143. *The Interaction of Aldehydes with Boron Trichloride.*

By M. J. FRAZER, W. GERRARD, and M. F. LAPPERT.

Eleven aldehydes have been treated with boron trichloride. All except tribromoacetaldehyde reacted with vigour, even at −80°. Tri- and dichloroacetaldehyde gave their respective tris-1-chloroalkyl borates, $(R\cdot CHCl\cdot O)_3B$, whereas monochloroacetaldehyde, acetaldehyde, and *n*- and *iso*-butyraldehyde each gave the appropriate α-chloro-ether $(R\cdot CHCl)_2O$. Benzaldehyde gave a 3 : 2 and crotonaldehyde a 1 : 1 compound. Pyrolysis of these compounds gave benzylidene dichloride and 1 : 3-dichlorobut-1-ene, respectively. Phenylacetaldehyde afforded hydrogen chloride and a resinous product, probably a poly(vinyl 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. Probable reaction sequences and mechanisms are discussed.

THE interactions of aldehydes with halides of non-metals and with organic acid halides are well known. In general three types of reaction have been established, but which aldehydes favour these particular reactions and whether the nature of the products depends on the halide or on the aldehyde are not known. The first type of reaction is the formation of the *gem.*-dichloride, *e.g.* the inter-reaction between silicon tetrachloride and benzaldehyde gives benzylidene dichloride.[1] The second type affords an organic derivative of a non-metal, *e.g.*, the formation of the compound $Ph\cdot CHCl\cdot P(:O)Cl_2$ from benzaldehyde and phosphorus trichloride.[2] Likewise the compound $Ph\cdot CHCl\cdot O\cdot SiCl_3$ has been suggested as precursor in the silicon tetrachloride–benzaldehyde reaction, mentioned above.[1] The third reaction leads to formation of α-chloro-ethers, $R\cdot CHCl\cdot O\cdot CHCl\cdot R'$ (for discussion, see ref. 3).

The present paper is concerned with the interaction of aldehydes with boron trichloride. Eleven aldehydes, having widely different steric and electronic features, were studied; with the exception of tribromoacetaldehyde, which was unreactive even at 20°, all reacted vigorously even at −80°. In the initial experiments, the reactants were mixed in equimolecular proportions, in the presence of an inert solvent if the reaction was uncontrollably violent in its absence, whereafter matter volatile at 20°/15—20 mm. was removed. The weight of the residue was indicative of the molar proportion in which the aldehyde and trichloride had combined, 1 : 1 for crotonaldehyde, 3 : 2 for benzaldehyde, 1 : 0 for bromal (*i.e.* no reaction), and 3 : 1 for acetaldehyde, *n*-butyraldehyde, *iso*butyraldehyde, mono-, di-, and tri-chloroacetaldehyde, phenylacetaldehyde, and β-phenylpropionaldehyde.

The residue was identified and the stoicheiometry of each reaction established. Five primary reactions were observed :

$$6R\cdot CHO + 2BCl_3 \longrightarrow 3(R\cdot CHCl)_2O + B_2O_3 \qquad (1)$$

$$3R\cdot CHO + BCl_3 \longrightarrow (R\cdot CHCl\cdot O)_3B \qquad (2)$$

$$3R\cdot CHO + 2BCl_3 \longrightarrow (R\cdot CHO)_3,(BCl_3)_2 \qquad (3)$$

$$R\cdot CHO + BCl_3 \longrightarrow R\cdot CHO,BCl_3 \qquad (4)$$

$$6R\cdot CHO + 2BCl_3 \longrightarrow B_2O_3 + \text{resinous product } (+HCl) \qquad (5)$$

---

[1] Zappel, *J. Amer. Chem. Soc.*, 1955, **77**, 4228.

[2] Kabachnik and Shepelera, *Izvest. Akad. Nauk, S.S.S.R., Otdel khim. Nauk*, 1950, 39.

[3] Summers, *Chem. Rev.*, 1955, **55**, 301.

With the exception of monochloroacetaldehyde each aldehyde reacted with stoicheiometric specificity and a mixture of two or more reactions was not observed.

