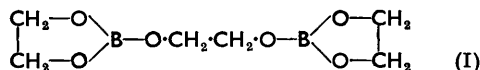


813. *The Interaction of Ethylene Glycol with Boron Trichloride and the Alkoxyboron Chlorides.*

By J. A. BLAU, W. GERRARD, and M. F. LAPPERT.

Compounds of the formula $(\text{CH}_2\cdot\text{O})_2\text{B}\cdot\text{X}$ [where $\text{X} = \text{Cl}, \text{OH}, \text{OR}, \text{OPh}, \text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}, \text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{B}(\text{O}\cdot\text{CH}_2)_2$, or $\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{B}(\text{OR})_2$] have been prepared. Their reactions resemble those of related compounds derived from monohydric alcohols and phenols, but there is much greater thermal stability.

THE reactions of boron trichloride and its alkoxy-derivatives with alcohols and phenol have been studied in considerable detail.¹⁻⁶ The present paper relates to ethylene glycol. In the course of this work, several derivatives of ethylene hydrogen borate, $(\text{CH}_2\cdot\text{O})_2\text{B}\cdot\text{OH}$, have been produced, namely, compounds wherein the hydroxyl group was replaced by chlorine, alkoxy-, or phenoxy-groups. Diborates⁷ have also been prepared, namely, the tetra-alkyl (and tetraphenyl) ethylene di(borates), $[(\text{RO})_2\text{B}\cdot\text{O}\cdot\text{CH}_2\cdot]_2$, and diethylene ethylene di(borate) (I).



The reaction of boron trichloride with ethylene glycol afforded either ethylene chloroboronate (scheme 1), or diethylene ethylene di(borate) (scheme 2), depending on the relative proportions of reactants, although the chloroboronate was obtained together with



di(borate) from equimolar amounts of reactants. It has been reported⁶ that boron trichloride and ethylene glycol (1 : 3) give tri-2-hydroxyethyl borate, $\text{B}(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_3$.

Addition of alkyl dichloroboronites, $\text{RO}\cdot\text{BCl}_2$ ($\text{R} = \text{Pr}^n, \text{Bu}^n$), to ethylene glycol, in absence (scheme 3) or presence (scheme 4) of pyridine, afforded alkyl ethylene borates; but dialkyl chloroboronates, $(\text{RO})_2\text{B}\cdot\text{Cl}$ ($\text{R} = \text{Bu}^n, \text{Bu}^i, n\text{-C}_5\text{H}_{11}$), gave tetra-alkyl ethylene di(borates) (scheme 5).

¹ Gerrard and Lappert, *J.*, 1951, 1020.

² Ebelmen and Bouquet, *Ann. Chim. Phys.*, 1846, **17**, 54; Counciler, *J. prakt. Chem.*, 1871, **18**, 371; Michaelis and Hillringhaus, *Annalen*, 1901, **315**, 41; Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1, 22, 31; Kinney, Thompson, and Cheney, *J. Amer. Chem. Soc.*, 1935, **57**, 2396; Martin and Mako, *ibid.*, 1951, **73**, 2674; Gerrard and Lappert, *J.*, 1951, 2545; Gerrard and Howe, *J.*, 1955, 505; Colclough, Gerrard, and Lappert, *J.*, 1955, 907; Edwards, Gerrard, and Lappert, *J.*, 1955, 1470; Frazer and Gerrard, *J.*, 1955, 2959; Gerrard, Lappert, and Silver, *J.*, 1956, 3285; 1957, 1647; Abel, Edwards, Gerrard, and Lappert, *J.*, 1957, 501.

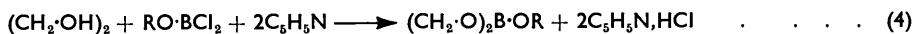
³ Lappert, *J.*, 1953, 667.

⁴ *Idem*, *J.*, 1956, 1768; Gerrard and Lappert, *J.*, 1955, 3084.

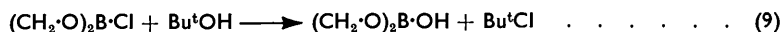
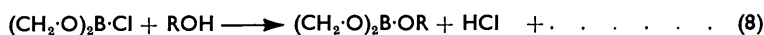
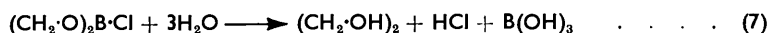
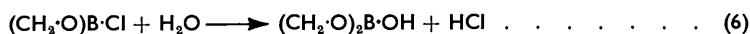
⁵ Colclough, Gerrard, and Lappert, *J.*, 1956, 3006.

