The Preparation and Stability of Alkyl Dichloroboronites.

By W. GERRARD and M. F. LAPPERT.

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The preparation of a number of alkyl dichloroboronites, $BCl_2{\cdot}OR$, by reaction of boron trichloride with alcohols, borates or chloroboronates has been investigated. The primary alkyl esters are stable at 20°, the secondary at −80°. There are two causes of this instability: decomposition (to alkyl chloride or to olefin) and disproportionation [to BCl_3 and $BCl(OR)_2$]; and which of these reactions predominates depends on experimental conditions. A probable mechanism for the formation of alkyl chloride is based on the relative stability of dichloroboronites when R is varied, stereochemical features (optical activity and molecular rearrangements), and the influence of electrophilic catalysts.

IN earlier papers (*J.*, 1951, 1020, 2545) we described experiments on alcohol (*sec.*-octyl, CHPhMe, Bu^n, Bu^i, Bu^t)–boron trichloride–borate systems, in the course of which alkyl dichloroboronites from primary (Bu^n and Bu^i), but not secondary or tertiary alcohols were isolated. The present paper is concerned with methods of preparation of dichloroboronites, stoicheiometries of their decomposition, and constitutional, stereochemical, and environmental factors influencing the decomposition; experiments are described. It deals with *n*- and *iso*-propyl, the four isomeric butyl, *neo*pentyl, 1 : 2-dimethylpropyl, 1 : 2 : 2-trimethylpropyl, *n*-octyl, and 1-methylheptyl systems.

Interaction between boron trichloride and any of these alcohols or their borates or chloroboronates, in the proportions indicated in equations (1)—(3), gave dichloroboronites quantitatively. As boron trichloride is difficult to handle, an excess of it was used and the residue was easily removed under reduced pressure after the reaction.

$$(1)\quad BCl_3 + ROH \longrightarrow BCl_2{\cdot}OR + HCl$$

$$(2)\quad 2BCl_3 + B(OR)_3 \longrightarrow 3BCl_2{\cdot}OR$$

$$(3)\quad BCl_3 + BCl(OR)_2 \longrightarrow 2BCl_2{\cdot}OR$$

The dichloroboronites could react further by decomposition to an alkyl halide (4), elimination, producing an olefin (5), or disproportionation (6):

$$(4)\quad 3BCl_2{\cdot}OR \longrightarrow B_2O_3 + BCl_3 + 3RCl$$

$$(5)\quad 3BCl_2{\cdot}OR \longrightarrow B_2O_3 + BCl_3 + 3HCl + 3\text{Olefin}$$

$$(6)\quad 2BCl_2{\cdot}OR \rightleftharpoons BCl_3 + BCl(OR)_2$$

Depending on experimental conditions either reaction (6) or reactions (4) and (5) together were observed, but the extent of the elimination (5) was not significant except with the *n*-octyl ester. When dichloroboronites were allowed to reflux (without heating in some cases), by reduction of pressure, boron trichloride (b. p. 12·5°/760 mm.) was gradually removed and dialkyl chloroboronates remained (6). At atmospheric or higher pressures, under reflux, or in sealed tubes, decomposition (4) [with (5)] occurred. Distillation, whether under reduced or at atmospheric pressure, gave all the possible products. Only reaction (6) was reversible, whence the influence of pressure on the equilibrium (because of the high volatility of the trichloride) is clear.

Occurrence of reaction (4) or (6) has previously been regarded as characteristic of a particular type of branching, methyl, ethyl (Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1, 22, 31), and *n*- and *iso*-butyl esters (Gerrard and Lappert, *loc. cit.*) undergoing reaction (4), and 2-chloroethyl (Edwards, Gerrard, and Lappert, *J.*, 1955, 1470) and phenyl esters (Colclough, Gerrard, and Lappert, *ibid.*, p. 907) undergoing reaction (6); and only with 4-chlorobutyl dichloroboronite (Edwards *et al.*, *loc. cit.*) have both types of reaction been recognised.

Tris-1 : 2 : 2-trimethylbutyl borate is new; four others used by us have not hitherto been prepared by the reaction $3ROH + BCl_3 \longrightarrow B(OR)_3 + 3HCl$ (cf. Wiberg and Sütterlin, Gerrard and Lappert, *loc. cit.*) which gives them in nearly quantitative yields.

Factors governing reaction (4) were studied and a number of conclusions emerge.

