REACTIONS OF BORON TRICHLORIDE WITH ORGANIC COMPOUNDS

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I. INTRODUCTION

Boron trichloride is rapidly proving to be one of the most reactive substances. It is a powerful Lewis acid and, as the majority of organic functional groups contain one or more of the elements oxygen, sulfur, nitrogen, phosphorus, or halogen, it might appear that compounds containing such functional groups should be potentially capable of reacting with the trichloride. Even olefins, acetylenes, aromatic hydrocarbons, and organometallic and organometalloidal compounds are generally responsive to attack by electrophilic reagents; therefore as a preliminary survey it appears that only the paraffins and cycloparaffins should possess no reactivity with boron trichloride. Although within most classes of organic compounds that have been investigated there are some members which do not react (or if so, only under the most forcing conditions), the above-stated expectations with regard to scope for reactivity with boron trichloride appear to have been realized.

The reactions would perhaps be only of limited interest if they commonly led merely to coördination compounds (i.e., products of equilibria between Lewis acid and base); although many such reactions are known (and were reviewed some time ago) (113), the majority are more complex, but in many cases proceed through initially formed coördination compounds. The reason for this complexity of reactions is due to a second factor (the first being the high strength of boron trichloride as a Lewis acid) which plays a part in boron trichloride reactions; this is the high polarizability of the boron–chlorine bonds. It is in this respect that boron trichloride differs so markedly from boron trifluoride. Although the latter is very reactive, it is less versatile and merely forms a wide range of coordination compounds (82); by virtue of these reactions the trifluoride has, of course, extensive applications as a catalyst (19).

As the reactions of boron trichloride with many of the simpler monofunctional organic compounds have already been described in the literature, a review is timely and should stimulate interest in their application to more complex systems.

II. HYDROCARBONS

The reactions of boron trichloride with hydrocarbons have not been extensively investigated. α-Olefins are generally polymerized, although the reactivity of boron trichloride as a catalyst is certainly less than that of boron trifluoride (129). *m*-Diisopropylbenzene was catalytically converted to the para isomer by boron trichloride (118). With acetylene, boron trichloride afforded β-chlorovinylboron compounds, $(ClCH{=}CH)_nBCl_{3-n}$ (n = 1, 2, or 3) and analogous reactions are probable for α-acetylenes generally (6). For example, the passage of acetylene and boron trichloride (in 1:1.5 molar ratio) over a mercurous chloride catalyst supported on activated charcoal in a glass tube at 150°C. gave 35 per cent conversion to chlorovinylboron dichloride in 6 hr.; the yield was 87 per cent on the basis of boron trichloride.

A mixture of benzene and boron trichloride when passed through a tube containing platinum asbestos or palladium black at 500–600°C. was said to give a 70 per cent yield of phenylboron dichloride (128); these high yields could not later be reproduced (136).

The reactions of boron trichloride and unsaturated hydrocarbons to produce organoboron compounds are of great potential value, because these methods are direct and avoid the use of the expensive and often hazardous organometallic intermediates.

III. ALCOHOLS

Some observations, mainly now of historical interest, were made in the last century regarding the reactions of boron trichloride with alcohols. The dissolution of the trichloride in ethanol was said to produce an ether-like odor (14). The first-reported organic boron compounds were some trialkyl borates, $B(OR)_3$ ($R = CH_3, C_2H_5, n\text{-}C_5H_{11}$), obtained by interaction of boron trichloride and the appropriate alcohol in a sealed tube (45). Under similar conditions, allyl alcohol afforded its borate, but benzyl alcohol gave benzyl chloride and dibenzyl (37).

The methanol- and ethanol–boron trichloride systems have been investigated using a high-vacuum line technique; the reactions were carried out at −60° to −80°C., owing to their exothermal nature, and were immediate and quantitative (163).

$$BCl_3 + nCH_3OH \rightarrow (CH_3O)_nBCl_{3-n} + nHCl \qquad (1)$$

$n = 1, 2,$ or 3.

Three further reactions (equations 7, 8, and 15) were recognized in the methanol system (133, 162, 163). The products of equations 7 and 8 are dialkyl chloroboronates and alkyl dichloroboronites, respectively; these as well as trialkyl borates may be used for synthesizing other organic boron compounds (102).

Interaction of isoamyl alcohol (2 moles) and boron trichloride (1 mole), both in chloroform at −20°C., produced the chloroboronate in only 15 per cent yield (96), whereas interaction of 2-chloroethanol and boron trichloride in equimolar proportions produced only a very small yield of the dichloroboronite and rather more of the chloroboronate (115). The low yields observed in these experiments are probably due to the procedures used during work-up, which caused appreciable decomposition of the alkoxyboron chlorides to take place (see below).

The reactions of boron trichloride with a wide range of alcohols having varied branching in the alkyl chain have been studied recently in considerable detail. In general, reaction according to equation 2 affords a method of obtaining trialkyl borates in almost quantitative yield; the reactions are highly exothermal and it is convenient to carry them out at −80°C. in an inert solvent such as *n*-pentane. It has been demonstrated with a selection of primary [R = n-C_3H_7 (64); n-C_4H_9, i-C_4H_9 (61); n-C_5H_{11} (2); t-$C_4H_9CH_2$, n-C_8H_{17} (64); $CH_2{=}CHCH_2$, $CH_2{=}C(CH_3)CH_2$ (71); $CH_3CH{=}CHCH_2$, $CH_2{=}CHCH_2CH_2$ (74); $CH{\equiv}CCH_2$ (71); $Cl(CH_2)_2$ (46); $Cl(CH_2)_3$ (2); $Cl(CH_2)_4$ (46); $Cl(CH_2)_5$, $CH_2ClCHClCH_2$ (2); CCl_3 (22); CF_3CH_2 (4); $C_2H_5OOCCH_2$, $C_2H_5OOC(CH_2)_2$ (52)] and also secondary alcohols [R = s-C_4H_9 (61); i-$C_3H_7(CH_3)CH$, t-$C_4H_9(CH_3)CH$ (64); n-$C_6H_{13}(CH_3)CH$ (60); $CH_2{=}CH(CH_3)CH$ (74); $(CH_2Cl)_2CH$ (2); $(CCl_3)_2CH$ (59); $C_2H_5OOC(CH_3)CH$, $C_2H_5OOCCH_2(C_2H_5OOC)CH$ (52)].

$$BCl_3 + 3ROH \rightarrow B(OR)_3 + 3HCl \qquad (2)$$

Exceptions were those alcohols [R = $C_6H_5CH_2$ (7), $C_6H_5(CH_3)CH$ (60)] which have a propensity for preionization, when the major product was the alkyl chloride (equation 3), this being the exclusive stoichiometry for an unsubstituted tertiary alcohol (R = t-C_4H_9 (61)). Boron trichloride may, however, be used for the preparation of *tert*-alkyl (as well as less highly branched) borates, by adding the trichloride (1 mole) to a mixture of the alcohol and pyridine (3 moles of each) in an inert solvent such as *n*-pentane, chloroform, or methylene dichloride at low temperature (−10° to −80°C.); this reaction is again rapid and gives a nearly quantitative yield of borate, pyridinium chloride being the other product (60, 99). A somewhat different reaction, also of general application and providing high yields, is illustrated by equation 4, but this requires prolonged heating of the components in chloroform (60, 62).

$$BCl_3 + 3ROH \rightarrow 3RCl + B(OH)_3 \qquad (3)$$

$$BCl_3 \cdot C_5H_5N + 3ROH + 2C_5H_5N \rightarrow B(OR)_3 + 3C_5H_5N \cdot HCl \qquad (4)$$

In general, methods according to equations 5 and 6 are available for obtaining dialkyl chloroboronates and alkyl dichloroboronites, respectively, in almost quantitative yield, the reaction conditions being similar to those described for equation 2. Reactions 5 [R = C_2H_5 (2, 141), n-C_3H_7 (101), n-C_4H_9 (61), n-C_5H_{11} (2), n-C_8H_{17} (101), i-C_4H_9 (61), t-$C_4H_9CH_2$ (101), $Cl(CH_2)_2$ (46); $Cl(CH_2)_3$, $Cl(CH_2)_4$, $Cl(CH_2)_5$ (2); s-C_4H_9, t-$C_4H_9(CH_3)CH$, n-$C_6H_{13}(CH_3)CH$ (101)] and 6 [R = C_2H_5 (2, 141), n-C_3H_7 (64), n-C_4H_9 (61), n-C_5H_{11} (2), n-C_8H_{17} (64), i-C_4H_9 (61), t-$C_4H_9CH_2$ (64), $Cl(CH_2)_2$ (46), $Cl(CH_2)_3$ (2), $Cl(CH_2)_4$ (46), $Cl(CH_2)_5$ (2)] have been demonstrated for a wide range of alcohols. These alkoxyboron chlorides could also arise in the alcohol–boron trichloride system as a result of any of reactions 7 to 12, each of which was independently demonstrated with a similar selection of alkyl groups; in addition the 3-butenyloxyboron chlorides were obtained by means of reactions 7 and 8 (74). Chloroboronates were not obtained as compounds stable at 20°C. if the alkyl group was powerfully electron-releasing [R = $CH_2{=}CHCH_2$, $CH_2{=}C(CH_3)CH_2$ (71); $CH_3CH{=}CHCH_2$, $CH_2{=}CH(CH_3)CH$ (74); $C_6H_5CH_2$ (7), $C_6H_5(CH_3)CH$ (60), t-C_4H_9 (61, 101)], although in some of these cases [R = $CH_2{=}CHCH_2$, $CH_2{=}C(CH_3)CH_2$ (71); $CH_2{=}CH(CH_3)CH$ (74)] it was possible to isolate their stable pyridine (1:1 or 1:2 py) complexes by addition of pyridine to the freshly prepared reaction mixture 7 at −80°C. *sec*-Alkyl [R = i-C_3H_7 (64), s-C_4H_9 (61, 64), n-$C_6H_{13}(CH_3)CH$, i-$C_3H_7(CH_3)CH$, t-$C_4H_9(CH_3)CH$ (64); $C_6H_5(CH_3)CH$ (60), $CH_2{=}CH(CH_3)CH$ (74)] and *tert*-butyl (61, 64) dichloroboronites could not be obtained, although analytical evidence [R = i-C_3H_7 (64), s-C_4H_9 (61)] and isolation of a pyridine complex [R = n-$C_6H_{13}(CH_3)CH$ (64)] at −80°C. demonstrated the existence of some of these at low temperatures; similar evidence could not be obtained for the *tert*-butyl (61), 1- and 3-methylallyl (74), benzyl (7), or carbethoxymethyl (52) dichloroboronites. The failure to obtain carbalkoxy-substituted alkyl dichloroboronites was attributed to the competing ester-fission reaction (see Section XI) (52).

$$BCl_3 + 2ROH \rightarrow (RO)_2BCl + 2HCl \tag{5}$$

$$BCl_3 + ROH \rightarrow ROBCl_2 + HCl \tag{6}$$

$$BCl_3 + 2B(OR)_3 \rightarrow 3(RO)_2BCl \tag{7}$$

$$2BCl_3 + B(OR)_3 \rightarrow 3ROBCl_2 \tag{8}$$

$$ROBCl_2 + ROH \rightarrow (RO)_2BCl + HCl \tag{9}$$

$$(RO)_2BCl + ROH \rightarrow B(OR)_3 + HCl \tag{10}$$

$$ROBCl_2 + B(OR)_3 \rightarrow 2(RO)_2BCl \tag{11}$$

$$(RO)_2BCl + BCl_3 \rightarrow 2ROBCl_2 \tag{12}$$

Of further significance to the boron trichloride–alcohol system is the mode of decomposition of the alkoxyboron chlorides (it has already been indicated that some of these decompose spontaneously). The dialkyl chloroboronates have available three possible modes of reaction: an alkyl chloride-producing decomposition (equation 13) (61, 101, 104), accompanied, to a relatively small extent, by an olefin-producing elimination (equation 14), and disproportionation (reverse of equations 11 and 12) (101). Disproportionation is encouraged by a reduction of pressure or distillation because the products contain the most volatile components of the equilibria, or alternatively by structural factors which inhibit the competing reactions (equations 13 and 14) [e.g., R = $Cl(CH_2)_2$ (46)]. Reaction 13 has been utilized for the preparation (100 per cent yield) of a number of alkyl metaborates (104).