The 3 : 2 benzaldehyde–trichloride product afforded on pyrolysis (see scheme 6) an almost quantitative yield of benzylidene dichloride and boron trioxide; the hydrolysis products are shown in scheme 7. With pyridine, no pyridine–boron trichloride was isolated.

$$(Ph\cdot CHO)_3,(BCl_3)_2 \longrightarrow 3Ph\cdot CHCl_2 + B_2O_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$(Ph\cdot CHO)_3,(BCl_3)_2 + 6H_2O \longrightarrow 3Ph\cdot CHO + 6HCl + 2B(OH)_3 \quad . \; . \; . \; . \quad (7)$$

The 1 : 1-crotonaldehyde–trichloride compound (scheme 4) afforded on pyrolysis (see scheme 8) a high yield of 1 : 3-dichlorobut-1-ene. This chloride could not be distinguished from its anionotropic isomer (see scheme 9), because of their known tendency to isomerise when heated.[4]

$$3CH_3\cdot CH{:}CH\cdot CH\cdot O\cdot BCl_3 \longrightarrow 3CH_3\cdot CHCl\cdot CH{:}CHCl + B_2O_3 + BCl_3 \quad . \; . \; . \quad (8)$$

$$CH_3\cdot CHCl\cdot CH{:}CHCl \rightleftharpoons CH_3\cdot CH{:}CH\cdot CHCl_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Hydrolysis gave a product, probably β-chlorobutyraldehyde, which was not identified because it polymerised; such polymerisation is a known reaction of β-chlorobutyraldehyde.[5] Only two-thirds of the total chlorine of the 1 : 1-crotonaldehyde–boron trichloride compound was instantly hydrolysed to hydrochloric acid by cold water, characteristic of chlorine attached to boron, whereas the remaining one-third was hydrolysed, still under mild conditions (cold aqueous-ethanolic potassium hydroxide; 12 hr.), typical of chlorine in β-chloro-aldehydes.

The tri-1-chloroalkyl borates (scheme 2), isolated from the reaction with di- and trichloroacetaldehyde, are novel and are of interest as esters of the unknown α-chloro-alcohols, RCHCl·OH. They are thermally stable, and were characterised since only the α-chlorine was easily hydrolysable. There was also evidence (molecular weight) for such a borate in the β-phenylpropionaldehyde system.

The symmetrical α-chloro-ethers (scheme 1) have easily hydrolysable α-chlorine atoms. In the monochloroacetaldehyde system there was evidence for the concurrent formation of the tris-1-chloroalkyl borate, as the initial product, which on pyrolysis afforded more boron trioxide and the bis-α-chloro-ether. This method of obtaining α-chloro-ethers has advantages over previous methods, particularly because of the mild conditions of the reaction.

Aldehyde	Primary product	Pyrolysis product
Acetaldehyde	Bis-1-chloroethyl ether	—
n-Butyraldehyde	Bis-1-chlorobutyl ether	—
*iso*Butyraldehyde	Bis-1-chloro-2-methylpropyl ether	—
Monochloroacetaldehyde	Bis-1 : 2-dichloroethyl ether (+ tris-1 : 2-dichloroethyl borate)	Bis-1 : 2-dichloroethyl ether
Dichloroacetaldehyde	Tris-1 : 2 : 2-trichloroethyl borate	—
Trichloroacetaldehyde	Tris-1 : 2 : 2 : 2-tetrachloroethyl borate	—
Tribromoacetaldehyde	No reaction	—
Phenylacetaldehyde	Resin	—
β-Phenylpropionaldehyde	Tris-1-chloro-3-phenylpropyl borate	Unidentified
Benzaldehyde	3 : 2-compound	Benzylidene dichloride
Crotonaldehyde	1 : 1-compound	1 : 3-Dichlorobut-1-ene

Reaction (5) was observed in the phenylacetaldehyde system. The resinous product was probably a poly(vinyl ether), formed by elimination of hydrogen chloride from the initial bis-1-chlorophenethyl ether obtained by reaction (1). This view is based on the known propensity[3] of α-chloro-ethers to lose hydrogen chloride, forming vinylic ethers, which are known to polymerise readily.[6] A β-bound phenyl group would assist the

---

[4] Kirrmann, *Compt. rend.*, 1934, **199**, 1228.

[5] Paul, *ibid.*, 1942, **215**, 303.

