98. *The Preparation and Properties of Certain Chloroalkoxyboron Chlorides and Trischloroalkyl Borates.*

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Certain novel trischloroalkyl borates, $B(OR)_3$, have been prepared from the appropriate alcohol and boron trichloride, whilst novel chloroalkoxyboron chlorides, $RO{\cdot}BCl_2$ and $(RO)_2BCl$, and also the ethyl and pentyl derivatives have been obtained from the appropriate borate and boron trichloride. Physical constants of the new compounds have been determined and molecular refractivity results calculated. The chloroalkoxyboron chlorides are unassociated in *cyclo*hexane; they fume in air, form complexes with pyridine, and decompose under the influence of ferric chloride in definite stoicheiometry. The relative rates of decomposition were measured, and the results are discussed.

Earlier work by Edwards, Gerrard, and Lappert [1] on chlorinated alkyl borates and chloroalkoxyboron chlorides has now been extended. Novel borates have now been prepared [see scheme (1)] in high yields (see Table 2) from boron trichloride and 3-chloropropan-1-ol, 5-chloropentan-1-ol, 2 : 2-dichloroethanol, 1 : 3-dichloropropan-2-ol, and 2 : 3-dichloropropan-1-ol.

$$3ROH + BCl_3 \longrightarrow B(OR)_3 + 3HCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Alkyl dichloroboronites [see scheme (2) and Table 3] and dialkyl chloroboronates [see scheme (3) and Table 4] were obtained quantitatively from boron trichloride and the appropriate borates in the stated proportions.

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

$$2B(OR)_3 + BCl_3 \longrightarrow 3(RO)_2B{\cdot}Cl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

All these esters were hydrolysed immediately by water, the borates into boric acid and the appropriate alcohol, and the alkoxyboron chlorides, which fumed in air, also to hydrochloric acid. Their molecular refractivities were estimated and these agreed well (see Table 1) with values calculated from Vogel's data [2] on the atomic refractivities of carbon, hydrogen, oxygen, and chlorine; a value of 2·65 was assumed for the atomic refractivity of boron.[3] Molecular-weight determinations showed the alkoxyboron chlorides to be unassociated in *cyclo*hexane (see Table 6). The alkoxyboron chlorides formed 1 : 1 or 1 : 2 complexes with pyridine.

Table 1. *Molecular refractivities, $[R_L]_D$, with calculated values in parentheses.*

$B(O{\cdot}[CH_2]_3{\cdot}Cl)_3$	$B(O{\cdot}[CH_2]_5{\cdot}Cl]_3$	$B(O{\cdot}CH_2{\cdot}CHCl_2)_3$	$B[O{\cdot}CH(CH_2Cl)_2]_3$	$B(O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2Cl)_3$
66·7 (66·9)	94·8 (94·8)	67·4 (67·5)	80·7 (81·4)	81·3 (81·4)
$n\text{-}C_5H_{11}O{\cdot}BCl_2$	$Cl{\cdot}[CH_2]_3{\cdot}O{\cdot}BCl_2$	$Cl{\cdot}[CH_2]_5{\cdot}O{\cdot}BCl_2$	$(n\text{-}C_5H_{11}O)_2B{\cdot}Cl$	$(Cl{\cdot}[CH_2]_3{\cdot}O)_2B{\cdot}Cl$
40·2 (40·2)	35·9 (35·8)	44·7 (45·1)	59·8 (60·3)	51·1 (51·4)
$(Cl{\cdot}[CH_2]_4{\cdot}O)_2B{\cdot}Cl$	$(Cl{\cdot}[CH_2]_5{\cdot}O)_2B{\cdot}Cl$			
60·6 (60·6)	70·5 (69·9)			

The stabilities and decomposition of unsubstituted alkyl dichloroboronites [4] and dialkyl chloroboronates [3] have been discussed before, and it was noted that there were two principal reactions—either decomposition [schemes (4) and (5)] or disproportionation [reverse of schemes (2) and (3)].

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

$$3(RO)_2B{\cdot}Cl \longrightarrow 3RCl + B_2O_3 + B(OR)_3 \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

With the present esters, disproportionation was observed on distillation, but heating under pressure favoured the decomposition. The 2-chloroethoxyboron chlorides were

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[1] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.

[2] Vogel, *J.*, 1946, 133; 1948, 616, 644, 654.

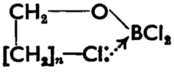
[3] Lappert, *J.*, 1956, 1768.

