# 271. *Fission of Mixed Ethers by Boron Trichloride.*

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Fission of ethers by boron trichloride is rapid and entails the reaction $ROR' + BCl_3 \longrightarrow RCl + R'O\cdot BCl_2$. The distribution of the hydrocarbon group appears to be decided during the electrophilic attack of the trichloride on the ether and is in accordance with the influence of the degree of electron release on the reactivity of the two relevant carbon atoms. Thus *n*-butyl *sec.*-butyl ether appears as *sec.*-butyl chloride and *n*-butyl dichloroboronite, $BCl_2\cdot OBu^n$. Results are compared with those from ether fission by hydrogen iodide in which system anionic attack by iodine on the cation $ROR'H^+$ appears to decide the distribution. The above-mentioned ether then appears as *n*-butyl iodide and *sec.*-butyl alcohol in accordance with accepted principles.

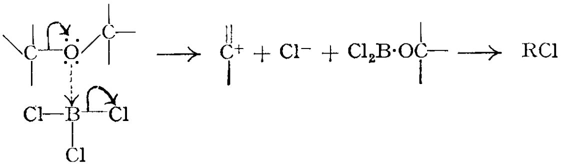
EBELMEN and BOUQUET (*Ann. Chim. Phys.*, 1846, [iii], **17**, 54) observed a reaction between diethyl ether and boron trichloride, hydrogen chloride being evolved and ethyl "protoborate" formed. Similarly the methyl and *n*-pentyl "protoborates" were prepared. Gattermann (*Ber.*, 1889, **22**, 186) reported co-ordination compound between boron trichloride and diethyl ether. Ramser and Wiberg (*Ber.*, 1930, **63**, 1136) carried out reactions in an enclosed low-pressure apparatus and found that the trichloride and diethyl ether formed an addition compound, $BCl_3,Et_2O$, m. p. 56°, which on melting decomposed to ethyl dichloroboronite, $BCl_2\cdot OEt$, and ethyl chloride. This dichloroboronite reacted with a further molecule of ether to give the complex, $(BCl_2\cdot OR)_2,R_2O$, which was less stable than the trichloride–ether complex and disproportionated to the latter and diethyl chloroboronate, $BCl(OEt)_2$. The chloroboronate did not, however, react with more ether even at 100°.

We have shown (*J.*, 1951, 1020) that the interaction of boron trichloride with ethyl 1-methylheptyl ether and with ethyl 1-phenylethyl ether afforded ethyl dichloroboronite, and the chloride of the other group. The 2-chloro-octane was obtained with inversion but with considerable loss in rotatory power. The 1-chloro-1-phenylethane was completely racemised, but this was probably due to the racemisation of the chloride itself, by free boron trichloride.

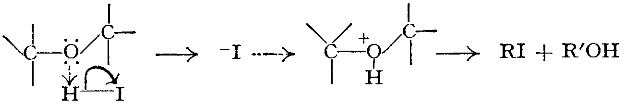
In the present experiments, the ether (1 mol.) was added to the trichloride (1 mol.) at −80°. Separation was effected by fractional distillation at low temperatures with differential changes in pressures, and we relied on our knowledge of the stability and nature of the relevant dichloroboronites and chloroboronates (Gerrard and Lappert, *J.*, 1951, 2545). In order to study the fission of *sec.*-butyl *tert.*-butyl ether, the reactants were mixed in proportions, ether (2 mols.) and trichloride (1 mol.), because neither of the dichloroboronites is stable at room temperature. When the reactants were mixed in proportions 3 : 1, as in the case of the *n*-butyl *iso*butyl ether, the ether (1 mol.) was recovered unchanged. It might therefore be concluded that the chloroboronates do not react with ether. The chloroboronates were not isolated as their stability is low. The phenyl ethers (anisole and phenetole) with boron trichloride formed a white solid which was stable at −80°, but decomposed on melting when allowed to warm to 20°.