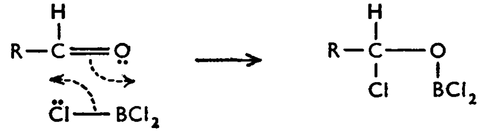
[6] Pepper, *Quart. Rev.*, 1954, **8**, 88.

hydrogen chloride elimination from the ether, because of conjugation with the developing olefinic double bond.[7]

Reactions (1) and (2) were also established when 3 : 1 molar proportions of reactants were employed in the acetaldehyde and chloral systems, respectively.

The results of equimolecular interaction are summarised in the Table.

Reaction Sequences and Mechanism.—It is suggested that the initial attack of boron trichloride on an aldehyde is either by means of a nucleophilic attack of chlorine on the α-carbon, followed by attachment of $[BCl_2]^+$ to the oxygen atom, or by means of a four-centre broadside collision as shown in scheme (10), to afford a 1-chloroalkyl dichloroboronite:


. . . . (10)

An alternative mechanism requires an initial electrophilic attack to give a co-ordination compound $R\cdot CHO{:}BCl_3$. Against this is the fact that bromal does not react with boron trichloride. Molecular models indicate that steric hindrance (*F*-strain) would prevent nucleophilic or broadside attack, but not electrophilic attack, of the carbonyl double bond in this aldehyde.

A 1 : 1 compound was isolated only from crotonaldehyde. The evidence (see above) favours the formulation of this compound as a dichloroboronite and not as a co-ordination compound. In accordance with known reactions of crotonaldehyde, this may be regarded as (I), the product of 1 : 4-addition, or as (II), the product of 1 : 2-addition.

(I) $CH_3\cdot CHCl\cdot CH{:}CHO\cdot BCl_2$ $CH_3\cdot CH{:}CH\cdot CHCl\cdot O\cdot BCl_2$ (II)

Alkyl dichloroboronites decompose [8] (slowly, or when heated) either to form an alkyl chloride (reaction 11) or by disproportionation (12). Reaction (11) is favoured by the presence of an electron-releasing group attached to the α-carbon atom (*e.g.* a vinyl group).

$$3RO\cdot BCl_2 \longrightarrow 3RCl + B_2O_3 + BCl_3 \quad . . . . \quad (11)$$

$$2RO\cdot BCl_2 \rightleftharpoons (RO)_2BCl + BCl_3 \quad . . . . \quad (12)$$

$$2(RO)_2BCl \rightleftharpoons (RO)_3B + RO\cdot BCl_2$$

The pyrolysis of the crotonaldehyde derivative is regarded as being of type (11) and this may be evidence for formula (II), although the selective hydrolysis seems more plausible in terms of formula (I), as α-chlorine atoms are generally readily hydrolysable, *e.g.* in the 1-chloroalkyl borates.

The structure of the 3 : 2-benzaldehyde compound is uncertain but its reactions would be explicable in terms of a 1 : 1-complex (III) of dichloroboronite and chloroboronate.

$Ph\cdot CHCl\cdot O\cdot BCl_2,(Ph\cdot CHCl\cdot O)_2BCl$ (III)

Dialkyl chloroboronates also decompose to alkyl chlorides,[9] and decomposition of the complex (III) therefore gives a satisfactory explanation of the pyrolysis products of the benzaldehyde complex.

Of the dichloroboronites corresponding to the aldehydes used, those from benzaldehyde and crotonaldehyde (II) have the greatest electron release at the α-carbon atom, and those are also the only two which give the appropriate chlorides on pyrolysis. This is in agreement with predictions as to the stability of dichloroboronites.

The formation of borates from di- and tri-chloroacetaldehyde is interpreted as being due to initial dichloroboronite formation, followed by disproportionation (scheme 12).

In the monochloroacetaldehyde reaction, the probable formation of borate and ether

---

[7] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, p. 436.

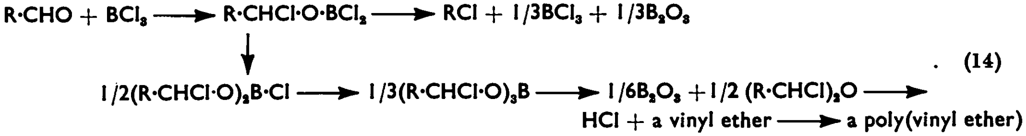
[8] Gerrard and Lappert, *J.*, 1955, 3084; Gerrard, Lappert, and Silver, *J.*, 1956, 3285.

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

as the initial products, which only on pyrolysis gives exclusively the ether, suggests that the borates are precursors in the formation of the ethers (see scheme 13).