[4] Gerrard and Lappert, *J.*, 1955, 3084.

previously shown not to decompose even on heating,[1] but it is now shown that the presence of ferric chloride (1—2% w/w) as catalyst (see refs. 3 and 4) induces a quantitative and rapid reaction at room temperature in this as well as in the other systems (see Tables 8 and 9).

The rates of decomposition of the pure alkoxyboron chlorides were determined (see Tables 10 and 11) and are available for comparison with earlier results.[3,4]

The rates of decomposition of the ω-chloroalkyl dichloroboronites are in the order R = $Cl{\cdot}[CH_2]_4 > Cl{\cdot}[CH_2]_5 \gg Cl{\cdot}[CH_2]_3 > Cl{\cdot}[CH_2]_2$. Other relations for relative reactivities of dichloroboronites are: $Et \gg Cl{\cdot}[CH_2]_2$; $Pr^n \gg Cl{\cdot}[CH_2]_3$; $Cl{\cdot}[CH_2]_4 \gg Bu^n$; $Cl{\cdot}[CH_2]_5 > n\text{-}C_5H_{11}$; $n\text{-}C_5H_{11} > Bu^n$; and $Cl{\cdot}[CH_2]_4 > Cl{\cdot}[CH_2]_5$. It has already been shown that the greater the electron-releasing power of the alkyl group in an alkyl dichloroboronite, the greater is the rate of decomposition.[4] We attribute the marked increase of stability of the 2-chloroethyl and the 3-chloropropyl ester mainly to stabilisation by intramolecular co-ordination as shown in (I).


(I; *n* = 1 or 2)

The greater stability of the *n*-butyl than the *n*-pentyl compound suggests that a steric acceleration factor must also be considered. However, this does not completely explain the results obtained with the ω-chloro-butyl and -pentyl homologues, which are homomorphs [5] of *n*-pentyl and *n*-hexyl compounds.

The rates of decomposition of the dialkyl chloroboronates are also available. Whilst these compounds are in general more stable than the corresponding dichloroboronites, the effect of chlorine substitution in the alkyl group is not so marked.

EXPERIMENTAL

Reagents and Procedures.—2 : 2-Dichloroethanol was obtained by Sroog, Chih, Short, and Woodburn's method;[6] 3-chloropropan-1-ol by that of Marvel and Calvery;[7] 2-chloropropan-1-ol by that of Pickett, Garner, and Lucas;[8] 4-chlorobutan-1-ol by that of Starr and Hixon;[9] and 5-chloropentan-1-ol by that of Anderson and Pollard.[10]

Triethyl borate was prepared by Wiberg and Sütterlin's procedure [12] and tripentyl borate by Johnson and Tompkins's method.[13] 2-Chloroethyl dichloroboronite, di-2-chloroethyl chloroboronate, and 4-chlorobutyl dichloroboronite were obtained as described previously.[1]

Analytical methods have been described elsewhere.[1,11]

Preparation of Trialkyl Borates.—The alcohol (3 mol.) in solvent (*n*-pentane or methylene dichloride), to moderate the reaction, was added to boron trichloride (1 mol.; 0·025—0·25 mole) in the same solvent at −80°. Hydrogen chloride and solvent were then removed at about 20°/20 mm., and the residue of crude borate was purified by distillation. The results are shown in Table 2. All the *borates* are new.[14]

Preparation of Alkyl Dichloroboronites.—The borate (1 mol., 0·025—0·05 mole) was added dropwise with shaking to boron trichloride (2 mol.) at −80°. The dichloroboronites were purified either by condensation (20°/0·5—1·0 mm.) or distillation at reduced pressure. The 5-chloropentyl ester was not treated in this way because of its lower volatility; distillation caused significant decomposition. In the other cases, after evaporation or distillation had been completed, substantial residues (5—30%) remained of the impure chloroboronate, resulting presumably from disproportionation. The results are shown in Table 3; except for the ethyl homologue, the *dichloroboronites* are new.[14]

Preparation of Dialkyl Chloroboronates.—The borate (2 mol.) was added to boron trichloride

