346. *The Preparation and Stability of Dialkyl Chloroboronates.*

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The preparation of a number of dialkyl chloroboronates, $BCl(OR)_2$, by reaction of either boron trichloride or alkyl dichloroboronites, $BCl_2{\cdot}OR$, with either alcohols or trialkyl borates has been investigated. The chloroboronates may further undergo either an alkyl chloride-producing reaction, accompanied by an olefin-producing elimination reaction, or a disproportionation reaction, depending upon the experimental conditions. The stability of dialkyl chloroboronates with respect to the former reaction depends on both electronic and steric factors. A probable mechanism for this reaction is offered, based on (1) the relative stability of chloroboronates when R is varied, (2) stereochemical features (optical activity and molecular rearrangements), and (3) the influence of catalysts. Results are compared with those obtained with alkyl dichloroboronites in a previous investigation.[1]

IN two earlier papers[2, 3] experiments on alcohol–boron trichloride–borate systems were described, in which dialkyl chloroboronates, $BCl(OR)_2$, containing primary (Bu^n and Bu^i), but not secondary or tertiary alkyl groups, were isolated. The present paper reports methods of preparation of chloroboronates, the stoicheiometry of their decomposition, and constitutional, stereochemical, and environmental factors influencing such decomposition reactions. Experiments are described concerning the systems involving *n*-propyl, the four isomeric butyl, *neo*pentyl, 1 : 2 : 2-trimethylpropyl, 1-octyl, and 1-methylheptyl radicals. The results are available for comparison with corresponding experiments[1] with alkyl dichloroboronites, $BCl_2{\cdot}OR$.

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[1] Gerrard and Lappert, *J.*, 1955, 3084.
[2] *Idem, J.*, 1951, 1020.
[3] *Idem, J.*, 1951, 2545.

Interaction between (*a*) boron trichloride or alkyl dichloroboronites and (*b*) alcohols or trialkyl borates, in the proportions indicated by (1)—(4), gave quantitative yields of the chloroboronates. In view of the difficulty in handling boron trichloride, methods (2) and (4) are preferred, but are only suitable for chloroboronates having primary alkyl groups, as the corresponding alkyl dichloroboronites, required as starting materials, are sufficiently stable only in those cases.[1]

$$\text{(1)}\quad BCl_3 + 2ROH \longrightarrow BCl(OR)_2 + 2HCl$$

$$\text{(2)}\quad BCl_2{\cdot}OR + ROH \longrightarrow BCl(OR)_2 + HCl$$

$$\text{(3)}\quad BCl_3 + 2B(OR)_3 \longrightarrow 3BCl(OR)_2$$

$$\text{(4)}\quad BCl_2{\cdot}OR + B(OR)_3 \longrightarrow 2BCl(OR)_2$$

The chloroboronates could react further in one of three ways—an alkyl chloride-producing decomposition (5), accompanied to a relatively small extent by an olefin-producing elimination reaction (6), and a disproportionation (7).

$$\text{(5)}\quad 3BCl(OR)_2 \longrightarrow B_2O_3 + B(OR)_3 + 3RCl$$

$$\text{(6)}\quad 3BCl(OR)_2 \longrightarrow B_2O_3 + B(OR)_3 + 3HCl + 3\ \text{Olefin}$$

$$\text{(7)}\quad 2BCl(OR)_2 \rightleftharpoons B(OR)_3 + BCl_2{\cdot}OR$$

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

According to experimental conditions either (7), or (5) and (6) together, were observed. At pressures equal to or greater than atmospheric and under reflux or sealed-tube conditions, decomposition (5) with (6) was observed. Under reflux, by reduction of pressure, slow disproportionation (7) was observed. Of these three reactions, (7) was reversible and so was (5), but in this case only when the group R was primary and straight-chained. The reversibility of the alkyl (primary) chloride-producing decomposition illustrates a difference from the dichloroboronites. A further difference is the far greater facility shown by the latter to disproportionate.

