137. *Further Experiments with Ethylene Derivatives of Boric Acid.*

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

Compounds $[\cdot CH_2\cdot O]_2BX$, where $X = SR, NR_2, O\cdot CO\cdot R$, or $O\cdot B[O\cdot CH_2\cdot]_2$, $Y^1Y^2B\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot BY^3Y^4$ where all the Y's are Cl or NR_2, or $Y^1 = Y^2 = Y^3 = Cl$ and $Y^4 = OR$, have been prepared and characterised; selected chemical properties are described.

THIS paper supplements our earlier one [1] on the interaction of ethylene glycol and boron trichloride and on the chemistry of related organic boron compounds. Previously [1] the preparations and selected properties of compounds (I) ($X = Cl$, OH, OR, OPh, or $O\cdot CH_2\cdot CH_2\cdot OH$) and (II) (each pair Y^1–Y^2 and Y^3–$Y^4 = O\cdot CH_2\cdot CH_2\cdot O$, or all Y's = OR or OPh) were described and this study is now extended to further similar compounds (see summary).

The new compounds of type (I) were prepared from ethylene chloroboronate (I; $X = Cl$) and the appropriate active-hydrogen compound. All the reactions except that with butane-1-thiol were fast and almost quantitative.

Although trialkyl borates and their trithio-analogues are well established,[2] *S*-n-butyl ethylene monothioborate (I; $X = SBu^n$) is the first aliphatic mixed thioborate. Ethylene boric anhydride (I; $X = O\cdot B[O\cdot CH_2]_2$) is of interest because it is the bicyclic ester of the as yet unknown diboric acid, $(HO)_2B\cdot O\cdot B(OH)_2$. The acyl ethylene borates (I; $X = OAc$, $O\cdot CO\cdot CHCl_2$, or $O\cdot CO\cdot CF_3$) are the first compounds of this type. Analogous acyclic compounds, $Bu^nO\cdot B(OAc)_2$ and $(Bu^nO)_2B\cdot OAc$, although not isolated, were postulated [3] as intermediates in the reactions of the n-butoxyboron chlorides with acetic acid to give acetic anhydride, tri-n-butyl borate, and tetra-acetyl diborate, $[(AcO)_2B]_2O$. That acetyl ethylene borate evolved acetic anhydride when heated suggests a similar disproportionation scheme, and one expected for a mixed acid anhydride. The other monocyclic compounds (I) had considerable thermal stability, thus further illustrating the proposition [1] that compounds $(RO)_2B\cdot Z$ are substantially more stable when the two groups R are joined than when they are not; the acyl ethylene borates are additionally stabilised by chelation (cf. III), this being demonstrated spectroscopically [4] (see also ref. 5).

Reaction of boron trichloride and ethylene glycol was shown previously [1] to give

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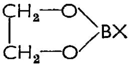
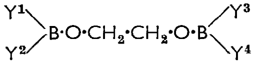
[1] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.
[2] Lappert, *Chem. Rev.*, 1956, **56**, 959.
[3] Gerrard, Lappert, and Shafferman, *J.*, 1958, 3648.
[4] Blau, Gerrard, Lappert, Mountfield, and Pyszora, *J.*, 1959, 380.
[5] Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, *J.*, 1958, 3652.

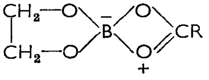
various products (I; X = Cl, or $O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; or II, each pair Y^1–Y^2 and Y^3–Y^4 = $O{\cdot}CH_2{\cdot}CH_2{\cdot}O$) depending on the relative proportions of the reactants, and it is now shown that with excess of boron trichloride, ethylene bisdichloroborinate (II; all Y's = Cl) is obtained. Previous reference (see ref. 2) to acyclic organic diboron compounds has been



(I)



(II)



(III)

restricted to compounds having the B–B, B–O–B, or B–C–C–B link, and to other compounds of type II (all Y's = OR or OPh,[1] or R[6]). The bisdichloroborinate is likely to prove a valuable intermediate because of the ease of replacement of its chlorine atoms. Thus reaction with ethylene glycol (2 mol.) or butan-1-ol (4 mol.) respectively gave hydrogen chloride and the known[1] di(borates) (II; Y^1–Y^2 and Y^3–Y^4 = $O{\cdot}CH_2{\cdot}CH_2{\cdot}O$ or all Y's = OBu^n), whilst with diethylamine (8 mol.) there was obtained the bisdiaminoborinate (II; all Y's = NEt_2) and ethylammonium chloride (4 mol.). Reaction with butan-1-ol (1 mol.) gave n-butyl 2-dichloroboro-oxyethylene chloroboronate (II; $Y^1 = Y^2 = Y^3$ = Cl, $Y^4 = OBu^n$), which contains both dichloroborinate and chloroboronate groups.