⁶ Counciler, *Ber.*, 1876, **9**, 485; 1877, **10**, 1655; 1878, **11**, 1106; Hartman, *J.*, 1957, 1918.

⁷ Lappert, *Chem. Rev.*, 1956, **56**, 959.

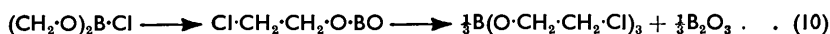


Ethylene chloroboronate is a colourless, viscous liquid and fumes in air owing to hydrolysis (schemes 6 and 7). With pyridine, it gave a solid 1 : 1 complex. With alcohols, it afforded borates (scheme 8); with *tert.*-butyl alcohol the major product was *tert.*-butyl

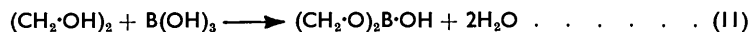


chloride (scheme 9); but the ester is obtained if pyridine is also present. The use of pyridine in ester (*e.g.*, borate) preparations is general and has been recommended particularly in connection with esters having highly electron-releasing alkyl groups.^{1,3,7}

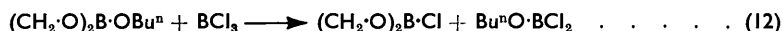
Ethylene chloroboronate has exceptional⁴ thermal stability: even ferric chloride has little effect. After prolonged heating, however, there was evidence for decomposition (10) although, owing to the limited stability of the products at 300°, this was not proved conclusively. Reaction (10) would be in accord with one frequently observed mode of chloroboronate decomposition.⁴



Ethylene hydrogen borate is crystalline. It was also obtained (scheme 11) by fractionation of a mixture of boric acid and ethylene glycol. Its existence and preparation by this method have been reported previously,⁸ but the physical characteristics were described differently.



The alkyl ethylene borates are viscous, unimolecular liquids, which hydrolyse readily and completely in air. Four such esters have previously been prepared, either by esterification of boron trioxide with a mixture of glycol and the alcohol or phenol in presence of benzene or toluene,⁹ or by displacing two alkoxy-groups from a trialkyl borate by distillation with glycol.¹⁰ *n*-Butyl ethylene borate is thermally stable. Reaction with ethylene glycol replaced the *n*-butoxy-group, affording crystalline ethylene 2-hydroxyethyl borate. With boron trichloride, reaction (12) occurred.



Tetra-alkyl ethylene di(borates) are unimolecular and have physical characteristics similar to those of alkyl ethylene borates; diethylene ethylene di(borate) is a solid. With water they were readily and completely hydrolysed, and distilling the *n*-butyl homologue with phenol gave the tetraphenyl homologue (*cf.* alcoholysis above).

In general, the reactions of the cyclic chloroboronates and borates are similar to those in the straight-chain series.⁷ The differences are: (*a*) the cyclic compounds are much more stable; and (*b*) the B-O bonds in the ring are broken less readily than others. These observations suggest that, in general, compounds of type $(\text{RO})_2\text{B}\cdot\text{Y}$ will prove more stable if the two groups R are joined than if they are not and in extreme cases it may be that compounds of such general formula which could not hitherto have been made, may now be prepared as stable compounds in corresponding cyclic forms. Two examples are already available. First, the dialkyl hydrogen borates (*i.e.*, Y = OH) do not exist;⁷

⁸ Rippere and LaMer, *J. Phys. Chem.*, 1943, **47**, 204.

⁹ Thomas, *J.*, 1946, 823.

¹⁰ Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174.

and, secondly, only one example of a stable acyclic mixed trialkyl borate (*i.e.*, Y = OR') is known.⁵

EXPERIMENTAL

Preparations and Procedures.—*n*-Butyl and *n*-propyl dichloroboronite and di-*n*-butyl, isobutyl, and *n*-pentyl chloroboronate were prepared by known methods.⁴ Boron trichloride was distilled before use. Analytical procedures have been described before;^{4,5} as has been noted with certain organic boron compounds, analyses for carbon were sometimes unreliable.¹¹ Molecular weights were determined cryoscopically in cyclohexane. M. p.s were determined in sealed capillary tubes.