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[5] H. C. Brown and co-workers, *J. Amer. Chem. Soc.*, 1953, **75**, 1.
[6] Sroog, Chih, Short, and Woodburn, *ibid.*, 1949, **71**, 1710.
[7] Marvel and Calvery, *Org. Synth.*, Coll. Vol. I, J. Wiley, New York, 1947, p. 533.
[8] Pickett, Garner, and Lucas, *J. Amer. Chem. Soc.*, 1951, **73**, 5063.
[9] Starr and Hixon, *Org. Synth.*, Coll. Vol. II, J. Wiley, New York, 1947 p. 571.
[10] Anderson and Pollard, *J. Amer. Chem. Soc.*, 1939, **61**, 3439.
[11] Edwards, Gerrard, and Lappert, *J.*, 1957, 377.
[12] Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1.
[13] Johnson and Tompkins, *Org. Synth.*, Coll. Vol. II, J. Wiley, New York, 1947, p. 106.
[14] Lappert, *Chem. Rev.*, 1956, **56**, 959.

TABLE 2. *Trialkyl borates.*

R in $B(OR)_3$	Yield (%)	B. p. (°/mm.)	n_D^{20}	d_4^{20}	Found (%) Cl	B	Required (%) Cl	B
$Cl\cdot[CH_2]_3$	88	96/0·075	1·4571	1·190	37·1	3·6	36·5	3·7
$Cl\cdot[CH_2]_5$	88	170/0·5	1·4626	1·090	28·6	2·9	28·4	2·9
$Cl_2CH\cdot CH_2$	90	118—120/0·5	1·4840 *	1·496	59·9	3·0	60·4	3·0
$(Cl\cdot CH_2)_2CH$	89 †	128/0·004	1·4891	1·417 *	53·6	2·8	53·9	2·7
$Cl\cdot CH_2\cdot CHCl\cdot CH_2$ ...	92	143/0·004	1·4952	1·419 *	54·0	2·8	53·9	2·7

* At 19°.

† Yield based on BCl_3. Preliminary experiments showed the yield, based on the alcohol, to be low. This was shown to be due to the presence in the alcohol of 6% of 1 : 5-dichloropentane, which is difficult to remove. Excess of the alcohol was therefore used.

(1 mol.; 0·026—0·05 mole) at −80°. The resultant product (*i.e.*, quantitative yield) was the pure chloroboronate; the results are shown in Table 4. Distillation of these led in some cases to slight decomposition (see Table 5). Except for the ethyl ester, the *chloroboronates* are new.[14]

Di-4-chlorobutyl chloroboronate (96%) (Found: e.h. Cl, 13·5; B, 4·1%) was also obtained from boron trichloride (1 mol.) by addition of 4-chlorobutanol (2 mol.) in methylene dichloride and subsequent removal of volatile matter.

TABLE 3. *Alkyl dichloroboronites.*

R in $RO\cdot BCl_2$	Yield (%)	B. p. (°/mm.)	n_D^{20}	d_4^{20}	Found (%): e.h. Cl *	Cl	B	Required (%): e.h. Cl	Cl	B
C_2H_5	92	78	1·3968	1·125	56·0	—	8·6	56·0	—	8·5
n-C_5H_{11}	85	52—55/28	1·4170	1·056	41·8	—	6·5	42·0	—	6·4
$Cl\cdot[CH_2]_3$ ...	56	—	1·4432	1·293	41·0	61·6	6·4	40·5	60·8	6·2
$Cl\cdot[CH_2]_5$ ...	100	—	1·4533	1·228	33·6	51·2	5·4	34·9	52·3	5·3

* e.h. = easily hydrolysed.

TABLE 4. *Dialkyl chloroboronates.*

R in $(RO)_2B\cdot Cl$	n_D^{20}	d_4^{20}	Found (%): e.h. Cl	B	Required (%): e.h. Cl	B
C_2H_5	1·3878	0·972	25·8	8·0	26·0	7·9
n-C_5H_{11}	1·4202	0·933	16·1	5·0	16·1	4·9
$Cl\cdot[CH_2]_3$	1·4564	1·240	14·9	4·6	15·1	4·6
$Cl\cdot[CH_2]_4$	1·4622	1·181	13·4	4·1	13·6	4·1
$Cl\cdot[CH_2]_5$	1·4621	1·127	11·8	3·7	11·9	3·8

TABLE 5. *Distillation of dialkyl chloroboronates.*

R in $(RO)_2B\cdot Cl$	B. p. (°/mm.)	n_D^{20}	Found (%): e.h. Cl	B
n-C_5H_{11}	62—64/0·2	1·4212	15·6	4·9
$Cl\cdot[CH_2]_3$	84/0·1	1·4576	14·3	4·7
$Cl\cdot[CH_2]_4$	101/0·04	1·4615	12·6	4·1
$Cl\cdot[CH_2]_5$	128/0·1	—	(Ratio e.h. Cl : B = 0·97)	