Distillation of the chloroboronates at atmospheric pressure was not possible in view of reactions (5)—(7), but at low pressures, such that the b. p. was below 45°, the *n*-propyl, *n*- and *iso*-butyl, *neo*pentyl, and 1 : 2 : 2-trimethylpropyl chloroboronates could be distilled without significant decomposition (<3%). The *sec.*-butyl and the 1-methylheptyl ester, however, decomposed [(5) and (6)], and the 1-octyl ester disproportionated (7) presumably because of the higher temperature that had to be used. In view of this difficulty, the experiments on the chloroboronates were carried out on undistilled samples, from which volatile materials (boron trichloride, hydrogen chloride, alkyl chlorides, or alkyl dichloroboronites) were removed by application of a suitable vacuum. The resultant samples were analytically very pure, and further, the molecular refractivities calculated from the measured refractive indices and densities were in good agreement (see Table 1) with the values calculated from Eisenlohr's data on carbon, hydrogen, oxygen, and chlorine atomic refractivities,[4] and an average value for boron of 2·65, calculated from Cowley and Partington's [5] and Arbuzov and Vinogradova's data [6] on trialkyl borates.

TABLE 1.*

R in $BCl(OR)_2$	Pr^n	Bu^n	Bu^i	Bu^s	$CMe_3{\cdot}CH_2$	$CHMeBu^t$	C_8H_{17}	$CHMe{\cdot}C_6H_{13}$
Found : $[R_L]_D$...	41·8	51·0	50·6	50·7	60·2	69·3	88·2	87·3
Calc. : $[R_L]_D$ ...	41·8	51·0	51·0	51·0	60·3	69·5	88·0	88·0

* The author is grateful to a referee for suggesting the advisability of computing these figures.

Either reaction (5) or (7) has previously been regarded as characteristic of a particular branching. Thus Bu^n and Bu^i were thought to afford reaction (5) only,[3] whilst for di-2-chloroethyl [7] and for diphenyl [8] chloroboronate the characteristic reaction was (7).

[4] Eisenlohr, *Z. phys. Chem.*, 1910, **75**, 585.
[5] Cowley and Partington, *Nature*, 1935, **136**, 643.
[6] Arbuzov and Vinogradova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1947, **55**, 411.
[7] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.
[8] Colclough, Gerrard, and Lappert, *ibid.*, p. 907.

Factors governing reaction (5) were studied under three headings.

(a) *Influence of Constitutional Factors.*—The stability of chloroboronates varied widely with change in the alkyl group, R. The *tert.*-butyl ester was unstable at 20° (88% decomposition in 20 min.). Of the esters having secondary alkyl groupings the stability increased with length of chain and extent of branching in the alkyl groups. Thus the *sec.*-butyl ester was less stable than the 1-methylheptyl ester and di-1 : 2 : 2-trimethylpropyl chloroboronate was completely unchanged after 6 days at 20° and indeed was more stable at 150° than short-chain primary esters such as the di-*n*-propyl and di-*n*-butyl chloroboronates. The primary dialkyl chloroboronates were stable at 20°, but at 150° the stability increased with length of chain and with extent of branching. Thus the 1-octyl and *neo*pentyl esters were unchanged after 5 hr. at 150°, whereas the *n*-propyl and *n*- and *iso*-butyl ester were almost completely decomposed. The *iso*- was more stable than the *n*-butyl ester which in turn was more stable than the *n*-propyl. Similar results were observed at 100°. The results are summarised in Table 9.

