# *Co-ordination Compounds of Boron Trihalides. Part III.* Compounds of Boron Trifluoride with Cyclic Ethers and Dioxan.*

By JOAN GRIMLEY and A. K. HOLLIDAY.

[Reprint Order No. 4772.]

Boron trifluoride forms 1 : 1 compounds with propylene oxide and tetrahydropyran; evidence for the existence of ethylene oxide–boron trifluoride below −78·5° has been obtained. Boron trifluoride also reacts with dioxan to form the compounds $C_4H_8O_2$, $BF_3$ and $C_4H_8O_2,2BF_3$.

A FEW addition compounds of boron trifluoride with cyclic ethers have been reported previously. Brown and Adams (*J. Amer. Chem. Soc.*, 1942, **64**, 2557) investigated tetrahydrofuran–boron trifluoride as one of a series of 1 : 1 ether–boron trifluoride compounds, and found tetrahydrofuran to be a stronger donor than dimethyl, diethyl or di*iso*propyl ether. The heat of dissociation of tetrahydrofuran–boron trifluoride was given as 13·4 kcal. Stone and Emeléus (*J.*, 1950, 2755), using a large excess of ethylene oxide, studied the reaction of boron trifluoride with ethylene oxide; it was highly exothermic, and dioxan and a liquid polymeric boron-containing material were formed; the latter depolymerised at room temperature to give more dioxan and an unidentified, less volatile material. Schmeisser and Jenkner studied this reaction more recently (*Z. Naturforsch.*, 1952, **76**, 583) but also failed to isolate the 1 : 1 compound $C_2H_4O,BF_3$; even at low temperatures white crystals of dioxan–di(boron trifluoride) were formed, which decomposed at 130° into dioxan and boron trifluoride. Greenwood and Martin (*J.*, 1951, 1915) reported the formation of a stable addition compound of boron trifluoride with dioxan. The compounds $C_4H_8O_2,BF_3,2H_2O$ and $C_4H_8O_2,BF_3,H_2O$ were prepared by Meerwein and Pannwitz (*J. pr. Chem.*, 1934, **141**, 123) by the interaction of dioxan and the appropriate hydrate of boron trifluoride.

The reactions of boron trifluoride with ethylene oxide, propylene oxide, tetrahydropyran, and dioxan are now described. When ethylene oxide is condensed on to a considerable

* Part II, preceding paper.

excess of boron trifluoride at −196° and the reaction temperature is kept below −78·5°, approximately equimolar quantities of the two react to form a white solid which is probably the 1 : 1 compound. On warming to 20°, this compound rapidly darkens; considerable heat is developed, droplets of a non-volatile liquid are formed, and boron trifluoride is evolved. When, however, equivalent amounts of ethylene oxide and boron trifluoride react at −78·5° there is formed a mixture of brown and white solids which rapidly changes to a purple liquid when warmed to 20°. Boron trifluoride is recovered from this mixture on re-cooling to −78·5°, and dioxan is identified at 20°. Since dioxan and boron trifluoride form solid addition compounds of negligible volatility at −78·5°, dioxan could not have been present at −78·5° when boron trifluoride was recovered, but must have been formed on rewarming to 20°.

Equimolar amounts of propylene oxide and boron trifluoride react at −112° to give a red, viscous, non-volatile liquid, stable at room temperature. The extremely low volatility of this (presumably) 1 : 1 compound precluded further purification in the vacuum-system, and no other physical properties were determined.

Tetrahydropyran and boron trifluoride form a stable 1 : 1-compound which dissociates reversibly when heated above 80°; the heat of dissociation is approximately 38 kcal. The heat of dissociation of tetrahydrofuran–boron trifluoride (Brown and Adams, *loc. cit.*) is much less (13·4 kcal.).

The 1 : 1 compound dioxan–boron trifluoride is prepared by direct addition; on sublimation *in vacuo* at 50—60° it yields a sublimate consisting of dioxan–di(boron trifluoride) and dioxan: $2C_4H_8O_2,BF_3 \longrightarrow C_4H_8O_2,2BF_3 + C_4H_8O_2$. The 1 : 2 compound is also prepared by the reaction of liquid boron trifluoride on the 1 : 1-compound at −112°. Both the 1 : 1 and the 1 : 2 compound are only sparingly soluble in benzene and light petroleum, but appreciably soluble in dioxan. Cryoscopic determinations of the molecular weight for dioxan–boron trichloride in dioxan as solvent gave normal values (Holliday and Sowler, *J.*, 1952, 11), yet the apparent molecular weights of both the dioxan–boron trifluoride compounds are abnormally high in this solvent, and decrease with increasing solute concentration. The expected values for monomeric 1 : 1 and 1 : 2 compounds are only approached at high solute concentrations. The cryoscopic solutions were too sensitive to moisture to permit analysis of the crystals obtained on freezing. Since the 1 : 1 compound is found to react with water to form the dihydrate $C_4H_8O_2,BF_3,2H_2O$ (m. p. 140°), previously obtained by Meerwein and Pannwitz (*loc. cit.*), it seems probable that dioxan molecules may also add on when either the 1 : 1 or the 1 : 2 compound is dissolved in dioxan. Formation of aggregates of the type $(dioxan)_n$–boron trifluoride would account for the high molecular weights observed in dilute solution, and with increasing solute concentration $n$ might reasonably be expected to fall, giving the observed decrease in molecular weight.