The bisdichloroborinate could not be distilled, since it disproportionated: $Cl_2B{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl_2 \longrightarrow$ (I; X = Cl) + BCl_3. That the bisdichloroborinate is a discrete compound and not a mixture was evident from the physical properties and from the replacement reactions and because it formed a 1 : 2 complex with pyridine.

n-Butyl 2-dichloroboro-oxyethylene chloroboronate also disproportionated when heated: $Cl_2B{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl{\cdot}OBu^n \longrightarrow$ (I; X = Cl) + $Bu^nO{\cdot}BCl_2$.

Although there was no perceptible reaction between gaseous hydrogen bromide and ethylene di(borates), there was complete dealkylation with liquid hydrogen bromide at room temperature and under pressure (a similar concentration effect for dealkylations has been noted with other boron esters[7]). From the tetra-n-butyl di(borate) there were obtained n-butyl bromide, ethylene dibromide, and boric acid (partly dehydrated), whilst triethylene diborate gave ethylene dibromide and boric acid. The main purpose of these experiments was to obtain ethylene di(boric acid) (II; all Y's = OH), but in this we were not successful.

The present results may be compared with those obtained in catechol–boron trichloride systems.[8]

EXPERIMENTAL

Preparations and Procedures.—Ethylene hydrogen borate, ethylene chloroboronate, tetra-n-butyl ethylene di(borate), and triethylene di(borate) were prepared as outlined in our earlier paper.[1] Analytical procedures have been described previously.[1,3] Gas chromatography was used for both qualitative and quantitative analysis of volatile products. In some cases identity of reaction products was confirmed by comparison of infrared spectra with those of authentic specimens.

Reactions of Ethylene Chloroboronate with Compounds having Active Hydrogen.—(a) *Butane*-1-*thiol.* As preliminary experiments showed that evolution of hydrogen chloride from a mixture of the chloroboronate and the thiol was slow, rather forcing conditions were used. A mixture of the chloroboronate (9·30 g., 1 mol.) and the thiol (16·4 g., 2·1 mol.) was heated (25 hr.) under reflux; hydrogen chloride (1·60 g., 50%) was absorbed in alkali. Two layers had been formed; the upper (18·4 g.) afforded a small forerun and then S-*n-butyl ethylene monothioborate* (7·50 g., 54%), b. p. 26°/0·002 mm., n_D^{22} 1·4872 (Found: C, 44·5; H, 8·0; S, 19·4; B, 6·7. $C_6H_{13}O_2SB$ requires C, 45·0; H, 8·2; S, 20·0; B, 6·8%). Butane-1-thiol (10·2 g.), n_D^{20} 1·4430 (gave the 2,4-dinitrophenyl sulphide, m. p. 67°), was collected as a condensate.

(b) *Diethylamine* (see also ref. 9). The chloroboronate (8·30 g., 1 mol.) in methylene

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[6] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174.
[7] Abel, Gerrard, and Lappert, *J.*, 1957, 3833; Lappert, *J.*, 1958, 3256.
[8] Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.
[9] Conklin and Morris. B.P. 790,090/1958.

dichloride (15 c.c.) was slowly added to the amine (11·40 g., 2 mol.) at −80°. Diethylammonium chloride (8·20 g., 96%) was filtered off and from the filtrate there was obtained *ethylene diethylaminoboronate* (5·50 g., 50%), b. p. 36°/0·4 mm., n_D^{20} 1·4284 (Found: N, 9·6; B, 7·5. $C_6H_{14}O_2NB$ requires N, 9·8; B, 7·6%).

