154. *Interaction of Boron Chlorides and Esters of Sulphonic Acids.*

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Alkyl alkane- and arene-sulphonates react readily with boron trichloride, to give the sulphonyl dichloroborinate, $R'\cdot SO_2\cdot O\cdot BCl_2$, and the alkyl choride, which is obtained as a mixture of isomers when rearrangement is possible. In contrast, 2-chloroethyl toluene-*p*-sulphonate slowly gave toluene-*p*-sulphonyl chloride and 2-chloroethyl esters of boron acids. Phenyl toluene-*p*-sulphonate and diphenyl sulphate did not form a complex or otherwise react with boron trichloride.

The mode of fission of the R–O–M bonds in esters of inorganic acids on reaction with boron trichloride depends on the electronegativity of the non-metal, M, and on the electron-releasing propensity of the group R. Thus n-butyl phosphate[1] and sulphate[2] undergo alkyl–oxygen fission and give a network of B–O–M linkages, whereas with less electronegative central atoms, as in tetra-n-butoxysilane,[3] tetra-n-butyl titanate,[4] n-butyl sulphite,[2] and n-butyl phosphite,[5] there is an exchange of chlorine and alkoxyl. However, a change from n-butyl to s-butyl is sufficient to cause formation of s-butyl chloride and a B–O–Si linkages in the tetra-alkoxysilane system,[6] whereas tris-2,2,2-trichloroethyl phosphate (strong electron-attraction in R) gave phosphoryl chloride and tris-2,2,2-trichloroethyl borate.[7]

Alkyl alkane- and arene-sulphonates, $R'\cdot SO_2\cdot OR$ ($R' = Me$, $R = Me$, Bu^n or Bu^i; $R' = Et$, $R = Bu^n$; $R' =$ tolyl, $R = Me$, Et, Pr^n, or Bu^n), reacted with boron trichloride in 1 : 1 ratio, giving alkyl chloride and the alkane- or arene-sulphonyl dichloroborinate. By contrast, alkanesulphinates undergo sulphur–oxygen fission with boron trichloride.[8]

$$R'\cdot SO_2\cdot OR + BCl_3 \longrightarrow RCl + R'\cdot SO_2\cdot O\cdot BCl_2 \quad . . . . (1)$$

The sulphonic esters ($R' = Me$, $R = Bu^s$ or 1-methylheptyl; $R' = Ph$, $R = Bu^n$) gave the alkyl chloride and an intractable residue.

The sulphonyl dichloroborinates are white solids, insoluble in the usual organic solvents, and rapidly hydrolysed by cold water to boric, hydrochloric, and sulphonic ($R'\cdot SO_3H$) acid. On pyrolysis they give the sulphonyl chloride ($R'\cdot SO_2Cl$), boron trichloride (0·33 mol.),

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[1] Gerrard and Griffey, *J.*, 1960, 3170.
[2] Charalambous, Davies, Frazer, and Gerrard, *J.*, 1962, 1505.
[3] Gerrard and Strickson, *Chem. and Ind.*, 1958, 860.
[4] Gerrard and Cooper, *Chem. and Ind.*, 1961, 320.
[5] Gerrard and Lindsay, *Chem. and Ind.*, 1960, 152.
[6] Frazer, Gerrard, and Strickson, *J.*, 1960, 4701.
[7] Gerrard and Griffey, *J.*, 1961, 4095.
[8] Frazer, Gerrard, and Ghaffar, unpublished work.

and boric oxide (0·33 mol.), a characteristic reaction of dichloroborinates. Support for the structure $R'\cdot SO_2\cdot O\cdot BCl_2$, in contrast to $R'\cdot SO_2Cl,BOCl$, comes from the reactivity of both chlorine atoms (R′ = tolyl) with diethyl ether. The related aluminium compound, $p\text{-}CH_3\cdot C_6H_4\cdot SO_2\cdot O\cdot AlCl_2$, has been prepared from aluminium chloride and the sulphonic acid.[9]

