666. *Cyclic Organic Boron Compounds. Part II.*[1] *Chemical Properties of* n-*Butyl Metaborate.*

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n-Butyl metaborate $(Bu^nO{\cdot}BO)_3$ is highly reactive, with affinity for reagents having nucleophilic activity (water; butan-1-ol; hydrogen, phosphorus, boron, and thionyl halides; carboxylic acids, chlorides, and anhydrides; and amines).

In Part I the preparation, physical properties, structures, and thermal and hydrolytic stability of a number of alkyl and phenyl metaborates were described.[1] The present paper concerns the chemical properties of the *n*-butyl homologue, which is regarded as typical of the alkyl compounds. For convenience, the empirical formula BuO·BO is used in the succeeding equations, in place of boroxole structure [1,2] $(BuO{\cdot}BO)_3$.

Reactions here reported are: with water or butan-1-ol to give butyl borate and boric acid; with non-metal halides to give butyl halides; with acids, acid chlorides, or anhydrides to give butyl esters; with boron trifluoride or trichloride to give butyl dihalogenoboronite; and with amines to give complex compounds. The metaborate did not react, under stated conditions, with *n*-butyl chloride, di-*n*-butyl ether, or hydrogen chloride; with propionamide, there was some dehydration to give propionitrile.

In the reactions with water and butan-1-ol there was no evidence that intermediate hydrogen or dihydrogen orthoborate had formed, although (—)-menthyl dihydrogen orthoborate has previously been obtained.[3] Hydrolysis to butan-1-ol and orthoboric acid was complete when a larger amount of water was used.

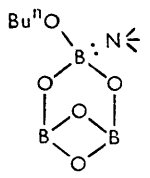
Hydrogen bromide did not react with the metaborate at 20°/760 mm., but dealkylation was rapid when the reaction was carried out under pressure; the observation is consistent with a mechanism involving rate-determining S_N2 attack of Br^- on the protonated metaborate. A similar concentration effect has previously been noted with alkyl diphenylboronites, $RO{\cdot}BPh_2$.[4]

Phosphorus penta-chloride and -bromide reacted readily and exothermally with the metaborate at 20°, but under similar conditions phosphorus trichloride and thionyl chloride did not, except in the presence of a trace of ferric chloride. In every case, the butyl chloride product contained 5—10% of the *sec.*-isomer; boron trioxide was invariably obtained together with phosphorus oxyhalide, phosphorus trioxide, or sulphur dioxide, respectively, in the several systems. The partial molecular rearrangement of the *n*-butyl group suggests that *n*-butyl carbonium ions are formed, which then undergo Wagner–Meerwein rearrangement. This suggestion would be consistent with the observed ferric chloride catalysis, as electrophilic catalysis of S_N1 reactions is general.[5] Catalysis by ferric chloride (and other Lewis acids) has previously been noted in certain other organic

[1] Lappert, *J.*, 1958, 2790.
[2] *Idem. Chem. Rev.*, 1956, **56**, 959.
[3] O'Connor and Nace, *J. Amer. Chem. Soc.*, 1955, **77**, 1578.
[4] Abel, Gerrard, and Lappert, *J.*, 1957, 3833.
[5] Ingold, "Structure and Mechanism in Organic Chemistry," p. 375, Bell and Sons, London, 1953.

boron systems.[6,7,8] Although the rearrangement *n*-butyl ⟶ *sec.*-butyl is not well known, it is likely that it has frequently not been detected in the past because of the lack of adequate methods of analysis, particularly gas chromatography.

With acetyl and benzoyl chloride (heating; no reaction at 20°), the *n*-butyl carboxylate formation was accompanied by that of boron trioxide and butyl chloride (90—95% *n*- and 5—10% *sec.*-). The formation from a metaborate of a carboxylic ester, by reaction with its parent acid (here demonstrated for R = Me or Ph), anhydride (R = Me), or acid chloride may prove to be of preparative value for esters which are not readily prepared by more direct methods.


(I)

The addition of pyridine to *n*-butyl metaborate instantly produced a white complex: $4Bu^nO{\cdot}BO + C_5H_5N \longrightarrow Bu^nO{\cdot}B_3O_4,NC_5H_5 + B(OBu^n)_3$. It was insoluble in organic solvents but was readily hydrolysed by cold water to give pyridine, butan-1-ol, and orthoboric acid. When heated it readily lost pyridine, and eventually butene and butan-1-ol. Other amines (Bu^nNH_2, Et_2NH, and Et_3N) reacted similarly, but precipitation of the complexes was much slower. For example, with *n*-butylamine, the reaction was not complete after 3 weeks at 20°. The complex may be formulated as (I) or as a polymer, formed by opening of the four-membered ring.

