62. *Reactions in Boron Trichloride–Cyclic Ether Systems.*
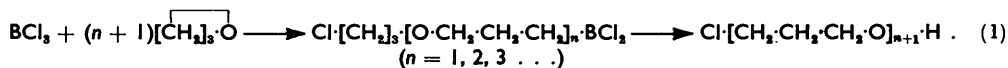
By J. D. Edwards, W. Gerrard, and M. F. Lappert.

Reactions of boron trichloride with ethylene, propene, and trimethylene oxides, epichlorohydrin (1-chloro-2 : 3-epoxypropane), tetrahydrofuran, and tetrahydropyran have been investigated; the results supplement our earlier work [1] with ethylene oxide and tetrahydrofuran. Only the ethers having five- or six-membered rings formed 1 : 1-complexes with the trichloride; these were solids stable at 20° and the stoicheiometries of pyrolysis, hydrolysis, and reaction with pyridine were established. The other cyclic ethers were cleaved by boron trichloride to give chloroalkoxyboron esters, the chloroalkoxy-groups of which contained either the same number of carbon atoms as the ether or a small integral multiple. Corresponding boron esters were obtained either when the boron trichloride complex of tetrahydrofuran or tetrahydropyran was heated with the ether, or from boron trichloride and tetrahydrofuran or tetrahydropyran, the ether being present in excess. These boron esters were identified by conversion into the appropriate alcohol by " methanolysis." The results are discussed.

EARLIER we [1] described reactions of boron trichloride with ethylene oxide and with tetrahydrofuran. These have now been examined in greater detail and the investigation has been extended to the corresponding propene oxide, epichlorohydrin, trimethylene oxide, and tetrahydropyran systems.

In many of the reactions to be described, products included chloroalkoxyboron chlorides, $RO \cdot BCl_2$ and $(RO)_2B \cdot Cl$, and trischloroalkyl borates, $(RO)_3B$. For identification, we used our earlier characterisation of some of these,[2] but identification was difficult, particularly if the esters were present in mixtures, and for this purpose a new technique was devised, which we term " methanolysis." The boron compound is treated with a large excess of methanol, so that all the boron in the esters is converted into methyl borate and chlorine attached to boron into hydrogen chloride. Fractional distillation affords initially the methanol–methyl borate azeotrope (b. p. 56°) and methanol (b. p. 65°) and subsequently the alcohols, ROH, as higher-boiling fractions. This method, by identifying the alcohol derived from the ester, is superior to the alternative of hydrolysis because of the high water-solubility of many of the alcohols and the losses inevitably incurred in extraction and drying.

The first series of experiments concerned the interaction in equimolecular proportions of the cyclic ether with boron trichloride. It had previously been shown that tetrahydrofuran afforded a solid 1 : 1-complex, whereas ethylene oxide underwent ring fission even at −80°, to produce 2-chloroethyl dichloroboronite.[1] It is now shown that tetrahydropyran, like tetrahydrofuran, forms a solid 1 : 1 complex, both having a finite stability at 20°. With trimethylene oxide there was no evidence for complex formation; evidence for ring fission was that the product had only approximately two-thirds of the total chlorine easily hydrolysable, suggesting that a dichloroboronite, or a mixture of these, had been formed (an ether complex would have all the chlorine easily hydrolysable). Methanolysis of the product afforded only a little 3-chloropropan-1-ol, the remainder of the alcoholic material being high-boiling, with the chlorine content diminishing with increasing boiling point. This suggests that polymerisation had taken place [see scheme (1)] particularly by analogy with other cyclic ether systems (see below).

$$BCl_3 + (n + 1)[\overline{CH_2]_3 \cdot O} \longrightarrow Cl \cdot [CH_2]_3 \cdot [O \cdot CH_2 \cdot CH_2 \cdot CH_2]_n \cdot BCl_2 \longrightarrow Cl \cdot [CH_2 \cdot CH_2 \cdot CH_2 \cdot O]_{n+1} \cdot H \quad . \quad (1)$$
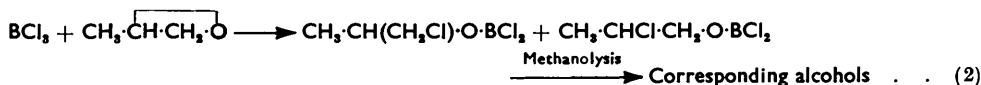$$(n = 1, 2, 3 \ldots)$$

Neither with epichlorohydrin nor with propene oxide was there evidence for complex formation. The product, in each case, had approximately two-thirds of the chlorine

[1] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.
[2] Abel, Edwards, Gerrard, and Lappert, *J.*, in the press.

easily hydrolysable, indicating the presence of dichloroboronites. Methanolysis of the epichlorohydrin product afforded 1 : 3-dichloropropan-2-ol (61%) as the major constituent and also 1-chloro-3-(2-chloro-1-chloromethylethoxy)propan-2-ol and the reactions may be represented by an equation analogous to scheme (1). Similar treatment of the propene oxide product afforded [see scheme (2)] a mixture of 2-chloropropan-1-ol and 1-chloro-propan-2-ol, with the latter isomer preponderating, and a small residue, probably consisting of higher-boiling alcohols.

$$BCl_3 + CH_3 \cdot \overset{\frown}{CH \cdot CH_2} \cdot O \longrightarrow CH_3 \cdot CH(CH_2Cl) \cdot O \cdot BCl_2 + CH_3 \cdot CHCl \cdot CH_2 \cdot O \cdot BCl_2$$

$$\xrightarrow{\text{Methanolysis}} \text{Corresponding alcohols} \quad . \quad . \quad (2)$$