Methyl methanesulphonate and methyl dichloroborinate gave methyl chloride and methanesulphonyl metaborate as a white solid. n-Butyl toluene-*p*-sulphonate reacted similarly with n-butyl dichloroborinate, but did not react with di-n-butyl chloroboronate:

$$R'\cdot SO_2\cdot OR + RO\cdot BCl_2 \longrightarrow 2RCl + (R'\cdot SO_2\cdot O\cdot BO)_x \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

There was a marked propensity to rearrangement during the formation of alkyl chloride. Thus the alkyl chloride comprised the proportion of isomer stated in parentheses, from Bu^n (Bu^s, 85—90%), from Pr^n (Pr^i, 84%), and from Bu^i (Bu^t, 86%). When R = 1-methylheptyl, 2-, 3-, and 4-chloro-octane were obtained in approximately equal proportions. The tendency to rearrangement in other related systems [10] may be compared with the pronounced tendency in the sulphate [2] and the sulphonate system.

In accordance with the electron-attracting propensity of the 2-chloroethyl group, the toluene-*p*-sulphonate reacted much more slowly with boron trichloride, even at 110°, and afforded toluene-*p*-sulphonyl chloride, 2-chloroethyl dichloroborinate, and other 2-chloroethyl esters of boron acids.

There was no evidence (precipitation, heat of mixing, shift in SO_2 stretching modes) of co-ordination or other reaction of boron trichloride with phenyl chlorosulphate,[2] phenyl toluene-*p*-sulphonate, diphenyl sulphate, toluene-*p*-sulphonyl chloride, or sulphuryl chloride. In contrast, aryl phosphates form stable 1 : 1 complexes with boron trichloride,[11] showing that the P=O group is a stronger donor than the SO_2 group in this respect; phosphoryl chloride forms a complex which is probably $POCl_2^+BCl_4^-$.[11,12] Aryl phosphates,[11] phenyl sulphate, and phenyl sulphonates do not undergo fission with boron trichloride; but triphenyl phosphite [13] and diphenyl sulphite [2] behave like the corresponding alkyl esters and undergo chlorine–phenoxy-exchange.

EXPERIMENTAL

Products were characterised by physical constants, chemical analysis, infrared spectroscopy, and gas chromatography. Chlorine formed by simple treatment with water is designated " e.h. Cl." The alkyl sulphonates [14] and diphenyl sulphate [15] were prepared by known procedures. *n-Butyl ethanesulphonate*, obtained in 82% yield, had b. p. 84°/0·5 mm., n_D^{20} 1·4295, d_4^{20} 1·074 (Found: S, 19·4. $C_6H_{14}O_3S$ requires S, 19·3%).

Boron Trichloride and Sulphonates.—The ester (Table 1) (10—20 g., 1 mol.) and boron trichloride (1 mol.) were mixed at −80°, and the mixture was held at room temperature, under an upright condenser (−80°) for 6 hr. Volatile matter was removed at 20° (boron trichloride, methyl or ethyl chloride), or at 20°/20 mm. (propyl or butyl chloride), or at 50°/1 mm. (octyl chloride), and suitably trapped. The residue was the white solid *alkane- or arene-sulphonyl dichloroborinate*, a jelly (nos. 4 and 7), or a tar (no. 5). The dichloroborinates were insoluble in carbon tetrachloride, methylene chloride, n-pentane, and benzene, but reacted quickly with cold water, giving boric, hydrochloric, and the sulphonic acid.

Results of pyrolysis of the sulphonyl dichloroborinates, $R'\cdot SO_2\cdot O\cdot BCl_2$, are given in Table 2.

Diethyl ether in excess was added to toluene-*p*-sulphonyl dichloroborinate (13·0 g.). Matter removed at 20°/20 mm. contained boron (0·38 g.) and chlorine (1·16 g.), and the white solid residue (8·9 g.) was essentially toluene-*p*-sulphonic acid.