It is clear that the stability of dialkyl chloroboronates is dependent both on the degree of electron release at the alcoholic carbon atom and also on steric factors, in contrast to the stability ranges found for alkyl dichloroboronites, where the electronic factor was the controlling, if not the only, criterion of stability.[1]

(b) *Influence of Stereochemical Factors.*—Wagner–Meerwein type rearrangement has previously been demonstrated in the decomposition of di*iso*butyl chloroboronate to *tert.*-butyl chloride.[3] Two other examples are now given :

$$\mathrm{Me_3C{\cdot}CH_2{-}} \longrightarrow \mathrm{Me_2EtC{-}} \quad \text{and} \quad \mathrm{Me_3C{\cdot}CHMe{-}} \longrightarrow \mathrm{Pr^iMe_2C{-}}$$

Whereas decomposition of (+)-1-methylheptyl dichloroboronite afforded much racemised 2-chloro-octane,[1] the decomposition of the corresponding chloroboronate is now shown to give (—)-2-chloro-octane with very little loss of activity.

(c) *Influence of Environmental Factors.*—The isomeric dibutyl chloroboronates are considerably more stable than has hitherto been believed. The lower stability reported earlier [3] is due to very small traces ($<0{\cdot}1\%$) of Lewis acid impurity then present, which catalysed decomposition. The influence of such catalysts on the decomposition of chloroboronates is general. Of the compounds tried, hydrogen chloride, alkyl chlorides, trialkyl borates, and *n*-pentane had no effect on the decompositions; Lewis acids such as ferric and aluminium chloride were very effective, as also to a smaller extent were alkyl dichloroboronites. For example, the addition of ferric chloride (0·05%) to di-*n*-butyl chloroboronate at 20° caused instant decomposition. Similar results were observed with the other esters; the results are summarised in Table 10. By contrast, diethyl ether, a Lewis base, had a stabilising effect.

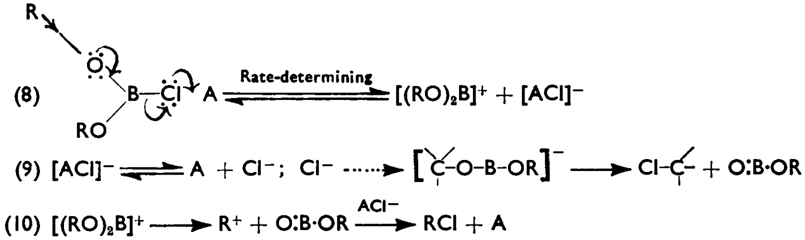
With the *iso*butyl, *neo*pentyl, and (+)-1-methylheptyl esters, such catalytic decomposition did not affect the steric course of the reactions.

The acceleration of decomposition produced by ferric and aluminium chloride is comparable to that observed with dichloroboronites.[1]

The Mechanism of Decomposition.—The mechanism of decomposition (5) of dialkyl chloroboronates is considered to involve a rate-determining initial fission of the 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 (8), which functions as an electrophilic catalyst and thus facilitates heterolysis of the B–Cl bond. Other Lewis acids, such as those mentioned in (c) (above) may also function as " A " in this way. The efficiency of " A " is dependent on two factors, its strength as an electrophile and the steric availability of the electron-deficient atom. If this atom is shielded, as in the uncatalysed decomposition of highly branched dialkyl chloroboronates, the power of " A " as an electrophile is low or negligible. This duality of mechanistic factors explains the observed influence of constitutional and environmental variations. The greater emphasis on steric factors in the decomposition of chloroboronates than in that of dichloroboronites is also clear.

Subsequent steps in the decomposition mechanism appear to depend on the nature of the alkyl group. Those groups which are normally not hindered with respect to S_N2

" in-line " attack choose this mode of reaction (9), whilst those hindered with respect to such attack react by an S_N1 carbonium-ion mechanism (10). These suggestions are put forward to account for the observed stereochemical influences.