The stability with respect to reaction according to equation 13 increased with both the length of the chain and extended branching (except at the α-carbon atom) of the alkyl group (101). Wagner–Meerwein rearrangements were demonstrated in the conversion of isobutyl (61), neopentyl and α-methylneopentyl (101) chloroboronates into *tert*-butyl, *tert*-amyl, and *tert*-hexyl chlorides, respectively. D(+)-1–Methylheptyl chloroboronate afforded L(−)-2-chloroöctane, with only very slight loss in optical rotatory power (101). Reaction 13 was remarkably catalyzed by traces of Lewis acids ($FeCl_3$, $AlCl_3$, $ROBCl_2$) and retarded by bases (ethyl ether); e.g., di-*n*-butyl chloroboronate showed no significant decomposition after 3 hr. at 100°C. when pure, but in the presence of 0.05 per cent ferric chloride decomposition was almost instantaneous at 20°C. (after a short induction period). ω-Chlorine substitution in the *n*-alkyl group had no marked effect for ethyl and propyl chloroboronates, but the chlorobutyl and chloroamyl compounds were somewhat less stable than their unsubstituted analogs; the chloroethyl and chloropropyl chloroboronates were more stable than their higher homologs (2). An olefinic double bond in the alkyl group has a considerable effect on the stability of chloroboronates when in the 2-position, but when in the 3-position it has little influence; the three isomeric bis(monomethylallyl) chloroboronates were each less stable (and stability was in the order $2\text{-CH}_3 > 1\text{-CH}_3 > 3\text{-CH}_3$) than the diallyl homolog (71, 74), and decomposition of the 1- and 3-methylallyl esters was accompanied by anionotropic rearrangement, there being obtained the same mixture of 1-methylallyl (ca. 30 per cent yield) and 3-methylallyl (ca. 70 per cent yield) chlorides from each.

The alkyl dichloroboronites have available analogous modes of decomposition to those of the chloroboronates [equations 15 (61, 64), 16, and the reverse of 11 and 12 (46, 64)].

$$3(RO)_2BCl \rightarrow 3RCl + (ROBO)_3 \rightarrow B(OR)_3 + B_2O_3 \qquad (13)$$

$$3(RO)_2BCl \rightarrow 3HCl + 3 \text{ olefin} + (ROBO)_3 \qquad (14)$$

$$3ROBCl_2 \rightarrow 3RCl + (BOCl)_3 \rightarrow BCl_3 + B_2O_3 \qquad (15)$$

$$3ROBCl_2 \rightarrow 3HCl + 3 \text{ olefin} + (BOCl)_3 \qquad (16)$$

The stability of dichloroboronites with respect to reaction according to equation 13 decreased with increasing electron release of the alkyl group and in the following respects obeyed similar criteria to the chloroboronates: propensity towards Wagner–Meerwein rearrangements [$i\text{-C}_4H_9 \rightarrow t\text{-C}_4H_9$ (61); $t\text{-C}_4H_9CH_2 \rightarrow$

t-C_5H_{11} (64); i-$C_3H_7(CH_3)CH \rightarrow t$-$C_5H_{11}$; (+)-$t$-$C_4H_9(CH_3)CH \rightarrow t$-$C_6H_{13}$]; tendency for anionotropic rearrangement (1- and 3-methylallyl) (74); and effect of traces of Lewis acid catalysts (64). Emphasis on these catalytic effects is important, because commercial boron trichloride usually contains substantial traces of foreign Lewis acids. D(+)-1-Methylheptyl dichloroboronite gave much racemized but inverted 2-chlorooöctane (60, 64). The effect of ω-chloro-substitution on the stability of n-alkyl dichloroboronites was (*a*) $Cl(CH_2)_2 > Cl(CH_2)_3 \gg Cl(CH_2)_5 > Cl(CH_2)_4$; (*b*) $Cl(CH_2)_2 \gg C_2H_5$; (*c*) $Cl(CH_2)_3 \gg n$-C_3H_7; (*d*) n-$C_4H_9 > Cl(CH_2)_4$; (*e*) n-$C_5H_{11} > Cl(CH_2)_5$ (2).

A further series of reactions which are significant in the alcohol–boron trichloride systems are those involving interaction between hydrogen chloride and reactants or products. Under the conditions of the experiments (i.e., rapid reaction, low temperature, and high dilution) reaction 17 can only be of importance for alcohols having great tendency for preionization (e.g., R = t-C_4H_9, $C_6H_5CH_2$, $C_6H_5(CH_3)CH$, allyl), and as water is a product of equation 17, it could initiate a chain reaction because boron trichloride is of course readily hydrolyzed to hydrochloric acid and boric acid. Trialkyl borates react (equation 18) with hydrogen chloride, but again only if the alkyl group is electron-releasing (7, 60, 61, 71). D(+)-Tri-1-phenylethyl borate gave much racemized but configuration-retained 1-chloro-1-phenylethane (a similar stereochemical result was obtained from ROH and BCl_3) (60), whereas the triallyl borate–hydrogen chloride reaction, which only proceeded at high temperature, was accompanied by anti-Markownikoff addition to give tri-3-chloropropyl borate and 1,2-dichloropropane (71).

$$ROH + HCl \rightarrow RCl + H_2O \tag{17}$$

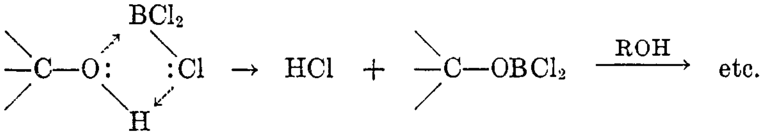
$$B(OR)_3 + 3HCl \rightarrow 3RCl + B(OH)_3 \tag{18}$$

The alkoxyboron chlorides did not react with hydrogen chloride at 20°C. (65). A final reaction is the possible interaction of boron trichloride with the alkyl chloride product (see Section XII).

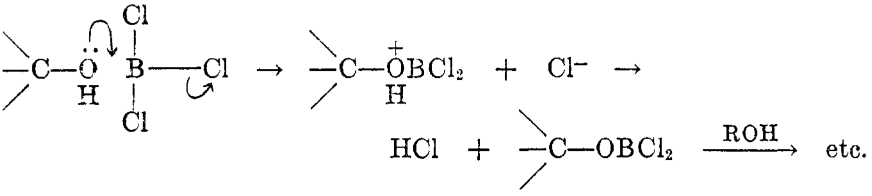
It will be evident that, with certain limitations, the reactions between any alcohol and boron trichloride can be utilized for the preparation, in very high yield and using very mild reaction conditions, of the following classes of compounds: (*a*) trialkyl borates, (*b*) dialkyl chloroboronates, (*c*) alkyl metaborates, (*d*) alkyl dichloroboronites, and (*e*) alkyl chlorides; of these the organic boron compounds are of application in the synthesis of more complex boron compounds.

Reaction mechanisms

The stepwise alkoxylation of the boron atom of boron trichloride may be viewed either as involving a broadside four-center approach of reagents (scheme 19) (58, 60, 61), or as an S_N2 replacement (scheme 20). With methanol and ethanol, it was suggested that 1:1 complexes with first boron trichloride and then alkoxyboron chlorides are intermediates; however, no evidence to this effect is available (166).



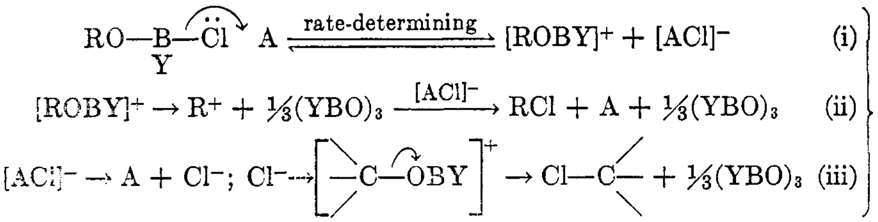
(19)



(20)

The function of pyridine, when used for the preparation of trialkyl borates, is considered to be one of polarizing the alcohol, in the extreme case to $RO^-(C_5H_5NH)^+$; an ancillary one is to remove chloride ion as pyridinium chloride (60, 99). Alternative possibilities are (*a*) that the pyridine first forms the complex $C_5H_5N \cdot BCl_3$, which subsequently reacts, and (*b*) that pyridine facilitates decomposition of alkoxyboron chloride intermediates; both must be rejected on the experimental evidence (62, 99).

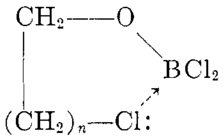
The alkyl chloride-producing decomposition (reactions 13 and 15) of the alkoxyboron chlorides was considered to involve scheme 20a, where A designates a Lewis acid catalyst or a second molecule of the alkoxyboron chloride, and Y = OR or Cl.



(20a)

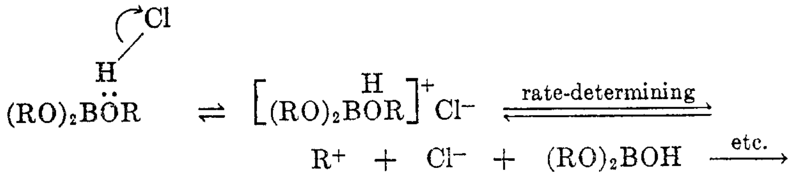
For dialkyl chloroboronates, the usual mode of decomposition was believed to be (i) and then (iii), but if the group R was hindered with respect to "in-line" approach of the attacking reagent, then the adopted mode was (i) and then (ii) (101); for alkyl dichloroboronites, (i) followed by (ii) was considered to be general, although an alternative mechanism involving synchronous boron–chlorine heterolysis and carbonium-ion formation was recognized as a possibility (64).

The increased stability of 2-chloroethyl and 3-chloropropyl dichloroboronites compared with their unsubstituted analogs was attributed to chelation (I: n = 1 or 2) (2); this suggestion is also in agreement with the observation that chlorine substitution on a more remote carbon atom has little influence on stability.

