# **568.** *Cyclic Organic Boron Compounds. Part I. Preparation, Characterisation, and Stability of Esters of Metaboric Acid.*

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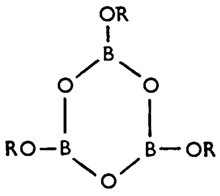
The lower alkyl (Me, Et, $Pr^n$, $Pr^i$, $Bu^n$, $Bu^i$, and $Bu^s$, but not $Bu^t$) metaborates, $(RO{\cdot}BO)_3$, have been prepared by thermal or catalytic decomposition of corresponding dialkyl chloroboronates, $(RO)_2BCl$, or by heating the orthoborates with boron trioxide. The last method was also successful for phenyl metaborate. Infrared spectra showed strong absorption bands near 720 and 735 cm.$^{-1}$ which appear to be diagnostic for metaborates. The esters, although thermally very stable, disproportionated when strongly heated under reduced pressure, and were also readily hydrolysed.

THIS paper * is the first in a series dealing with the chemistry of cyclic organic boron compounds, and in particular with six-membered ring compounds having alternate boron atoms and atoms capable of " back-co-ordinating " to boron.

Until recently the existence of alkyl metaborates, $RO{\cdot}BO$, had not definitely been established,[1] although the orthoborates, $(RO)_3B$, have been known since 1846 [2] and numerous detailed investigations have been reported concerning their preparation, structure, and chemical and physical behaviour.[1] By contrast, in inorganic chemistry, the meta-(or 1 : 1)borates are better known than the ortho(or 3 : 1)borates.[3]

Goubeau and Keller obtained methyl metaborate by heating the orthoborate and boron trioxide in equimolecular proportions in a sealed tube.[4] It was trimeric and this, taken in conjunction with its Raman spectrum,[5] was evidence for a formulation (I; R = Me). Trimeric (—)-menthyl and *cyclo*hexyl metaborate, prepared by azeotropic removal (with toluene) of water from an equimolecular mixture of orthoboric acid and the appropriate alcohol, were considered to have no characteristic infrared B=O absorption and were also formulated as (I) [6]; this view of the spectra was taken because all the bands in the 2—9 μ region were attributed to CH absorption. Alkyl metaborates have also been postulated as intermediates in the decomposition of dialkyl chloroboronates, $(RO)_2B{\cdot}Cl$, producing alkyl chloride, this being markedly catalysed by traces of Lewis acids.[7]


(I)

The alkyl metaborates were obtained by reaction (1) $3(RO)_2B{\cdot}Cl \longrightarrow (RO{\cdot}BO)_3 + 3RCl$ or (2) $(RO)_3B + B_2O_3 \longrightarrow (RO{\cdot}BO)_3$; attempted preparation of the *n*-butyl homologue by hydrolysis of the orthoborate with a limited amount of water failed, orthoboric acid being precipitated. Reaction (1) was carried out (*a*) at 150—250°, under pressure if necessary, depending on the boiling point of the reactant, or (*b*) without heat, by the addition of a trace of anhydrous ferric or aluminium chloride. Reaction (2) was carried out by heating the mixture under reflux, or under pressure if necessary, until the trioxide had dissolved (a slight excess of boron trioxide is recommended).

Neither of the methods was suitable for the preparation of *tert.*-butyl metaborate; di-*tert.*-butyl chloroboronate does not exist [7] and reaction of the orthoborate with boron trichloride produced mainly boron trioxide. Reaction (1) is not suitable for aryl metaborates, in view of the different mode of decomposition of diaryl chloroboronates.[8]

Some physical constants of the metaborates are shown in Table 1, including molecular

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* Partly covered by B.P. Application 22444/57.

[1] Lappert, *Chem. Rev.*, 1956, **56**, 959.

[2] Ebelmen and Bouquet, *Ann. Chim. Phys.*, 1846, **3**, 17, 54; *Annalen*, 1846, **60**, 251.

[3] Kemp, " The Chemistry of Borates," Part I, Borax Consolidated Ltd., London, 1956.