In no cases were dichloroboronites or alkyl halides from both the alkyl groups obtained by direct fission of the ether. In addition all the reactions appeared to have gone to completion. Experimental results are recorded in the Table, and are available for comparison with fission experiments with cold hydrogen iodide. Benton and Dillon (*J. Amer. Chem. Soc.*, 1942, **64**, 1128) treated with water the primary product from the interaction of ethers and boron tribromide, and obtained phenol and alkyl bromide from phenyl *iso*propyl and *n*-butyl phenyl ether. From benzyl *n*-propyl ether they got benzyl bromide and *n*-propyl alcohol.

The postulated mechanism for fission by boron trichloride is depicted in (1), whereas that for fission with hydrogen iodide is shown in (2) :



. . . . . . . (1)



. . . . (2)

Fission of the C–O bond in the trichloride system will be favoured by electron accession to that carbon atom. In anisole, the phenyl group can cope with electron demand without materially weakening the nuclear C–O bond and therefore fission occurs by formation of the methyl cation. In the hydrogen iodide fission we do not expect protonisation of the oxygen normally to be sufficient to effect fission, so the process is visualised as an end-on ($S_N2$) anionic exchange (2). The halogen may therefore appear on that hydrocarbon group having the weaker electron release. Whereas boron trichloride fission of *n*-butyl *sec.*-butyl ether gives *sec.*-butyl chloride, it is *n*-butyl iodide which results in the hydrogen iodide system. With *iso*butyl *sec.*-butyl ether both reagents give *sec.*-butyl halide, presumably because the *iso*butyl structure offers a measure of steric hindrance in the $S_N2$ process, which is ineffective in the carbonium-cation mechanism of the boron trichloride reaction, which also leads to rearrangement of *iso*butyl to *tert.*-butyl radical. The formation of alkyl halide from phenyl alkyl ethers in both systems is in accord with the greater electron release by the alkyl group in mechanism (1) and its greater susceptibility to nucleophilic attack in mechanism (2).

The matter may be considered in terms of complex ions, $R^+[BCl_3{\cdot}OR']^-$ and $[R\text{–}\underset{H}{O}\text{–}R']^+I^-$. The complex anion could ionise unimolecularly ($S_N1$) to $R^+ + Cl^- + R'O{\cdot}BCl_2$; but which alkyl group separates as a cation during the formation of the anion will be determined by its relative electron-release capacity. The $S_N2$ attack of the iodine anion on the cation will also be in accord with known principles (Hughes and Ingold, cf. Hughes, *J.*, 1946, 968). Greenwood, Martin, and Emeléus (*J.*, 1950,

3030) concluded that the boron trifluoride–diethyl ether complex has the structure $(C_2H_5)^+[BF_3\cdot O\cdot C_2H_5]^-$. In the boron trichloride system distribution of hydrocarbon group would be decided during the formation of the corresponding complex *anion*, whereas in the hydrogen iodide system the decision is made during the $S_N2$ attack on the complex *cation*. Nevertheless the detailed career of the approaching molecules in the boron system is still somewhat elusive. Ramser and Wiberg's solid ether complex (*loc. cit.*) was stable up to the m. p. (56°), and with water gave back the ether. Whether the complex salt referred to could do this is a matter of opinion. Our solid compounds with anisole and phenetole were decomposed by water to give back the ether. We found no sign of such addition compounds with the other ethers.