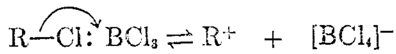


I

The dealkylation (equation 18) of those trialkyl borates having highly electron-releasing alkyl groups is attributed to a preionization mechanism (scheme 21); the evidence, apart from constitutional considerations, is based on the optical activity result (60) and the demonstration of an S_N1' mechanism for R = $CH_3CH{=}CHCH_2$ (74). The racemization of (+)-1-chloro-1-phenylethane by boron trichloride (60) was thought to involve scheme 22.



$$(RO)_2B\overset{\overset{Cl}{|}}{\overset{H}{\ddot{O}}}R \rightleftharpoons \left[(RO)_2B\overset{H}{O}R\right]^+ Cl^- \xrightleftharpoons{\text{rate-determining}} R^+ + Cl^- + (RO)_2BOH \xrightarrow{\text{etc.}} RCl \tag{21}$$



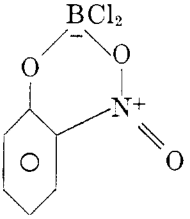
$$R{-}Cl{:}BCl_3 \rightleftharpoons R^+ + [BCl_4]^- \tag{22}$$

IV. PHENOLS

Of historical interest is the preparation of the first triaryl borates (Ar = C_6H_5, m-$CH_3C_6H_4$, β-$C_{10}H_7$), from boron trichloride and the appropriate phenol or β-naphthol, by heating in a sealed tube at 100°C.; no yields were given and chlorinated by-products were claimed (123). More recently it was found that phenols react (equation 23) rapidly, exothermally, and nearly quantitatively with boron trichloride to produce stepwise dechlorination of the trichloride, and that the nature of the product depended upon the proportions in which the reagents were mixed (33, 34). In this respect there is marked resemblance between the phenols and alcohols, and differences in the two systems arise mainly out of the different behavior of the aryloxyboron chlorides and triaryl borates compared with their aliphatic analogs. The preferred procedure for preparing triaryl borates was to employ an inert solvent such as methylene dichloride and to add the solution of the phenol to the trichloride at −70°C. (34). The following borates (96 to 100 per cent yields) were prepared: phenyl (33), *p*-chlorophenyl (34), 2,5-dichlorophenyl, 2,4,6-trichlorophenyl, *o*-iodophenyl, 2,6-dimethylphenyl, 4-*n*-octylphenyl, *o*-nitrophenyl, 2,6-dimethoxyphenyl, α-naphthyl, and β-naphthyl.

In general, reactions analogous to those represented by equations 5 and 6, under experimental conditions similar to those for preparing triaryl borates, are suitable for the preparation of aryloxyboron chlorides; these esters may also arise by reactions analogous to equations 7 and 12, and the reverse of 12. The aryloxyboron chlorides are usually much more prone to undergo disproportionation reactions (analogous to the reverse of each of equations 7, 8, 11, and 12) than are the alkoxyboron chlorides. On the other hand, there is no tendency for aryl chloride (or aryl metaborate (104)) formation (i.e., equations 13, 14, 15, and 16 have no counterpart in the aromatic field) even in the presence of Lewis acids, and this is undoubtedly due to the comparative difficulty of nucleophilic aromatic substitution.

Diphenyl chloroboronate, on prolonged heating, gave boron trichloride and triphenyl borate, whilst on distillation it gave some phenyl dichloroboronite (33); *o*-chlorophenyl and *o*-tolyl chloroboronates underwent disproportionation similarly at 130°C. (10 hr.) (34). The 2,4,6-trichlorophenyl and *p*-nitrophenyl compounds were, however, stable under similar conditions. Phenyl dichloroboronite was less stable than the chloroboronate, undergoing disproportionation readily at −15°C. (33); similar results were obtained with the *o*-chlorophenyl, *o*-tolyl, and *p*-nitrophenyl dichloroboronites (34), but *o*-nitrophenyl dichloroboronite was remarkably stable (e.g., at 100°C. and 20 mm. pressure for 5 hr.), a result attributed to chelation (II).



II

The formation of the unstable aryloxyboron chlorides mentioned in this paragraph was confirmed by isolating their stable 1:1 pyridine complexes (33, 34).

The use of pyridine offers no advantage for preparing borates from phenols and boron trichloride. In fact, difficulties were encountered in obtaining even a small yield of triphenyl borate, both when the trichloride (1 mole) was added to phenol and pyridine (3 moles of each), and when using a procedure analogous to that given in equation 4 (65). This is attributed to the known (33, 34) tendency for most triaryl borates to coördinate with pyridine. Hydrogen chloride was shown to give no reaction with triphenyl borate or the phenyloxyboron chlorides (35).

The 3:1 reaction resulting in the formation of triaryl borates is probably of even greater importance with the phenols than with the alcohols (because triaryl borates are solids of low volatility and therefore distillation methods are not suitable). Advantages over alternative methods (102) for preparing triaryl borates are that (*i*) nearly quantitative yields are obtained, (*ii*) the only other product is gaseous hydrogen chloride, which together with the low-boiling solvent can be readily removed, (*iii*) the reaction is quick and easily controlled at low temperatures, and (*iv*) functional groups may be present (34).

$$BCl_3 \xrightarrow[-HCl]{ArOH} ArOBCl_2 \xrightarrow[-HCl]{ArOH} (ArO)_2BCl \xrightarrow[-HCl]{ArOH} B(OAr)_3 \qquad (23)$$

V. POLYHYDRIC ALCOHOLS AND PHENOLS

Ethylene glycol was said to react with boron trichloride to produce tri-2-hydroxyethyl borate, $B(OCH_2CH_2OH)_3$ (38). This experiment has recently been repeated (88), and surprisingly it was stated that an excess of boron trichloride was used; a by-product was stated to be the diborate formulated as $B(OCH_2CH_2O)_3B$. No evidence for either of these structures is available.

Investigation of the interaction of boron trichloride with ethylene glycol, in varying proportions, indicates the existence of the following stoichiometries [equations 24 (17), 25 to 27 (16), and 28 (38, 88)]:

$$2BCl_3 + (CH_2OH)_2 \rightarrow Cl_2BO(CH_2)_2OBCl_2 + 4HCl \tag{24}$$

$$BCl_3 + (CH_2OH)_2 \rightarrow (CH_2O)_2BCl + 2HCl \tag{25}$$

$$2BCl_3 + 3(CH_2OH)_2 \rightarrow (CH_2O)_2BO(CH_2)_2OB(OCH_2)_2 + 6HCl \tag{26}$$

$$BCl_3 + 2(CH_2OH)_2 \rightarrow (CH_2O)_2BO(CH_2)_2OH + 3HCl \tag{27}$$

$$BCl_3 + 3(CH_2OH)_2 \rightarrow B(OCH_2CH_2OH)_3 + 3HCl \tag{28}$$

The structures of the products of equations 24 to 27 have been established by physical characterization and by chemical reactions (16, 17).

Further complications in the system arise from the fact that ethylene bisdichloroboronite, a product of equation 24, readily and reversibly underwent disproportionation (equation 29) on distillation (17). A reaction analogous to scheme 25 has also been carried out with propylene and butylene glycols, although the products were not characterized but were immediately used for synthesizing further cyclic boron compounds (36).

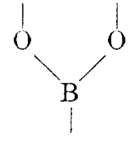
$$Cl_2BO(CH_2)_2OBCl_2 \rightleftharpoons BCl_3 + (CH_2O)_2BCl \tag{29}$$

Experiments with catechol and boron trichloride revealed a similar pattern to that observed with ethylene glycol (66). A remarkable feature in both systems was the great thermal stability of the ethylene (product of equation 25) and *o*-phenylene chloroboronates compared with that of dialkyl and diaryl chloroboronates (see Sections III and IV); this affords an interesting example of stabilization by chelation.

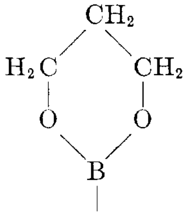
Resorcinol, quinol, and pyrogallol each reacted with boron trichloride in equimolar proportions, with liberation of hydrogen chloride and formation of polymeric products (66). The degree of polymerization appeared to increase when these materials were heated.

Boron trichloride reacted with 4-hydroxyazobenzene to give two types (1:2 and 1:3) of addition compounds; their structure is uncertain (51).

The reactions between boron trichloride and 1,2- and 1,3-glycols and catechol appear to offer the most convenient routes for synthesizing and studying the chemistry of the only little known (16, 17, 36, 66) 1,3,2-dioxaborolanes (III) and 1,3,2-dioxaborinanes (IV) and their derivatives, whereas reactions involving dihydric or polyhydric compounds having the hydroxyl groups more remote from one another may lead to interesting polymers.



III



IV

VI. HYDROPEROXIDES

Boron trichloride reacted with alkyl (*n*- and *t*-C_4H_9) hydroperoxides (3 moles) to give the trialkyl peroxyborate, $B(OOR)_3$, and hydrogen chloride (42); cumyl hydroperoxide behaved differently and phenol was the only isolated product.

VII. ETHERS

The reaction between ethers (R in R_2O = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_5H_{11}) and boron trichloride was originally thought to produce hydrogen chloride (45), but later it was recognized that diethyl ether forms a 1:1 complex (56). A detailed study of the diethyl ether– and dimethyl ether–boron trichloride systems was made, using a high-vacuum technique; the initial reaction was extremely rapid and exothermal, and the complete sequence is represented by scheme 30 (133, 164).

$$BCl_3 \xrightarrow[-80^\circ C.]{R_2O} R_2O\cdot BCl_3 \xrightarrow[-RCl]{56^\circ C.} ROBCl_2 \xrightarrow[-80^\circ C.]{R_2O}$$

$$R_2O\cdot(ROBCl_2)_2 \xrightarrow[-RCl]{0^\circ C.} (RO)_2BCl + R_2O\cdot BCl_3 \rightarrow \text{etc.} \qquad (30)$$

It was also independently shown that ethyl dichloroboronite forms an unstable 2:1 complex with diethyl ether, whereas diethyl chloroboronate does not react with the ether even at 100°C. Similar observations were made concerning the methoxyboron chlorides and dimethyl ether (163). Subsequent investigations of the ether–boron trichloride system have been directed to (*a*) a study to determine whether ether fission is invariable for all ethers and, if not, what other reactions are available, (*b*) the effect of constitutional and stereochemical factors upon carbon–oxygen fission and hence the mechanism of the reaction, and (*c*) a study of the ether complexes, particularly with reference to their stability. The answer to problem (*a*) may be summarized as follows:

(i) Diaryl (33) and bis(1-chloroalkyl) (48, 53) ethers did not react with boron trichloride; this was attributed to their low basic strength.
(ii) Aralkyl ethers gave alkyl chloride and aryloxyboron compounds (equation 31) (63).
(iii) 1-Chloroalkyl methyl ethers reacted according to equation 32 (48).
(iv) Mixed dialkyl (48, 60, 63), diallyl (71), or alkyl allyl (72) ethers gave alkyloxy(or allyloxy)boron compounds and alkyl(or allyl) chlorides [the chlorides from the more electron-releasing (R′ in ROR′) of the two groups], according to equations 33 or 34; chloroboronates did not react with ethers. In certain cases, depending on the stabilities (see Section III) of the particular alkoxyboron chloride (or on the addition of a trace of Lewis acid), the reactions were modified according to scheme 33a (71, 74) or 34a (63, 71, 72).
(v) The complex between di-2-chloroethyl ether and boron trichloride dissociated into its components as well as decomposing according to equation 33 (48).