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[9] Drahowzal, Klamann, and Haas, *Annalen*, 1953, **580**, 210.

[10] Gerrard, Hudson, and Murphy, *J.*, 1962, 1099.

[11] Frazer, Gerrard, and Patel, *J.*, 1960, 762.

[12] Gerrard, Mooney, and Willis, *J.*, 1961, 4255.

[13] Frazer, Gerrard, and Patel, *Chem. and Ind.*, 1959, 90.

[14] Tipson, *J. Org. Chem.*, 1944, **9**, 235.

[15] Denivelle, *Compt. rend.*, 1934, **199**, 211.

TABLE 1.

Reaction of boron trichloride and sulphonates, $R'\cdot SO_2\cdot OR$.

	Reactant $R'\cdot SO_2\cdot OR$				$R'\cdot SO_2\cdot O\cdot BCl_2$ Found (%) *		RCl		
No.	R′	R	Temp.	**	B	e.h. Cl	Yield (%)	Found (%) Cl †	Compn. of RCl
1	Me	Me	30—50°	S	6·2	39·7	85	—	—
2	Me	Bu^n	0—20	I	6·1	39·5	85	37·5	Bu^sCl (89%)
3	Me	Bu^i	20	S	6·1	39·7	75	38·9	‡
4	Me	Bu^s	20	S	—	—	50	37·9	Bu^sCl (100%)
5	Me	2-Oc §	20	S	—	—	65	23·5	¶
6	Et	Bu^n	0—20	I	5·5	36·8	86	37·8	Bu^sCl (85%)
7	Ph	Bu^n	0—20	I	—	—	81	37·5	Bu^sCl (86%)
8	To §	Me	20	S	4·2	28·1	100	—	—
9	To	Et	20	S	4·3	27·1	96	53·5	—
10	To	Pr^n	−10 to 0	I	4·5	25·2	100	44·7	Pr^iCl (84%)
11	To	Bu^n	−10 to 0	I	4·4	24·2	90	37·9	Bu^sCl (85%)

** Formation of residue: S = slow, I = instantaneous. * $CH_3BCl_2O_3S$ requires B, 6·1; Cl, 40·0%. $C_2H_5BCl_2O_3S$ requires B, 5·7; Cl, 37·2%. $C_7H_7BCl_2O_3S$ requires B, 4·3; Cl, 28·0%. † Cl: Calc. for C_2H_5Cl, 54·9; for C_3H_7Cl, 45·1; for C_4H_9Cl, 38·3; for $C_8H_{17}Cl$, 23·8%. ‡ Bu^tCl, 86; $Bu^sCl + Bu^iCl$, 14%. § 2-Oc = 1-methylheptyl; To = *p*-tolyl. ¶ 2-Chloro-octane, 36; 3-chloro-octane, 36; 4-chloro-octane, 28%.

TABLE 2.

Pyrolysis of the sulphonyl dichloroborinates, $R'\cdot SO_2\cdot O\cdot BCl_2$.

	Pyrolysis		Products		
R′ in $R'\cdot SO_2\cdot O\cdot BCl_2$ (1 mol.)	Temp./mm.	Time (hr.)	$R'SO_2Cl$ (mol.)	B_2O_3 (mol.)	BCl_3 (mol.)
Me	50—70°/1·0	3	0·70	0·32	0·30
Et	100°/1·0	2	0·60	0·33	0·33
p-$Me\cdot C_6H_4$	40°/20	8	0·90	0·32	0·33

When n-butyl toluene-*p*-sulphonate (2 mol.) and boron trichloride (1 mol.) were mixed, alkyl chloride (1·8 mol.) (Found: Cl, 38·0%) (Bu^sCl, 88%) and a tar were obtained; from 3 mol. of the ester, alkyl chloride (1·9 mol.) (Found: Cl, 38·2%) (Bu^sCl, 86%) and a tar were obtained.

