4·36. Calc. for $C_6H_{12}O_3Cl_3B$: Cl, 42·7; B, 4·33%), as a residue, which upon distillation had b. p. 76°/0·1 mm., n_D^{20} 1·4542 (Found : Cl, 43·0; B, 4·38%).

(c) 2-*Chloroethyl ethyl*. The complex (11·8 g.) was heated (2 hr.) at 100° and then (0·5 hr.) at 150° in an apparatus similar to that described in (b). A condensate (4·55 g.) (Found : e.h. Cl, 25·8; B, 2·68%; *i.e.*, e.h. Cl : B = 2·93 : 1) was collected at −80°. From this, a portion (4·15 g.) was treated as described in (b), to afford ethyl chloride (2·40 g., 78%) (Found : e.h. Cl, none; Cl, 53·3; B, 0. Calc. for C_2H_5Cl : Cl, 55·0%). The original residue (7·00 g.) was a mixture of 2-chloroethyl dichloroboronite and di-2-chloroethyl chloroboronate (Found : e.h. Cl, 33·9; Cl, 60·5; B, 6·5%), which was confirmed by treating a portion (6·65 g.) at −80° with 2-chloroethanol (5·15 g., equiv. to the e.h. Cl in mixture), to afford tri-2-chloroethyl borate (8·76 g., 92%), b. p. 73°/0·15 mm., n_D^{20} 1·4556 (Found : Cl, 44·2; B, 4·33%).

(d) *Di-2-chloroethyl*. The complex (7·05 g.) was heated (2·75 hr.) at 120—130° in an apparatus similar to that described in (b). During this time, a condensate (2·25 g.), substantially boron trichloride (Found : Cl, 87·7; B, 9·12%), had collected at −80°. A portion (4·50 g.) of the residue (4·70 g.) (Found : e.h. Cl, 10·25; B, 2·2%) was heated with 2-chloroethanol (1·05 g., equiv. to the e.h. Cl in mixture). Distillation afforded 1 : 2-dichloroethane (0·83 g., 31%), b. p. 80—85°/760 mm., n_D^{20} 1·4453, di-2-chloroethyl ether (2·15 g., 56%, based on dissociation of complex), b. p. 94—97°/43 mm., n_D^{20} 1·4570 (Found : Cl, 49·0. Calc. for $C_4H_8OCl_2$: Cl, 49·7%), tri-2-chloroethyl borate (1·60 g., 25%), b. p. 72°/0·1 mm., n_D^{20} 1·4559 (Found : Cl, 44·6; B, 4·3%), and a residue (0·25 g.).

The yields in (b), (c), and (d) are based on reaction (1).

Relative Stability of Ether Complexes.—The thermal stabilities of the complexes were ascertained by heating sealed samples at the stated temperatures and for the stated times, whereafter the samples were broken under water in stoppered flasks and the equivalence ratio of e.h. chlorine to boron was estimated in each case by titration with N/20-sodium hydroxide to successively methyl-orange and phenolphthalein, the latter in presence of mannitol. A ratio of e.h. Cl : B = 3 : 1 was taken as the pure complex and of 2 : 1 as the completely decomposed specimen. The results are shown in Table 2.

TABLE 2. *Stability of ether complexes.*

ROR′ in ROR′, BCl_3	Temp.	Time (hr.)	Decomp. (%)	ROR′ in ROR′, BCl_3	Temp.	Time (min.)	Decomp. (%)
$MeO{\cdot}CH_2{\cdot}CH_2Cl$ ...	20°	20·1	40	$(Cl{\cdot}CH_2{\cdot}CH_2)_2O$	20°	fairly stable	
,, ...	20	29·0	75	,, ...	100	2·5	18
,, ...	20	41·75	85	,, ...	100	9	37
,, ...	20	68·1	100	,, ...	100	24	61
,, ...	100	0·083	100	,, ...	100	62	77
$EtO{\cdot}CH_2{\cdot}CH_2Cl$	20	1·75	65	,, ...	100	175	90
,, ...	100	0·083	100	$(n\text{-}C_4H_9)_2O$	20	2	12
				,, ...	20	2·25	12
				,, ...	20	19·25	63
				,, ...	20	25·25	91

Interaction of Ether Complexes with Pyridine (4).—(a) 2-*Chloroethyl methyl*. The ether complex was prepared *in situ* by addition of the ether (4·23 g., 1 mol.) in methylene dichloride (20 c.c.) to boron trichloride (5·25 g., 1 mol.) in the same solvent (20 c.c.) at −80°. Pyridine (5·55 g., 1 mol.) in methylene dichloride (10 c.c.) was then added to the mixture at −80°. Material volatile at 20°/12 mm. was evaporated and condensed at −80°. The remaining solid, washed with *n*-pentane, was substantially pyridine–boron trichloride (8·53 g., 97%), m. p. 106—112° (Found : Cl, 52·6; C_5H_5N, 39·9%); this was purified by washing it with water, to leave the purer, water-insoluble complex, m. p. 112° (Found : Cl, 53·0; C_5H_5N, 41·6%). Distillation of the pentane washings combined with the condensate gave no satisfactory separation of 2-chloroethyl methyl ether, but its presence in solution was demonstrated by adding the solution to boron trichloride (5·15 g.) in *n*-pentane (30 c.c.) at −80°, whereupon the ether complex (7·35 g., equiv. to 75% yield of ether) (Found : e.h. Cl, 49·8; B, 5·4%) was precipitated.

(b) *Di-2-chloroethyl.* The complex was prepared *in situ* by addition of the ether (4·88 g., 1 mol.) in methylene dichloride (10 c.c.) to boron trichloride (4·00 g., 1 mol.) in the same solvent (10 c.c.) at −80°. After this product had been at −80° for ½ hr., pyridine (2·70 g., >1 mol.) in methylene dichloride (10 c.c.) was added thereto. Volatile matter was removed at 20°/20 mm., whereafter the residue was washed by decantation with *n*-pentane. Pyridine–boron trichloride remained as a water-insoluble, white solid (6·59 g., 99%) (Found : Cl, 51·0; B, 5·24; C_5H_5N, 41·3. Calc. for $C_5H_5NCl_3B$: Cl, 54·2; B, 5·50; C_5H_5N, 40·2%). The pentane extract was concentrated and distilled, affording di-2-chloroethyl ether (4·15 g., 85%), b. p. 92°/40 mm., n_D^{18} 1·4582 (Found : Cl, 49·3%).

*Interaction of the 2-Chloroethyl Methyl Ether Complex with Butan-*1-*ol* (5).—The complex (7·90 g., 1 mol.) was treated with butan-1-ol (8·28 g., 3 mols.) at −80°. The product was set aside at 15° for 17 hr., whereafter it was heated at 65°/13 mm. Hydrogen chloride (88%) was absorbed in potassium hydroxide and a condensate (3·75 g.) was collected in a trap at −80°. There remained a residue of tri-*n*-butyl borate (8·10 g., 100%), n_D^{20} 1·4083 (Found : B, 4·81. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%), which was distilled (b. p. 111—112°/14 mm., n_D^{20} 1·4082) (Found : B, 4·7%). The condensate was purified by successive recondensation from lead carbonate, calcium chloride, and phosphoric oxide, leaving a final residue of 2-chloroethyl methyl ether (2·60 g., 74%), which distilled without leaving a residue and had b. p. 87—88°, n_D^{20} 1·4072 (Found : Cl, 37·7%).

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