(vi) Phenyl allyl ether underwent an ortho-Claisen rearrangement (equation 35) (73).

$$\mathrm{ArOR + BCl_3 \rightarrow RCl + ArOBCl_2 \rightarrow} \text{ disproportionation} \tag{31}$$

$$\mathrm{6ClCH_2OCH_3 + 2BCl_3 \rightarrow 6CH_3Cl + 3(ClCH_2)_2O + B_2O_3} \tag{32}$$

$$\mathrm{ROR' + BCl_3 \xrightarrow{(33)} R'Cl + ROBCl_2 \xrightarrow{(33a)}}$$
$$\mathrm{R'Cl + RCl + \tfrac{1}{3}(BOCl)_3\ [\rightarrow \tfrac{1}{3}BCl_3 + \tfrac{1}{3}B_2O_3]}$$

$$\mathrm{2ROR' + BCl_3 \xrightarrow{(34)} 2R'Cl + (RO)_2BCl \xrightarrow{(34a)}}$$
$$\mathrm{2R'Cl + 2RCl + \tfrac{1}{3}(ROBO)_3\ [\rightarrow \tfrac{1}{3}B(OR)_3 + \tfrac{1}{3}B_2O_3]}$$

$$\mathrm{3C_6H_5OCH_2CH{=}CH_2 + BCl_3 \rightarrow B(OC_6H_4CH_2CH{=}CH_2\text{-}\mathit{o})_3 + 3HCl} \tag{35}$$

The fission of mixed ethers (schemes 33 and 34) invariably proceeded according to only one mode, i.e., never leading to a mixture of dichloroboronites or chloroboronates but invariably to a single ester; as to selection of the group giving rise to the boron ester, the data are summarized in table 1 with the italicized group (i.e., R′) indicating the one which produces the alkyl or alkenyl chloride. Boron trichloride reacted with "diglyme," $CH_3(OCH_2CH_2)_2OCH_3$, to produce methyl chloride and presumably $CH_3(OCH_2CH_2)OBCl_2$ and $[CH_3(OCH_2CH_2)_2O]_2BCl$ (26).

The steric course of the fission was followed for ethyl (+)-1-methylheptyl and ethyl (+)-1-phenylethyl ethers. From the former there was obtained inverted but much racemized 2-chlorooöctane, and from the latter racemic 1-chloro-1-phenylethane (60). A Wagner–Meerwein rearrangement occurred with *n*-butyl isobutyl ether, the isobutyl radical giving rise to a mixture of *tert*-butyl and isobutyl chlorides (63). With di-3-methylallyl ether there was observed an anionotropic rearrangement, and the mixture of 1- and 3-methylallyl chlorides was of such composition as to indicate that a mesomeric methylallyl carbonium ion had been an intermediate (74).

Work on complex formation between alkyl dichloroboronites and ethers has so far been restricted to the methyl and ethyl homologs (133, 163), as already described. This is perhaps not surprising in view of the stability of such complexes; it is likely that the stability of a complex would decrease the more electron-releasing the alkyl group in the ether, whereas with electron-attracting groups the basic strength of the ether would probably be inadequate to permit complex formation.

The zero dipole moment of boron trichloride in benzene gave way to one of 5.89 D in diethyl ether (126, 152), and this was of the right order for a tetrahedral structure for the 1:1 complex. Complexes generally underwent further reaction (equations 32 to 35) near their melting points. Complexes of the following ethers have been characterized: $(CH_3)_2O$ (163), $(C_2H_5)_2O$ (133), CH_3OCH_2Cl (48), $CH_3OCH_2CH_2Cl$, $C_2H_5OCH_2CH_2Cl$, $(ClCH_2CH_2)_2O$, $(n\text{-}C_4H_9)_2O$. The relative ease of decomposition of the 2-chloroethyl ether complexes was ethyl > methyl >

TABLE 1

Fission of ROR′ *according to equations 33 and 34*

$n\text{-}\mathrm{C_4H_9O}C_4H_9\text{-}i$ (63)
$n\text{-}\mathrm{C_4H_9O}C_4H_9\text{-}s$ (63)
$n\text{-}\mathrm{C_4H_9O}C_4H_9\text{-}t$ (63)
$i\text{-}\mathrm{C_4H_9O}C_4H_9\text{-}s$ (63)
$i\text{-}\mathrm{C_4H_9O}C_4H_9\text{-}t$ (63)
$s\text{-}\mathrm{C_4H_9O}C_4H_9\text{-}t$ (63)
$n\text{-}C_8H_{17}\mathrm{OC_2H_5}$ (63)

$n\text{-}C_6H_{13}(CH_3)CH\mathrm{OC_2H_5}$ (60)
$C_6H_5(CH_3)CH\mathrm{OC_2H_5}$ (60)
$\mathrm{CH_2{=}CHCH_2O}CH_2(CH_3)C{=}CH_2$ (71)
$CH_2{=}CHCH_2\mathrm{OC_4H_9}\text{-}n$ (72)
$\mathrm{CH_2{=}CHCH_2O}C_4H_9\text{-}s$ (72)
$\mathrm{CH_2{=}CHCH_2O}C_4H_9\text{-}t$ (72)
$CH_2{=}CHCH_2\mathrm{OC_3H_7}\text{-}n$ (72)

$\mathrm{CH_2{=}CHCH_2O}C_3H_7\text{-}i$ (72)
$\mathrm{ClCH_2CH_2O}CH_3$ (48)
$\mathrm{ClCH_2CH_2O}C_2H_5$ (48)
$\mathrm{C_6H_5O}CH_3$ (63)
$\mathrm{C_6H_5O}C_2H_5$ (63)

2-chloroethyl (48). Although *n*-butyl isobutyl ether formed an unstable 1:1 complex with boron trichloride at −80°C., there was no evidence that such a complex formed with ethyl 1-methylheptyl ether under similar conditions.

It is the view of the authors that the reaction of boron trichloride with ethers, particularly those of complex structure, is likely to be of synthetic value for converting alkoxy groups to either chlorine or hydroxy (by hydrolysis of the intermediate dichloroboronite or chloroboronate), depending on structural features. Alternative reagents to boron trichloride for effecting fission of ether linkages are hydriodic acid and more recently mixtures of alkali metal and ammonia (15). Both these may, for purposes where specific reaction is required, suffer from the disadvantage of being powerful reducing agents. In any case, the reaction conditions involved when using boron trichloride are exceedingly mild and yields are nearly quantitative. A point of contrast between the trichloride and the hydriodic acid reactions which may be of importance is that the alkyl halide from the former reaction arises from an S_N1 mechanism (see below), whereas from the latter it does so by an S_N2 mechanism (30, 63); as a simple example of the consequence of such a difference, whereas *n*-butyl *sec*-butyl ether with hydriodic acid gave *n*-butyl iodide and *sec*-butyl alcohol (108), with boron trichloride it produced *sec*-butyl chloride and *n*-butyl alcohol (63). Another potential use of boron trichloride–ether reactions is with certain allylic ethers for effecting ortho-Claisen rearrangements. Prior to the observation that boron trichloride converted phenyl allyl ether at low temperature and in high yield into *o*-allylphenol (produced by hydrolysis or methanolysis of the borate) (73), it was necessary to heat the ethers for a considerable period at about 200°C. in order to effect similar rearrangements (148).

Some examples of the use of boron trichloride for synthetic purposes involving ethers have already appeared. Thus *p*-hydroxyphenylboronic acid was prepared as shown in scheme 36 (40).

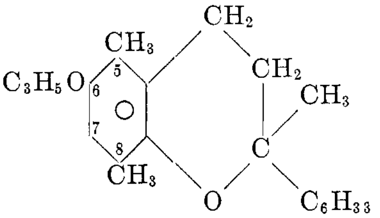
$$p\text{-}\mathrm{CH_3OC_6H_4MgBr} \xrightarrow{\mathrm{B(OC_4H_9}\text{-}n)_3} p\text{-}\mathrm{CH_3OC_6H_4B(OC_4H_9}\text{-}n)_2 \xrightarrow{\mathrm{H_2O}}$$

$$p\text{-}\mathrm{CH_3OC_6H_4B(OH)_2} \xrightarrow{-\mathrm{H_2O}} (p\text{-}\mathrm{CH_3OC_6H_4BO})_3 \xrightarrow{\mathrm{BCl_3}}$$

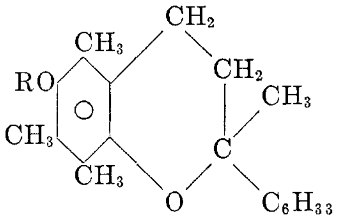
$$p\text{-}\mathrm{Cl_2BOC_6H_4BCl_2} \xrightarrow{\mathrm{H_2O}} p\text{-}\mathrm{HOC_6H_4B(OH)_2} \quad (36)$$

Demethylation of methylated sugar derivatives to parent sugars has been reported; with methylated polysaccharides, simultaneous degradation to monosaccharides also took place (5).

β-Tocopherol allyl ether (V) and the isomeric γ-ether (which instead of having a 5-methyl has a 7-methyl group) underwent the ortho-Claisen rearrangement with boron trichloride to give, after subsequent hydrolysis, 7-allyl-β-tocopherol and 5-allyl-γ-tocopherol, respectively (80). By contrast, with α-tocopherol allyl and *n*-propyl ethers (VI: R = C_3H_5 or *n*-C_3H_7) cleavage took place to give, after subsequent hydrolysis, α-tocopherol. It is interesting to note that the chroman rings were not attacked and that when an aryl allyl ether has the ortho positions blocked as in VI (R = C_3H_5), cleavage (equation 33) takes place.



V

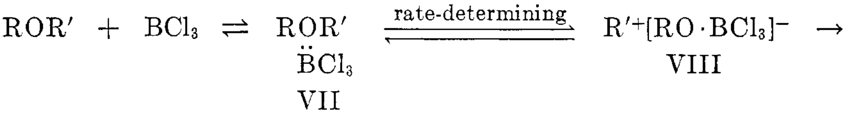


VI

A further use of the ether–boron trichloride reaction is to provide a method of determining relative electron-release of hydrocarbon radicals, by studying the mode of fission of appropriate mixed ethers (72).

Reaction mechanisms

The carbon–oxygen fission reaction is considered to involve scheme 37.



$$ROR' + BCl_3 \rightleftharpoons \underset{\substack{\overset{\cdot\cdot}{BCl_3}\\ \text{VII}}}{ROR'} \overset{\text{rate-determining}}{\rightleftharpoons} \underset{\text{VIII}}{R'^{+}[RO\cdot BCl_3]^{-}} \rightarrow$$

$$R'^{+} + Cl^{-} + ROBCl_2 \rightarrow R'Cl + ROBCl_2 \quad (37)$$

The essential feature is the postulate of carbonium-ion formation (S_N1) (63). The evidence rests on (*i*) the selection (see table 1) of the more electron-releasing group (R′) as that found in the alkyl chloride; (*ii*) the Wagner–Meerwein rearrangement of *i*-C_4H_9 to *t*-C_4H_9 (63); (*iii*) the evidence (composition of mixture of chlorides) of formation of a mesomeric cation in the di-3-methylallyl ether system (S_N1') (74); and (*iv*) the optical activity data (60). An alternative (S_N2) scheme has been proposed (30) but is not supported by the evidence. As to the structure of the complex, chemical evidence (replacement reactions with pyridine, 1-butanol, and water) supports the view that the equilibrium VII ⇌ VIII lies very much to the left; and in any case an alternative mechanism involving synchronous carbonium-ion and chloride-ion formation would be consistent with the data, in which case the intermediate (or transition state) VIII is not invoked.