The metaborates, BO·OR, suggested as intermediates, are finally considered to decompose :

$$(11)\quad 3BO{\cdot}OR \longrightarrow B(OR)_3 + B_2O_3$$

The probability of preponderance of either the S_N2 (9) or the S_N1 mechanism (10) for a particular group R, will depend on the relative rates of these reactions. The stability of $[(RO)_2B]^+$ is evidently sufficient to permit (9) to take place if the group R is such that it is normally responsive to S_N2 replacements. This is a contrasting result to that found[1] with dichloroboronites, where even with such groups, an S_N1 result was obtained. This is doubtless due to the lower stability of $[BCl{\cdot}OR]^+$ than of $[(RO)_2B]^+$; the greater stability of the latter may be due to its symmetry.

EXPERIMENTAL

General Procedure.—Reagents were prepared or purified by the methods outlined earlier.[1] Compounds containing boron, or boron as well as chlorine atoms attached to a boron atom, were analysed by cold-water hydrolysis in an enclosed system and titration with carbonate-free sodium hydroxide to successively a methyl-orange (Cl) and a phenolphthalein (B) end-point, the latter titration being carried out in the presence of mannitol. Compounds containing a chlorine atom attached to a carbon atom were analysed for chlorine by the Volhard method, after previous hydrolysis with boiling ethanolic potassium hydroxide.

Dialkyl Chloroboronates by Reaction (1).—The alcohol (2 mols.) was added dropwise to boron trichloride (1 mol.) at −80°. The outlet to the reaction vessel was connected to potassium hydroxide absorption tubes in order to collect the liberated hydrogen chloride. At the end of the addition, the mixture was allowed to warm to 20° and was then kept at 20°/15—20 mm. for 30 min., whilst being mechanically shaken. The residual oil was the chloroboronate. The results are shown in Table 2 (for Bu^n and Bu^i, see ref. 3 ; for Me and Et, see ref. 9 ; for 2-chloroethyl, see ref. 7) ; all the *esters* are new compounds. Reagents were used in 0·01—0·05-molar amounts and the reverse order of addition gave substantially similar results.

TABLE 2.

R in $BCl(OR)_2$	Yield (%)	Yield of HCl (%)	Properties of $BCl(OR)_2$					
					Found (%) :		Required (%) :	
			n_D^{20}	d_4^{20}	Cl	B	Cl	B
Pr^n	98	100	1·4028	0·959	21·4	6·6	21·6	6·6
Bu^s	98	99	1·4017	0·924	18·4	5·8	18·4	5·6
$CMe_3{\cdot}CH_2$ *	100	100	1·4102	0·906	16·1	5·1	16·1	4·9
CHMeBu^t	100	98	1·4165	0·901	14·2	4·4	14·3	4·4
C_8H_{17}	99	98	1·4380	0·906	11·6	3·7	11·7	3·6
$CHMe{\cdot}C_6H_{13}$ † ...	100	97	1·4277	0·897	11·6	3·7	11·7	3·6

* Pentane used as solvent, as alcohol is a solid.
† α_D^{20} +20·0° from ROH having α_D^{20} +7·72°.

Dialkyl Chloroboronates by Reaction (2).—The alcohol (1 mol.) was added to the dichloroboronite[1] (1 mol.) at −80°. Further procedure was similar to that described for reaction (1).

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[9] Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 31.

Results are shown in Table 3. The method was not satisfactory for the esters having secondary alkyl groups, as the corresponding dichloroboronites are unstable.[1]

TABLE 3.

R in	Yield	Yield of HCl		Found (%):		R in	Yield	Yield of HCl		Found (%):	
BCl(OR)$_2$	(%)	(%)	n_D^{20}	Cl	B	BCl(OR)$_2$	(%)	(%)	n_D^{20}	Cl	B
Pr^n	98	100	1·4024	21·5	6·6	CMe$_3$·CH$_2$ *	100	100	1·4100	16·1	5·0
Bu^n	100	100	1·4132	18·4	5·7	C$_8$H$_{17}$	100	100	1·4378	11·6	3·7
Bu^i	98	99	1·4055	18·3	5·7						

* Pentane used as solvent.