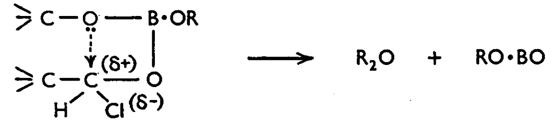
$$2(RO)_3B \longrightarrow 3R_2O + B_2O_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

The probable reaction sequences are summarised in scheme (14).



$$\begin{tikzcd}[column sep=small] R{\cdot}CHO + BCl_3 \arrow[r] & R{\cdot}CHCl{\cdot}O{\cdot}BCl_2 \arrow[r] \arrow[d] & RCl + 1/3BCl_3 + 1/3B_2O_3 \\ & 1/2(R{\cdot}CHCl{\cdot}O)_2B{\cdot}Cl \arrow[r] & 1/3(R{\cdot}CHCl{\cdot}O)_3B \arrow[r] & 1/6B_2O_3 + 1/2\,(R{\cdot}CHCl)_2O \arrow[r] & HCl + \text{a vinyl ether} \arrow[r] & \text{a poly(vinyl ether)} \end{tikzcd} \quad (14)$$

It would appear that the decomposition of borate to ether is governed by electronic rather than steric factors, because whereas dichoroacetaldehyde gives the borate, *iso*butyraldehyde gives the ether, although their borates are homomorphs (the methyl and chlorine groups have similar spatial requirements [10]). The decomposition may be regarded as of S_Ni type (scheme 15); metaborates decompose [11] to orthoborates and boron trioxide.



(15)

The suggestion is made that a decrease in the electron density on the oxygen atom of the borate hinders the ether-forming reaction, which is therefore not observed when groups attached to the β-carbon atom are sufficiently electronegative, as for the borates derived from di- and tri-chloroacetaldehyde.

EXPERIMENTAL

General Procedures.—Tribromoacetaldehyde was prepared by Lord and Howard's method; [12] dichloroacetaldehyde was obtained by dry distillation of the trimer. The other aldehydes were purified commercial samples. Boron trichloride was redistilled before use. In the reactions of the aldehydes with boron trichloride volatile material (solvent and unchanged trichloride) were removed at 20°/15 mm.

Boron, and chlorine attached to boron, were estimated by cold-water hydrolysis to hydrochloric and boric acid, which were analysed acidimetrically. The α-chlorine in α-chloro-ethers (and also allylic chlorine) was estimated by Volhard's method after hydrolysis with cold ethanolic potassium hydroxide. Total chlorine, as distinct from easily-hydrolysable chlorine (e.h. Cl) (except vinylic), was determined similarly, except that complete hydrolysis was ensured by prolonged refluxing with potassium hydroxide–ethanol.

The Interaction of Aldehydes (1 *mol.*) *with Boron Trichloride* (1 *mol.*).—*Acetaldehyde.* This (4·34 g.) was slowly added to boron trichloride (11·6 g.) at −80°; a vigorous reaction ensued, and a white solid formed. The mixture was allowed to warm to 20°, whereafter volatile matter was removed. The residue (8·27 g.) was a colourless liquid mixed with white solid, which afforded bis-1-chloroethyl ether (6·04 g., 86%), b. p. 111—114°, and a residue (2·11 g.) which contained boron trioxide (1·13 g., 98%). The ether on redistillation had b. p. 113—114°, n_D^{20} 1·4232, d_4^{20} 1·132 (Found: Cl, 49·4. Calc. for $C_4H_8OCl_2$: Cl, 49·7%). Yields are based on (scheme 1).

n-*Butyraldehyde.* This (2·76 g.) in *n*-pentane (10 c.c.) was added to boron trichloride (4·50 g.) in *n*-pentane (10 c.c.) at −80°. A vigorous reaction ensued, and the reaction mixture was kept at 20° for ½ hr. Volatile matter [including BCl_3 (2·96 g., 97%)] was then removed. On distillation, solid separated in the still as the temperature was raised. The distillate was *bis*-1-*chlorobutyl ether* (3·13 g., 83%), b. p. 75—78°/16 mm., and the dark residue (0·67 g.) contained boron trioxide (0·432 g., 97%). The ether on redistillation had b. p. 90°/24 mm., n_D^{20} 1·4406, d_4^{20} 1·033 (Found: C, 48·8; H, 8·2; Cl, 35·6. $C_8H_{16}OCl_2$ requires C, 48·3; H, 8·1; Cl, 35·7%). In another experiment ferric chloride (10% by weight of the aldehyde) was

---

[10] H. C. Brown and his co-workers, *J. Amer. Chem. Soc.*, 1953, **75**, 1.