The lack of reaction between chloroboronates and ethers is probably not due solely to steric reasons, but also to the relatively low strength of the esters as

Lewis acids. Thus, the acid strengths of boron trichloride, the alkoxyboron chlorides, and trialkyl borates are believed to be in the order $BCl_3 > ROBCl_2 > (RO)_2BCl > B(OR)_3$, because of the greater back-coördination to boron from oxygen than from chlorine.

VIII. CYCLIC ETHERS

Reactions of boron trichloride have been studied with ethers having one oxygen atom in the molecule [ethylene oxide (46, 47, 85), propylene oxide (47, 85), epichlorohydrin (1-chloro-2,3-epoxypropane) (47), trimethylene oxide, tetrahydrofuran (46, 47, 85), and tetrahydropyran (47, 85)] and with two in the molecule [1,3-dioxalane (54), 1,4-dioxan (54, 91, 98), and catechol methylene, dimethylene, propylene, and trimethylene ethers (54)]. Perfluoro-1-butyltetrahydrofuran, $C_8F_{16}O$, did not react with the trichloride even at 350°C. (24 hr.) (149).

Interaction in equimolecular proportions of boron trichloride and ethers afforded moderately stable 1:1 complexes with tetrahydrofuran and tetrahydropyran, but with the other monoethers ring fission (reaction 38 with $n = 2$ or 3, $m = 1, 2, 3 \cdots$, and reaction 39 with $Y = CH_3$ or Cl) prevailed even at −80°C. (46, 47).

$$\overline{(CH_2)_nO} + BCl_3 \rightarrow Cl[(CH_2)_nO]_mBCl_2 \qquad (38)$$

$$YCH_2\overline{CHCH_2O} + BCl_3 \rightarrow \underset{\text{IX}}{YCH_2CH(Cl)CH_2OBCl_2} + \underset{\text{X}}{YCH_2(CH_2Cl)CHOBCl_2} + \text{polymeric products} \qquad (39)$$

With trimethylene oxide (equation 38, $n = 3$), 3-chloropropyl dichloroboronite ($m = 1$) was obtained only as a minor product, the polymeric materials predominating (47), whereas with ethylene oxide ($n = 2$), 2-chloroethyl dichloroboronite was the sole product (46). With propylene oxide (equation 39, $Y = CH_3$), the mixture of IX and X was richer in IX (55–70 per cent of the total) and there was almost complete absence of polymeric (similar to scheme 38, with $m = 1$) material, whereas epichlorohydrin ($Y = Cl$) afforded X and no IX and a substantial quantity of polymeric products (ca. 30 per cent of the total), consisting mainly of 1-chloro-3-(2-chloro-1-chloromethylethoxy)propan-2-yl dichloroboronite (XI) (47).

$$\underset{\text{XI}}{(ClCH_2)_2CHOCH_2(CH_2Cl)CHOBCl_2}$$

In many cases the identification of the boron compounds arising from cyclic ether–boron trichloride reactions, particularly those of higher molecular weights, was carried out by converting into the corresponding alcohols; this was conveniently effected by adding methanol and distilling.

It must further be borne in mind that the dichloroboronite products mentioned above may either undergo disproportionation (reverse of equations 8 and 12) or decompose (equation 15), particularly if a catalyst is added.

The 1:1 complex of boron trichloride with tetrahydropyran was more thermally stable than that with tetrahydrofuran; both however readily decomposed according to scheme 40 (x = 4 or 5) when heated (46, 47).

$$\overline{(CH_2)_xO}\cdot BCl_3 \rightarrow \underset{\text{(not isolated)}}{Cl(CH_2)_xOBCl_2} \rightarrow Cl(CH_2)_xCl + [(BOCl)_3] \qquad (40)$$

In view of the formation of polymeric compounds in some of the 1:1 reactions, experiments were carried out in which a large excess (5 to 6 moles) of cyclic ether was used (47). The results (scheme 41) with tetrahydrofuran and tetrahydropyran were identical, irrespective of whether their complexes or the free trichloride was used.

$$BCl_3 + (3n+3)\overline{[CH_2]_xO}$$
$$\rightarrow (Cl[CH_2]_x\{O[CH_2]_m\}_nO)_3B \xrightarrow{\text{methanolysis}} 3Cl\{[CH_2]_xO\}_{n+1}H \qquad (41)$$

With tetrahydrofuran the main product was 4,4′-chlorobutoxy-1-butanol (the dimer), with the monomer and higher polymers also present, whereas with tetrahydropyran only slightly more 5,5′-chloropentyloxy-1-pentanol than 5-chloro-1-pentanol was obtained. Ethylene oxide, epichlorohydrin, and propylene oxide reacted similarly, although the major product in each case was the monomer (obtained as borate). 4-Trichlorosilylmethyltetrahydropyran gave 1,5-dichloro-3-trichlorosilylmethylpentane, on treatment first with boron trichloride and then with thionyl chloride (143).

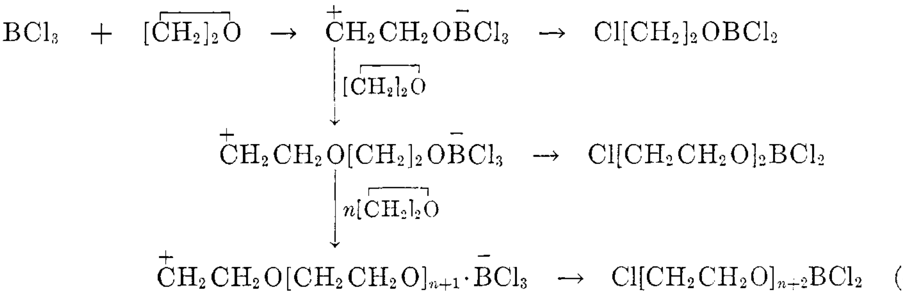
Boron trichloride had a dipole moment of 4.86 D in dioxan, which agreed well with a value (5.2 D) calculated from a 1:1 complex (98). The complex has been isolated in the form of colorless hexagonal crystals, m.p. 78.5°C. (91). At the melting point it decomposed with loss of hydrogen chloride and formation of a material believed to be 2-vinyloxyethyl dichloroboronite. The 1:1 complex did not react with further boron trichloride at 70°C. and 760 mm. pressure (91), but at a low temperature it gave a 1:1.5 complex, $(C_4H_8O_2)_2\cdot(BCl_3)_3$ (54). The other cyclic diethers mentioned in the first paragraph of this section formed 1:1 complexes with the trichloride. With the exception of the 1,3-dioxalane compound, they reversibly dissociated on heating, but the 1,3-dioxalane compound afforded what was believed to be 2-chloroethoxymethyl dichloroboronite (54).

The reactions of boron trichloride with cyclic monoethers may prove of interest for synthesizing certain ω-chloroalkoxyboron compounds, α,ω-dichlorides, ω-chloro alcohols, ω-chloroalkoxy alcohols, and ω-chloropolyalkoxy alcohols, whereas the reaction with some of the cyclic diethers (particularly those that form complexes which dissociate on heating) might prove of interest for separating the trichloride from impurities, or alternatively for removing traces of boron trichloride present as an impurity in materials such as silicon tetrachloride.

Reaction mechanisms

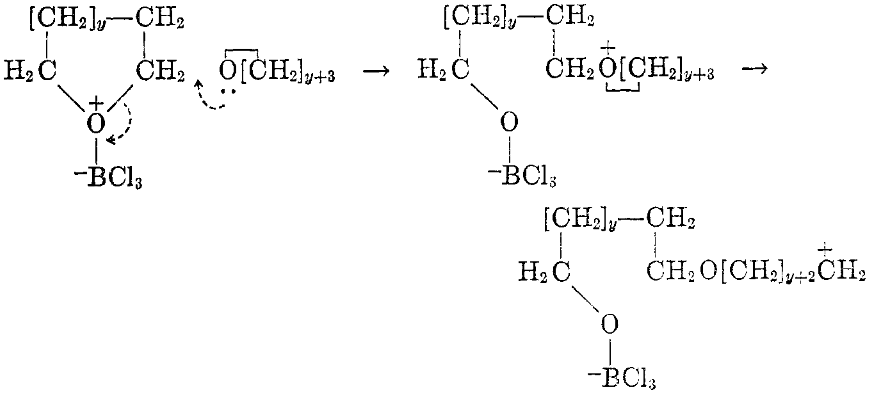
The relative stabilities of the tetrahydropyran and tetrahydrofuran complexes and the nonformation (or lack of stability) of complexes in the other cyclic monoether systems have been interpreted in terms of *I* steric strain (47).

A mechanism for the carbon–oxygen fission in cyclic monoether systems must satisfy the condition that ω-chloroalkyl dichloroboronites, and also polymeric products, are obtained by equimolecular interaction; a mechanism has been proposed and is illustrated for the case of ethylene oxide in scheme 42 (47).



$$\begin{array}{l} \mathrm{BCl_3} + \overline{\mathrm{[CH_2]_2O}} \rightarrow \overset{+}{\mathrm{C}}\mathrm{H_2CH_2O}\overset{-}{\mathrm{B}}\mathrm{Cl_3} \rightarrow \mathrm{Cl[CH_2]_2OBCl_2} \\ \qquad\qquad\qquad \downarrow \overline{\mathrm{[CH_2]_2O}} \\ \overset{+}{\mathrm{C}}\mathrm{H_2CH_2O[CH_2]_2O}\overset{-}{\mathrm{B}}\mathrm{Cl_3} \rightarrow \mathrm{Cl[CH_2CH_2O]_2BCl_2} \\ \qquad\qquad\qquad \downarrow n\overline{\mathrm{[CH_2]_2O}} \\ \overset{+}{\mathrm{C}}\mathrm{H_2CH_2O[CH_2CH_2O]_{\mathit{n}+1}\cdot}\overset{-}{\mathrm{B}}\mathrm{Cl_3} \rightarrow \mathrm{Cl[CH_2CH_2O]_{\mathit{n}+2}BCl_2} \end{array} \quad (42)$$

In the five- and six-membered rings the formation of the dipolar intermediate must proceed through the 1:1 complexes. Thus scheme 42 might be modified as shown in scheme 43 ($y = 1$ or 2).



(43)

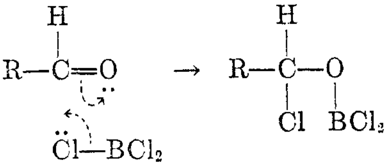
The nonformation of a 1:2 complex between dioxan (1 mole) and boron trichloride (2 moles) has been interpreted as due to the unusual character of oxygen coördination compounds (91). Thus, coördination compounds of oxygen are believed to differ from those of other donor atoms in that binding is regarded as electrostatic rather than covalent (32).

IX. ALDEHYDES AND KETONES

The reactions of eleven aldehydes with boron trichloride have been studied (53.) All except tribromoacetaldehyde reacted vigorously even at −80°C.