Dialkyl Chloroboronates by Reaction (3).—Boron trichloride (1 mol.) was added to the trialkyl borate (2 mols.) at −80°. Further procedure was similar to that described for reaction (1), except that instead of potassium hydroxide absorption tubes, a silica-gel drying tube was attached to the apparatus. Results are shown in Table 4 (for Bu^n and Bu^i, see ref. 3; for Me and Et, see ref. 10; for 2-chloroethyl, see ref. 7).

TABLE 4.

R in	Yield		Found (%):		R in	Yield		Found (%):	
BCl(OR)$_2$	(%)	n_D^{20}	Cl	B	BCl(OR)$_2$	(%)	n_D^{20}	Cl	B
Pr^n	97	1·4027	21·3	6·6	CHMeBu^t ...	100	1·4169	14·2	4·5
Bu^s	98	1·4013	18·3	5·7	C$_8$H$_{17}$	100	1·4379	11·4	3·6
CMe$_3$·CH$_2$ ...	100	1·4106	16·1	4·9	CHMe·C$_6$H$_{13}$ *	99	1·4283	11·6	3·7

* α_D^{20} +20·4° from B(OR)$_3$ having α_D^{20} +28·7°.

Dialkyl Chloroboronates by Reaction (4).—The dichloroboronite (1 mol.) was added to the trialkyl borate (1 mol.) at −80° and subsequent procedure was as described for reaction (3). Results are shown in Table 5. The method was not tried for chloroboronates having secondary alkyl groupings.

TABLE 5.

R in	Yield		Found (%):		R in	Yield		Found (%):	
BCl(OR)$_2$	(%)	n_D^{20}	Cl	B	BCl(OR)$_2$	(%)	n_D^{20}	Cl	B
Pr^n	97	1·4020	21·5	6·6	CMe$_3$·CH$_2$ ...	100	1·4106	16·0	5·0
Bu^n	99	1·4134	18·3	5·7	C$_8$H$_{17}$	100	1·4384	11·6	3·6
Bu^i	100	1·4055	18·4	5·6					

Decomposition (5) *and* (6) *of Dialkyl Chloroboronates*.—The purpose of these experiments was to establish the stoicheiometry of the decompositions. Conditions (*e.g.*, absence or presence of various catalysts) are not stated (except that in none was reduced pressure used) because, as a result of many experiments, it was seen that these did not affect the stoicheiometry of the reactions or the nature of the halide (optical activity and molecular rearrangement results) obtained. The present results are additional to those on the four isomeric butyl esters.[3] Yields are recorded in Table 6, and the results for the characterisation of the alkyl halides and trialkyl borates are shown in Table 7.

TABLE 6.

R in BCl(OR)$_2$		Pr^n	CMe$_3$·CH$_2$	CHMeBu^t	C$_8$H$_{17}$	CHMe·C$_6$H$_{13}$
Yield (%) of	B$_2$O$_3$	95	98	96	100	98
	B(OR)$_3$ ...	93	84	90	98	92
	RCl	79	88	89	97	51 *

* Also octene (35%). The mixture was separated by distillation and by bromination. The dibromide had b. p. 110—111°/13 mm., n_D^{16} 1·4894.

The proportion of olefin formed [reaction (6)] in the decomposition of chloroboronates was small, except for the 1-methylheptyl ester. That it is formed was demonstrated with the *n*-butyl ester. The chloroboronate (11·30 g.) was heated for 4 hr. at 100° under reflux in the presence of a trace of ferric chloride. The outlet of the condenser was connected through a soda-lime trap (to absorb hydrogen chloride) to two Herschel bottles, each containing bromine (4 c.c.) in chloroform (10 c.c.). The bromine solutions were combined and the chloroform and

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[10] Wiberg and Smedsrud, *ibid.*, 1935, **225**, 204.

TABLE 7.