(c) *Carboxylic acids.* Glacial acetic acid (2·48 g., 1 mol.) was slowly added to ethylene chloroboronate (4·40 g., 1 mol.) in methylene dichloride (10 c.c.) at 15°. Removal of volatile matter at 15°/0·04 mm. (2 hr.) left *acetyl ethylene borate* (5·10 g., 95%), m. p. ~77° (sealed tube) (Found: OAc, 43·5; B, 8·3. $C_4H_7O_4B$ requires OAc, 45·4; B, 8·3%).

Similarly monochloroacetic acid (5·00 g.) gave *chloroacetyl ethylene borate* (8·50 g., 98%) (Found: C, 28·4; H, 3·9; $O{\cdot}CO{\cdot}CH_2Cl$, 55·0; B, 6·4. $C_4H_6O_4ClB$ requires C, 29·2; H, 3·7; $O{\cdot}CO{\cdot}CH_2Cl$, 56·8; B, 6·6%), and trifluoroacetic acid (4·60 g.) gave *ethylene trifluoroacetyl borate* (7·30 g., 99%), n_D^{20} 1·3500 (Found: C, 25·4; H, 2·9; $O{\cdot}CO{\cdot}CF_3$, 58·4; B, 5·6. $C_4H_4O_4F_3B$ requires C, 26·1; H, 2·2; $O{\cdot}CO{\cdot}CF_3$, 61·5; B, 5·9%), which decomposed on distillation.

When acetyl ethylene borate (4·53 g.) was heated at 100°/0·5 mm. for 9·5 hr., acetic anhydride (0·77 g.; identified by gas chromatography and its infrared spectrum), b. p. 136°, was condensed at −80° and there was a glassy solid residue (3·72 g.) (Found: OAc, 34·0; B, 8·8%). These results are consistent with: $6[CH_2{\cdot}O]_2B{\cdot}OAc \longrightarrow Ac_2O + [(AcO)_2B]_2O + 2([CH_2{\cdot}O]_2B{\cdot}O{\cdot}CH_2)_2$; but separation of the solid was not achieved.

(d) *Ethylene hydrogen borate.* The chloroboronate (9·50 g., 1 mol.) in methylene dichloride (20 c.c.) was added to the acid (7·85 g., 1 mol.) at 10°. Hydrogen chloride (3·40 g., calc.: 3·26 g.) was trapped in potassium hydroxide, and removal of volatile matter was completed at 50°/0·5 mm. Di-*O*-ethyleneboric anhydride (13·73 g., 98%) (Found: B, 13·1. Calc. for $C_4H_8O_5B_2$: B, 13·7%) was obtained as a white, gelatinous solid. Attempts to recrystallise it did not improve purity.

Preparation of Derivatives of $Y_2B{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BY_2$. Ethylene glycol (1·70 g., 1 mol.) was added to boron trichloride (6·45 g., 2 mols.) at −80°. The mixture was warmed to 20° and liberated hydrogen chloride (1·90 g., 95%) was trapped in alkali. The residual liquid was *ethylene bisdichloroborinate,* n_D^{20} 1·4392 (Found: Cl, 63·8; B, 9·7. $C_2H_4O_2Cl_4B_2$ requires Cl, 63·6; Br, 9·7%).

Ethylene bisdichloroborinate (5·60 g., 1 mol.) in methylene dichloride (15 c.c.) was added to diethylamine (14·63 g., 8 mols.) at −10°. The precipitated diethylammonium chloride (10·60 g., 97%) was filtered off and the filtrate afforded *ethylene bisdiethylaminoborinate* (7·40 g., 80%), b. p. 67°/0·3 mm., n_D^{21} 1·4348 (Found: N, 15·2; B, 5·7. $C_{18}H_{44}O_2N_4B_2$ requires N, 15·1; B, 5·9%).

Addition of butan-1-ol (1·00 g., 1 mol.) to the bisdichloroborinate (3·00 g., 1 mol.) at −80° afforded hydrogen chloride (0·49 g., 100%) and (after removal of volatile matter at 18°/16 mm., *n-butyl* 2-*dichloroboro-oxyethylene chloroboronate* (3·42 g., 97%), n_D^{20} 1·4339 (Found: Cl, 39·8; B, 8·3. $C_6H_{13}O_3Cl_3B_2$ requires Cl, 40·7; B, 8·3%).