Tri- and dichloroacetaldehydes gave their respective α-chloroalkyl borates, $B(OCHClR)_3$, whereas monochloroacetaldehyde, acetaldehyde, and *n*- and isobutyraldehyde each gave the appropriate α-chloro ether, $(RCHCl)_2O$. Benzaldehyde gave $3C_6H_5CHO:2BCl_3$ and crotonaldehyde a 1:1 compound; these on pyrolysis gave benzylidene dichloride and 1,3-dichloro-1-butene, respectively. Phenylacetaldehyde afforded hydrogen chloride and a resin, probably a polyvinyl ether. There was evidence for the formation of borate from β-phenylpropionaldehyde and for the formation of the borate together with the ether in the monochloroacetaldehyde system. The effect of structural factors on the nature of the products was interpreted on the basis of the reaction sequence shown in scheme 44; the 1:1 crotonaldehyde complex was regarded as XII and the benzaldehyde complex as $C_6H_5CHClOBCl_2 \cdot (C_6H_5CHClO)_2BCl$. The initial approach of reagents was believed to be either by means of a nucleophilic attack of chlorine on the carbon atom of the carbonyl group, followed by attachment of $[BCl_2]^+$ to the oxygen atom, or by means of the four-center attack (scheme 45); alternative initial electrophilic attack to give a complex $RCHO:BCl_3$ was discounted because of the nonreactivity of tribromoacetaldehyde.

$$\begin{array}{l} RCHO + BCl_3 \rightarrow RCHClOBCl_2 \rightarrow RCl + \tfrac{1}{3}[(BOCl)_3] \\ \qquad\qquad\qquad\qquad \downarrow XII \\ \qquad\qquad \tfrac{1}{2}(RCHClO)_2BCl \rightarrow \tfrac{1}{3}B(OCHClR)_3 \rightarrow \tfrac{1}{6}B_2O_3 + \\ \qquad \tfrac{1}{2}(RCHCl)_2O \rightarrow HCl + \text{a vinyl ether} \rightarrow \text{a polyvinyl ether} \end{array} \qquad (44)$$

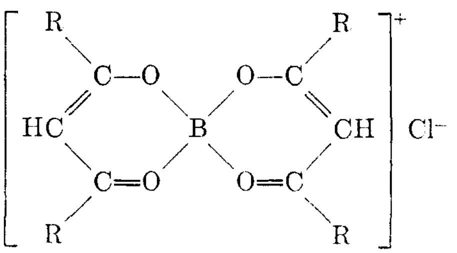


$$R-\overset{H}{C}=O + Cl-BCl_2 \rightarrow R-\underset{Cl}{\overset{H}{C}}-\underset{BCl_2}{O} \qquad (45)$$

The boron trichloride–aldehyde reactions appear to offer the only route to α-chloroalkyl borates; these compounds are of interest as esters of the unknown α-chloro alcohols, RCHClOH. The synthesis of α-chloro ethers from boron trichloride has advantages over other methods (147), particularly because of the mild reaction conditions.

Little detail is available about the reaction of ketones and boron trichloride. Benzophenone gave a 1:1 complex, which appeared to be $(C_6H_5)_2CClOBCl_2$, because there was no characteristic carbonyl absorption in the infrared spectrum, whereas *n*-butyl ethyl ketone gave a mixture of condensation dimers (i.e., mesityl oxide analogs) (67).

Acetylacetone reacted with boron trichloride, liberating hydrogen chloride; the product was believed to be $(CH_3COCHCOCH_3)_2BCl$ or its hydrogen chloride adduct (43, 135). Benzoylacetone behaved similarly, but the nature of the products with dibenzoylmethane was uncertain (43). It has been suggested that these 1,3-diketone products are boronium salts (XIII) (138). Ethyl acetoacetate afforded a crystalline product when treated with boron trichloride (135); this was probably a similar boronium salt.

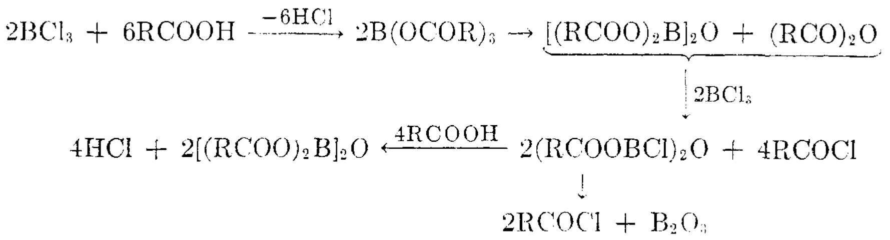


XIII

Boron trichloride (in ethereal solution) was among the compounds which catalyzed the depolymerization of paraldehyde (13). Degradation of cyclic acetals and ketals of hexitols to parent hexitols was achieved by use of boron trichloride (5).

X. CARBOXYLIC ACIDS AND ANHYDRIDES

Boron trichloride was originally said to react with acetic acid to give acetyl chloride (87), but later work showed that this was only one of several possible products. When the acid was used in excess there was obtained tetraacetyl diborate, $[(CH_3COO)_2B]_2O$ (76); triacetyl borate, however, could not be prepared. By contrast, trifluoroacetic acid gave $B(OCOCF_3)_3$, which on sublimation *in vacuo* gave the diborate (70). From acetic acid (3 moles) and the trichloride (2 moles) there was obtained dichlorodiacetyl diborate, $(CH_3COOBCl)_2O$, which when heated gave acetyl chloride and when treated with acetic acid gave the tetraacetyl diborate (77). It was shown by infrared spectra that these acyloxyboron compounds were chelated, e.g., XIV (44). Probable reaction sequences are shown in scheme 46, but complications in the boron trichloride–carboxylic acid system are also due to interactions of anhydride and acyl chloride with boron trichloride (see later).



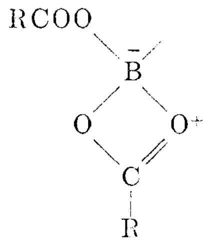
$$2BCl_3 + 6RCOOH \xrightarrow{-6HCl} 2B(OCOR)_3 \rightarrow \underbrace{[(RCOO)_2B]_2O + (RCO)_2O}_{}$$

$$\Big\downarrow 2BCl_3$$

$$4HCl + 2[(RCOO)_2B]_2O \xleftarrow{4RCOOH} 2(RCOOBCl)_2O + 4RCOCl \tag{46}$$

$$\Big\downarrow$$

$$2RCOCl + B_2O_3$$



XIV

Acetic anhydride gave acetyl chloride when treated with boron trichloride (87). It was shown that this arose from reaction according to equation 47, and if the mixture was heated, then also from pyrolysis of the dichlorodiacetyl diborate, as shown in equation 46 (77). An excess of acetic anhydride was used for preparing tetraacetyl diborate (equation 48) (76).

$$3(RCO)_2O + 2BCl_3 \rightarrow (RCOOBCl)_2O + 4RCOCl \qquad (47)$$

$$5(RCO)_2O + 2BCl_3 \rightarrow [(RCOO)_2B]_2O + 6RCOCl \qquad (48)$$

XI. CARBOXYLIC ESTERS

The initial reaction between a carboxylic ester and boron trichloride was shown to be one of complex formation. When heated, the complex decomposed with either acyl–oxygen (equation 49) [R′ in CH_3COOR' = C_2H_5 (52, 77), n-C_4H_9 (77), i-C_4H_9, n-C_8H_{17}, t-$C_4H_9CH_2$, $Cl(CH_2)_2$, CCl_3CH_2 (77), C_6H_5 (52), o-$NO_2C_6H_4$ (77); R in $RCOOC_2H_5$ = n-C_3H_7, t-C_4H_9, $CHCl_2$, CCl_3, C_6H_5; and $HCOOC_4H_9$-n] or alkyl–oxygen (equation 50) [R′ in CH_3COOR' = i-C_3H_7, s-C_4H_9, t-C_4H_9, n-$C_6H_{13}(CH_3)CH$, t-$C_4H_9(CH_3)CH$ (77)] fission of the ester. Ethyl trichloroacetate was exceptional in being inert to boron trichloride, whereas the decomposition of the complexes obtained from ethyl dichloroacetate and benzyl acetate was accompanied by reversible dissociation (77). The benzyl acetate reaction was further complicated by the formation of hydrogen chloride and a polymer, probably polybenzyl. There was some difficulty in establishing the reaction according to equation 49, mainly because, at the temperature of decomposition of the complex, decomposition (equations 15 and reverse of 8 and 12) of the dichloroboronite was also well advanced (52, 77); however, in the case of *o*-nitrophenyl acetate the exceptionally stable (q.v.) *o*-nitrophenyl dichloroboronite was isolated in high yield (77). From the point of view of ease of operation, the pyrolysis of the complex was carried out in presence of ester as shown in equation 50, in order to establish the alkyl–oxygen fission reaction; the reaction in absence of ester was also demonstrated for *sec*-butyl acetate. It may be significant that the alkyl–oxygen fission reaction was observed only when the group R′ was *sec*- or *tert*-alkyl, because corresponding dichloroboronites, $R'OBCl_2$ (unlike the primary alkyl), are known to be unstable and it is possible that the products of equation 50 may result from dichloroboronite–acyl chloride (the products of equation 49) interaction, rather than from a different mode of fission. From the infrared spectrum of the ethyl acetate–boron trichloride complex it was evident that its structure involves coördination with the oxygen of the carbonyl group and not the alkyl oxygen (106).

$$RCOOR' \cdot BCl_3 \rightarrow RCOCl + R'OBCl_2 \qquad (49)$$

$$2RCOOR' \cdot BCl_3 + RCOOR' \rightarrow (RCOOBCl)_2O + 3R'Cl + RCOCl \qquad (50)$$

Deacylation of acylated sugar derivatives has been effected by using boron trichloride (5).

XII. ALKYL AND ACYL HALIDES

Boron trichloride did not react with methyl fluoride or chloride in the range −60° to 300°C. (157), nor with *n*-propyl chloride (117), but there was evidence (phase diagrams) for complex formation with ethyl (116) and isopropyl (90) chlorides at low temperature (less than −100°C.), although not in stoichiometric proportions. Triphenylmethyl fluoride and chloride, however, formed moderately stable (F > Cl) crystalline compounds with the trichloride (157). There appeared to be a correlation between dipole moments and hence polarizabilities of alkyl [CH_3, C_2H_5 (116), *n*- and *i*-C_3H_7 (117)] chlorides and their tendencies to form complexes with the trichloride. It was suggested that when alkyl halides have a dipole moment greater than 2.0 D, they may be expected to complex (114). In the presence of a trace of boron trichloride, (+)-1-chloro-1-phenylethane was rapidly racemized (scheme 22) (18, 60), but its bromo analog polymerized, with liberation of hydrogen chloride, when left in a sealed tube (65). Similar polymerizations have been noted with benzyl chloride (7, 77) and also the triphenylmethyl chloride–boron trichloride complex (on heating) (157). The polymerizations are probably due to Friedel–Crafts activity subsequent to reaction according to scheme 22; the polymerization of 1-methylallyl chloride (74) probably also proceeds by means of scheme 22 and subsequent electrophilic addition to the olefinic linkage as the means of propagation. The optical rotatory power of neither (+)-2-chlorooöctane nor (+)-2-iodooöctane was affected by contact (24 hr.) with an equimolar quantity of boron trichloride at 18°C. (65).