Because of the isolation of polymeric products in the already described reactions, in the next series of experiments boron trichloride was treated with excess of the cyclic ether. The interaction of boron trichloride (1 mol.) with tetrahydropyran or tetrahydrofuran (6 mols.), and subsequent removal of ether which had not reacted, gave a product which contained only a small fraction of the total chlorine as easily hydrolysable, indicating that borates had been formed and that alkoxyboron chlorides were virtually absent. Methanolysis of each product gave a mixture of the monomeric and dimeric alcohols and a higher-boiling residue, probably comprising higher molecular-weight polyalkoxy-alcohols. The two systems differed in that with tetrahydrofuran 4-4'-chlorobutoxybutan-1-ol was by far the major product, whereas with tetrahydropyran 5-5'-chloropentyloxypentan-1-ol was obtained in only slightly greater amount than the 5-chloropentan-1-ol. The two reactions are represented by scheme (3), with $m = 4$ or 5 :
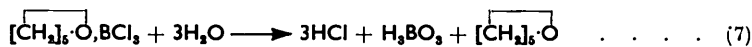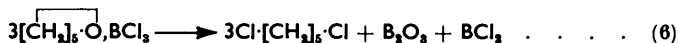
$$BCl_3 + (3n + 3)[\overset{\frown}{CH_2}]_m \cdot O \longrightarrow (Cl \cdot [CH_2]_m \cdot \{O \cdot [CH_2]_m\}_n \cdot O)_3 B \xrightarrow{\text{Methanolysis}} 3Cl \cdot \{[CH_2]_m \cdot O\}_{n+1} \cdot H . \quad (3)$$

A corresponding experiment in the ethylene oxide system ($m = 2$) produced a like result; however almost all the alcohol isolated was 2-chloroethanol, although some 2-(2-chloro-ethoxy)ethanol was identified. Tri-(2-chloro-1-chloromethylethyl) borate was present (about 50% w/w) in the primary product obtained in the epichlorohydrin system, the remainder being higher-boiling material, which on methanolysis yielded fractions having decreasing chlorine content and increasing molecular weights as the boiling points rose. This suggests that fission and polymerisation of the type analogous to scheme (3) had occurred.

The interaction of boron trichloride with propene oxide in the stated proportions (schemes 4 and 5) afforded mainly the chloropropoxyboron esters.
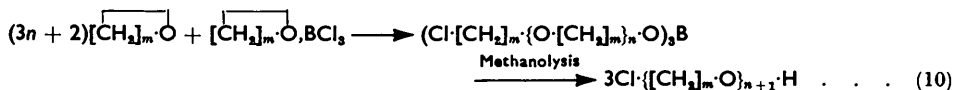
$$BCl_3 + 2CH_3 \cdot \overset{\frown}{CH \cdot CH_2} \cdot O \longrightarrow (ClC_3H_6O)_2B \cdot Cl \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$BCl_3 + 3CH_3 \cdot \overset{\frown}{CH \cdot CH_2} \cdot O \longrightarrow (ClC_3H_6O)_3B \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We had previously investigated certain reactions (hydrolysis, n-butanolysis, and pyrolysis) of the tetrahydrofuran–boron trichloride complex.[1] It is now shown that the pyrolysis of the tetrahydropyran complex is similar [scheme (6)]. The tetrahydropyran complex underwent no appreciable decomposition after 2 days at 20°, and for a period of weeks thereafter it retained its crystalline appearance. By contrast, the tetrahydrofuran complex became dark and sticky after only a few days. Hydrolysis of the tetrahydro-pyran complex [see scheme (7)] was similar in its stoicheiometry to the hydrolysis of the tetrahydrofuran complex; however the latter complex was noticeably less readily hydrolysed than the former. The liberation of 3 mol. of hydrogen chloride by action of cold water on the complex is evidence for its formulation as a co-ordination compound; 5-chloropentyl dichloroboronite (like its 4-chlorobutyl homologue) which is isomeric with the complex, liberates only two mol. of hydrogen chloride on cold aqueous hydrolysis. The two complexes differed in their reactions with pyridine. Whereas boron trichloride was
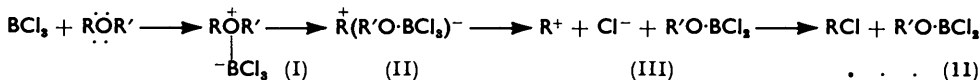
displaced from the tetrahydropyran complex [see scheme (8)], ring fission occurred with the tetrahydrofuran complex [see scheme (9)].

$$3[\overline{CH_2]_5 \cdot O},BCl_3 \longrightarrow 3Cl \cdot [CH_2]_5 \cdot Cl + B_2O_3 + BCl_3 \quad \dots \quad (6)$$

$$[\overline{CH_2]_5 \cdot O},BCl_3 + 3H_2O \longrightarrow 3HCl + H_3BO_3 + [\overline{CH_2]_5 \cdot O} \quad \dots \quad (7)$$

$$[\overline{CH_2]_5 \cdot O},BCl_3 + C_5H_5N \longrightarrow C_5H_5N,BCl_3 + [\overline{CH_2]_5 \cdot O} \quad \dots \quad (8)$$

$$[\overline{CH_2]_4 \cdot O},BCl_3 + C_5H_5N \longrightarrow C_5H_5N,Cl \cdot [CH_2]_4 \cdot O \cdot BCl_2 \quad \dots \quad (9)$$

The tetrahydrofuran–boron trichloride complex reacted exothermally with tetrahydrofuran (5 mol.). Only a small percentage of the total chlorine present in the product was easily hydrolysable. Methanolysis afforded [scheme (10), $m = 4$] 4-chlorobutan-1-ol and 4-4'-chlorobutoxybutan-1-ol in roughly equal amounts as well as a small quantity of higher-boiling material having less chlorine than either alcohol. Similar results were obtained with tetrahydropyran [scheme (10), $m = 5$], but the reaction was slower and heating was required to convert most of the chlorine, present in the primary reaction product, into non-easily hydrolysable form.

$$(3n + 2)[\overline{CH_2]_m \cdot O} + [\overline{CH_2]_m \cdot O},BCl_3 \longrightarrow (Cl \cdot [CH_2]_m \cdot \{O \cdot [CH_2]_m\}_n \cdot O)_3B$$

$$\xrightarrow{\text{Methanolysis}} 3Cl \cdot \{[CH_2]_m \cdot O\}_{n+1} \cdot H \quad \dots \quad (10)$$