Reactions of Ethylene Bisdichloroborinate.—There was little apparent reaction when butan-1-ol (6·90 g., 4 mol.) was added to the bisdichloroborinate (5·20 g., 1 mol.) at −80° but at 15° a vigorous reaction ensued and hydrogen chloride was liberated. The residue, when three times distilled, afforded tetra-n-butyl ethylene di(borate) (6·9 g., 79%) (Found: C, 57·8; H, 10·8; B, 5·8. Calc. for $C_{18}H_{40}O_6B_2$: C, 57·8; H, 10·8; B, 5·8%) (infrared spectrum), b. p. 57°/0·1 mm., n^{20} 1·4199.

Ethylene glycol (1·42 g., 2 mol.) in methylene dichloride (30 c.c.) was added to the bisdichloroborinate (2·60 g., 1 mol.). Removal of volatile matter at 16°/0·01 mm. afforded triethylene di(borate) (2·35 g., 100%) (Found: B, 10·1. Calc. for $C_6H_{12}O_6B_2$: B, 10·7%) (infrared), m. p. 160°.

The bisdichloroborinate (4·60 g.) was heated under reflux at 110° for 2 hr. and there was only slight dissociation as evident from analysis (Found: Cl, 58·5; B, 11·0%). Further heating at 130°/5 mm. afforded boron trichloride (1·70 g., 70%) as a condensate (−80°); the trichloride was characterised as the pyridine complex [10] (Found: Cl, 53·1; C_5H_5N, 41·3; B, 5·4. Calc. for $C_5H_5NCl_3B$: Cl, 54·2; C_5H_5N, 40·3; B, 5·5%) (infrared). The pyrolysis residue (2·80 g.), n_D^{20} 1·4500, was crude ethylene chloroboronate (Found: Cl, 43·7; B, 9·9%) and was purified by twice distilling it (Found: Cl, 34·1; B, 10·4. Calc. for $C_2H_4O_2ClB$: Cl, 33·4; B, 10·2%).

The bisdichloroborinate (2·50 g., 1 mol.) in methylene dichloride (10 c.c.) was added to

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[10] Gerrard and Lappert, *J.*, 1951, 1020.

pyridine (1·77 g., 2 mol.) in the same solvent (15 c.c.) at −80° The white solid *pyridine complex* (4·27 g., 100%) [Found: Cl, 37·7; C_5H_5N, 41·7; B, 5·9. $C_2H_4O_2Cl_4B_2,2C_5H_5N$ requires Cl, 37·2; C_5H_5N, 41·5; B, 5·7%] was filtered off.

Disproportionation of n-Butyl 2-Dichloroboro-oxyethylene Chloroboronate.—Distillation of this chloroboronate (2·90 g.) afforded n-butyl dichloroborinate (1·60 g., 93%) (Found: Cl, 44·3; B, 7·2. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%) (infrared), n_D^{20} 1·4160, as a condensate (−80°), and ethylene chloroboronate (1·10 g., 93%), b. p. 62°/0·9 mm., n_D^{20} 1·4628 (Found: Cl, 32·4; B, 10·5%) (infrared).

Dealkylations.—Liquid hydrogen bromide (9·16 g.) and tetra-n-butyl ethylene di(borate) (2·80 g.) were stored in a sealed tube at 20° for 112 hr. Condensation at 15°/10 mm. afforded (at −80°) a mixture (5·09 g.; n_D^{20} 1·4385) of n-butyl bromide and ethylene dibromide (gas chromatography) and a residual solid (3·67 g.), which when heated gave more ethylene dibromide (0·23 g.), b. p. 26°/9 mm., n_D^{20} 1·4902 (gas chromatography), a condensate (−80°) of n-butyl bromide (2·41 g.), n_D^{20} 1·4362 (gas chromatography), and a mixture (0·70 g.) of boric acid and boric oxide (Found: B, 22·8%).

Similarly from liquid hydrogen bromide (9·60 g.) and triethylene di(borate) (1·00 g.) at 18° (76 hr.), there were obtained ethylene dibromide (2·80 g., 100%), b. p. 125°, and boric acid (0·63 g. Calc.: 0·613 g.) (Found: B, 16·9. Calc. for H_3O_3B: B, 17·5%).

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

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