The passage of a gaseous mixture of an alkyl halide and boron trichloride over an aluminum or zinc catalyst at about 350°C. was said to provide an economical method for preparing alkylboron halides and trialkylborons, BR_3 (92). Although experiments with methyl and ethyl chlorides were described, no yields were stated nor were the products characterized.

Boron trichloride formed with acetyl chloride a crystalline 1:1 complex which reversibly dissociated at room temperature (119). A phase diagram of the boron trichloride–acetyl chloride system failed to reveal compounds other than the 1:1 complex, m.p. −54°C. (83). The melting point was thought also to be the dissociation temperature, since there was no evidence for association in the liquid or vapor phase. In the solid phase, the complex was regarded as a lattice compound, stabilized by favorable packing. In contrast with the acetyl chloride system, there was no definite evidence for complex formation with benzoyl chloride.

It does not seem possible on the available evidence to decide whether the 1:1 complexes contain the tetrachloroborate anion.

XIII. TERTIARY AMINES

In general, boron trichloride forms 1:1 complexes with tertiary amines, but it has recently been shown that the 1:1 complex with triethylamine absorbs a second molecule of boron trichloride at −78°C. (25).

Reactions have been carried out at −10° to −80°C. in a high-vacuum line [$N(CH_3)_3$ (165)] or in solution using a solvent such as *n*-pentane (60, 62). Complexes have been obtained from aliphatic, aromatic, and heterocyclic amines [$N(CH_3)_3$ (131, 165), $N(C_2H_5)_3$ (55, 68, 132), $N(C_3H_7\text{-}n)_3$ (55), $N(C_4H_9\text{-}n)_3$, C_5H_5N (8, 24, 60, 62), $C_6H_5N(CH_3)_2$ (93), quinoline (106), 2-$CH_3C_5H_4N$, 3-$CH_3C_5H_4N$, 4-$CH_3C_5H_4N$ (8), 4-$CH_3OC_5H_4N$, 4-ClC_5H_4N, 4-$C_2H_5CO_2C_5H_4N$, 4-CNC_5H_4N]. The only tertiary amine which has behaved differently has been 4-acetylpyridine which, on attempted purification of its complex by recrystallization, gave 4-acetylpyridine hydrochloride (8). The complexes were generally exceptionally stable, both hydrolytically and thermally (60, 62, 165). The dipole moments of the complexes of the 4-substituted pyridines have been measured in order to compare the effect of nitrogen donation to (*i*) boron and (*ii*) oxygen (the *N*-oxides) (8) and the dipole moment values have also been compared with those obtained with the trimethylamine complex (9). It was established that the relative strengths of the boron halides and borine as Lewis acids was $BBr_3 > BCl_3 \geqslant BH_3 > BF_3$, by subtracting from the dipole moments of the BX_3 complexes the moments of the molecules CHX_3. This order had also been derived from heats of formation of pyridine and trimethylamine complexes (24). The electrical conductivity of molten pyridine–boron trichloride showed that there is about 1 per cent dissociation into kinetically free ions, believed to be $[py_2BCl_2]^+$ and $[BCl_4]^-$ (81); however, in benzene solution the conductivity was of such order as to indicate the presence of kinetically free ions to an extent of only about one part in 10^8 and moreover the complex was monomeric (9). The dimeric ionic structure was also indicated from infrared spectra (84).

XIV. SECONDARY AMINES

By interaction of boron trichloride and secondary amines (R in R_2NH = C_2H_5, n-C_3H_7, i-C_4H_9), a number of dialkylaminoboron dichlorides were obtained (124). With dimethylamine, it was shown that as the proportion of amine with respect to boron trichloride was increased, a stepwise amination of the boron resulted (scheme 51) (160). Yields, however, were low (less than 50 per cent), because the hydrogen chloride that formed reacted with both the amine and the dialkylaminoboron compounds; these reactions were carried out in a high-vacuum line (160, 167), but dimethylaminoboron dichloride has been prepared also by using n-pentane as solvent (31). Reactions of higher amines with boron trichloride have usually been carried out in n-pentane or some other inert solvent (68). Scheme 51 may also involve extremely unstable 1:1 complexes of amine with each of boron trichloride, and the two dimethylaminoboron chlorides.

$$BCl_3 \xrightarrow{(CH_3)_2NH} (CH_3)_2NBCl_2 \xrightarrow{(CH_3)_2NH} [(CH_3)_2N]_2BCl \xrightarrow{(CH_3)_2NH} B[N(CH_3)_2]_3 \quad (51)$$

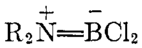
Reaction according to equation 52 appears to provide the most convenient method for preparing tris(dialkylamino)borons [R = CH_3 (140, 160), C_2H_5 (68), n-C_4H_9], the preferred procedure being to add the trichloride to the amine in n-pentane at −80°C. and to remove the amine hydrochloride by filtration. For preparing aminoboron dichlorides, the use of triethylamine in addition to the secondary amine has simplified the procedure (equation 53). Thus for dimethylaminoboron dichloride, the 1:1 amine–boron trichloride complex in benzene was added to triethylamine (27). The same method has been used for pyrrolidino-, piperidino-, and morpholinoboron dichlorides (125). In a similar way (equation 54) interference by hydrogen chloride was avoided during the preparation of bis(dimethylamino)boron chloride (140). Diphenylamine gave with the trichloride a 1:1 complex which when heated in boiling benzene gave diphenylaminoboron dichloride and hydrogen chloride (12).

$$BCl_3 + 6R_2NH \rightarrow B(NR_2)_3 + 3R_2NH\cdot HCl \qquad (52)$$

$$BCl_3\cdot(CH_3)_2NH + (C_2H_5)_3N \rightarrow (CH_3)_2NBCl_2 + (C_2H_5)_3N\cdot HCl \qquad (53)$$

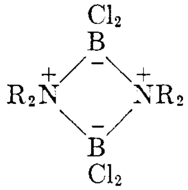
$$(CH_3)_2NBCl_2 + (C_2H_5)_3N + (CH_3)_2NH \rightarrow [(CH_3)_2N]_2BCl + (C_2H_5)_3N\cdot HCl \qquad (54)$$

A complication with the aminoboron dichlorides is their isomerism. Thus, when initially prepared, these compounds are monomeric (XV) but may undergo dimerization (XVI), particularly when heated [the evidence for these structures has been reviewed elsewhere (102)]. It has recently been shown that tendency for the dimerization to occur is related to steric effects (125) [i.e., dimers are formed with R_2NBCl_2 when $R_2 = (CH_3)_2$ (161), $—(CH_2)_4—$ (125), $—(CH_2)_5—$, $—O(CH_2CH_2—)_2$, but not when $R_2 = (C_2H_5)_2$ (127, 154), $(n\text{-}C_3H_7)_2$ (125), $(n\text{-}C_4H_9)_2$, $—CH(CH_3)(CH_2)_4—$].



$$R_2\overset{+}{N}{=}\overset{-}{B}Cl_2$$

XV



XVI

The aminoboron dichlorides may also be formed in the secondary amine–boron trichloride system as a result of equations 55 [$R = CH_3$ (78), C_2H_5 (68)] or 56 [$R = C_2H_5$ (68)]. Unlike corresponding reactions (equations 7 and 8) with trialkyl borates, these are highly exothermal and appear to go through an intermediate complex.

$$B(NR_2)_3 + 2BCl_3 \rightarrow 3R_2NBCl_2 \qquad (55)$$

$$2B(NR_2)_3 + BCl_3 \rightarrow 3(R_2N)_2BCl \qquad (56)$$

Apart from the dimeric aminoboron dichlorides, all other aminoboron compounds react with hydrogen chloride. The dimethylaminoboron compounds were each thought to add on one molecule of hydrogen chloride for each nitrogen atom, i.e., to form compounds $[(CH_3)_2N]_nBCl_{3-n}\cdot nHCl$, where $n = 1, 2,$ or 3 (160). This has been confirmed with dialkylaminoboron dichlorides [$R = CH_3$ (23, 78), C_2H_5 (68, 127)] and the compounds have been formulated as XVII (68, 102).

$$R_2H\overset{+}{N}-\overset{-}{B}Cl_3$$

XVII

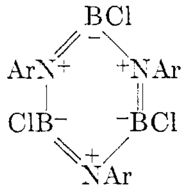
Tris(diethylamino)boron reacted according to equation 57 (68).

$$B[N(C_2H_5)_2]_3 + 5HCl \rightarrow C_2H_5NBCl_2\cdot HCl + 2(C_2H_5)_2NH\cdot HCl \qquad (57)$$

XV. PRIMARY AMINES

The reaction of boron trichloride with ethylamine was said to give a product which, when heated, gave ethyl chloride and boron nitride (87). Aniline with boron trichloride was said to give C_6H_5NBCl (134), but later investigations showed that the system was more complicated (scheme 58) (86, 93). Thus, when the two reagents were mixed in benzene at −15°C., a 1:1 complex formed; when the solution was boiled, hydrogen chloride was evolved and *N*,*N*′,*N*″-triphenyl-*B*,*B*′,*B*″-trichloroborazole [XVIII: $Ar = C_6H_5$] was formed. This was the first borazole to be established. *p*-Toluidine (94) and *p*-anisidine (95) reacted similarly, but the addition of excess of *p*-anisidine to boron trichloride at 0°C. in benzene gave tris(*p*-anisidino)boron. Benzylamine also formed a 1:1 complex and this on heating lost hydrogen chloride (2 moles), but the other product could not be identified. Methylamine when heated with the trichloride to 250°C. gave *N*,*N*′,*N*″-trimethyl-*B*,*B*′,*B*″-trichloroborazole (94). Dodecylamine and boron trichloride when mixed in benzene solution were said to form a range of addition compounds: 1:1BCl$_3$, 2:1BCl$_3$, 3:1BCl$_3$, 4:1BCl$_3$ (144).

$$3ArNH_2 + 3BCl_3 \rightarrow 3ArNH_2\cdot BCl_3 \rightarrow$$



$$+ 6HCl \qquad (58)$$

XVIII

XVI. ORGANIC AMMONIUM SALTS

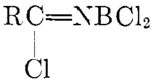
The reaction between boron trichloride and *p*-anisidine hydrochloride gave the amine–boron trichloride complex, which on heating gave a borazole (see Section XV) (95). Addition of the trichloride to pyridinium chloride dissolved in methylene dichloride gave a 1:1 complex, formulated as $[C_5H_5NH]^+[BCl_4]^-$ (103); when this was heated, hydrogen chloride was lost and pyridine–boron trichloride was formed, but this reaction was not reversible. The structure was supported by infrared spectra, which showed the presence of quaternary nitrogen (106). By contrast, tetraethylammonium chloride did not react with boron trichloride (84). Methylammonium chloride and boron trichloride at 180°C. in the presence of a catalyst of metallic iron, nickel, or cobalt, gave a 60 per cent yield of *N*,*N*′,*N*″-trimethyl-*B*,*B*′,*B*″-trichloroborazole (50); alkylated hydrazine hydrochlorides were also suggested as reagents for preparing alkylated borazoles. Heating amine (CH_3NH_2, $C_2H_5NH_2$, *n*-$C_4H_9NH_2$) hydrochlorides with boron trichloride in boiling chlorobenzene afforded the 1:1 amine–boron trichloride complexes, which when treated with triethylamine gave the borazoles $(RNBCl)_3$ and triethylammonium chloride (150).