Discussion.—Extensive studies on the reactions in equimolecular proportions between non-cyclic ethers, ROR', and boron trichloride have indicated that the mechanism follows scheme (11), wherein R is more electron-releasing than R'.[3]

$$BCl_3 + R\ddot{O}R' \longrightarrow R\overset{+}{O}R' \longrightarrow \overset{+}{R}(R'O \cdot BCl_3)^- \longrightarrow R^+ + Cl^- + R'O \cdot BCl_2 \longrightarrow RCl + R'O \cdot BCl_2$$

$$\phantom{BCl_3 + R\ddot{O}R' \longrightarrow} \overset{|}{-}BCl_3 \quad \text{(I)} \qquad \text{(II)} \qquad\qquad \text{(III)} \qquad\qquad\qquad \dots \quad (11)$$

It is reasonable to expect that there will be a mechanistic similarity between these reactions and those involving cyclic ethers. In the three- and four-membered ring systems there was no evidence for the formation of complexes of the type (I) even at very low temperatures (see also ref. 1) although they may be formed as reaction intermediates. The relative stabilities of the tetrahydropyran and tetrahydrofuran complexes and the non-formation (or lack of stability) of complexes in the other cyclic ether systems may be interpreted in terms of *I*-steric strain and the results are available for comparison with those obtained by H. C. Brown and Gerstein on the stability of cyclic amine–trimethylboron complexes.[4]

The products of fission in the cyclic ether systems, when the reactants are present in equimolecular proportions, should be the ω-chloroalkyl dichloroboronites, by analogy with (III) in scheme (11). These were in fact isolated, but a mechanism must satisfy the condition that dimeric and polymeric esters are also isolated [scheme (1)]. The mechanism shown in scheme (12) for ethylene oxide accounts for the experimental observations and similar mechanisms may be postulated to operate in the other three- and four-membered ring systems.
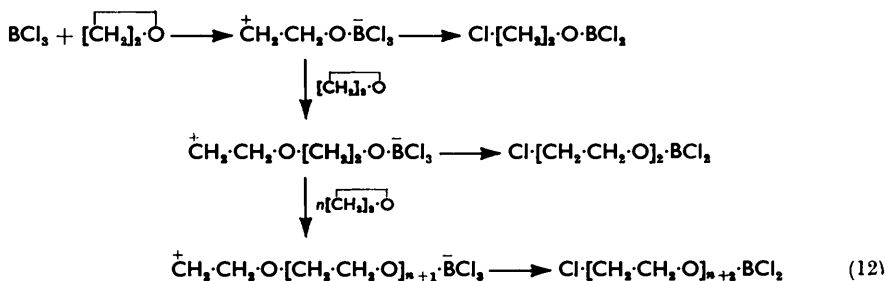
In each of the propene oxide and epichlorohydrin reactions two isomeric dichloroboronites may be formed. Whereas predictions based on scheme (11) (S_N1) would suggest

$$\text{CH}_3 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{BCl}_2 \qquad \text{CH}_3 \cdot \text{CH(CH}_2\text{Cl)} \cdot \text{O} \cdot \text{BCl}_2 \qquad \text{CH}_2\text{Cl} \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{BCl}_2 \qquad \text{(CH}_2\text{Cl)}_2\text{CH} \cdot \text{O} \cdot \text{BCl}_2$$
$$\text{(IV)} \qquad\qquad\qquad \text{(V)} \qquad\qquad\qquad\qquad \text{(VI)} \qquad\qquad\qquad\qquad \text{(VII)}$$

that compounds (IV) and (VI) should be formed, predictions based on S_N2 decomposition of the complex (I) would point to compounds (V) and (VII), respectively, in the two systems. The experimental results indicate that in the epichlorohydrin system the S_N2 mechanism is

[3] Gerrard and Lappert, *J.*, 1951, 1020; 1952, 1486; Edwards, Gerrard, and Lappert, *J.*, in the press; Gerrard, Lappert, and Silver, *J.*, 1956, 4987.
[4] H. C. Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2926.

the controlling one, whilst both mechanisms appear to be of importance in the case of propene oxide.

$$BCl_3 + [CH_2]_2 \cdot O \longrightarrow \overset{+}{C}H_2 \cdot CH_2 \cdot O \cdot \overset{-}{B}Cl_3 \longrightarrow Cl \cdot [CH_2]_2 \cdot O \cdot BCl_2$$

$$\downarrow [CH_2]_2 \cdot O$$

$$\overset{+}{C}H_2 \cdot CH_2 \cdot O \cdot [CH_2]_2 \cdot O \cdot \overset{-}{B}Cl_3 \longrightarrow Cl \cdot [CH_2 \cdot CH_2 \cdot O]_2 \cdot BCl_2$$

$$\downarrow n[CH_2]_2 \cdot O$$

$$\overset{+}{C}H_2 \cdot CH_2 \cdot O \cdot [CH_2 \cdot CH_2 \cdot O]_{n+1} \cdot \overset{-}{B}Cl_3 \longrightarrow Cl \cdot [CH_2 \cdot CH_2 \cdot O]_{n+2} \cdot BCl_2 \qquad (12)$$

In the five- and six-membered ring systems, a mechanism analogous to (12) may operate also. However, as in these reactions, complexes of type (I) are stable and because polymeric products are formed in larger proportions than in the other systems, mechanisms (13) or (14) ($m = 2$ or 3) may be more likely.

Scheme (13)

and continues as in Scheme (12)

Scheme (14)