[4] Goubeau and Keller, *Z. anorg. Chem.*, 1951, **267**, 1.

[5] *Idem, ibid.*, 1953, **272**, 303.

[6] O'Connor and Nace, *J. Amer. Chem. Soc.*, 1955, **77**, 1578.

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

[8] Colclough, Gerrard, and Lappert, *J.*, 1955, 907; 1956, 3006.

TABLE 1.

| R in $(RO{\cdot}BO)_3$ | $n_D^{20}$ | $d_4^{20}$ | M. p. | $[R_L]_D$ Found | $[R_L]_D$ Calc. |
|---|---|---|---|---|---|
| Me | 1·4038 | 1·233 | — | 34·4 | 34·1 |
| Et | 1·4071 | 1·113 | — | 47·7 | 48·0 |
| $\text{Pr}^n$ | 1·4129 | 1·025 | — | 62·6 | 62·0 |
| $\text{Pr}^i$ | — | — | 52—54° | — | — |
| $\text{Bu}^n$ | 1·4236 | 1·014 | — | 75·3 | 75·9 |
| $\text{Bu}^i$ | 1·4170 | 0·997 | — | 75·8 | 75·9 |
| $\text{Bu}^s$ | 1·4151 | 0·985 | — | 76·1 | 75·9 |
| Ph | — | — | 98—101 | — | — |

refractivities calculated from the measured refractive indices and densities which are in reasonable agreement with the values calculated from accepted atomic and structural constants [9] and a value of 2·20 for the atomic refractivity of boron (this is substantially lower than the 2·65 for boron in orthoborates [7]). The three isomeric butyl metaborates were shown to be trimeric, their formulæ thus being (I). The metaborates were soluble in many organic solvents, including diethyl ether, benzene, *n*-pentane, and methylene dichloride.

Strong bands between 1500 and 1300 cm.$^{-1}$ in the infrared spectrum of methyl metaborate are undoubtedly due to the modes involving B–O stretching and mask the methyl deformation bands. A band at 1486 cm.$^{-1}$ with a shoulder at 1520 cm.$^{-1}$ is at a considerably higher frequency than is usual [10,11] for B–O single-bond stretching frequencies, suggesting bonds of higher order. The spectra of the higher alkyl metaborates contain more bands in the regions 1300—1500 cm.$^{-1}$ than does the spectrum of methyl metaborate owing, probably, to the wider occurrence of rotational isomers as the alkyl group becomes larger. It seems that *cyclo*hexyl and menthyl metaborate [6] should have similar absorptions in this region of the spectrum which, of course, is within the range 2—9 $\mu$. All the alkyl metaborates absorb strongly in the region 1050—1100 cm.$^{-1}$ (C–O bond stretching). In phenyl metaborate the corresponding bands occur at 1225 and 1209 cm.$^{-1}$ as expected for ether links. Further strong absorption which appears highly characteristic for metaborates occurs near 720 and 735 cm.$^{-1}$, the intensities being of the same order as those of the C–O bands near 1100 cm.$^{-1}$. Such bands do not occur in the spectra of trialkyl orthoborates [10] and it is possible that they arise from the out-of-plane vibrations of the $B_3O_6$ skeleton. However, whatever the cause of these bands, strong absorption near 720 and 735 cm.$^{-1}$ is of good diagnostic value for metaboric esters.

Attempted distillation under reduced pressure of the metaborates caused disproportionation [reverse of reaction (2)]; in order to distil the orthoborate, a bath temperature substantially higher than its boiling temperature had to be employed. This result explains the stoicheiometry proposed previously for decomposition of dialkyl chloroboronates.[7] When heated at high temperature under reflux, on the other hand, the metaborates were stable; for example the *n*-butyl homologue showed no significant decomposition after 5 hours at 280—290° (cf. ref. 6).

The metaborates, like most orthoborates,[1] were hydrolysed readily by cold water, to boric acid and the alcohol or phenol.