XVII. NITRILES, AMIDES, NITRO COMPOUNDS, AND DIAZOMETHANE

Boron trichloride was shown to form a 1:1 complex with acetonitrile (126, 151, 152). This was prepared either in the gas phase in a high-vacuum apparatus at -70°C. (107), or by addition of the nitrile to the trichloride at -80°C. in an inert solvent such as benzene or methylene dichloride (75, 126). The dipole moment of the complex in benzene has been determined (126, 151, 152), although its solubility in that solvent is very small (107). By electron diffraction and vapor pressure measurements it was shown that the complex was almost completely dissociated in the vapor state, and its stability in the solid state has been attributed to the high crystal lattice energy (139). The crystalline structure of the complex by x-ray diffraction has been described (57). A number of other nitriles [R in RCN = CH_3CH_2 (126), n-C_3H_7 (75), n-C_4H_9, n-C_5H_{11}, C_6H_5, $C_6H_5CH_2$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, p-$NO_2C_6H_4$, $CH_2{=}CH$] have likewise been shown to form 1:1 complexes with boron trichloride. The result with the p-methoxybenzonitrile is interesting, as it demonstrates that the nitrile group has a greater affinity for boron trichloride than the ether linkage (75). The nitrile complexes were pyrolytically stable, and their infrared spectra showed that they had the structure XIX and not XX; furthermore, the relative intensities of the bands due to the nitrile group in the various complexes were a measure of their relative basic strengths.

$RC{\equiv}N{:}BCl_3$

XIX



$$\mathrm{R}\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{C}}\mathrm{{=}NBCl_2}$$

XX

Acetamide formed a 1:1 complex with boron trichloride, but its structure is still uncertain (75). On heating, the complex lost 1 mole of hydrogen chloride at 100°C. at 15 mm. pressure and a second mole after several hours at 200°C. Acetanilide also formed a complex, which likewise lost hydrogen chloride on heating.

Nitrobenzene formed a 1:1 complex with boron trichloride (93); the molar heat of reaction was measured (24). It is interesting to note that the trifluoride does not react with nitrobenzene. The trichloride complex dissociated when heated. The formation and dissociation of the complex have been used as a method for purifying boron trichloride.

Boron trichloride polymerized diazomethane to a polymethylene (168).

XVIII. SULFUR COMPOUNDS

Boron trichloride formed a 1:1 complex with methyl mercaptan, which on melting (-20°C.) gave hydrogen chloride and methyl dichlorothioboronite, CH_3SBCl_2 (79). It was not possible to replace more than one chlorine atom of the trichloride with methyl mercaptan (79), but with lead *n*-butyl mercaptide, a high yield of tri-*n*-butyl thioborate was obtained (equation 59), by mixing at 0°C., with the mercaptide in suspensions in *n*-pentane (106). Reactions analogous to those represented by equations 7 and 8 were used for preparing the *n*-butylmercaptoboron chlorides in good yields from the thioborate. The interaction of 1,2- and 1,3-dithiols with boron trichloride has been suggested (but no details given) as a route to 1,3,2-dithiaborolanes and 1,3,2-dithiaborinanes (the dithio analogs of III and IV) (36). 1,2- and 1,3-Monothioglycols might likewise afford routes to 1,3,2-oxathiaborolanes and borinanes (monothio analogs of III and IV).

$$3Pb(SC_4H_9\text{-}n)_2 + 2BCl_3 \rightarrow 3PbCl_2 + 2B(SC_4H_9\text{-}n)_3 \qquad (59)$$

Dialkyl sulfides [R in R_2S = CH_3 (79), C_2H_5 (131), *n*-C_4H_9 (100), *i*-C_4H_9 (131)] formed 1:1 complexes with boron trichloride. These, unlike ether complexes, were extremely stable to heat and carbon–sulfur fission has not yet been realized; for example, the di-*n*-butyl sulfide complex withstood 32 hr. heating at 215°C., there being only some slight dissociation (100).

Tri-*n*-butyl sulfonium chloride formed a 1:1 complex with boron trichloride, which probably has structure XXI, although XXII is a possible alternative (100).

$$\underset{\text{XXI}}{[(n\text{-}C_4H_9)_3S]^+[BCl_4]^-} \qquad \underset{\text{XXII}}{[(n\text{-}C_4H_9)_3S\!:\!BCl_3]^+Cl^-}$$

Mercaptans have been removed from "sour" petroleum distillates by interaction with olefins in the presence of boron trichloride (137).

XIX. ORGANOMETALLIC AND ORGANOMETALLOIDAL COMPOUNDS

The reactions of organometallic compounds with boron trichloride have been used for preparing organoboron compounds, although other methods (e.g., using the trifluoride or trialkyl borates) are currently preferred.

Arylboron dichlorides [Ar = C_6H_5 (120), *o*-$CH_3C_6H_4$ (122), *p*-$CH_3C_6H_4$ (121), *o*- and *p*-$CH_3OC_6H_4$ (122), *o*- and *p*-$C_2H_5OC_6H_4$, the isomeric $(CH_3)_2C_6H_3$, α-$C_{10}H_7$, and β-$C_{10}H_7$] have been obtained from appropriate diarylmercury compounds, but it was difficult to replace a second chlorine atom from the trichloride (122). 2-Chlorovinylboron dichloride was prepared from 2-chlorovinylmercuric chloride and bis-2-chlorovinylboron chloride from di-2-chlorovinylmercury (20). Boron trichloride with a dialkylzinc (R = CH_3, C_2H_5) gave the trialkylboron (145, 156, 159) and the same reagents (R = CH_3), when used in appropriate proportions, were said to give high yields of the methylboron chlorides (155), although later work has cast doubt on this (10). Trialkylaluminum compounds have also been recommended as reagents for preparing the alkylboron chlorides (155). Grignard reagents [C_6H_5MgBr (146), CH_3MgBr (159), CH_3MgI (142), and *n*-C_4H_9MgBr] have been used to replace one chlorine atom (by C_6H_5), or all three chlorine atoms (by CH_3, *n*-C_4H_9) of boron trichloride. The addition of a mixture of boron trichloride and *tert*-butyl chloride in ether to magnesium afforded triisobutylboron (89). The trichloride and sodiophenylacetylide afforded sodium tetraphenylacetylenylboron, $Na[B(C{\equiv}CC_6H_5)_4]$; the presumed intermediate $B(C{\equiv}CC_6H_5)_3$ could not be isolated (97).

Extensive use has been made of the reactions of boron trichloride with organic boron compounds (for references up to the end of 1955, see reference 102; for later work, excluding papers already referred to, see references 1, 3, 11, 21, 28, 39, 69, 105, 109, 110, 111, 130), and in general these have involved a mutual replacement reaction of the type shown in equations 60 (where X, Y, and Z are the same or different and each is OR, NR_2, SR, R, Ar, Hal) equation 61 (1, 105, 109, 111, 130), or equation 62 (1, 69). Reaction according to equation 60 proceeded rapidly at low temperature unless the group in BXYZ to be replaced by chlorine was alkyl or aryl.

$$BXYZ + BCl_3 \rightarrow XBCl_2 + ZYBCl \xrightarrow{BCl_3} ZBCl_2 + YBCl_2 \qquad (60)$$

$$(QBO)_3 + BCl_3 \rightarrow QBCl_2 + \tfrac{1}{3}[(BOCl)_3];\ Q = R, \text{Ar or OR} \qquad (61)$$

$$\{[R(\text{or Ar})]_2B\}_2O + BCl_3 \rightarrow R_2(\text{or Ar}_2)BCl + \tfrac{1}{3}[(BOCl)_3] \qquad (62)$$

Trisilylamine and boron trichloride reacted according to equation 63 at −78°C. and there was evidence for an intermediate 1:1 complex (29); with methyldisilylamine, scheme 64 was observed.

$$(SiH_3)_3N + BCl_3 \rightarrow SiH_3Cl + (SiH_3)_2NBCl_2 \qquad (63)$$

$$CH_3(SiH_3)_2N + BCl_3 \xrightarrow{-78^\circ C.} SiH_3Cl + CH_3(SiH_3)NBCl_2 \xrightarrow{20^\circ C.} SiH_3Cl + \tfrac{1}{3}(CH_3NBCl)_3 \qquad (64)$$

Boron trichloride and trimethylethoxysilane at 80°C. gave trimethylchlorosilane in nearly quantitative yield (158). As an application of this reaction it has been proposed that the technically interesting separation of the three methylchlorosilanes and silicon tetrachloride might be effected by first esterifying, then separating the esters, and finally reconverting these, as shown in equation 65 ($n = 1, 2,$ or 3). 1,1′,2,2′-Tetramethyldisiloxane, $[(CH_3)_2SiH]_2O$, gave dimethylchlorosilane and a mixture of boron compounds, probably containing the dichloroboronite, $(CH_3)_2SiHOBCl_2$ (49). Boron trichloride reacted with two disiloxanes at −78°C. as shown in equations 66 and 67. In the reaction according to equation 66, there was evidence for an intermediate dichloroboronite, $CH_3SiH_2OBCl_2$. With 1,1′-dimethyldisilthiane, $(CH_3SiH_2)_2S$, there was no reaction at low temperature; at 100°C. a complex mixture was obtained.

$$(CH_3)_nSi(Cl)_{4-n} \underset{BCl_3}{\overset{ROH}{\rightleftharpoons}} (CH_3)_nSi(OR)_{4-n} \qquad (65)$$

$$3(CH_3SiH_2)_2O + 2BCl_3 \rightarrow 6CH_3SiH_2Cl + B_2O_3 \qquad (66)$$

$$[(CH_3)_3Si]_2O + BCl_3 \rightarrow (CH_3)_3SiCl + (CH_3)_3SiOBCl_2 \qquad (67)$$

Phosphine $[P(CH_3)_3, P(C_6H_5)_3]$ (131) and arsine $[As(CH_3)_3]$ (90) 1:1 complexes with boron trichloride have been obtained, either by reaction in benzene solution

$[P(C_6H_5)_3$ (131)] or in a high-vacuum apparatus. These complexes were high melting and were thermally and hydrolytically stable.

Arylchlorosilanes have been obtained by treatment of chlorosilanes (or substituted chlorosilanes) with aromatic hydrocarbons in the presence of boron trichloride (41, 153).

Organocyclosiloxanes, $(R_2SiO)_n$ ($R = CH_3$ or C_2H_5; $n = 3$ or 4), reacted with the trichloride according to scheme 68 (112); these reactions appear to have similarity with those between aldehydes and boron trichloride (q.v.).

$$(R_2SiO)_n + nBCl_3 \rightarrow nR_2Si(Cl)OBCl_2 \rightarrow B[O(Cl)SiR_2]_3 + 2BCl_3$$

$$\downarrow$$

$$B_2O_3 + 3[R_2Si(Cl)]_2O \rightarrow 3R_2SiCl_2 + (R_2SiO)_3 \qquad (68)$$

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