Polymeric products

(i) Loses; (ii) gains $[CH_2]_{m+3} \cdot O$
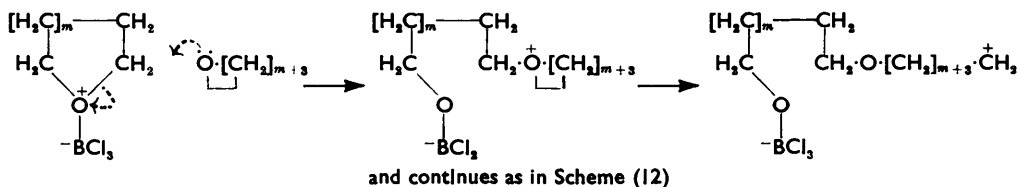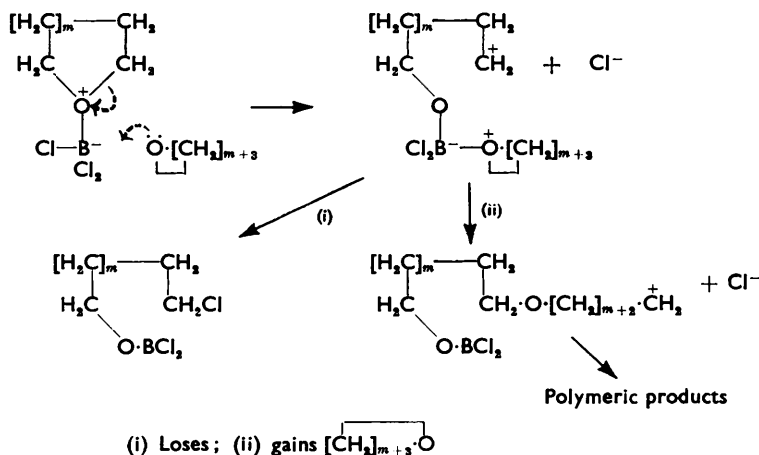
The polymerisation is of greater significance with tetrahydrofuran than tetrahydropyran. This may be related to the fact that different products [reactions (8) and (9)] are obtained by action of pyridine on the complexes. Reaction (9) may follow a similar path to that put forward in (14), pyridine being the nucleophilic reagent replacing a chlorine anion in the complex.

The reactions (3), involving boron trichloride and excess of the cyclic ether, evidently imply that the borate end-products are formed step-wise. Whereas in corresponding non-cyclic ether systems, similar reactions between ethers and either boron trichloride or alkyl dichloroboronites are well known, dialkyl chloroboronates have hitherto proved unreactive with ethers.

Polymerisations of tetrahydrofuran and tetrahydropyran with certain acyl and

inorganic chlorides have previously been observed [for summary see ref. (5)] and a growing cation has been suggested as the means of propagation.

The dimeric alcohols, except 2-chloroethoxyethanol, are new compounds and the methods disclosed herein may prove of synthetic value.

Our observations and conclusions differ very markedly from those of Grimley and Holliday.[6] These authors reported the formation of co-ordination complexes between boron trichloride and ethylene and propene oxide, tetrahydrofuran, and tetrahydropyran and studied their modes of decomposition. The ethylene oxide complex was said to dissociate reversibly, and the others irreversibly, each evolving hydrogen chloride as well as boron trichloride.

<h1 align="center">EXPERIMENTAL</h1>

Trimethylene oxide was prepared by Noller's method.[7] The tetrahydrofuran–boron trichloride complex [1] and 3-chloropropyl dichloroboronite [3] were obtained by methods already reported. 1-Chloropropan-2-ol (28·85 g., 44%), b. p. 69°/90 mm., n_D^{21} 1·4372, d_4^{20} 1·114 (Found : Cl, 37·4. Calc. for C_3H_7OCl : Cl, 37·6%), was prepared by addition of monochloroacetone (64·7 g., 0·697 mole) in ether (30 c.c.) to a stirred, ice-cooled solution of lithium aluminium hydride (10·00 g., 0·264 mole) in ether (250 c.c.), whereafter the mixture was treated with concentrated sulphuric acid (35 c.c.) in water (200 c.c.) and the ether layer separated; this was dried ($MgSO_4$), concentrated, and distilled. 2-Chloropropan-1-ol was obtained by the method of Pickett, Garner, and Lucas.[8]

Analytical procedures have been described previously;[1,2,3] e.h. Cl refers to chloride-ion estimation of easily (cold water) hydrolysable chlorine. Molecular weights were determined cryoscopically in benzene or *cyclo*hexane.

Interaction of Cyclic Ethers (1 *mol.*) *with Boron Trichloride* (1 *mol.*).—*Tetrahydropyran.* The ether (3·55 g., 1 mol.) in *n*-pentane (15 c.c.) was added to the trichloride (4·85 g., 1 mol.) in *n*-pentane (25 c.c.) at −80°. The precipitated *tetrahydropyran–boron trichloride complex* (8·15 g., 97%), m. p. 62—63° (Found : e.h. Cl, 51·8; B, 5·5. $C_5H_{10}OCl_3B$ requires e.h. Cl, 52·4; B, 5·3%), was filtered off and washed with *n*-pentane. After 2 days at room temperature no appreciable decomposition was noted. The complex was immediately hydrolysed by cold water.

Trimethylene oxide. The ether (1·90 g.) was added to the trichloride (3·85 g.) at −80°, whereupon a violent reaction took place. At 20°, a solid which had formed melted with evolution of heat to produce two layers, but after 2 hr. the mixture became homogeneous. During this time, boron trichloride (0·55 g.) (Found : Cl, 89·8; B, 9·5. Calc. for Cl_3B : Cl, 90·2; B, 9·2%) had distilled from the mixture and was condensed at −80°. A portion (4·85 g.) of the residue (5·05 g.) (Found : e.h. Cl, 35·8; Cl, 61·1; B, 6·0%) gave at 26°/0·5 mm. a condensate (2·80 g.), collected at −80°, having n_D^{21} 1·4460 (Found : e.h. Cl, 35·8; Cl, 58·9; B, 5·54%; equivalence ratio e.h. Cl : B = 2 : 1), and a residue (1·75 g.), n_D^{21} 1·4722 (Found : e.h. Cl, 26·7; Cl, 48·2; B, 6·6%). A portion (1·80 g.) of the condensate, when treated with methanol (7 c.c.), afforded a large forerun of methanol–methyl borate azeotrope and 3-chloropropan-1-ol (0·50 g.), b. p. 67°/19 mm., n_D^{20} 1·4455 (Found : Cl, 37·7. Calc. for C_3H_7OCl : Cl, 37·6%).

In a second experiment the ether (1·95 g.) and the trichloride (3·95 g.) were mixed in the presence of methylene dichloride (40 c.c.) at −80°, whereafter 3-chloropropan-1-ol (6·37 g., 2 mol.) was added to the mixture still at −80°. The product was set aside for 40 min. at 20°; matter volatile at 20°/15 mm. was then removed, leaving a residue (9·95 g.), n_D^{16} 1·4575 (Found : e.h. Cl, 5·3; Cl, 35·8; B, 3·7%). Distillation of a portion (8·65 g.) afforded a forerun (3·95 g.), b. p. up to 102°/0·075 mm., n_D^{16} 1·4575 (Found : e.h. Cl, 10·2; Cl, 42·1; B, 4·2%); tris-3-chloropropyl borate (2·90 g.), b. p. 102—103°/0·075 mm., n_D^{16} 1·4593 (Found : Cl, 36·1; B, 3·7. Calc. for $C_9H_{18}O_3Cl_3B$: Cl, 36·5; B, 3·7%); and a residue (1·45 g.) (Found : Cl, 17·0; B, 2·4%).