TABLE 6. *Molecular weights.*

$Cl\cdot[CH_2]_2\cdot O\cdot BCl_2$	$Cl\cdot[CH_2]_3\cdot O\cdot BCl_2$	$Cl\cdot[CH_2]_4\cdot O\cdot BCl_2$	$Cl\cdot[CH_2]_5\cdot O\cdot BCl_2$
162 (161)	172 (175)	192 (189)	249 (203)
$(Cl\cdot[CH_2]_2\cdot O)_2B\cdot Cl$	$(Cl\cdot[CH_2]_3\cdot O)_2B\cdot Cl$	$(Cl\cdot[CH_2]_4\cdot O)_2B\cdot Cl$	$(Cl\cdot[CH_2]_5\cdot O)_2B\cdot Cl$
204 (205)	244 (233)	262 (261)	293 (289)

TABLE 7. *Pyridine complexes.*

Compound	Found (%): e.h. Cl	Cl	py	B	Required (%): e.h. Cl	Cl	py	B
$Cl\cdot[CH_2]_3\cdot O\cdot BCl_2$,py	27·3	39·1	30·2	4·3	27·5	39·1	31·1	4·3
$(Cl\cdot[CH_2]_3\cdot O)_2B\cdot Cl$,py	12·2	32·5	29·6	3·5	11·4	34·2	25·3	3·5
$(Cl\cdot[CH_2]_4\cdot O)_2B\cdot Cl$,py	10·1	30·7	21·2	3·1	10·4	31·3	23·2	3·2
$(Cl\cdot[CH_2]_5\cdot O)_2B\cdot Cl$,py	—	—	21·9	3·0	—	—	21·4	2·9

Molecular Weights of Alkoxyboron Chlorides.—These were determined cryoscopically in *cyclo*hexane under anhydrous conditions, with a dry nitrogen pulse as a means of agitation. The results are shown in Table 6; the calculated values (in parentheses) are for the monomers.

Interaction of Pyridine and Alkoxyboron Chlorides.—Pyridine (1 mol.; 0·01—0·05 mole) in solvent (*n*-pentane or methylene dichloride) was added to the appropriate alkoxyboron chloride (1 mol.) in the same solvent at −80°, whereupon a viscous oil, insoluble in *n*-pentane but soluble in methylene dichloride, was formed. Solvent was removed under vacuum and the remainder was washed several times by decantation with *n*-pentane. This residue, freed from all matter volatile at 20°/0·01 mm., was the 1 : 1 *complex*. The results are shown in Table 7.

When pyridine (0·332 g., 2 mol.) was added to 5-chloropentyl dichloroboronite (0·427 g., 1 mol.) in *n*-pentane (15 c.c.) at −80°, a white solid formed, which separated into a solvent-insoluble layer at 20°. This oil crystallised after 2 days, and was thoroughly washed with *n*-pentane, to give the 1 : 2 *complex* (0·743 g., 98%) (Found: equivalence ratio, e.h. $Cl : B : C_5H_5N = 1 : 0{\cdot}99 : 2{\cdot}03$).

Catalytic Decomposition of Dichloroboronites.—To the dichloroboronite (about 10 g.) at −80° was added anhydrous ferric chloride (0·1 g.). When the mixture was allowed to attain room temperature, a vigorous reaction took place. Boron trichloride was evolved and absorbed in alkali absorption tubes; the alkyl halide formed in the reaction was distilled off and a white solid residue of crude boron trioxide (slightly more than theoretical, possibly owing to the presence of undecomposed boron oxychloride) remained. Results are shown in Table 8; yields are based on scheme (4).