R in $BCl(OR)_2$	Characterisation of RCl B. p. (mm.)	n_D^{20}	Found : Cl (%)	Calc. : Cl (%)	Characterisation of $B(OR)_3$ B. p. (mm.)	n_D^{20}	Found : B (%)	Calc. : B (%)
Pr^n	45—47°	1·3878	—	—	175—177°	1·3969	5·6	5·8
$CMe_3{\cdot}CH_2$ * ...	85	1·4054	32·8	33·2	113(12)	— (m.p. 53—54°)	4·1	4·0
CHMeBu^t * ...	109	1·4180	29·0	29·4	72—74(0·3)	1·4150	3·3	3·2
C_8H_{17}	69—71(15)	1·4302	23·8	23·9	158—160(0·1)	1·4377	3·2	2·7
$CHMe{\cdot}C_6H_{13}$ †	61(14)	1·4275	23·7	23·9	135—137(0·1)	1·4298	2·8	2·7

* The chlorides were also analysed for tertiary alkyl chloride, by hydrolysing weighed samples in dilute nitric acid in the cold (48 hr.) and a subsequent Volhard titration. Earlier work had shown that under these conditions only a tertiary and not a secondary chloride was thus hydrolysed.[1] The results were 85% *neo*pentyl chloride in the *neo*pentyl system and 98% of a *tert.*-hexyl chloride in the 1 : 2 : 2-trimethylpropyl system.

† The chloroboronate was prepared from a (+)-tri-1-methylheptyl borate sample [reaction (3)] having α_D^{20} +14·6°. The borate from decomposition of the chloroboronate had the same activity, whilst the 2-chloro-octane had α_D^{20} −11·8°.

much of the excess of bromine were removed in a vacuum. The small residue was dissolved in ether (10 c.c.), washed ($NaHSO_3$), and dried ($CaCl_2$). The ether was removed by distillation and the residue (0·50 g.) was 1 : 2-dibromobutane, b. p. 164°/760 mm., n_D^{18} 1·5138, equivalent to but-1-ene (0·13 g., 4%).

Disproportionation (7) *of Dialkyl Chloroboronates.*—(a) n-*Butyl.* The ester (4·00 g.) was heated for 28 hr. at 80° under reflux at 1 mm. A residue (2·40 g.), n_D^{20} 1·4101, remained, which was a mixture of tri-*n*-butyl borate (59%) and di-*n*-butyl chloroboronate (41%) (Found : Cl, 7·5; B, 5·1. Calc. for such a mixture : Cl, 7·5; B, 5·1%; n_D^{20} 1·4121). A condensate had collected in a trap cooled to −80°, which after two distillations afforded *n*-butyl dichloroboronite (0·46 g.), b. p. 38—41°/19 mm., n_D^{20} 1·4160 (Found : Cl, 45·3; B, 6·9. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%).

(b) Very similar results were obtained with the *iso*butyl and the *n*-propyl ester.

Distillation of Chloroboronates.—The chloroboronates shown in Table 8 were distilled. In each case the reduced pressure employed was so chosen that the compounds could be distilled in the range 30—45°. Under these conditions the corresponding dichloroboronites and alkyl chlorides are gaseous, except the 1-octyl ester, which consequently underwent appreciable disproportionation (7). In the cases where distillation was possible, significant disproportionation (about 15%) was noted (*i.e.*, a dichloroboronite condensate and a trialkyl borate residue). The di-*sec.*-butyl and di-1-methylheptyl chloroboronates could not be distilled owing to decomposition [(5) and (6)].

TABLE 8.

R in $BCl(OR)_2$	B. p. (mm.)	n_D^{20}	Found (%) : Cl	B	R in $BCl(OR)_2$	B. p. (mm.)	n_D^{20}	Found (%) : Cl	B
Pr^n	36°(6)	1·4018	21·3	6·5	$CMe_3{\cdot}CH_2$	30°(0·2)	1·4110	16·0	4·8
Bu^n	40(0·25)	1·4128	18·1	5·5	CHMeBu^t	35(0·015)	1·4180	14·2	4·4
Bu^i	32(0·2)	1·4070	18·2	5·6	[C_8H_{17} ...	40—75(0·01)	1·4338	18·3	4·0]

TABLE 9.