In a final experiment, to the mixture at −80°, obtained from the ether (3·61 g.) and the trichloride (7·30 g.) in methylene dichloride (40 c.c.), methanol (30 c.c.) was immediately added. Removal of volatile matter left a residue (4·40 g.) (Found : Cl, 15·1%). A portion (3·80 g.)

[5] Alexander and Schniepp, *J. Amer. Chem. Soc.*, 1948, **70**, 1839; Delfs, P. B. 717, O.T.S., U.S. Department of Commerce.
[6] Grimley and Holliday, *J.*, 1954, 1212.
[7] Noller, *Org. Synth.*, 1949, **29**, 92.
[8] Pickett, Garner, and Lucas, *J. Amer. Chem. Soc.*, 1951, **73**, 5066.

afforded a forerun (0·25 g.), b. p. up to 63°/14 mm., n_D^{20} 1·4428 (Found : Cl, 30·1%) ; 3-chloro-propan-1-ol (0·85 g.), n_D^{20} 1·4447 (Found : Cl, 37·6%) ; a liquid (0·45 g.), b. p. 68—123°/14 mm., n_D^{20} 1·4462 (Found : Cl, 31·0%) ; a liquid (0·45 g.), b. p. up to 130°/0·005 mm., n_D^{20} 1·4540 (Found : Cl, 18·7%) ; a liquid (0·50 g.), b. p. 130—205°/0·0075 mm., n_D^{20} 1·4576 (Found : Cl, 11·1%) ; a liquid (0·60 g.), b. p. 205—234°/0·005 mm., n_D^{20} 1·4593 (Found : Cl, 5·0%) ; and a residue (0·55 g.).

Epichlorohydrin. The ether (6·54 g.) at −60° was added to boron trichloride (8·3 g.) at −80° ; a violent reaction ensued. At 20°, boron trichloride (0·15 g.) (Found : Cl, 91·0 ; B, 9·4%) distilled off, leaving a residue (14·3 g.), n_D^{21} 1·4708, d_4^{18} 1·424 (Found : e.h. Cl, 35·7 ; Cl, 66·3 ; B, 5·2%). To a portion (10·40 g.) at −80°, methanol (20 c.c.) was added. Matter volatile at 20°/20 mm. was removed to leave a residue (6·25 g.) which afforded a forerun (0·26 g.), n_D^{21} 1·4788 ; 1 : 3-dichloropropan-2-ol [4·00 g., 61% based on BCl$_3$ + epichlorohydrin $\longrightarrow$ (ClCH$_2$)$_2$CH·O·BCl$_2$ $\longrightarrow$ (ClCH$_2$)$_2$CH·OH], b. p. 64—70°/10 mm., n_D^{21} 1·4823, d_4^{22} 1·410 (Found : Cl, 55·5. Calc. for C$_3$H$_6$OCl$_2$: Cl, 55·0%) (the infrared spectrum was identical with that of an authentic specimen) ; a liquid (1·30 g.), probably 1-chloro-3-(2-chloro-1-chloromethylethoxy)-propan-2-ol, b. p. 140°/10·5 mm. to 100°/0·4 mm. (mainly having b. p. 98°/0·4 mm.), n_D^{21} 1·4911 (Found : Cl, 48·5. Calc. for C$_6$H$_{11}$O$_2$Cl$_3$: Cl, 48·1%) ; and a residue (0·20 g.).

Propene oxide. The ether (2·87 g.) at −40° was added to the trichloride (5·80 g.) at −80°. A portion (7·90 g.) of the product (8·60 g.), n_D^{20} 1·4392 (Found : e.h. Cl, 39·1 ; Cl, 58·7 ; B, 6·07%), afforded at 20°/0·5 mm. a dichloroboronite (5·40 g.) (2-chloropropyl, 2-chloro-1-methyl-ethyl, or a mixture of the two), n_D^{20} 1·4369, d_4^{20} 1·276 (Found : e.h. Cl, 41·7 ; Cl, 62·0 ; B, 6·2. Calc. for C$_3$H$_6$OCl$_3$B : e.h. Cl, 40·5 ; Cl, 60·8 ; B, 6·2%), which was condensed at −80°, and a residue (2·05 g.), probably the crude chloroboronate, n_D^{20} 1·4483 (Found : e.h. Cl, 16·2 ; Cl, 44·3 ; B, 4·9. Calc. for C$_6$H$_{12}$O$_2$Cl$_3$B : e.h. Cl, 15·2 ; Cl, 45·6 ; B, 4·6%).

In a separate experiment, the product obtained by mixing the ether (5·31 g.) and the tri-chloride (10·75 g.) at −80° was set aside for 15 min. at 15°, whereafter water (15 c.c.) was added and the mixture again cooled to −80°. After 1 hr. at 20°, the precipitated boric acid was filtered off and washed with ether ; the filtrate was extracted with ether (8 × 25 c.c.). The combined ethereal solutions were dried (MgSO$_4$), concentrated, and distilled giving a chloro-propanol (5·20 g., 60% based on BCl$_3$ + oxide $\longrightarrow$ C$_3$H$_6$ClO·BCl$_2$ $\longrightarrow$ C$_3$H$_6$Cl·OH), b. p. 64—65°/90 mm., n_D^{20} 1·4381, d_4^{20} 1·111 (Found : Cl, 37·6%) ; and a trischloropropyl borate (0·56 g.), n_D^{20} 1·4469 (Found : Cl, 35·8 ; B, 3·64. Calc. for C$_9$H$_{18}$O$_3$Cl$_3$B : Cl, 36·5 ; B, 3·70%).