Interaction of Boron Trichloride and Ethylene Glycol. Reactions (1) and (2).—(a) The glycol (23.6 g., 1 mol.) was added in $\frac{1}{2}$ hr. to boron trichloride (47.0 g., slightly >1 mol.) at -80° . The mixture was allowed to attain 20° , whereupon hydrogen chloride was evolved and was completely removed at $18^\circ/18$ mm. to leave a yellow liquid containing a white solid (38.89 g.). Distillation afforded *ethylene chloroboronate* (29.13 g., 72%), b. p. $70-74^\circ/1$ mm., n_D^{20} 1.4640 (Found: Cl, 33.3; B, 10.5. $C_2H_4O_2ClB$ requires Cl, 33.4; B, 10.2%), and a white residue (5.72 g.) of *diethylene ethylene di(borate)*, which after being washed with methylene dichloride had m. p. $162-164^\circ$ (Found: B, 10.7. $C_6H_{12}O_6B_2$ requires B, 10.7%). The chloroboronate was insoluble in *n*-pentane and diethyl ether, but soluble in methylene dichloride. Its analysis by aqueous hydrolysis established reaction (7).

(b) The glycol (7.27 g., 2 mols.) was added in $\frac{3}{4}$ hr. to the trichloride (6.86 g., 1 mol.) in methylene dichloride (25 ml.) at -80° to afford a clear solution, which at 20° deposited, as a white solid, impure ethylene 2-hydroxyethyl borate (7.30 g., 95%) (Found: C, 33.3; H, 7.4; B, 8.4. Calc. for $C_4H_9O_4B$: C, 36.4; H, 6.9; B, 8.2%). During the reaction, hydrogen chloride [5.63 g., 88% based on: $2(CH_2OH)_2 + BCl_3 \rightarrow (CH_2O)_2B \cdot O \cdot CH_2 \cdot CH_2 \cdot OH + 3HCl$] was evolved. This solid (9.79 g.) when heated at $100^\circ/0.4$ mm. left diethylene ethylene di(borate) (5.45 g.) (Found: C, 35.0; H, 5.6; B, 10.7. $C_6H_{12}O_6B_2$ requires C, 35.7; H, 5.7; B, 10.7%) as a non-volatile residue.

The diethylene ethylene di(borate) was also obtained in almost quantitative yield when the reactants were mixed in the proportions according to scheme (2).

Interaction of Alkyl Dichloroboronites with Ethylene Glycol. Reactions (3) and (4).—(a) *n*-Butyl. Ethylene glycol (5.82 g.) was added slowly to *n*-butyl dichloroboronite (14.55 g.) at -80° , whereafter matter volatile at $20^\circ/20$ mm. was removed, leaving a viscous oil (13.69 g. Calc. for $C_6H_{13}O_3B$: 13.52 g.). Distillation afforded *n*-butyl ethylene borate (10.86 g., 80%), b. p. $96-100^\circ/16$ mm., which when twice redistilled had b. p. $98^\circ/18$ mm., n_D^{20} 1.4293, d_4^{20} 1.006 (Found: C, 51.6; H, 9.5; B, 7.3%; M, 143. Calc. for $C_6H_{13}O_3B$: C, 50.1; H, 9.1; B, 7.5%; M, 143).

(b) *n*-Propyl. (i) *n*-Propyl dichloroboronite (9.7 g.) in *n*-pentane (20 ml.) was added in $1\frac{1}{2}$ hr. to ethylene glycol (4.3 g.) at 0° . Hydrogen chloride (4.80 g., 95%) was trapped in potash absorption tubes. Distillation afforded, as the main fraction, *ethylene n*-propyl borate (4.92 g., 55%), b. p. $85^\circ/16$ mm., $n_D^{21.5}$ 1.4180 (Found: B, 8.7. $C_5H_{11}O_3B$ requires B, 8.3%).

(ii) The dichloroboronite (14.75 g.) in methylene dichloride (25 ml.) was added in 1 hr. to the glycol (6.5 g.) and pyridine (16.6 g.) in methylene dichloride (25 ml.) at 0° . Matter volatile at $21^\circ/16$ mm. was removed, whereafter *n*-pentane (100 ml.) was added. The white precipitate of pyridinium chloride (27.51 g., 100%) was filtered off; the filtrate, when freed from solvent comprised ethylene *n*-propyl borate (5.93 g., 100%), n_D^{20} 1.4220 (Found: B, 8.3%).

Interaction of Dialkyl Chloroboronates with Ethylene Glycol. Reaction (5).—(a) *n*-Butyl. Di-*n*-butyl chloroboronate (4.00 g.) in *n*-pentane (10 ml.) was added to ethylene glycol (0.65 g.) at 20° , whereafter the mixture was kept at $20^\circ/20$ mm. for 3 hr. The residue was *tetra-n*-butyl ethylene diborate (3.83 g., 99%), b. p. $92^\circ/0.5$ mm., n_D^{21} 1.4190, d_4^{20} 0.9222 (Found: C, 57.3; H, 10.8; B, 5.8%; M, 371. $C_{18}H_{40}O_6B_2$ requires C, 57.8; H, 10.8; B, 5.8%; M, 374).