[11] Lappert, *Chem. Rev.*, 1956, **56**, 959.

[12] Lord and Howard, *Org. Synth.*, Coll. Vol. II, New York, 1947, p. 87.

incorporated in the reaction mixture. The ether was obtained in only 20% yield and there was a resin in the still; hydrogen chloride was liberated. Yields are based on scheme (1).

iso*Butyraldehyde*. To boron trichloride (4·50 g.) in *n*-pentane (10 c.c.) at −80°, was added the aldehyde (2·76 g.) in *n*-pentane (10 c.c.). The mixture was stored at 20° for ½ hr., whereafter volatile matter [including boron trichloride (2·96 g. 99%)] was removed. The residue (4·30 g.) comprised a white solid and a supernatant liquid. Matter volatile at 20°/0·01 mm. was condensed into a trap at −80°. This condensate was *bis-1-chloro-2-methylpropyl ether* (2·88 g., 75%), b. p. 72°/13 mm., n_D^{20} 1·4392, d_4^{20} 1·045 (Found: C, 48·1; H, 8·05; Cl, 35·6%). The residue (1·28 g.) contained boron trioxide (0·441 g., 99%). Yields are based on scheme (1).

Monochloroacetaldehyde. The aldehyde (6·88 g.) in suspension in *n*-pentane (15 c.c.) was added to boron trichloride (10·30 g.) in pentane (30 c.c.) at −80°. The mixture was kept at 20° for ½ hr., whereafter volatile matter, including boron trichloride (6·83 g., 99%), was removed at 20°/20 mm. A white, pasty solid remained; this was washed with ether to afford a clear solution and boron trioxide (0·444 g., 43·5%). Evaporation of solvent left a viscous, pale yellow liquid, which was heated at 120° for ½ hr. under reflux. Hydrogen chloride was evolved, but no precipitate resulted. Cooling and addition of ether precipitated more boron trioxide (0·573 g., 56·2%). The ethereal filtrate afforded *bis-1 : 2-dichloroethyl ether* (5·75 g., 62%), b. p. 62—64°/0·1 mm., leaving a brown residue (2·53 g.). The ether on redistillation had b. p. 62°/0·1 mm., n_D^{20} 1·4918, d_4^{20} 1·457 (Found: C, 23·1; H, 3·0; Cl, 66·5; e.h. Cl, 33·0. $C_4H_6OCl_4$ requires C, 22·6; H, 2·85; Cl, 67·0; e.h. Cl, 33·5%). Yields are based on scheme (1).

Dichloroacetaldehyde. Boron trichloride (6·50 g.) at —80° was added to the aldehyde (6·25 g.) also at −80°; a vigorous reaction produced a viscous liquid. Volatile matter [boron trichloride (4·30 g., 99%)] was removed, and subsequent distillation afforded *tris-1 : 2 : 2-trichloroethyl borate* (7·19 g., 85%), as a viscous liquid, b. p. 116—118°/11 mm., n_D^{20} 1·5052, d_4^{20} 1·647 (Found: C, 16·3; H, 1·45; Cl, 69·7; e.h. Cl, 22·8; B, 2·34. $C_6H_6O_3Cl_9B$ requires C, 15·8; H, 1·3; Cl, 70·0; e.h. Cl, 23·3; B, 2·37%) and a brown solid (1·03 g.). The yield is based on scheme (2). The borate was instantly hydrolysed on exposure to the atmosphere. Heating at 200° for 1 hr. caused no significant decomposition.

Trichloroacetaldehyde. Boron trichloride (5·60 g.) was added to the aldehyde (7·03 g.) at −80°, whereupon a viscous solution was obtained. Volatile matter [boron trichloride (3·70 g., 99%)] was removed (20°/15 mm.) and subsequent distillation afforded *tris-1 : 2 : 2 : 2-tetrachloroethyl borate* (8·00 g., 90%) as a viscous liquid, b. p. 98—105°/0·5 mm., n_D^{20} 1·5090, d_4^{20} 1·702 (Found: C, 12·4; H, 0·9; Cl, 75·8; e.h. Cl, 20·0; B, 2·0. $C_6H_3O_3Cl_{12}B$ requires C, 12·8; H, 0·5; Cl, 76·1; e.h. Cl, 19·0; B, 1·9%). There was a brown residue (0·89 g.). The yield is based on scheme (2). The borate was instantly hydrolysed on exposure to the atmosphere, but was recovered almost quantitatively after 3 hr. at 200°. There was no reaction with triethylamine.