In a further experiment the product obtained by mixing the ether (3·71 g.) and the tri-chloride (7·50 g.) at −80° and allowing the mixture to attain room temperature was treated with methanol (20·4 g.) at −80°. After removal of matter volatile at <70°/95 mm., a mixture of chloropropanols (4·35 g., 71%), b. p. 70—73·5°/95 mm., n_D^{19} 1·4375, d_4^{20} 1·114 (Found : Cl, 37·4%), was obtained, together with a residue (0·55 g.) (Found : Cl, 20·1%). This mixture was shown to consist of 2-chloropropan-1-ol and 1-chloropropan-2-ol (55—70%) by examination of an infrared spectrum and comparison with the spectra of authentic specimens.

Interaction of Cyclic Ethers (6 *mols.*) *with Boron Trichloride* (1 *mol.*).—*Tetrahydropyran.* The trichloride (4·25 g.) at −60° was added to the ether (18·70 g.) at −80°. The mixture was allowed to warm to room temperature and was then heated (14·25 hr.) under reflux, whereafter it was set aside for 22 days at 20°. Tetrahydropyran (10·10 g.), b. p. 84—90°/760 mm., d_4^{14} 0·889, was removed at 20°/10 mm., leaving a residue (11·65 g.) (Found : e.h. Cl, 3·2 ; B, 3·7%). A portion (11·45 g.) of the latter was treated with methanol (50 c.c.) ; a residue (10·45 g.) was left after removal of material volatile at 50°/16 mm., and afforded fractions : (1) (4·25 g.), b. p. 99—110°/15 mm. ; (2) (5·10 g.), b. p. 110°/15—110°/0·25 mm. ; (3) a residue (0·60 g.) of higher-boiling material. Careful fractionation of (1) gave 5-chloropentan-1-ol (2·90 g.), b. p. 96—97°/13 mm., n_D^{18} 1·4545, d_4^{17} 1·046 (Found : Cl, 28·5. Calc. for C$_5$H$_{11}$OCl : Cl, 29·0%). This alcohol was further characterised by heating it (1·90 g.) with acetyl chloride (2·20 g., 2 mol.) for 4 hr. under reflux, and subsequent fractionation to give 5-chloropentyl acetate (1·90 g.), b. p. 96—98°/12 mm., n_D^{21} 1·4368, d_4^{21} 1·061 (Found : C, 51·6 ; H, 8·0 ; Cl, 21·1. Calc. for C$_7$H$_{13}$O$_2$Cl : C, 51·1 ; H, 7·9 ; Cl, 21·6%). Fraction (2) on redistillation was identified as 5-5′-*chloropentyl-oxypentan-1-ol* (4·81 g.), b. p. 104—106°/0·25 mm., n_D^{18} 1·4615, d_4^{17} 1·019 (Found : Cl, 17·5. C$_{10}$H$_{21}$O$_2$Cl requires Cl, 17·0%).

Tetrahydrofuran. The trichloride (4·15 g.) at −60° was added to the ether (15·10 g.) at −80°. A vigorous reaction developed ; the mixture was heated at 115—150° for 11·9 hr. under reflux. A loss of 1·95 g. was noted—possibly tetrahydrofuran. From the remainder

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(17·30 g.), unconsumed tetrahydrofuran (0·75 g.) was removed. A portion (16·00 g.) of the remainder (16·55 g.) (Found : e.h. Cl, 0·4; Cl, 20·1; B, 2·00%) was treated with methanol (50 c.c.). Matter volatile at 20°/20 mm. was removed, leaving a residue (15·70 g.), which contained no boron. . Distillation gave : (1) (1·25 g.), b. p. 70—92°/7 mm.; (2) (11·45 g.), b. p. 92—146°/7 mm.; (3) (0·40 g.), b. p. 140—160°/7 mm.; (4) (0·90 g.), b. p. 120—140°/0·15 mm., n_D^{18} 1·4600 (Found : Cl, 15·6%); (5) a higher-boiling residue (0·85 g.). During the distillation a condensate (0·50 g.), apparently tetrahydrofuran contaminated with hydrogen chloride, was collected at −80°. Redistillation of (2) afforded : (6) (1·80 g.), b. p. up to 90°/0·15 mm.; (7) 4-4'-*chlorobutoxybutan*-1-*ol* (8·27 g.), b. p. 90°/0·15 mm., n_D^{20} 1·4591, d_4^{21} 1·044 (Found : C, 53·2; H, 9·4; Cl, 19·9%; *M*, 200, 201, 206, 210. $C_8H_{17}O_2Cl$ requires C, 53·2; H, 9·4; Cl, 19·7%; *M*, 180·5); and a higher boiling residue (0·95 g.). Fractions (1) and (6) were combined and distillation gave 4-chlorobutan-1-ol (1·50 g.), b. p. 73—74°/7 mm., n_D^{18} 1·4512 (Found : Cl, 32·5. Calc. for C_4H_9OCl : Cl, 32·7%). The alcohol (7) was further characterised by adding acetyl chloride (2·20 g.) in ether (30 c.c.) to a mixture of it (5·00 g., 1 mol.) and pyridine (2·20 g., 1 mol.) in ether (30 c.c.) at 0°, whereupon the pyridinium chloride (3·30 g., 100%) which had been precipitated was filtered off, and distillation of the filtrate gave 4-4'-*chlorobutoxybutyl acetate* (4·70 g.), b. p. 80°/0·15 mm., n_D^{20} 1·4472, d_4^{19} 1·048 (Found : C, 54·3; H, 8·6; Cl, 16·2%; *M*, 219. $C_{10}H_{19}O_3Cl$ requires C, 53·7; H, 8·5; Cl, 15·9%; *M*, 223).