*Boron Trichloride and 2-Chloroethyl Toluene-*p*-sulphonate.*—After 6 hr. at 20°, an equimolecular mixture afforded the ester (82%) and boron trichloride (95% recovery). The ester (13·0 g., 1 mol.) and boron trichloride (1·8 mol.) were heated at 110° under reflux for 36 hr. 2-Chloroethyl dichloroborinate (2·0 g., 22%) (Found: B, 7·0; e.h. Cl, 45·0. Calc. for $C_2H_4BCl_3O$: B, 6·7; e.h. Cl, 44·0%) was removed at 20°/1 mm., and boron trichloride (6·2 g., 0·95 mol.) was absorbed by alkali. A mixture (3·6 g.) of di-2-chloroethyl chloroboronate and tri-2-chloroethyl borate was extracted by n-pentane, leaving toluene-*p*-sulphonyl chloride (9·8 g., 90%), m. p. and mixed m. p. 70°.

Alkoxyboron Chlorides and Sulphonates.—A mixture of methyl methanesulphonate (8·8 g., 1 mol.) and methyl dichloroborinate (1 mol.) gave, during 12 hr. at 20°, methyl chloride (6·0 g., 1·5 mol.) (trapped at −80°) and *methanesulphonyl metaborate* (8·8 g., 100% weighed after being held at 20°/20 mm. for 3 hr.) (Found: B, 8·6; S, 26·0. CH_3BO_4S requires: B, 8·8; S, 26·2%), a white solid, insoluble in benzene, carbon tetrachloride, methylene chloride, and n-pentane, and with cold water readily affording boric acid and methanesulphonic acid.

A mixture of n-butyl toluene-*p*-sulphonate (12·8 g., 1 mol.) and n-butyl dichloroborinate (1·0 mol.) (20°, 1·5 hr.) gave, at 20°/10 mm., butyl chloride (9·4 g., 1·8 mol.) (Found: Cl, 37·6%; Bu^sCl, 88%), and a white solid (12·0 g.) (Found: B, 5·2; e.h. Cl, 1·5; S, 14·6. Calc. for $C_7H_7BO_4S$: B, 5·5; S, 16·2%). The same sulphonate (7·0 g.) and di-n-butyl chloroboronate (1 mol.) showed no loss in weight when heated at 90—100° for 6 hr.; boron trichloride (0·33 g.), hydrogen chloride (0·3 g.), di-n-butyl chloroboronate (2·45 g., 43% recovery), b. p. 60—64°/1·5 mm., n_D^{22} 1·4125 (Found: B, 5·7; Cl, 17·2. Calc. for $C_8H_{18}BClO_2$: B, 5·65; Cl, 18·4%), tri-n-butyl borate (1·6 g.), b. p. 90°/1·4 mm., n_D^{22} 1·4120 (Found: B, 4·8. Calc. for $C_{12}H_{27}BO_3$: B, 4·7%), and n-butyl toluene-*p*-sulphonate (80% recovery), b. p. 156°/1·3 mm., n_D^{22} 1·4975, d_{20}^{22} 1·173, were obtained.

Examples of Non-reactivity.—Diphenyl sulphate (100% recovery) (Found: S, 13·3. Calc. for $C_{12}H_{10}O_4S$: S, 12·8%) and boron trichloride (96%) were separated after their mixture had been heated at 50° for 6 hr. Phenyl toluene-*p*-sulphonate (96%) and boron trichloride (93%) were separated after being heated together in carbon tetrachloride at 60° for 36 hr. Sulphuryl chloride (95%) and boron trichloride (84%) were separated after the mixture had been held at 20° for 24 hr. Toluene-*p*-sulphonyl chloride (91%) and boron trichloride (94%) were similarly separated. There was no evidence of complex formation in these systems, *e.g.*, no solid formation, no heat of mixing, and no infrared spectral shift.

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