(a) *Constitutional Factors.*—Changing the alkyl group, R, in the dichloroboronites showed that the stability is primary > secondary > tertiary. Tertiary dichloroboronites were not isolated (Gerrard and Lappert, *loc. cit.*). Evidence for the existence of secondary dichloroboronites at —80° was obtained (see also Gerrard and Lappert, *loc. cit.*), but they decomposed very rapidly at 20°. Primary alkyl dichloroboronites were stable at 20° for indefinite periods and the relative order of stabilities at 150° was estimated by heating weighed samples in sealed tubes and analysing the mixtures after arbitrary time intervals (dichloroboronites yield all their chlorine in ionic form on hydrolysis by cold water, whereas of the products of decomposition only the boron trichloride is so hydrolysed). The results are shown in Table 1.

TABLE 1.

R in $RO{\cdot}BCl_2$	Pr^n	Bu^n	n-C_8H_{17}	Bu^i	$Bu^t{\cdot}CH_2$
Decomp. (%) (½ hr.)	14	2	1	5·5	2
Decomp. (%) (1½ hr.)	46	24	15	62	29
Decomp. (%) (5 hr.)	93	100	95	92	81

(b) *Stereochemical Factors.*—Wagner–Meerwein rearrangement has already been shown to occur (Gerrard and Lappert, *loc. cit.*) in the decomposition of *iso*butyl dichloroboronite to *tert.*-butyl chloride. Other examples [$Bu^t{\cdot}CH_2 \longrightarrow CMe_2Et$; $CHMePr^i \longrightarrow CMe_2Et$; $(+)$-$CHMeBu^t \longrightarrow CMe_2Pr^i$] are now given.

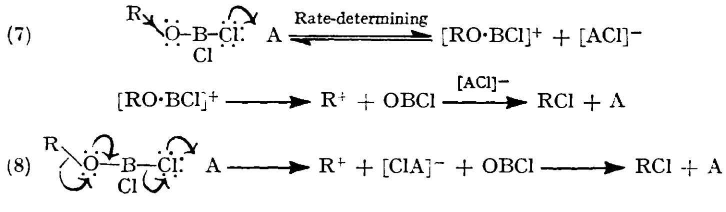
Reactions (1) and (2) with (+)-1-methylheptyl compounds have previously (Gerrard and Lappert, *loc. cit.*) been shown to give the configurationally inverted, but much racemised, 2-chloro-octane. It is now shown that these reactions involved 1-methyl heptyl dichloroboronite as an intermediate in that a stable 1 : 1 complex with pyridine has been isolated (see Lappert, *J.*, 1953, 667, and Edwards *et al.*, *loc. cit.*, regarding pyridine–primary alkyl dichloroboronite adducts).

Both these stereochemical factors indicate a carbonium-ion intermediate in alkyl halide formation.

(c) *Environmental Factors.*—*n*-Butyl and *iso*butyl dichloroboronites are more stable than hitherto believed (Gerrard and Lappert, *loc. cit.*). The lower stability reported earlier is due to very small traces (<0·1%) of Lewis acid impurity, then present, which catalysed decomposition. Thus, it is now shown that the *n*-butyl ester is stable for 9 hr. at 100°, if prepared from rigorously purified boron trichloride. However, when a small quantity (1% by weight) of ferric or aluminium chloride was added decomposition was complete within ½ min. at room temperature. With *iso*butyl, *neo*pentyl, and 1-methylheptyl dichloroboronites, such catalytic decomposition did not affect the steric course of the reactions. Earlier work on the stability of dichloroboronites was repeated, but results for *sec.*- and *tert.*-butyl and *sec.*-octyl esters were substantially the same as already reported (Gerrard and Lappert, *loc. cit.*).

The Mechanism of Decomposition.—It is suggested that the mechanism of decomposition (4) of dichloroboronites involves a rate-determining initial fission of one B–Cl bond, depending on two factors : the degree of electron release (+*I*) from the alkyl group, and the action of a second molecule of the ester, designated A in representations (7) and (8), which functions as an electrophilic catalyst and thus facilitates heterolysis of the B–Cl bond. Ferric and aluminium chloride (A) may also function in this way. If the alkyl group of the ester is bulky, the boron atom may be sterically shielded to some degree and thus its efficiency as an electrophilic catalyst may be decreased. This duality of mechanistic factors explains the observed influence of constitutional and environmental variations.

For later steps in the decomposition it is necessary to postulate that a carbonium cation be formed, either as a separate step (7) or by a process synchronous with B–Cl heterolysis (8).