TABLE 8. *Decomposition of alkyl dichloroboronites.*

R in $RO\cdot BCl_2$	Yield of BCl_3 (%)	RCl Yield (%)	RCl B. p. (°/mm.)	n_D^{20}
$Cl\cdot[CH_2]_2$	90	81	83/760	1·4451
$Cl\cdot[CH_2]_3$	83	89	118/760	1·4472
$Cl\cdot[CH_2]_5$	91	91	74/18	1·4558

TABLE 9. *Decomposition of dialkyl chloroboronates.*

R in $(RO)_2B\cdot Cl$	Yield (%)	RCl B. p. (°/mm.)	n_D^{20}	Yield (%)	$B(OR)_3$ B. p. (°/mm.)	Found: B (%)
$Cl\cdot[CH_2]_2$	83	82/760	1·4454	73	70/0·1	4·3
$Cl\cdot[CH_2]_3$	88	118/760	1·4465	61	96/0·075	3·7
$Cl\cdot[CH_2]_4$	66	150/760	1·4557	54	136—140/0·1	3·2
$Cl\cdot[CH_2]_5$	95	78/24	1·4563	72	162/0·1	2·9

TABLE 10. *Stability of alkyl chloroboronites.*

R in $RO\cdot BCl_2$	Time (hr.)	Temp.	Decompn. (%)	R in $RO\cdot BCl_2$	Time (hr.)	Temp.	Decompn. (%)	R in $RO\cdot BCl_2$	Time (hr.)	Temp.	Decompn. (%)
C_2H_5	1	150°	39	$Cl\cdot[CH_2]_4$	$\frac{1}{3}$	100°	9	n-C_5H_{11}	$2\frac{1}{2}$	100°	8
,,	3	150	94	,,	$\frac{1}{2}$	100	24	,,	5	100	24
$Cl\cdot[CH_2]_2$	3	150	9	,,	$\frac{2}{3}$	100	41	,,	$6\frac{1}{2}$	100	40
,,	6	150	17	,,	$\frac{5}{6}$	100	56	$Cl\cdot[CH_2]_5$	$\frac{1}{4}$	100	0
,,	10	150	21	,,	1	100	63	,,	1	100	11
$Cl\cdot[CH_2]_3$	3	150	19	,,	$1\frac{1}{6}$	100	72	,,	$2\frac{1}{2}$	100	35
,,	6	150	46	,,	$1\frac{1}{3}$	100	85	,,	5	100	68
,,	10	150	90	n-C_5H_{11}	$\frac{1}{4}$	100	0	,,	$6\frac{1}{2}$	100	87
$Cl\cdot[CH_2]_4$	$\frac{1}{6}$	100	6	,,	1	100	2				

TABLE 11. *Stability of dialkyl chloroboronates.*

R in $(RO)_2B\cdot Cl$	Time (hr.)	Temp.	Decompn. (%)	R in $(RO_2)B\cdot Cl$	Time (hr.)	Temp.	Decompn. (%)	R in $(RO)_2B\cdot Cl$	Time (hr.)	Temp.	Decompn. (%)
C_2H_5	1	150°	1	$Cl\cdot[CH_2]_3$	5	150°	9	n-C_5H_{11}	4	150°	7
,,	3	150	2	$Cl\cdot[CH_2]_4$	$\frac{1}{4}$	100	5	,,	6	150	20
,,	5	150	6	,,	1	100	5	$Cl\cdot[CH_2]_5$	7	100	6
$Cl\cdot[CH_2]_2$	3	150	7	,,	5	100	9	,,	10	100	9
,,	5	150	8	,,	$7\frac{1}{2}$	100	14	,,	1	150	14
,,	7	150	10	,,	$12\frac{1}{2}$	100	22	,,	2	150	27
$Cl\cdot[CH_2]_3$	$\frac{1}{2}$	150	2	n-C_5H_{11}	1	150	3	,,	4	150	64
,,	$1\frac{1}{2}$	150	2	,,	2	150	6	,,	8	150	83

Catalytic Decomposition of Chloroboronates.—To the chloroboronate (about 5 g.) at −80° was added anhydrous ferric chloride (0·1 g.). After the mixture had been warmed to room temperature, the alkyl halide and the borate were distilled off and a white solid or viscous oil remained, whose weight was generally about twice that expected for boron trioxide and was probably a mixture of this and the metaborate; this was indicated by the remarkably high bath-temperature required for distillation of the orthoborate from the mixture. The results are shown in Table 9; yields are based on scheme (5).

Uncatalysed Decomposition of Alkoxyboron Chlorides.—In order to ascertain the thermal stability of these compounds when pure, with respect to reactions (4) and (5), small (0·1—0·2 g.) samples in sealed tubes were heated for stated times and temperatures and analysed for e.h. chlorine and boron; this permits the extent of decomposition to be calculated (see refs. 3 and 4). The results are shown in Tables 10 and 11.

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