R in $BCl(OR)_2$	Time (hr.)	Temp.	Decompn. (%)	R in $BCl(OR)_2$	Time (hr.)	Temp.	Decompn. (%)
Bu^s	1/3	20°	0·5	$CMe_3{\cdot}CH_2$	5	150°	0
Bu^s	2½	20	2	CHMeBu^t	1	150	2
Bu^s	22	20	13	,, ...	2	150	35
Bu^s	72	20	37	,, ...	5	150	68
$CHMe{\cdot}C_6H_{13}$	72	20	1	C_8H_{17}	5	150	0
,,	42 days	20	26	Bu^n	1	100	5
CHMeBu^t ...	144	20	0	Bu^n	3	100	23
Pr^n *	1	150	90	Bu^n	5	100	38
Pr^n	2	150	95	Bu^i	1	100	0
Bu^n *	1	150	62·5	Bu^i	3	100	1
Bu^n	2	150	88	Bu^i	5	100	1·5
Bu^i	1	150	3	$CMe_3{\cdot}CH_2$	28	200	92
Bu^i	2	150	56				

* Only in these examples was there evidence of reversibility. Thus samples which had been heated for 5 hr. at 150°, when subsequently left for 36 hr. at 20°, contained more chloroboronate (Pr^n, 80%; Bu^n, 60%).

Stability of Dialkyl Chloroboronates.—The only tertiary ester investigated was di-*tert.*-butyl chloroboronate. This was not isolated at 20°, when method (4) was used, the mixture being 88% decomposed after 20 min. For the other esters, the results for non-catalysed decompositions are shown in Table 9, and, for decompositions at 20° in presence of added substances, in Table 10. At 20° all the primary esters (Pr^n, Bu^n, and Bu^i, $CMe_3{\cdot}CH_2$, and C_8H_{17}) were still pure after 3 weeks.

TABLE 10.

R in $BCl(OR)_2$	Time (hr.)	Added substance and amount	Decompn. (%)	R in $BCl(OR)_2$	Time (hr.)	Added substance and amount	Decompn. (%)
Bu^n ……	1	HCl (saturated)	<2	Bu^n ………	<5 min.	$AlCl_3$ (2%)	99
Bu^n * …	1 min.	$FeCl_3$ (0·05%)	98	$CMe_3{\cdot}CH_2$ …	1	$FeCl_3$ (2%)	96
Bu^n …	48	$FeCl_3$ (0·05%) $B(OBu^n)_3$ (1 mol.)	98	Bu^s ………	2½	BCl_3 † (4%)	45
				$CHMe{\cdot}C_6H_{13}$	2½	BCl_3 † (4%)	25
Bu^n …	48	$FeCl_3$ (0·05%) Bu^nCl (1 mol.)	94	Bu^s ………	23	BCl_3 † (4%)	95
				$CHMe_3{\cdot}C_6H_{13}$	12 days	BCl_3 † (4%)	95
Bu^n …	48	$FeCl_3$ (0·05%) $C_5H_{12}{}^n$ (1 mol.)	93	,,	23	BCl_3 † (4%)	55
Bu^n …	48	$FeCl_3$ (0·05%) Et_2O (1 mol.)	34				

* Temp. rose from 16° to 68°.

† The addition of BCl_3 to chloroboronates has been considered as equivalent to formation of $BCl_2{\cdot}OR$ in the mixture (see discussion).

The stabilities were estimated by heating weighed samples in sealed tubes and analysing the mixtures after arbitrary time intervals by breaking the tubes under water in stoppered flasks and titrating the liberated hydrogen chloride to a methyl-orange end-point (the chloroboronates on hydrolysis in cold water instantly evolve all the chlorine as HCl; the alkyl halides do not).

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