Boron oxychloride which is here suggested as an intermediate, is supposed to decompose subsequently ($3BOCl \longrightarrow B_2O_3 + BCl_3$). A similar postulate was made by Wiberg and Sütterlin and by Gerrard and Lappert (*locc. cit.*), although the existence of an oxychloride was doubtful; but it appears now more probable in view of the isolation (Lappert, *loc. cit.*) of its stable 1 : 1 pyridine complex.

EXPERIMENTAL

Reagents.—*neo*Pentyl alcohol was prepared by Whitmore and Badertscher's method (*J. Amer. Chem. Soc.*, 1933, **55**, 1559), 3-methylbutan-2-ol by Drake and Cooke's method (*Org. Synth.*, Coll. Vol. II, 1943, p. 406), and 3 : 3-dimethylbutan-2-ol by reduction of pinacolone. The last-named alcohol was optically resolved by Pickard and Kenyon's method (*J.*, 1912, **101**, 620). Boron trichloride was carefully redistilled before use.

Preparation of Trialkyl Borates.—Boron trichloride (1 mol.) in *n*-pentane was added (20—30 min.) to the alcohol (3 mols.) in *n*-pentane at −80°. The reaction was strongly exothermic. The mixture having been kept at −80° for 20 min., hydrogen chloride and solvent were removed at 10—15 mm. and the crude borate was distilled. Results are shown in Table 2. From 0·025 to 0·10 mole of reagents was used, and the volume of solvent was 6 times that of the combined reactants. Reversal of addition (a more convenient procedure in view of the low b. p. of boron trichloride) gave substantially similar results. Physical constants are those obtained with redistilled samples.

TABLE 2. *Alkyl borates.*

					Found (%)			Calc. (%)		
Alkyl	Yield (%)	B. p. (°/mm.)	n_D^{20}	d_4^{20}	C	H	B	C	H	B
Pr^n	96	176/760	1·3969	0·861	57·2	11·2	5·7	57·4	11·3	5·8
CH_2Bu^t	88	104/12	(m. p. 58—58·5°)		66·5	11·8	4·1	66·2	12·1	4·0
$CHMePr^i$	85	59—61/0·4	1·4080	0·844	66·5	12·1	4·0	66·2	12·1	4·0
$CHMeBu^t$	86	122/9	1·4151	0·841	68·5	12·3	3·3	68·8	12·4	3·2
n-C_8H_{17}	95	182—184/0·5	1·4377	0·855	72·8	12·9	2·7	72·4	12·9	2·7

Dichloroboronites by Reaction (1).—The alcohol (1 mol.) was added (20—30 min.) to boron trichloride (1 mol.) in absence of solvent at −80°. The mixture was allowed to warm to 20° and then kept at 20°/15—20 mm. (75 mm. for Pr^n) for 10 min. whilst mechanically shaken to remove hydrogen chloride and any excess of boron trichloride, which were collected in potassium hydroxide absorption tubes. Reagents were used in 0·01—0·05 mole amounts and the reverse order of addition gave substantially similar results. For primary esters the results are shown in Table 3 (for Me, Et, Bu^n, and Bu^i see Wiberg and Sütterlin, and Gerrard and Lappert, *locc. cit.*), but for secondary esters (for Bu^s see Gerrard and Lappert, *loc. cit.*) decomposition at 20° was rapid.

*iso*Propyl alcohol (1·03 g., 1 mol.) was added to boron trichloride (1·90 g., 1 mol.) at −80°, After 5 min., dry nitrogen was passed for 15 min. through the mixture, still at −80°, and hydrogen chloride (0·60 g., 97%) was absorbed in traps containing potassium hydroxide. Hydrolysis of the residue in an enclosed system revealed that iso*propyl dichloroboronite* (Found: Cl, 49·4; B, 7·9. $C_3H_7OBCl_2$ requires Cl, 50·2; B, 7·7%) had been formed.

TABLE 3. *Alkyl dichloroboronites.*

Alkyl	Yield (%)	Yield of HCl (%)	n_D^{20}	d_4^{20}	Found (%) Cl	Found (%) B	Required (%) Cl	Required (%) B
Pr^n †	100	99	1·4094	1·138	49·6	7·6	50·2	7·7
CH_2Bu^t † *	98	97	1·4097	1·032	41·2	6·3	41·8	6·4
n-C_8H_{17}	99	98	1·4316	1·015	34·3	4·9	33·6	5·2

* Pentane used as solvent, as the alcohol is a solid.
† Purified by condensation (0·1 mm.) into a trap at −80°.