## EXPERIMENTAL

*Preparations, Boron Analysis, and Hydrolysis.*—The orthoborates (Me,[12] Et,[13], $\text{Bu}^t$,[14] Ph,[8] and the others [15]) and dialkyl chloroboronates (Me and Et,[16] and the others [7]) were prepared

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

[10] Webster and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355; 1956, **9**, 137.

[11] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872; Abel, Gerrard, and Lappert, *J.*, 1957, 3833.

[12] Vaughn, U.S.P. 2,088,935/1937.

[13] Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1.

[14] Brown, Mead, and Shaaf, *J. Amer. Chem. Soc.*, 1956, **78**, 3613.

[15] Scattergood, Miller, and Gammon, *ibid.*, 1945, **67**, 2150.

[16] Wiberg and Smedsrud, *Z. anorg. Chem.*, 1935, **225**, 204.

by established methods. Boron in phenyl metaborate,[17] the alkyl metaborates,[7] and boron trioxide was estimated by procedures described previously. All the metaborates were readily hydrolysed by cold water; this was shown analytically. M. p.s were determined in sealed capillary tubes.

*Preparation* (1) *of Alkyl Metaborates.*—Details of these experiments are shown in Tables 2 and 3; the general procedure was to decompose the dialkyl chloroboronate (4—30 g.) either under reflux for a stated time or by adding a catalyst. The metaborate was separated from the alkyl chloride by filtration (Pr$^{\text{i}}$) or evaporation of the chloride under reduced pressure. When a catalyst was used, this was removed by dissolving the metaborate in an inert anhydrous solvent, such as methylene dichloride or diethyl ether and filtering the whole. The solvent was removed from the filtrate under reduced pressure.

*Preparation* (2) *of Alkyl and Phenyl Metaborates.*—A mixture of the orthoborate (1 mol.) and boron trioxide (slightly >1 mol.) was heated under stated conditions as shown in Table 4. Purification of the metaborate was effected by dissolving the product in a large volume of an inert anhydrous solvent, filtering, and evaporating the filtrate under reduced pressure.

*Unsuccessful Attempts to prepare Metaborates.*—(*a*) *tert.*-Butyl orthoborate (6·25 g.) and boron trioxide (1·90 g.) were heated under reflux for 6 hr. The supernatant liquid was substantially the orthoborate (Found: B, 4·93. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%). (*b*) Boron trichloride (1·35 g.) in methylene dichloride (10 c.c.) at −80° was added to *tert.*-butyl orthoborate (5·28 g.) in the same solvent (25 c.c.) at −80°. Evaporation of volatile material at 20°/1 mm. left crude boron trioxide (Found: B, 24·3%). (*c*) Addition of water (0·76 g.) in

TABLE 2.

| R in $(RO{\cdot}BO)_3$ | Time (hr.) | Temp. | Catalyst (% w/w) | Yield (%) | Yield * (%) of RCl |
|---|---|---|---|---|---|
| Me | 10 | 250° (sealed) | — | 99 | — |
| Et | 10 | 250° (sealed) | — | 100 | — |
| Pr$^{\text{n}}$ | 10 | 250° (sealed) | — | 99 | 80 |
| Pr$^{\text{i}}$ | 5 | 200° (sealed) | — | 98 | 76 |
| Bu$^{\text{n}}$ | 10 | 250° (sealed) | — | 100 | 85 |
| Bu$^{\text{n}}$ † | 3 | 20° | $FeCl_3$ (0·28) | 93 | — |
| Bu$^{\text{i}}$ | 10 | 250° (sealed) | — | 99 | 83 |
| Bu$^{\text{s}}$ | 3 | 20° | $AlCl_3$ (0·16) | 96 | — |

* RCl characterised by $n_D^{20}$. † $(RO{\cdot}BO)_3$ had $n_D^{20}$ 1·4235 (Found: B, 10·8%).