The present results should be compared with established reactions for other boroxoles [*e.g.*, $(Bu^n{\cdot}BO)_3$] and orthoborates [*e.g.*, $B(OBu^n)_3$].[2,4,9]

Experimental

General Procedures.—*n*-Butyl metaborate was prepared from boron trioxide.[1] In addition to constants and standard analytical procedures,[6,10] gas chromatography was used for both qualitative and quantitative analysis of all products having b. p. <140°/760 mm.

Hydrolysis and Alcoholysis.—Water (0·56 g.) in diethyl ether (10 c.c.) was added to the metaborate (3·11 g.) at 20°. A white precipitate (1·061 g.) was formed instantly and was filtered off. Removal of solvent from the filtrate afforded more precipitate, which was separated by addition of *n*-pentane (20 c.c.) and filtration. The combined precipitate was identified as orthoboric acid (1·273 g., 100%) (Found: B, 17·1. Calc. for H_3O_3B: B, 17·5%); the filtrate afforded tri-*n*-butyl borate (1·76 g., 74%), b. p. 110—114°/12 mm., n_D^{20} 1·4103 (Found: B, 4·70. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%). Yields are based on: $3Bu^nO{\cdot}BO + 3H_2O \longrightarrow B(OBu^n)_3 + 2B(OH)_3$.

By similar technique, addition of *n*-butyl alcohol (1·85 g.) to the metaborate (2·55 g.) afforded orthoboric acid (0·462 g., 88%) and the orthoborate (3·41 g., 87%), b. p. 112°/10 mm., n_D^{20} 1·4100. Yields are based on: $3Bu^nO{\cdot}BO + 3Bu^nOH \longrightarrow 2B(OBu^n)_3 + B(OH)_3$.

Hydrogen Halides.—The metaborate did not react with gaseous hydrogen chloride at 20° even in presence of ferric chloride.

Liquid hydrogen bromide (4·61 g.) and the metaborate (2·03 g.) were mixed at −80° and the vessel was sealed. Within 30 min. at 20° the mixture set to an opaque solid. After 24 hr. at 20°, the vessel was opened at −80°, and unchanged hydrogen bromide was allowed to escape, whereafter volatile matter was condensed at 20°/10 mm. into a trap at −80°. The condensate was distilled from lead carbonate and dried ($CaCl_2$); redistillation gave *n*-butyl bromide (1·84 g., 66%), b. p. 95—98°/760 mm., n_D^{20} 1·4403. The residue (1·34 g.) contained boron, equivalent to metaboric acid (0·833 g., 94%). Yields are based on: $Bu^nO{\cdot}BO + HBr \longrightarrow Bu^nBr + HO{\cdot}BO$.

[6] Lappert, *J.*, 1956, 1768.
[7] Gerrard and Lappert, *J.*, 1955, 3084.
[8] Brindley, Gerrard, and Lappert, *J.*, 1956, 1540; Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.
[9] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697; Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2893; Gerrard, Lappert, and Shafferman, *ibid.*, p. 3828; McCusker and Glunz, *J. Amer. Chem. Soc.*, 1955, **77**, 4253; McCusker, Ashby, and Makowski, *ibid.*, 1957, **79**, 5182; McCusker and Makowski *ibid.*, p. 5185.
[10] Gerrard and Lappert, *J.*, 1951, 2545; Gerrard, Lappert, and Silver, *J.*, 1956, 3285; 1957, 1647; Abel, Edwards, Gerrard, and Lappert, *J.*, 1957, 501.

Boron Trihalides.—When boron trifluoride was passed into the metaborate in absence of solvent, working-up was difficult owing to incomplete reaction caused by gelation. Accordingly, the gas was passed through the ester (5·00 g.) in *n*-pentane (25 c.c.), whereupon precipitation of a white solid was rapid. Solvent was removed at 20°/20 mm., and distillation gave *n*-butyl difluoroboronite (4·42 g., 73%), b. p. 45—48°/10 mm., n_D^{14} 1·3882, which was also characterised by comparing its infrared spectrum with that of an authentic specimen.[11] The white, solid distillation residue (2·12 g.) was washed with diethyl ether to give, as an amorphous powder, boron trioxide (1·13 g., 97%) (Found: B, 30·6. Calc. for O_3B_2: B, 31·1%).