Dichloroboronites by Reaction (2).—The borate (1 mol.) was added (5 min.) to boron trichloride (slightly more than 2 mols.) at −80°. The mixture was warmed to 20° and excess of trichloride removed at 15—20 mm. (40 mm. for Pr^n) in 10 min.; the residue in the case of a primary alkyl compound was the dichloroboronite, but decomposition products (4) were obtained from secondary alkyl compounds. The results are shown in Table 4 (for Me, Et, Bu^n, Bu^i, and Bu^s see Wiberg and Smedsrud, *Z. anorg. Chem.*, 1935, **225**, 204; Gerrard and Lappert, *loc. cit.*). Reversal of addition or the use of a solvent (*n*-pentane) made no significant difference.

TABLE 4.

R in BCl_2·OR	Yield (%)	n_D^{20}	d_4^{20}	Found (%) Cl	Found (%) B
Pr^n	98	1·4110	1·140	49·6	7·6
CH_2Bu^t	98	1·4090	1·031	41·7	6·4
n-C_8H_7	99	1·4316	1·013	34·0	5·1

Boron trichloride (4·13 g., 2 mols.) was added to tris-1-methylheptyl borate (7·00 g., 1 mol.) in *n*-pentane (30 c.c.) at −80° and the mixture was kept at −80° for a further 1 hr., whereafter pyridine (4·14 g., 3 mols.) in *n*-pentane (15 c.c.) was added. A white, pasty solid was formed instantly. After being kept for 3 hr. at 20° this was washed with more pentane and solvent then removed under reduced pressure. The precipitate (14·07 g.), which was treated with water, was a mixture of 1-methylheptyl dichloroboronite–pyridine (13·4 g., 87%) and pyridine–boron trichloride (Gerrard and Lappert, *Chem. and Ind.*, 1952, 53) (0·67 g.), m. p. 115°; the latter compound was insoluble; the former was hydrolysed, and gave analytical results corresponding to the 1 : 1 *complex* of dichloroboronite and pyridine (Found: Cl, 23·8; B, 3·7; C_5H_5N, 27·2. $C_{13}H_{22}ONCl_2B$ requires Cl, 24·3; B, 3·75; C_5H_5N, 27·2%).

Dichloroboronites by Reaction (3).—*n*- or *iso*-Butyl chloroboronate (Gerrard and Lappert, *J.*, 1951, 2545) (1 mol.) was added (5 min.) to boron trichloride (slightly more than 2 mols.) at −80°. The subsequent procedure was as described for reaction (2) and the results are shown in Table 5.

TABLE 5.

R in BCl_2·OR	Yield (%)	n_D^{20}	d_4^{20}	Found (%) Cl	Found (%) B	Calc. (%) Cl	Calc. (%) B
Bu^n	98	1·4161	1·079	45·7	7·0	45·8	7·0
Bu^i	99	1·4088	1·046	45·5	7·0	,,	,,

Decomposition (4) *and* (5) *of Dichloroboronites.*—The evidence for reaction (4) is shown in Table 6, which gives the data relating to yields and purity of end-products. These results are only some of many obtained in order to demonstrate that the stoicheiometry and the nature of the halide (*i.e.*, rearranged or not) was the same whether or not a catalyst was also present; conditions are not here stated as they were found to have no significant effect; in none of these experiments was reduced pressure used. 0·02—0·1 Mole of reagents was employed. The present results are additional to the earlier ones (Wiberg and Sütterlin, and Gerrard and Lappert, *locc. cit.*). Notes to Table 6 are: (*a*) These results are for sealed tube or catalysed reactions in open systems. (*b*) Octene (34%) was also formed, having b. p. 125—127°/760 mm., n_D^{20} 1·4157, d_4^{20} 0·723, which was further characterised as the dibromide, b. p. 108—109°/12 mm., n_D^{20} 1·4936, d_4^{20} 1·415. (*c*) When the optically active 3 : 3-dimethylbutan-2-ol, $[\alpha]_D^{20}$ +5·5°, was used the resulting halide was completely racemised. (*d*) These chlorides were also analysed for tertiary alkyl chloride by hydrolysing weighed samples in dilute nitric acid in the cold (48 hr.) with subsequent Volhard titration. Blank experiments on authentic samples revealed that only a tertiary and not a secondary halide was thus hydrolysed. The results were 87% and 93% of *tert.*-pentyl chloride in the *neo*pentyl and 1 : 2-dimethylpropyl systems respectively and 74% of a *tert.*-hexyl chloride in the 1 : 2 : 2-trimethylpropyl system. (*e*) In these examples the dichloroboronites were not isolated at 20°.