TABLE 3.

| R in $(RO{\cdot}BO)_3$ | $n_D^{20}$ | Found (%) | | | Required (%) | | |
|---|---|---|---|---|---|---|---|
| | | C | H | B | C | H | B |
| Me | 1·4060 | 20·6 | 4·97 | 19·4 | 20·7 | 5·23 | 18·7 |
| Et | 1·4083 | 32·9 | 6·84 | 15·4 | 33·3 | 6·95 | 15·0 |
| Pr$^{\text{n}}$ | 1·4143 | 42·8 | 8·1 | 12·4 | 42·6 | 8·1 | 12·6 |
| Pr$^{\text{i}}$ | (M. p. 52—54°) | 41·2 | 8·0 | 12·9 | 41·8 | 8·1 | 12·6 |
| Bu$^{\text{n}}$ | 1·4238 | 47·6 | 9·1 | 11·3 | 48·1 | 9·1 | 10·8 |
| Bu$^{\text{i}}$ | 1·4180 | 47·9 | 9·1 | 11·0 | 48·1 | 9·1 | 10·8 |
| Bu$^{\text{s}}$ | 1·4151 | 47·7 | 9·0 | 11·1 | 48·1 | 9·1 | 10·8 |

TABLE 4.

| R in $(RO{\cdot}BO)_3$ | Time (hr.) | Temp. | Yield (%) | $n_D^{22}$ | $n_4^{22}$ | Found (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | B |
| Me | 6 | 180° (sealed) | 98 | 1·4020 | 1·233 | 20·7 | 5·05 | 18·9 |
| Et | 10 | 250° (sealed) | 98 | 1·4069 | 1·113 | 32·5 | 6·94 | 15·3 |
| Pr$^{\text{n}}$ | 3 | Reflux | 93 | 1·4128 | 1·017 | 42·6 | 8·3 | 12·3 |
| Pr$^{\text{i}}$ | 3 | Reflux | 93 | (M. p. 52—54°) | | 41·2 | 7·9 | 13·0 |
| Bu$^{\text{n}}$ | 8 | 240° | 96 | 1·4236* | 1·014* | 47·6 | 8·9 | 11·2 |
| Bu$^{\text{i}}$ | 8 | Reflux | 95 | 1·4170 | 0·997 | 48·5 | 9·4 | 11·2 |
| Bu$^{\text{s}}$ | 8 | Reflux | 96 | 1·4160 | 0·985 | 47·6 | 9·1 | 11·0 |
| Ph † | 14 | 400° (sealed) | 88 | (M. p. 98—101°) | | 59·2 | 4·34 | 9·3 |

* At 20°. † $C_6H_5O_2B$ requires C, 60·0; H, 4·17; B, 9·0%.

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[17] Thomas, *J.*, 1946, 820.

diethyl ether (10 c.c.) to *n*-butyl orthoborate (9·71 g.) at 20° afforded instantaneously a precipitate of boric acid (Found: B, 18·9%).

*Molecular Weights.*—These were determined cryoscopically in *cyclo*hexane, in a Beckmann apparatus designed to operate under anhydrous conditions [Found: *M*, 315 (Bu$^{n}$), 306 (Bu$^{i}$), 305 (Bu$^{s}$). $C_{12}H_{27}O_6B_3$ requires *M*, 300].

*Infrared Spectra.*—The spectra of the metaborates were measured in the region of 2—15 $\mu$ on a Grubb–Parsons double-beam spectrometer with a rock-salt prism. With the exception of the two solid compounds (Pr$^{i}$, Ph), these were measured in the liquid state. The solids were dissolved in methylene dichloride or carbon disulphide, or dispersed in "Nujol." The spectra of metaborates obtained by the two methods were identical, as follows (max. in cm.$^{-1}$; vs = very strong; s = strong; m = medium; w = weak; sh = shoulder):

*Methyl.* ~1520 sh, 1486 vs, ~1427 sh, 1351 vs, 1304 s, 1221 w, 1186 w, 1085 s, 1037 m, 1021 sh, 975 w, 898 w, 879 w, 863 w, 799 w, ~736 sh, 718 s.