| | Fission products (*a*) | | Fission products (*b*) | | |
|---|---|---|---|---|---|
| Ether | RCl | $RO\cdot BCl_2$ | Iodide | ROH | Ref. (*b*) |
| Et, Pr$^i$ ......... | — | — | Et | Pr$^i$ | Lippert (*Annalen*, 1893, **276**, 157). |
| Et, Bu$^i$ ......... | — | — | Et | Bu$^i$ | ,, ,, ,, |
| Bu$^n$, Bu$^i$ ......... | Bu$^i$ + Bu$^t$ | Bu$^n$ | Bu$^n$ | Bu$^i$ | ,, ,, ,, |
| Bu$^n$, Bu$^s$ ......... | Bu$^s$ | Bu$^n$ | Bu$^n$ | Bu$^s$ | ,, ,, ,, |
| Bu$^i$, Bu$^s$ ......... | Bu$^s$ | Bu$^i$ | Bu$^s$ | Bu$^i$ | ,, ,, ,, |
| Allyl, Pr$^i$ ...... | — | — | allyl | Pr$^i$ | ,, ,, ,, |
| Bu$^n$, Bu$^t$ ......... | Bu$^t$ | Bu$^n$ | — | — | — |
| Bu$^i$, Bu$^t$ ......... | Bu$^t$ | Bu$^i$ | — | — | — |
| Bu$^s$, Bu$^t$ ......... | Bu$^t$ | Bu$^s$ (borate) | — | — | — |
| Oct$^n$, Et ......... | Oct$^n$ | Et | — | — | — |
| Oct$^s$, Et ......... | Oct$^s$ | Et | — | — | — |
| PhEt, Et ......... | PhEt | Et | — | — | — |
| Et, Pr$^n$ ......... | — | — | Et | Pr$^n$ | Silva (*Ber.*, 1876, **8**, 1352). |
| Me, Et ............ | — | — | Me | Et | ,, ,, |
| Ph, Me ......... | — | Ph | Me | Ph | Graebe (*Annalen*, 1866, **139**, 149). |
| Ph, Et ............ | — | Ph | — | — | |

## EXPERIMENTAL

*Preparation of Ethers.*—*iso*Butyl *tert.*-butyl and *sec.*-butyl *tert.*-butyl ether were prepared by Norris and Rigby's procedure (*J. Amer. Chem. Soc.*, 1932, **54**, 2088), the others by Williamson's synthesis. The *tert.*-butyl ethers were purified by thorough washing with water and final distillation from sodium, the others by treatment with phthalic anhydride to remove alcohol.

*Fission of Ethers by Boron Trichloride.*—*Ethyl* n-*octyl ether.* The ether (Found: C, 76·0; H, 13·9. Calc. for $C_{10}H_{22}O$: C, 75·9; H, 14·0%) (2·38 g., 1 mol.) was added to boron trichloride (3·4 g., >1 mol.) at −10°. The reaction was vigorous and a dark liquid remained. Direct distillation after 2 hours afforded ethyl dichloroboronite (1·7 g., 89%), b. p. 60—80° (redistilled), 78—80° (Found: Cl, 56·0; B, 8·34. Calc. for $C_2H_5OCl_2B$: Cl, 55·9; B, 8·5%), *n*-octyl chloride (1·8 g., 80%), b. p. 64—67°/10 mm. (redistilled), 58—60°/8 mm., $n_D^{18\cdot5}$ 1·4300 (Found: Cl, 23·8. Calc. for $C_8H_{17}Cl$: Cl, 23·9%), and a dark residue (0·55 g.). Unless otherwise stated, yields are expressed on: $ROR' + BCl_3 \longrightarrow RO\cdot BCl_2 + R'Cl$.

n-*Butyl* iso*butyl ether.* This ether (4·91 g., 1 mol.) was added to boron trichloride (4·44 g., 1 mol.) at −80°. The mixture was kept at 20° for 1½ hours. The reaction vessel was then cooled to −10° and was connected to the water-pump (20 mm.) for 3 hours. A liquid (3·4 g., 98%) consisting of a mixture of *tert.*- and *iso*-butyl chlorides, b. p. 50—65°, $n_D^{20}$ 1·3880 (Found: as *tert.*-$C_4H_9Cl$, cold KOH hydrolysable Cl, 30·5; total Cl, 38·1. Calc. for $C_4H_9Cl$: Cl, 38·4%), had collected in a trap at −80°. At −10°/0·2 mm. crude *n*-butyl dichloroboronite (4·21 g., 73%) was collected (Found: Cl, 36·8; B, 6·0. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%). On two redistillations, the purer ester, b. p. 35—38°/12 mm. (Found: Cl, 45·0; B, 6·8%), was obtained. To show that this dichloroboronite was indeed the *n*-butyl ester, it was heated for 40 hours at 110°. On distillation, *n*-butyl chloride, b. p. 76—78°, $n_D^{24}$ 1·3968, was obtained.