Epichlorohydrin. The trichloride (4·05 g.), in *n*-pentane (40 c.c.) at −60°, was carefully added to the ether (19·05 g.) at −80°. The mixture was allowed to warm to 20°; it contained no easily hydrolysable chlorine. Evacuation at 20°/0·5 mm. afforded a residue (20·25 g.). A portion (19·15 g.) of this yielded : (1) crude tri-(2-chloro-1-chloromethylethyl) borate (8·55 g.), b. p. 137—148°/0·004 mm., which on redistillation gave a purer sample (7·50 g.), b. p. 128—130°/0·004 mm., n_D^{17} 1·4902 (Found : Cl, 52·5; B, 2·8. Calc. for $C_9H_{15}O_3Cl_6B$: Cl, 53·9; B, 2·7%); (2) a liquid (3·55 g.), b. p. 148—220°/0·004 mm.; and (3) a viscous residue (5·30 g.). During the distillation epichlorohydrin (1·50 g.) had collected in a trap at −80°. Fractions (2) and (3) were combined and treated with methanol (70 c.c.). Matter volatile at 20°/20 mm. was removed leaving a residue (9·20 g.) which was fractionated into : (4) 1 : 3-dichloropropan-2-ol (2·20 g.), b. p. 62—73°/10·5 mm., n_D^{19} 1·4820 (Found : Cl, 55·5. Calc. for $C_3H_6OCl_2$: Cl, 55·0%); (5) (0·55 g.), b. p. 86—106°/0·05 mm., n_D^{19} 1·4935 (Found : Cl, 50·0%); (6) (2·30 g.), b. p. 106—234°/0·05 mm., n_D^{19} 1·5024 (Found : Cl, 44·2%; *M*, 318, 308, 307); (7) (0·6 g.), b. p. >234°/0·01 mm., n_D^{19} 1·5058 (Found : Cl, 44·0%). Distillation was discontinued at this stage, owing to apparent decomposition; there was a residue (2·00 g.) (*M*, 782, 792).

Ethylene oxide. The trichloride (5·70 g.) in methylene dichloride (30 c.c.) was added to the ether (12·65 g.) in the same solvent (20 c.c.). A residue (14·20 g.) (Found : e.h. Cl, 0; Cl, 35·8; B, 3·7%) remained after evacuation at 20°/20 mm. Methanol (50 c.c.) was added; after removal of matter having b. p. up to 126°/760 mm. from the mixture, there were obtained : (1) 2-chloroethanol (9·0 g.), b. p. 126—127°/760 mm. (after redistillation), n_D^{21} 1·4400 (Found : Cl, 42·6. Calc. for C_2H_5OCl : Cl, 44·0%); (2) (0·36 g.), b. p. 130°/760—91°/13 mm.; (3) (0·72 g.), b. p. 91—106°/13 mm.; (4) (0·56 g.), b. p. 106—144°/13 mm., n_D^{19} 1·4570 (Found : Cl, 22·8%); (5) (0·41 g.), b. p. 166°/13 mm., n_D^{21} 1·4590 (Found : Cl, 15·8%). There was a higher-boiling residue (0·87 g.), n_D^{21} 1·4640 (Found : Cl, 10·6%). Fractions (2) and (3) were combined and redistilled affording a fraction (0·55 g.) which appeared to be 2-2'-chloroethoxyethanol, b. p. 91—92°/13 mm., n_D^{19} 1·4505 (Found : C, 37·8; H, 7·15; Cl, 27·9. Calc. for $C_4H_5O_2Cl$: C, 38·5; H, 7·2; Cl, 28·5%).

Interaction of Propene Oxide (2 *mol.*) *with Boron Trichloride.*—The oxide (4·55 g.) in *n*-pentane (40 c.c.) was added to the trichloride (4·60 g.) in *n*-pentane (30 c.c.) at −80°. A small amount of gummy precipitate was removed by filtration at −40°. The filtrate was concentrated at 20°/15 mm., and the residue (7·95 g.), n_D^{20} 1·4457 (Found : e.h. Cl, 12·9; Cl, 43·3; B, 4·6%) was probably impure dichloropropyl chloroboronate (Calc. for $C_6H_{12}O_2Cl_3B$: e.h. Cl, 15·2; Cl, 45·6; B, 4·6%), contaminated with tri(dichloropropyl) borate.

Interaction of Propene Oxide (3 *mol.*) *with Boron Trichloride.*—The oxide (8·15 g.) in *n*-pentane (40 c.c.) was added to the trichloride (5·50 g.) in *n*-pentane (20 c.c.) at −80°. A small amount of solid which had formed dissolved at 20°. The mixture was heated under reflux for 10·5 hr., whereafter matter volatile at 20°/10 mm. was removed. The residue was crude trischloropropyl borate (13·40 g., 98%), n_D^{20} 1·4428 (Found : Cl, 35·3; B, 3·8%). A portion (12·4 g.) gave the pure borate (10·2 g.), b. p. 102—103°/1·0 mm., n_D^{21} 1·4437 (Found : Cl, 36·5; B, 3·7. Calc. for $C_9H_{18}O_3Cl_3B$: Cl, 36·6; B, 3·7%). There was a residue (1·05 g.).

Reactions of the Tetrahydropyran–Boron Trichloride Complex.—(a) *Pyrolysis.* The complex (6·25 g.) was heated (5·25 hr. at 115° and 6 hr. at 140°) to afford a condensate (1·10 g.), collected at −80°, from which, by recondensation, there was obtained impure boron trichloride (0·95 g., 79%) (Found : Cl, 88·6; B, 8·9%). The residue was extracted with *n*-pentane and of this, a solid (0·95 g.) (Found : e.h. Cl, 9·6; B, 26·2%), which was largely boron trioxide and boron oxychloride, remained insoluble. The *n*-pentane extract was fractionated to afford 1 : 5-dichloropentane (3·80 g., 87%), b. p. 56—58°/9 mm., n_D^{20} 1·4525 (Found : Cl, 49·6. Calc. for $C_5H_{10}Cl$: Cl, 49·7%). Yields are based on scheme (6).

(b) *With pyridine.* The complex (6·12 g.) in methylene dichloride (25 c.c.) at −80° was treated with pyridine (2·38 g., 1 mol.) in the same solvent (25 c.c.). On removal of material volatile at 20°/10 mm., which was collected as a condensate at −80°, impure pyridine–boron trichloride (5·92 g., 100%), m. p. 110° (Found : Cl, 51·3; C_5H_5N, 40·7. Calc. for $C_5H_5Cl_3NB$: Cl, 54·2; C_5H_5N, 40·2%), remained. In order to characterise tetrahydropyran in the condensate, it was treated with boron trichloride (6·70 g.) at −80° and, after removal of volatile matter, there was a residue comprising the tetrahydropyran–boron trichloride complex (5·92 g., corresponding to 97% yield of tetrahydropyran), m. p. 57—62° (Found : e.h. Cl, 50·5; B, 5·5%).