Boron trichloride (3·00 g.) was added to the metaborate (1·73 g.) at −80°. Matter volatile at 20°/1 mm. was condensed into a trap at −80°. The condensate was twice distilled, giving *n*-butyl dichloroboronite (1·34 g., 50%), b. p. 40—42°/20 mm., n_D^{20} 1·4142 (Found: Cl, 44·8; B, 6·8. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%). The distillation residue (2·28 g.) was a fuming white solid and appeared to be impure boron oxychloride.

Phosphorus Pentahalides.—When phosphorus pentachloride (11·36 g.) and the metaborate (5·45 g.) were mixed, an exothermal reaction took place. The mixture was set aside for 24 hr. at 15°, whereafter matter volatile at 20°/0·01 mm. was condensed into a trap at −80°. The condensate (10·74 g.) was a mixture of butyl chlorides (90—95% of *n*- and 5—10% of *sec.*-butyl) (2·94 g., 59%) and phosphorus oxychloride (7·80 g., 93%). The residue (5·24 g.) contained boron, equivalent to boron trioxide (1·90 g., 100%). Yields are based on: $Bu^nO{\cdot}BO + PCl_5 \longrightarrow Bu^nCl + POCl_3 + [BOCl]$.

Similarly, from the pentabromide (6·20 g.) and the metaborate (1·46 g.), there was obtained a mixture of butyl bromides (1·20 g., 61%), b. p. 80—100°/760 mm., n_D^{20} 1·4393, separated from other products by aqueous treatment.

Phosphorus Trichloride.—The trichloride (4·75 g., 1 mol.) and the metaborate (3·46 g., 1 mol.) were mixed at 20° and set aside for 72 hr.; there was no sign of reaction. Ferric chloride (0·050 g.) was added and after 4 hr. at 20° the mixture became gelatinous and after 24 hr. semi-solid. It was then heated under reflux for 1 hr. and subsequent distillation afforded a mixture of phosphorus trichloride (3·20 g., 0·675 mol.) and butyl chloride (90—95% of *n*- and 5—10% of *sec.*-butyl) (2·63 g., 82%), b. p. 72—78°/760 mm., n_D^{21} 1·4627. There was a white residue (2·22 g.), which contained boron, equivalent to boron trioxide (1·20 g., 99%), and phosphorus, equivalent to phosphorus trioxide (0·632 g., 100%). Yields are based on: $6Bu^nO{\cdot}BO + 2PCl_3 \longrightarrow 6Bu^nCl + 3B_2O_3 + P_2O_3$.

Thionyl Chloride.—The metaborate did not react with thionyl chloride under reflux during 3½ hr.

A mixture of the metaborate (3·01 g.), thionyl chloride (3·52 g.), and ferric chloride (0·033 g.) was heated under reflux for 1 hr. Distillation afforded a mixture of thionyl chloride (1·36 g.) and butyl chloride (90—95% of *n*- and 5—10% of *sec.*-butyl) (1·80 g., 65%), b. p. 68—78°/760 mm., n_D^{22} 1·4358. There was a residue (1·65 g.), which contained boron, equivalent to boron trioxide (1·01 g., 95%). During the work-up, sulphur dioxide was evolved. Yields are based on: $2Bu^nO{\cdot}BO + SOCl_2 \longrightarrow 2Bu^nCl + B_2O_3 + SO_2$.

Acetyl Chloride.—The metaborate (3·38 g., 1 mol.) and acetyl chloride (2·66 g., 1 mol.) were set aside for 24 hr. at 20°; there was no sign of reaction. The whole was then heated under reflux for 4 hr. and on cooling became solid. A condensate comprising a mixture of acetyl chloride (1·07 g.), *n*-butyl acetate (2·84 g., 64%), and butyl chloride (90—95% *n*- and 5—10% *sec.*-butyl) (0·56 g.), n_D^{20} 1·3962, was obtained by heating at 110°/1 mm. There was a residue (1·33 g.), containing boron, equivalent to boron trioxide (1·12 g., 95%).