n-*Butyl* sec.-*butyl ether.* Boron trichloride (2·5 g., >1 mol.) was added to this ether (1·7 g., 1 mol.) at −10°. The mixture was sealed and set aside for 12 hours at 20°. Distillation afforded a mixture of *n*-butyl and *sec.*-butyl chlorides (2·2 g., 92%), b. p. 70—80° (which on treatment with water and redistillation had b. p. 70—77°, $n_D^{20}$ 1·4012), and a residue (0·53 g.) containing boron trioxide (0·297 g., 96%) as shown by analysis. (Yields in this experiment were based on: $3ROR' + 2BCl_3 \longrightarrow 3RCl + 3R'Cl + B_2O_3$.) The mixture of halides obtained in the above experiment was thought to be formed by decomposition of an intermediate dichloroboronite caused by distillation at atmospheric pressure (Gerrard and Lappert, *loc. cit.*)

and so another sample of *n*-butyl *sec.*-butyl ether (4·0 g., 1 mol.) was added to boron trichloride (3·6 g., 1 mol.) at −80°. After 1 hour at −10°, the flask was evacuated (20 mm.) while at −10°, with a trap at −80°. After 2 hours, a liquid (2·48 g.), mainly *sec.*-butyl chloride (Calc.: 2·82 g.) but containing dissolved boron trichloride (15%) (Found: cold-water hydrolysable Cl, 13·7; B, 1·43%), was collected in the trap, and on treatment with moist lead carbonate afforded pure *sec.*-butyl chloride, b. p. 66—68°, $n_D^{24}$ 1·3964. The remainder (4·80 g.) afforded, at 20°/0·5 mm., crude *n*-butyl dichloroboronite (4·4 g., 92%) (Found: Cl, 39·4; B, 6·1%) which on two redistillations afforded the pure compound, b. p. 38—39°/15 mm., $n_D^{20}$ 1·4164 (Found: Cl, 45·0; B, 6·9%). On hydrolysis a portion (3·15 g.) gave *n*-butyl alcohol (1·12 g., 75%), b. p. 117°, $n_D^{20}$ 1·4000. A residue (0·7 g.) remained from the primary distillation.

n-*Butyl* tert.-*butyl ether.* This ether (4·35 g., 1 mol.) was added to boron trichloride (3·89 g., 1 mol.) at −80°. After 1 hour at 20° the flask was cooled to −10°/20 mm. and a condensate (3·90 g.) was collected in a trap at −80°. On treatment with moist lead carbonate this afforded *tert.*-butyl chloride (2·50 g., 81%), b. p. 50—51°, $n_D^{20}$ 1·3860 (Found: Cl, 38·0%). The remainder from the original distillation was crude *n*-butyl dichloroboronite (4·27 g., 82%) (Found: Cl, 39·0; B, 6·0%) which on two redistillations gave the pure ester, b. p. 38—40°/15 mm., $n_D^{26}$ 1·3972 (Found: Cl, 45·2; B, 7·0%). The latter (1·5 g.) on hydrolysis gave *n*-butyl alcohol, b. p. 116°, $n_D^{26}$ 1·3964.

iso*Butyl* sec.-*butyl ether.* The ether (3·27 g., 1 mol.) was added to boron trichloride (2·96 g., 1 mol.) at −80°. After 10 minutes at 20°, the flask was cooled to −10°/20 mm. and a condensate (1·91 g.) was collected at −80°. This was largely *sec.*-butyl chloride but contained boron trichloride (0·29 g.), as shown by chlorine and boron analysis in the cold. On treatment with moist lead carbonate the pure chloride, b. p. 68—70°, $n_D^{21}$ 1·3957, was obtained. The remainder from the original distillation was further distilled at 0·5 mm., and crude *iso*butyl dichloroboronite (3·90 g.; Calc., 3·90 g.) (Found: Cl, 38·7; B, 6·0%) was obtained; this, purified by two distillations, had b. p. 32—34°/20 mm., $n_D^{20}$ 1·4087, $d_4^{20}$ 1·042 (Found: Cl, 45·1; B, 6·9%). A portion on aqueous treatment yielded *iso*butyl alcohol, b. p. 105—106°, $n_D^{21}$ 1·4148.