*Ethyl.* 1521 sh, 1495 vs, 1433 vs, 1383 vs, 1341 vs, 1289 s, 1215 w, ~1164 w, 1107 s, 1080 s, ~1055 sh, ~961 w, ~824 w, 804 w, ~736 sh, 722 s.

n-*Propyl.* 1520 sh, 1486 vs, 1427 vs, 1355 vs, 1333 vs, 1297 s, 1256 m, 1215 w, 1167 w, 1151 w. 1103 s, 1083 s, 1075 sh, 1052 sh, 1016 w, ~993 w, 969 w, ~911 w, ~889 w, ~870 w, ~734 sh, 722 s.

iso*Propyl.* 1580 sh, ~1508 sh, ~1429 vs, 1406 vs, 1366 vs, 1335 vs, ~1232 sh, 1175 m, 1135 s, 1119 s, 1025 m, ~924 w, 898 m, 789 m, 733 m, 723 s.

n-*Butyl.* 1515 sh, 1488 s, 1425 vs, ~1365 vs, 1344 s, 1299 sh, 1264 sh, 1233 w, 1214 w, 1147 w, 1117 m, 1088 s, 1029 w, 963 w, ~895 w, ~827 w, ~810 w, 734 sh, 723 s.

iso*Butyl.* 1520 sh, 1481 s, 1427 vs, 1385 vs, 1353 vs, ~1337 vs, 1299 s, 1267 s, 1214 w, 1175 w, 1112 m, 1083 s, 1036 m, ~1014 sh, 962 w, ~952 w, 925 w, 908 w, ~876 w, 823 w, ~736 sh, 724 s.

sec.-*Butyl.* 1511 s, ~1459 sh, 1409 vs, 1377 vs, 1337 vs, 1302 s, ~1276 sh, ~1215 w, 1174 m, 1129 s, 1105 s, 1052 m, 1031 sh, ~1005 w, 994 m, ~977 w, 959 w, ~912 w, 865 m, 831 w, 822 m, ~778 w, 735 s, 724 s.

*Phenyl.* 1592 m, 1494 s, ~1409 sh, 1378 vs, 1355 vs, 1321 s, 1225 s, 1209 m, ~1196 w, 1149 w, ~1096 w, 1068 m, 1020 m, ~1002 w, 977 w, 898 w, ~824 w, 789 w, 757 s, ~715 sh, 700 s, 690 s.

*Pyrolysis of* n-*Butyl Metaborate.*—The ester (2·34 g.) was heated under reflux at 280—290° for 6 hr. There was no change in appearance, refractive index, or infrared spectrum. In a bromine trap there was collected dibromobutane (0·051 g.), which was separated by washing with sodium thiosulphate, dried, and identified ($n_D^{20}$ 1·5128).

*Attempted Distillation of Metaborates.*—The results are shown in Table 5. In order to distil the orthoborate at all completely, a bath-temperature about 100° higher than the b. p. of the orthoborate had to be used. The residual boron trioxide was freed from ortho- and metaborates by washing it with diethyl ether.

TABLE 5.

| | $(RO)_3B$ | | | | $B_2O_3$ (Calc.: B, 31·1%) | |
|---|---|---|---|---|---|---|
| R in $(RO{\cdot}BO)_3$ | Yield (%) | $n_D^{20}$ | Found: B (%) | Calc.: B (%) | Yield (%) | Found: B (%) |
| Me | 91 | 1·3615 | 10·2 | 10·4 | 100 | 30·6 |
| Et | 92 | 1·3738 | 7·3 | 7·4 | 98 | 30·7 |
| Pr$^{n}$ | 92 | 1·3948 | 5·8 | 5·8 | 100 | 30·9 |
| Pr$^{i}$ | 93 | 1·4067 | 5·8 | 5·8 | 99 | 30·9 |
| Bu$^{n}$ | 92 | 1·4081 | 4·7 | 4·7 | 100 | 30·4 |
| Bu$^{i}$ | 94 | 1·4035 | 4·8 | 4·7 | 100 | 30·8 |
| Bu$^{s}$ | 92 | 1·3967 | 4·7 | 4·7 | 99 | 30·6 |
| Ph | 85 | (M. p. 92—95°) | 3·7 | 3·7 | 95 | 30·2 |

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