Tribromoacetaldehyde. Boron trichloride (2·67 g.) was added to the aldehyde (6·39 g.) at −80°. After ½ hr. at 20°, volatile matter [boron trichloride (2·46 g., 92%)] was removed, and the aldehyde (5·34 g., 84%), b. p. 62—66°/12 mm., n_D^{20} 1·5890, d_4^{20} 2·729 (Found: Br, 84·8. Calc. for C_2HOBr_3: Br, 85·4%), and a dark liquid (1·04 g.) were obtained.

Phenylacetaldehyde. Boron trichloride (9·30 g.) was added to phenylacetaldehyde (9·50 g.) at −80°. Volatile matter [boron trichloride (6·20 g., 100%)] was rapidly removed, and the residue then set aside at 20° for 12 hr.; hydrogen chloride was continuously evolved. A solution of the gum in chloroform (50 c.c.) was refluxed (2 hr.) until evolution of hydrogen chloride had ceased. The solvent was removed (at 0·1 mm.) and a reddish-brown oil remained, which upon extraction with water–ether afforded an ethereal solution and an aqueous portion which contained boric acid equivalent to boron trioxide (0·799 g., 87%). The ethereal solution was dried ($MgSO_4$) and freed from solvent affording a reddish-brown resin (7·84 g.). Yields are based on scheme (5).

β-*Phenylpropionaldehyde*. Boron trichloride (3·91 g.) was added to the aldehyde (4·46 g.) at −80°. The volatile matter contained boron trichloride (2·58 g., 99%). The brown viscous residue was probably tris-1-chloro-3-phenylpropyl borate (5·79 g.) (Found: Cl, 20·8; B, 2·15; *M*, 500. Calc. for $C_{27}H_{30}O_3Cl_3B$: Cl, 20·5; B, 2·1%; *M*, 519·5). The molecular weight was determined cryoscopically (in *cyclo*hexane) in an atmosphere of nitrogen, agitation being effected by a nitrogen pulse in order to avoid hydrolysis. The yield is based on scheme (1). Attempted distillation led to decomposition products which have not been identified.

Benzaldehyde. Boron trichloride (6·20 g.) in *n*-pentane (20 c.c.) at −80° was added to the aldehyde (5·60 g.) also in *n*-pentane (20 c.c.), at −80°. Volatile matter was removed (20°/0·5 mm.) leaving a 3 : *2-benzaldehyde–boron trichloride* compound (9·91 g. Calc., 9·76 g.) (Found : Cl, 38·0; B, 4·5. $3C_7H_6O,2BCl_3$ requires Cl, 38·5; B, 3·9%) as a white solid. All the chlorine in the compound was converted into hydrogen chloride by hydrolysis with cold water. The compound was insoluble in *n*-pentane and ether, but soluble in methylene dichloride. The yield is based on scheme (3).

Crotonaldehyde. This (5·06 g.) in *n*-pentane (25 c.c.) was added to boron trichloride (8·50 g.) in pentane (25 c.c.) at −80°, whereupon a white solid was precipitated. After the mixture had remained at 20° for 3 hr. volatile matter was removed. The residue (12·69 g., 94%; based on equimolecular interaction) was a white solid.

In several similar experiments the original precipitate was filtered off. Its weight varied, but on the average, was equivalent to about 50% of that required for a 1 : 1-compound. The analysis, which was also somewhat variable (Found : Cl, 54·3—60·4; e.h. Cl, 38·1—41·6; B, 5·6—6·2. Calc. for C_4H_6O,BCl_3 : C, 56·8; e.h. Cl, 37·9; B, 5·8%), identified it as 1-chloro-3-methylallyl dichloroboronite or its anionotropic isomer.