iso*Butyl* tert.-*butyl ether.* This ether (4·00 g., 1 mol.) was added to boron trichloride (3·60 g., 1 mol.) at −80°. Evacuation (20 mm.) of the reaction vessel at 0° gave crude *tert.*-butyl chloride (3·0 g.) which was condensed at −80° and, when treated with moist lead carbonate, yielded the pure chloride (2·3 g., 80%), b. p. 50—51°, $n_D^{21}$ 1·3852 [Found: Cl (cold KOH hydrolysable), 38·2%]. The residue from the primary distillation was crude *iso*butyl dichloroboronite (4·87 g.; Calc., 4·76 g.) (Found: Cl, 37·5; B, 7·0%) which on two redistillations afforded the pure ester, b. p. 32—33°/19 mm., $n_D^{21}$ 1·4090 (Found: Cl, 45·1; B, 7·1%).

*Interaction of Boron Trichloride* (1 *mol.*) *and* n-*Butyl* iso*Butyl Ether* (3 *mols.*).—*n*-Butyl *iso*butyl ether (9·14 g., 3 mols.) was added to boron trichloride (2·75 g., 1 mol.) at −80°. The mixture was kept for 1 hour at 20°. Distillation afforded a liquid (6·1 g.), b. p. 55—85°, which was probably a mixture of *tert.*-, *n*-, and *iso*-butyl chlorides (Calc., 6·46 g.), a second fraction [unchanged ether (2·5 g.; Calc., 3·05 g.)], b. p. 25—35°/20 mm., $n_D^{25}$ 1·3950 (Found: Cl, 0%), and a final fraction of tri-*n*-butyl borate (1·65 g., 92%), b. p. 71°/0·5 mm. (redistilled), 105—106°/10 mm., $n_D^{25}$ 1·4030 (Found: B, 4·8. Calc. for $C_{12}H_{27}O_3B$: B, 4·7%). This borate on hydrolysis gave *n*-butyl alcohol, b. p. 117°, $n_D^{20}$ 1·3993. A residue (0·60 g.) remained from the primary distillation, containing boron trioxide (0·551 g.; Calc., 0·545 g.) as shown by analysis. The chloride fraction was shaken with moist lead carbonate and fractionated, giving (i) (2·0 g.) b. p. 53—64°, $n_D^{25}$ 1·3855 (Found: Cl, as *tert.*-$C_4H_9Cl$, 21·4; total Cl, 38·2%), (ii) (3·0 g.) b. p. 64—69°, $n_D^{25}$ 1·3910 (Found: Cl, as *tert.*-$C_4H_9Cl$, 15·3; total Cl, 38·4%), and (iii) (0·91 g.) b. p. 69—78°, $n_D^{25}$ 1·3917 (Found: Cl, as *tert.*-$C_4H_9Cl$, 0·87; total Cl, 37·9%).

The *tert.*-butyl chloride was estimated by hydrolysis in cold aqueous potassium hydroxide, and the total chloride was found by hydrolysis in hot alcoholic potassium hydroxide in a sealed tube. Yields in the above experiment are based on: $3ROR' + BCl_3 \longrightarrow ROR'$ (unchanged) $+ (RO)_2BCl + R'Cl$; $3(RO)_2BCl \longrightarrow (RO)_3B + 3RCl + B_2O_3$.