(c) *With tetrahydropyran* (4 *mol.*). To the complex (12·80 g.) at 20° was added tetrahydropyran (21·66 g., 4 mol.). After 140 hr. at 20°, the ratio of e.h. chlorine to boron (initially 3 : 1) had dropped to 2·24 : 1. A portion (18·15 g.) was taken and from it tetrahydropyran (8·49 g.), b. p. 84—87°/760 mm., was withdrawn; the residue (9·71 g.) was treated with methanol (45 c.c.). Removal of matter volatile at 20°/20 mm., left a residue (4·37 g.), which afforded on distillation : (1) (0·19 g.), b. p. up to 88°/10 mm.; (2) 5-chloropentan-1-ol (1·22 g.), b. p. 88—90°/10 mm., n_D^{22} 1·4528 (Found : Cl, 28·7%); (3) (0·48 g.), b. p. 90°/10—110°/0·5 mm.; (4) 5-5′-*chloropentyloxypentan-1-ol* (1·57 g.), b. p. 110—114°/0·3 mm., n_D^{22} 1·4604 (Found : C, 57·4; H, 9·9; Cl, 17·4. $C_{10}H_{21}O_2Cl$ requires C, 57·5; H, 9·2; Cl, 17·0%).

A second portion (14·63 g.) of the original reaction product was heated at 120° for 20·5 hr., the ratio of e.h. chlorine to boron having then fallen to 0·165 : 1. Tetrahydropyran (2·41 g.), b. p. 84—86°/760 mm., was evaporated to leave a residue (12·22 g.) which was treated with methanol (50 c.c.). Easily volatile matter was removed and subsequent distillation gave : (1) (0·98 g.), b. p. 60—87°/10 mm., n_D^{20} 1·4535 (Found : Cl, 35·6%); (2) 5-chloropentan-1-ol (3·22 g.), b. p. 87—91°/10 mm., n_D^{20} 1·4540 (Found : Cl, 29·8%); (3) (1·13 g.), b. p. 91°/10—106°/0·25 mm., n_D^{20} 1·4597 (Found : Cl, 27·1%); (4) (0·62 g.), b. p. 106—108°/0·25 mm., n_D^{20} 1·4609 (Found : Cl, 24·2%); (5) crude 5-5′-chloropentyloxypentan-1-ol (2·77 g.), n_D^{20} 1·4608 (Found : Cl, 18·9%), which on redistillation gave the pure alcohol, b. p. 106°/0·15 mm., n_D^{19} 1·4612 (Found : Cl, 16·9%).

(d) *With tetrahydropyran* (5 *mol.*). Tetrahydropyran (17·00 g., 5 mol.) was heated under reflux (19·75 hr.) at 120° with the complex (8·05 g.) and was subsequently set aside for 13 hr. at 20°. The ratio of e.h. chlorine to boron (initially 3 : 1) had dropped to 0·22 : 1. After removal of unconsumed tetrahydropyran (8·44 g.) there remained a residue (14·37 g.) which was treated with methanol (50 c.c.). Distillation gave two major fractions : 5-chloropentan-1-ol (3·7 g.), b. p. 92°/13 mm., n_D^{19} 1·4545 (Found : Cl, 28·6%); and 5-5′-chloropentyloxypentan-1-ol (4·50 g.), b. p. 104—107°/0·25 mm., n_D^{19} 1·4615 (Found : Cl, 18·4%). A portion (3·34 g.) of the latter fraction was converted into its acetate (3·25 g.), b. p. 103—104°/0·15 mm., n_D^{18} 1·4502, d_4^{20} 1·027 (Found : Cl, 15·1%), by refluxing (3 hr.) with acetyl chloride (2·49 g.).

Further Reactions of the Tetrahydrofuran–Boron Trichloride Complex.—(a) *With pyridine.* To the complex (8·62 g.) in methylene dichloride (30 c.c.) at −80° was added pyridine (3·59 g., 1 mol.) in the same solvent (25 c.c.). The viscous, liquid residue (12·04 g.), which remained after removal of matter volatile at 20°/10 mm., was treated with methanol (50 c.c.). After evaporation at 20°/10 mm., there remained material (10·65 g.) which, when extracted with ether, left a semi-solid (6·18 g.) (Found : e.h. Cl, 29·6; Cl, 30·4; C_5H_5N, 51·3%). The ether extract contained 4-chlorobutan-1-ol (3·05 g.), b. p. 75°/10 mm., n_D^{21} 1·4540 (Found : Cl, 32·4%).

In a separate experiment, the methanolysis step was omitted. The product of reaction between pyridine and the tetrahydrofuran complex was the 1 : 1-complex, 4-chlorobutyl dichloroboronite–pyridine (Found : e.h. Cl, 28·5; Cl, 39·3; B, 4·03; C_5H_5N, 27·7. Calc. for $C_4H_8OCl_3B,C_5H_5N$: e.h. Cl, 26·4; Cl, 39·7; B, 4·02; C_5H_5N, 29·4%); it was completely water-soluble.

(b) *With tetrahydrofuran.* The complex (8·47 g.) was treated with tetrahydrofuran (16·11 g.,

5 mol.) at −80°. On removal of the cooling bath, the mixture warmed spontaneously to 60°, and was again cooled (to 20°). After 45 hr. at 20°, the ratio of e.h. chlorine to boron (initially 3 : 1) was 0·55 : 1. At this stage, unconsumed tetrahydrofuran (7·88 g.), b. p. 64—68°/760 mm., was removed from a portion (24·21 g.) of the reaction mixture, thus leaving a less volatile residue (16·0 g.). This was treated with methanol (50 c.c.) and after removal of the more easily volatile matter afforded 4-chlorobutan-1-ol (5·66 g.), b. p. 76—78°/10 mm., n_D^{21} 1·4505 (Found : Cl, 31·9%) ; a middle cut (0·67 g.), b. p. 78—134°/10 mm.; and 4-4′-chlorobutoxybutan-1-ol (6·11 g.), b. p. 91°/0·25 mm., n_D^{21} 1·4585 (Found : Cl, 19·9%). A condensate (0·33 g.), probably tetrahydrofuran, was collected in a trap at −80° during the distillation; there was a distillation residue (1·13 g.) (Found : Cl, 15·8%).

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