Interaction of Aldehydes (3 *mol.*) *and Boron Trichloride* (1 *mol.*).—*Acetaldehyde.* This (3·15 g.) was cautiously added to the trichloride (2·80 g.) at −80°. At 20° there was some white solid; at 50° there was no loss of weight but the mixture had become brown and gelatinous. Distillation afforded bis-1-chloroethyl ether (4·50 g., 88%), and a residue (1·00 g.) which contained boron trioxide (0·815 g., 98%). The ether had b. p. 112—114°, n_D^{20} 1·4230, d_4^{20} 1·132 (Found : Cl, 49·2%), after redistillation. The yield is based on scheme (1).

Chloral. This (24·90 g.) was added to boron trichloride (6·60 g.) at −80°. Distillation afforded tris-1 : 2 : 2 : 2-tetrachloroethyl borate (24·3 g., 77%), b. p. 155—160°/0·5 mm., a brown residue (0·40 g.), and a condensate (at −80°) of chloral (2·30 g.). Redistillation afforded the pure borate (21·7 g.), b. p. 100°/0·05 mm., n_D^{20} 1·5020, d_4^{20} 1·702 (Found : e.h. Cl, 20·5; Cl, 75·8; B, 3·35%). The yield is based on scheme (2).

Properties of the Benzaldehyde–Boron Trichloride Compound.—Pyrolysis. When the 3 : 2-compound (see above) (3·60 g.) was heated benzylidene dichloride (3·12 g., 99%; based on $3Ph{\cdot}CHO,2BCl_3 \longrightarrow 3Ph{\cdot}CHCl_2 + B_2O_3$), b. p. 88—90°/17 mm., n_D^{20} 1·5488, d_4^{20} 1·246 (Found : Cl, 43·1. Calc. for $C_7H_6Cl_2$: Cl, 44·0%) was obtained, and boron trioxide (0·455 g., 100%) remained. The yields are based on scheme (6).

Addition of benzaldehyde (8·25 g., 3 mol.) to boron trichloride (6·10 g., 2 mol.) at −80° afforded a white solid, which when heated in a vacuum gave benzylidene dichloride (12·30 g., 98%), b. p. 87°/12 mm., n_D^{20} 1·5488 (after redistillation).

Hydrolysis. Water (10 c.c.) and *n*-pentane (10 c.c.) were added to the compound (3·15 g.). The washed and dried *n*-pentane extract afforded benzaldehyde (1·68 g., 93%), b. p. 172—180°, n_D^{20} 1·5464. The yield is based on scheme (7).

Action of pyridine. To the compound (7·38 g., 1 mol.) in methylene dichloride (60 c.c.) was added pyridine (2·11 g., 2 mol.) in the same solvent (20 c.c.) at 20°. There was considerable evolution of heat, and the mixture remained homogeneous. The solvent was removed in a vacuum and a viscous oil remained. Addition of water to a mixture of the residue with *n*-pentane gave two liquid phases. The upper (pentane) layer contained benzaldehyde (3·63 g.), b. p. 176—180°.

Properties of the Crotonaldehyde–Boron Trichloride Compound.—Pyrolysis. When the 1 : 1-compound (see above) (2·51 g.) was heated there was obtained 1 : 3-dichlorobut-1-ene (1·31 g., 79%; based on $3C_4H_6O,BCl_3 \longrightarrow 3CH_3{\cdot}CHCl{\cdot}CH{:}CHCl + BCl_3 + B_2O_3$), b. p. 58—60°/25 mm., n_D^{20} 1·4647, d_4^{20} 1·12 [Found : e.h. Cl (cold potassium hydroxide in ethanol), 28·0. Calc. for $C_4H_6Cl_2$: e.h. Cl (allylic), 28·4%]. The maximum value for " total " chlorine obtained was 35·5%, after 92 hours' refluxing in strong ethanolic potassium hydroxide A carbonaceous residue (0·45 g.) contained boron trioxide (0·31 g., 99%). Yields are based on scheme (8).

Hydrolysis. The compound (7·21 g.) was shaken with a mixture of water and ether. The ether layer was dried ($MgSO_4$), and the solvent was removed at 20 mm. The residue (1·82 g.) was volatile at 0·1 mm. and may have been β-chlorobutyraldehyde (Found : Cl, 32·3. Calc. for C_4H_7OCl : Cl, 33·3%). It slowly decomposed to a tar.

THE NORTHERN POLYTECHNIC, HOLLOWAY, LONDON, N.7.

[*Received, June 13th,* 1956.]