*Interaction of Boron Trichloride* (1 *mol.*) *and* sec.-*Butyl* tert.-*Butyl Ether* (2 *mols.*).—*sec.*-Butyl *tert.*-butyl ether (3·54 g., 2 mols.) was added to boron trichloride (1·60 g., 1 mol.) at −80°. After 1½ hours at 20°, the mixture was kept at 20°/20 mm. A liquid (3·70 g.; Calc., 3·75 g.) consisting probably of a mixture of *tert.*- and *sec.*-butyl chlorides was condensed at −80°. After shaking with moist lead carbonate and redistillation, this mixture had b. p. 51—67°, $n_D^{20}$ 1·3929 (Found: Cl, as *tert.*-$C_4H_9Cl$, 23·2; total Cl, 38·2%). The remainder of the original distillation gave tri-*sec.*-butyl borate (0·91 g., 87%), b. p. 82°/10 mm., $n_D^{20}$ 1·3970 (Found: B, 4·8%), and a residue (0·51 g.) containing boron trioxide (0·33 g.; Calc., 0·317 g.) as shown by analysis. The tributyl borate on hydrolysis gave *sec.*-butyl alcohol, which was immiscible in water (contrast *tert.*-butyl alcohol). Yields in this experiment are based on: $2ROR' + BCl_3 \longrightarrow (RO)_2BCl + R'Cl$; $3(RO)_2BCl \longrightarrow (RO)_3B + 3RCl + B_2O_3$.

*Interaction of Boron Trichloride* (1 *mol.*) *and Anisole* (1 *mol.*).—Anisole (4·50 g., 1 mol.) was added to boron trichloride (4·90 g., 1 mol.) at $-80°$. A white solid formed instantly, but this slowly melted when allowed to warm to room temperature and gave a purple, clear liquid. The mixture was kept at 20°/20 mm. for 40 minutes. The remainder (6·55 g.; *i.e.*, loss in weight, 2·85 g.; Calc. loss for $CH_3Cl$ only, 2·12 g.) was phenyl dichloroboronite and the products [diphenyl chloroboronate and triphenyl borate (boron trichloride being also removed at the pump)] of its apparent disproportionation $2RO{\cdot}BCl_2 \longrightarrow (RO)_2BCl + BCl_3$; $3(RO)_2BCl \longrightarrow 2(RO)_3B + BCl_3$ [Found: Cl (cold water hydrolysable) 31·2; B, 4·8. $C_6H_5OBCl_2$ requires Cl, 40·1; B, 6·3%]. Distillation afforded a forerun (1·3 g.), b. p. 30—65°/0·2 mm. (Found: Cl, 27·0; B, 5·7%), and a solid (triphenyl borate) (3·5 g.) (Calc., 4·5 g. for complete disproportionation), b. p. 160—170°/0·2 mm. (Found: B, 3·9. Calc. for $C_{18}H_{15}O_3B$: B, 3·8%).

*Interaction of Boron Trichloride* (1 *mol.*) *and Phenetole* (1 *mol.*).—Phenetole (3·85 g., 1 mol.) was added to boron trichloride (3·7 g., 1 mol.) at $-80°$. A white solid formed. This solid, as the corresponding one in the preceding experiment with anisole, may be the boron trichloride–ether complex, which decomposes on melting. The mixture which was purple was kept for 15 hours at 20°. Free boron trichloride was then present. The mixture was kept at 15 mm. and a residue (3·34 g.) (loss in weight, 4·21 g.; Calc. loss in weight due to $C_2H_5Cl$ and remainder of Cl as $BCl_3$, 4·51 g.), which on distillation afforded a forerun (1·04 g.) of diphenyl chloroboronate and triphenyl borate, b. p. 120—150°/0·2 mm. (Found: Cl, 7·6; B, 4·3%), and triphenyl borate (2·3 g.; total triphenyl borate, 3·04 g., for complete disproportionation), b. p. 178°/0·4 mm. (Found: B, 3·8%).

Addition of water to the white solid formed at $-80°$ (25 minutes after its formation) showed that no alkyl chloride had been formed (Found: Cl, 43·9; B, 4·4. $C_8H_{10}OCl_3B$ requires Cl, 44·5; B, 4·5%); unchanged phenetole, b. p. 170°, $n_D^{19}$ 1·5083, was obtained. Similarly the anisole–boron trichloride *complex* with water (Found: Cl, 47·0; B, 4·7. $C_7H_8OCl_3B$ requires Cl, 47·4; B, 4·8%) gave the ether, b. p. 154°, $n_D^{19}$ 1·5182.

THE NORTHERN POLYTECHNIC, LONDON, N.7.

[*Received, January 2nd*, 1952.]