The 1 : 1 compound melts over the range 91·4—96·1°, with a small amount of irreversible decomposition. The 1 : 2 compound does not melt below 117°; saturated vapour-pressure measurements for this compound are reproducible between 25° and 117°. The 1 : 1 compound undoubtedly dissociated when heated to give dioxan and boron trifluoride, but in view of the low value of the saturated vapour pressure of this compound at relatively high temperatures (*e.g.*, 17 mm. at 75°), no measurements of the dissociation constant were attempted. It seems clear that dioxan–di(boron trifluoride) is more stable than the 1 : 1 compound, since it is formed when the latter is heated in an open system.

The stability of cyclic ether–boron trifluoride compounds appears to increase with increase of ring size, as was observed in the boron trichloride–cyclic ether series (Part II, *loc. cit.*). The increase in stability observed in passing from ethylene oxide–boron trifluoride to tetrahydropyran–boron trifluoride is much more marked than the corresponding transition in the boron trichloride series. Again, the introduction of a methyl group into ethylene oxide, to form propylene oxide, has a different effect, since propylene oxide–boron trifluoride is certainly more stable than ethylene oxide–boron trifluoride. Replacement of a ring methylene group in tetrahydropyran by an oxygen atom, to form dioxan, increased the thermal stability of the boron trichloride addition compound, but this effect is not so obvious in the case of the boron trifluoride addition compounds, as the stability is already large. The most marked difference between the two sets of compounds is the complete

absence of decomposition of the boron trifluoride addition compounds by ring fission, followed by elimination of hydrogen fluoride. This can doubtless be ascribed to the different effects of the two boron trihalides on the ring atoms, leading to differences in the ease with which carbon-attached hydrogen atoms can be attacked. Certainly there is a notable difference in the effect of single co-ordination to the dioxan ring, in that a 1 : 2 compound with *two* co-ordinated boron trihalide molecules can be made from the 1 : 1 compound for the trifluoride but not for the trichloride. This does not necessarily imply a marked difference in the character of the unco-ordinated oxygen atoms of dioxan–boron trifluoride and dioxan–boron trichloride, as non-formation of dioxan–di(boron trichloride) may be explained equally well in terms of the difference in " co-ordinating power " or electronegativity of the two trihalides. A study of oxygen-containing rings with *both* boron trifluoride and boron trichloride co-ordinated simultaneously is now in progress.

## Experimental

The experimental methods were as described by Holliday and Sowler (*J.*, 1952, 11). Boron trifluoride was estimated volumetrically by the method of Swinehart, Bumblis, and Flisik (*Analyt. Chem.*, 1947, **19**, 28). As an additional check fluoride was estimated gravimetrically as calcium fluoride, and boron was determined in the filtrate.

Commercial boron trifluoride was purified by fractionation in a high-vacuum apparatus, and then stored in a mercury-sealed bulb.

*Reaction of Boron Trifluoride with Ethylene Oxide.*—Ethylene oxide (5·6 mmoles) was condensed on to excess (34·7 mmoles) of boron trifluoride (v. p. 292 mm. at −111·8°) at liquid-nitrogen temperature. After 3 hr. at −111·8°, a white solid remained at the bottom of the reaction vessel and a brown residue at the top. 28·1 mmoles of unchanged boron trifluoride were recovered at −111·8°; hence 6·6 mmoles had reacted with the ethylene oxide (ratio $C_2H_4O : BF_3 = 1 : 1{\cdot}18$). When the vessel was warmed to −78·5°, 2·0 mmoles of boron trifluoride were evolved, and the white solid became discoloured (ratio $C_2H_4O : BF_3 = 1 : 0{\cdot}82$). When the temperature rose to that of the room only boron trifluoride (1·1 mmoles) was isolated.

*Reaction of Boron Trifluoride with Propylene Oxide.*—Propylene oxide (6·3 mmoles) was condensed on boron trifluoride (34·8 mmoles) at liquid-nitrogen temperature. Warming to −111·8° produced dense brown fumes; after 30 min. at this temperature, excess of boron trifluoride (28·4 mmoles) was recovered. No further evolution of boron trifluoride occurred when warmed to 20°. Hence 6·4 mmoles of boron trifluoride react with 6·3 mmoles of propylene oxide.