(b) *n*-Pentyl. By similar technique, but with reversed order of addition, from di-*n*-pentyl chloroboronate (12.4 g.) and glycol (1.75 g.) there was obtained *ethylene tetra-n*-pentyl diborate (9.0 g., 75%), b. p. $86-88^\circ/1$ mm., n_D^{21} 1.4248, d_4^{20} 0.9189 (Found: C, 60.6; H, 11.2; B, 5.0. $C_{22}H_{48}O_6B_2$ requires C, 61.4; H, 11.2; B, 5.0%).

(c) *iso*Butyl. Similarly the addition of ethylene glycol (0.80 g.) to diisobutyl chloroboronate

¹¹ Rothstein and Saville, *J.*, 1952, 2987; Gerrard, Lappert, and Shafferman, *J.*, 1957, 3828.

(4.70 g.) gave *tetraisobutyl ethylene diborate* (4.20 g., 88%), b. p. 56°/0.1 mm., n_D^{20} 1.4158, d_4^{20} 0.9231 (Found: C, 57.0; H, 10.4; B, 6.0%).

The boron analyses, by aqueous hydrolysis, of these esters established complete hydrolysis.

Preparation of Ethylene Hydrogen Borate.—(a) To the chloroboronate (1.49 g.) in methylene dichloride (10 ml.) was added water (0.252 g.) in ether (10 ml.) at 25°. Volatile matter was removed at 20°/20 mm., to leave a sticky solid (1.26 g. Calc. for $C_2H_5O_3B$: 1.23 g.). By thorough washing with ether, *ethylene hydrogen borate* (0.60 g.), m. p. 114—118° (Found: C, 24.0; H, 5.7; B, 12.2. $C_2H_5O_3B$ requires C, 27.3; H, 5.7; B, 12.3%), was obtained as a hard, crystalline solid.

(b) Ethylene glycol (62 g.) and boric acid (61 g.) were heated at 130—190° for 4 hr. Water was distilled off and ethylene hydrogen borate (89 g., 100%) was obtained as a crystalline residue (Found: C, 25.4; H, 5.8; B, 12.3%).

Complex of Pyridine and Ethylene Chloroboronate.—The chloroboronate (2.02 g.) in methylene dichloride (15 ml.) was added to pyridine (1.50 g.) in the same solvent (10 ml.) at 20°. There was some heat of mixing but no precipitation. Volatile matter was removed at 20°/20 mm., leaving a white, solid residue which was washed with *n*-pentane and filtered. The precipitate (3.43 g., 97%) was the 1:1 complex, m. p. 91° (Found: Cl, 18.9; B, 5.6; C_5H_5N , 43.2. $C_7H_9O_2NClB$ requires Cl, 19.2; B, 5.8; C_5H_5N , 42.7%). It was soluble in cold water and hydrolysed thereby.

Alcoholysis of Ethylene Chloroboronate.—(a) The alcohol was added slowly to the chloroboronate in methylene dichloride (ca. 50%) at -80°. Volatile matter was removed at 18°/20 mm. and hydrogen chloride was trapped. The residue was distilled to afford the ester, which was characterised. The reactions were carried out on a 0.05—0.1 molar scale; results are shown in the Table.

R in ROH	Yield (%) of HCl	Yield (%) of $(CH_2O)_2B\cdot OR$	B. p./mm.	n_D^{20}	Found (%)			Calc. (%):		
					C	H	B	C	H	B
Et *	89	51	38°/0.1	1.4190	41.8	7.9	9.3	41.5	7.8	9.3
Bu ⁿ	—	73	84°/0.7	1.4300	—	—	7.3	—	—	7.5
Bu ¹ *	95	91	56°/0.8	1.4230	51.2	9.4	7.4	50.1	9.1	7.5
Bu ^s *	88	53	45—50°/0.8	1.4227	50.2	9.1	7.4	50.1	9.1	7.5
Ph	85	30	112—114°/0.5	1.5200	58.0	5.5	6.7	58.6	5.5	6.6

* New compounds.

The boron analyses, by aqueous hydrolysis, of these esters established complete hydrolysis.

(b) The chloroboronate (6.0 g.) was added to *tert.*-butyl alcohol (4.18 g.) at 16°. *tert.*-Butyl chloride (2.40 g., 46%), b. p. 51°, n_D^{21} 1.3860, was condensed at -80°. The white, solid residue, after being washed with methylene dichloride, appeared to be impure ethylene hydrogen borate (Found: B, 14.4%).