Benzoyl Chloride.—Similarly, when the metaborate (1·55 g., 2 mols.) and benzoyl chloride (1·09 g., 1 mol.) were mixed there appeared to be no reaction. After heating, under reflux, for 4 hr., distillation afforded *n*-butyl benzoate (1·32 g., 96%), b. p. 70—72°/0·01 mm., n_D^{22} 1·4962, and a residue (0·58 g.), containing boron, as the trioxide (0·540 g., 99%). There was a condensate of *n*- (90—95%) and *sec.*-butyl chloride (5—10%) (0·59 g., 83%). Yields are based on: $2Bu^nO{\cdot}BO + Ph{\cdot}COCl \longrightarrow Bu^nCl + Bu^nO{\cdot}COPh + B_2O_3$.

Acetic Anhydride.—There was no heat of mixing when acetic anhydride (1·34 g.) was added to the metaborate (2·73 g.) at 20°, but after ½ hr. under reflux there was obtained *n*-butyl acetate (2·54 g., 80%), b. p. 120—122°/760 mm., n_D^{20} 1·3936, and a white residue (1·23 g.), which contained boron, equivalent to boron trioxide (0·953 g., 100%). Yields are based on: $2Bu^nO{\cdot}BO + (CH_3{\cdot}CO)_2O \longrightarrow 2Bu^nO{\cdot}CO{\cdot}CH_3 + B_2O_3$.

[11] Lappert, *J.*, 1955, 784.

Carboxylic Acids.—A mixture of acetic acid (1·54 g.) and the metaborate (2·57 g.) was heated under reflux for 2 hr. Distillation afforded a mixture of *n*-butyl acetate (2·22 g., 66%) and acetic acid (0·635 g.), b. p. 124—126°/760 mm., n_D^{20} 1·3892. There was a white solid residue (1·17 g.) containing boron, equivalent to metaboric acid (1·12 g., 100%).

A mixture of benzoic acid (1·12 g.) and the metaborate (0·915 g.) was heated under reflux for 3 hr. at 150°. Distillation afforded *n*-butyl benzoate (1·10 g., 62%), b. p. 120°/10 mm., n_D^{20} 1·4973, and a white solid residue (0·76 g.) containing boron, equivalent to metaboric acid (0·615 g. Calc. for HO·BO: 0·401 g.). Yields are based on: $Bu^nO{\cdot}BO + R{\cdot}CO_2H \longrightarrow Bu^nO{\cdot}COR + HO{\cdot}BO$.

Amines.—Pyridine (1·20 g.) was added to the metaborate (5·14 g.) in *n*-pentane (20 c.c.) at 20°. Reaction was slightly exothermal and a voluminous white precipitate was immediately formed. Filtration afforded the *complex* (3·165 g., 99%) (Found: C, 43·1; H, 5·60; C_5H_5N, 31·4; B, 13·2. $C_9H_{14}O_5NB_3$ requires C, 43·4; H, 5·62; C_5H_5N, 31·8; B, 13·1%) and from the filtrate there was obtained tri-*n*-butyl borate (2·60 g., 88%), b. p. 105—107°/12 mm., n_D^{23} 1·4082 (Found: C, 62·2; H, 11·7; B, 4·7. Calc. for $C_{12}H_{27}O_3B$: C, 62·7; H, 11·7; B, 4·7%). The complex was insoluble in *n*-pentane, diethyl ether, methylene dichloride, *cyclo*hexane, camphor, benzene, and nitrobenzene.

In a similar manner, from diethylamine (0·63 g.) and metaborate (3·45 g.) in *n*-pentane (20 c.c.), there was formed the diethylamine *complex* (1·692 g., 81%) (Found: Et_2NH, 25·9; B, 13·2. $C_8H_{20}O_5NB$ requires Et_2NH, 26·8; B, 13·4%), tri-*n*-butyl borate (1·74 g., 88%), b. p. 104—110°/9 mm., n_D^{20} 1·4110 (Found: B, 4·8%), and a residue (0·52 g.). This reaction differed from the pyridine system in that precipitation of the complex was incomplete even after the mixture had been kept at 48 hr. at 20°.

Similar results were obtained with triethylamine and *n*-butylamine, as already described.

Other Reagents.—There was no reaction between the metaborate and *n*-butyl chloride at 20° during 4 days or di-*n*-butyl ether under reflux during 6 hr.

A mixture of propionamide (1·63 g.) and the metaborate (4·47 g.) was heated at 220° for 48 hr. in a sealed tube. The tube was opened and heated for 1 hr. at 220°/0·1 mm. There was a condensate (2·58 g.), trapped at −80°, which on distillation afforded a fraction (1·69 g.), b. p. 100—130°/760 mm., which contained propionitrile (10—15%).

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