*Reaction of Boron Trifluoride with Tetrahydropyran.*—Boron trifluoride (15·4 mmoles) was passed slowly through tetrahydropyran (11·8 mmoles) at −40°; the liquid gradually became yellow. On warming to 20°, only 3·6 mmoles of boron trifluoride were recovered; hence equimolecular amounts (11·8 mmoles) had reacted, and no other material was formed. Molecular-weight determinations in nitrobenzene gave $M$ = 165 ($C_5H_{10}O,BF_3$ requires $M$, 154), hence the 1 : 1 compound *tetrahydropyran–boron trifluoride*, m. p. ~ −18°, has been formed. The compound fumes in moist air, and finally leaves a residue of boric acid. Saturated vapour pressures were reproducible between 46° and 122°, and are represented by the equation $\log p + 2550/T = 8{\cdot}74$; the molar latent heat (46—122°) is 11·7 kcal./mole and Trouton's constant is 26·8. The " boiling point," 162° at 760 mm. (by extrapolation), is not a true one, as tetrahydropyran–boron trifluoride is largely dissociated before the b. p. is reached. Vapour densities were measured over the range 83—118°, and the results are tabulated below. The calculated vapour density for the monomer $C_5H_{10}O,BF_3$ is 77; hence dissociation occurs above 83°, and to the extent of 91% at 118°. The heat of dissociation, based on a small number of readings, is 38 kcal.

| Temp. | 83° | 94° | 111·5° | 118° |
|---|---|---|---|---|
| V.d., obs. | 75·5 | 53 | 42·2 | 40·2 |

*Reaction of Boron Trifluoride with Dioxan.*—Boron trifluoride (15·1 mmoles) was passed through a 1 : 7 mixture of dioxan (14·1 mmoles) and light petroleum at 11°, until absorption of boron trifluoride ceased. A gelatinous mass formed and volatile products were removed at −30° and fractionated; only 0·51 mmole of boron trifluoride and unchanged light petroleum were recovered. The white solid residue in the reaction vessel was analysed [Found: $BF_3$, 43·4; B, 7·05; F, 36·2%; $M$, 321 (1·84% solution) 211 (3·86%). $C_4H_8O_2,BF_3$ requires $BF_3$, 43·6; B, 7·05; F, 36·6%; $M$, 156]. *Dioxan–boron trifluoride* fumes in moist air, and finally

leaves a residue of boric acid. Saturated vapour-pressure readings between 15° and 107° indicate slight irreversible secondary decomposition. The compound melts over the range 91—96°; the log $p$–$(1/T)$ plot is slightly curved, and indicates an apparent m. p. at 93°. A sample of the 1 : 1 compound, heated at 120° for 2½ hr. in a sealed tube, yielded only a trace of decomposition product on cooling; yet a sample heated in an open system at 50—60° yielded a colourless volatile liquid (v. p. 9 ± 2 mm. at 0°. Dioxan has v. p. 10 mm. at 0°) and a white solid (Found: $BF_3$, 58·9. $C_4H_8O_2,2BF_3$ requires $BF_3$, 60·7%).

*Reaction of dioxan–boron trifluoride with water.* A slight excess of water was condensed on to a sample of the 1 : 1 compound, and reaction allowed to proceed for several hours. Excess of water was removed at 60°, and the colourless crystals which separated, m. p. 140° (decomp.), were analysed (Found: F, 30·7. Calc. for $C_4H_8O_2,BF_3,2H_2O$: F, 29·7%); the dihydrate is reported to have m. p. 142° (decomp.) (Meerwein and Pannwitz, *loc. cit.*).

*Reaction of dioxan–boron trifluoride with excess of boron trifluoride.* Excess (142·4 mmoles) of boron trifluoride was condensed on dioxan–boron trifluoride (7·67 mmoles) at liquid-nitrogen temperature. The mixture was allowed to react at −112° for 6 hr., and unchanged boron trifluoride was removed at −112° and then at −78·5°. The reaction vessel was warmed to 20° and then re-cooled to −78·5°, until no more boron trifluoride was evolved; in all, 136·0 mmoles of boron trifluoride were recovered, so 6·4 mmoles react with 7·67 mmoles of dioxan–boron trifluoride. The white solid remaining in the reaction vessel was analysed [Found: $BF_3$, 59·7; F, 49·6%; $M$, 611 (1·83% solution), 272 (2·92%). $C_4H_8O_2,2BF_3$ requires $BF_3$, 60·7; F, 50·8%; $M$, 224]. For *dioxan–di(boron trifluoride)* saturated vapour-pressure readings are reproducible between 25° and 117°, and are represented by the equation $\log p + 2700/T = 9{\cdot}81$. The solid darkens slightly above 75°, but no m. p. is observed below 117°.

Department of Inorganic and Physical Chemistry,
The University of Liverpool. [*Received, November 6th,* 1953.]