(c) The chloroboronate (8.8 g.) in methylene dichloride (10 ml.) was added in 1¼ hr. to *tert.*-butyl alcohol (6.1 g.) and pyridine (6.5 g.) in the same solvent (25 ml.) at -80°. The mixture was allowed to attain room temperature, whereafter *n*-pentane (25 ml.) was added and the mixture was filtered. The precipitate was pyridinium chloride (9.3 g., 98%) (Found: Cl, 29.4; C_5H_5N , 67.7. Calc. for C_5H_6NCl : Cl, 30.7; C_5H_5N , 68.4%). The filtrate was freed from solvent and repeated distillation afforded *tert.*-butyl ethylene borate (46%), b. p. 32—33°/1 mm., $n_D^{20.5}$ 1.4189, d_4^{20} 1.022 (Found: C, 50.1; H, 9.3; B, 7.5. $C_6H_{13}O_3B$ requires C, 50.1; H, 9.1; B, 7.5%).

Butan-1-ol similarly afforded pyridinium chloride and *n*-butyl ethylene borate (94%), b. p. 98°/16 mm., n_D^{20} 1.4291 (Found: B, 7.3%).

Pyrolysis of Ethylene Chloroboronate. Reaction (10).—When the chloroboronate was heated in presence of anhydrous ferric chloride (0.15 g.) at 120° for 2 hr., it was recovered in 69% yield. When it (19.3 g.) was heated at 300° for 30 hr., removal of volatile matter at 20°/20 mm. left a residue (16.58 g.), which on distillation gave what appeared to be impure tri-2-chloroethyl borate (7.29 g., 44%), b. p. 170°/0.8 mm., n_D^{21} 1.4580 (Found: easily hydrolysable Cl, 0; total Cl, 41.0; B, 6.0. Calc. for $C_6H_{12}O_3Cl_3B$: Cl, 42.7; B, 4.4%), and a black residue (7.84 g.). In another experiment, from chloroboronate (6.0 g.) there was obtained ethylene, characterised as the dibromide (0.95 g.), n_D^{21} 1.5390, after 37 hr. at 305—310°.

Alcoholysis of n-Butyl Ethylene Borate.—The borate (22.44 g.), glycol (8.64 g.), and benzene (21.26 g.) were fractionated, through a Snyder-Schriner column fitted with a total-reflux partial-ratio head. The benzene (22.12 g.) distilled first (b. p. 78—80°, n_D^{20} 1.4925), then butanol

(10.41 g., 100%; b. p. 110—117°, n_D^{20} 1.4000), finally a fraction (2.43 g.), b. p. up to 52°/1 mm. (Found: B, 5.2%). The residue was crude ethylene 2-hydroxyethyl borate (15.62 g., 84%), which was purified by washing it with hot *n*-pentane. Filtration afforded pure *ethylene 2-hydroxyethyl borate* (8.73 g., 47%), m. p. 128° (Found: C, 36.4; H, 6.9; B, 8.4. $C_4H_8O_4B$ requires C, 36.4; H, 6.9; B, 8.2%), insoluble in ether, pyridine, and anisole.

Interaction of Boron Trichloride with n-Butyl Ethylene Borate. Reaction (12).—Boron trichloride (5.1 g.) at -80° was added to the borate (6.3 g.) at -80° . Distillation afforded crude ethylene chloroboronate (4.3 g., 94%), b. p. 40°/0.1 mm., n_D^{21} 1.4565 (Found: Cl, 36.8; B, 10.3%). A condensate (at -80°) of *n*-butyl dichloroboronite (6.7 g., 100%), $n_D^{20.5}$ 1.4150 (Found: Cl, 44.3; B, 7.2. Calc. for $C_4H_8OCl_2B$: Cl, 45.8; B, 7.0%), was also obtained.

Reaction of Tetra-n-butyl Ethylene Di(borate) with Phenol.—The diborate (1.49 g.) and phenol (1.66 g.), when distilled, gave butanol (0.90 g., 75%), b. p. 116°, n_D^{23} 1.3990. The residue (1.80 g.) (Found: B, 4.7; C_6H_5O , 68.3%) afforded *tetraphenyl ethylene di(borate)* (1.30 g., 77%), b. p. 124°/0.05 mm., $n_D^{22.5}$ 1.4998, d_4^{20} 1.053 (Found: C, 64.0; H, 5.9; B, 4.9; C_6H_5O , 81.7. $C_{26}H_{24}O_6B_2$ requires C, 68.8; H, 5.3; B, 4.8; C_6H_5O , 82.0%).

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