TABLE 6.

R in $BCl_2 \cdot OR$	Yield of B_2O_3 (%)	Yield of BCl_3 (%)	RCl Yield (%)	B. p. (°/mm.)	n_D^{20}	Found : Cl (%)	Calc. : Cl (%)
Pr^n	96	—	84	46—47	1·3864	44·8	45·3
$Pr^{i\ c}$	98	—	90	38—42	1·3782	45·0	45·3
$CH_2Bu^{t\ a}$	98	98	90	83—84	1·4045	32·7 [d]	33·2
$CHMePr^{i\ a,e}$	99	98	88	82—84	1·4042	32·8 [d]	33·2
$CHMeBu^{t\ a,c,e}$ ...	98	96	85	108—110	1·4183	28·7 [d]	29·4
n-C_8H_{17} [b]	98	100	53	68/12	1·4311	23·4	23·9

For notes see text.

Disproportionation (6) *of Dichloroboronites.*—(a) n-*Octyl.* The dichloroboronite (9·52 g.) was heated (150°) under reflux at 15° for 7 hr. in order to allow boron trichloride to escape. On distillation at 0·5 mm. *n*-octyl chloride (1·00 g.), b. p. 40°/0·5 mm., and a middle fraction (1·00 g.), b. p. 128—132°/0·5 mm., n_D^{15} 1·4393 (Found : Cl, 13·9; B, 3·5%), were obtained. The final fraction (3·0 g., 50%) was tri-*n*-octyl borate, b. p. 178—182°/0·5 mm., n_D^{15} 1·4401 (Found : B, 3·2. Calc. for $C_{24}H_{51}O_3B$: B, 2·7%). The yield of borate is based on : $3BCl_2 \cdot OR \longrightarrow B(OR)_3 + 2BCl_3$.

(b) neo*Pentyl.* The dichloroboronite (2·53 g.) was allowed to reflux for 4½ hr. at 20°/2 mm., a solid carbon dioxide–acetone cold-finger condenser and a mechanical shaker being employed. A residue (1·65 g., 100%) of *dineopentyl chloroboronate*, n_D^{16} 1·4125 (Found : Cl, 17·4; B, 5·2. $C_{10}H_{22}O_2ClB$ requires Cl, 16·1; B, 4·9%), remained. From an absorption tube at −80° containing pyridine, attached to the apparatus, pyridine–boron trichloride, m. p. 114° was isolated. The yield is based on equation (6).

(c) n-*Butyl.* As in (*b*), the dichloroboronite (5·47 g.) after 4½ hr. at 20°/14 mm., and then 3 hr. at 20°/0·2 mm., gave a residue (3·38 g.) of crude di-*n*-butyl chloroboronate (Gerrard and Lappert, *loc. cit.*) which was purified by removing the dichloroboronite by condensation (0·2 mm.). The residue (2·30 g.) was the pure chloroboronate (Found : Cl, 18·7; B, 5·8. Calc. for $C_8H_{18}O_2ClB$: Cl, 18·4; B, 5·65%).

Stability of Dichloroboronites.—In addition to information on p. 3085, catalytic acceleration of decomposition by aluminium or ferric chloride is shown in Table 7. The method of estimation is by an analytical procedure as described on p. 3085, employing sealed samples (0·1—0·3 g.). The results were in satisfactory agreement with those of larger-scale experiments, wherein the extent of decomposition was estimated by isolation of the products. These decompositions were shown to be irreversible, because decomposed samples of pure dichloroboronites when kept at 20° for several days did not to any measurable extent re-form the esters.

TABLE 7.

Time	Temp.	Catalyst	Catalyst (% w/w)	Decomp. (%)	Time	Temp.	Catalyst	Catalyst (% w/w)	Decomp. (%)
		n-*Butyl dichloroboronite*					neo*Pentyl dichloroboronite*		
<1 min.	20°	$FeCl_3$	1	100	5 hr.	17°	$AlCl_3$	0·7	20
9 hr.	100	—	—	<5	25 days	100	—	—	75
1 hr.	100	$FeCl_3$	0·2	98	4 days	17	$AlCl_3$	0·7	65
1 hr.	100	$AlCl_3$	0·2	96					

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

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