138. *The Trialkylsilyl Esters of Boron.*

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The tristrialkylsilyl borates, $[(R_3Si{\cdot}O)_3B]$, have been obtained in good yield by a number of methods, and their thermal stability and ease of hydrolysis investigated. Bistriethylsilyl phenylboronate $[(Et_3Si{\cdot}O)_2B{\cdot}Ph]$ and triethylsilyl diphenyborinate $[Et_3Si{\cdot}O{\cdot}BPh_2]$ have been prepared. The trialkylsilyl metaborates have been formed from boric oxide and the corresponding orthoborates at high temperature; they are trimeric.

Since the first report of tristrimethylsilyl borate by Krieble,[1] there has been little systematic investigation of the chemistry of the trialkylsilyl compounds of boron. The few preparative methods reported [2,3] have been peculiar to the silyl system, only one reaction [3] being related to the normal methods of preparing organic borates. We have now prepared the trialkylsilyl borates by a number of methods analogous to those used for the alkyl borates.[4]

[1] Krieble, U.S.P. 2,440,101/1946.
[2] Voronkov and Zgonnik, *Zhur. obshchei Khim.*, 1957, **27**, 1476.
[3] Wiberg and Krüerke, *Z. Naturforsch.*, 1953, **8**, *b*, 608.
[4] Lappert, *Chem. Rev.*, 1956, **56**, 959.

Triethylsilanol and boric acid gave tristriethylsilyl borate in good yield, $3Et_3Si{\cdot}OH + H_3BO_3 \longrightarrow (Et_3Si{\cdot}O)_3B + 3H_2O$, the water being continuously removed as the benzene–water azeotrope. This reaction is much simpler than the analogous reaction leading to tertiary alkyl borates.[4] We found the reported [2] action of silanols on trialkyl borates to give only moderate yields of silyl borate, but good yields were obtained in the silanolysis of tristrimethylsilyl borate to tristriethylsilyl borate with triethylsilanol, $(Me_3Si{\cdot}O)_3B + 3Et_3Si{\cdot}OH \longrightarrow (Et_3Si{\cdot}O)_3B + 3Me_3Si{\cdot}OH$.

The preparation of alkyl borates from boron trichloride, alcohols, and pyridine has given [5] excellent yields, but the corresponding reaction with triethylsilanol gave a poor yield (34%) of the silyl borate; considerable amounts of boron trichloride–pyridine and hexaethyldisiloxane were isolated as by-products. Boron trichloride and sodium triethylsiloxide, however, afforded a good yield (73%) of the pure borate: $BCl_3 + 3Et_3Si{\cdot}ONa \longrightarrow 3NaCl + (Et_3Si{\cdot}O)_3B$. Sodium triethylsiloxide also gave bistriethylsilyl phenylboronate, $Ph{\cdot}B(O{\cdot}SiEt_3)_2$, and triethylsilyl diphenylborinate, $Ph_2B{\cdot}O{\cdot}SiEt_3$, from phenylboron dichloride and diphenylboron chloride, respectively.

The most convenient preparation of tristrialkylsilyl borates was the silanolysis of trisdiethylaminoboron: [6] $3Et_3Si{\cdot}OH + (Et_2N)_3B \longrightarrow (Et_3Si{\cdot}O)_3B + 3Et_2NH$. The reaction required no solvent, and removal of diethylamine at reduced pressure gave the pure borate, which distilled unchanged.

Phenylboronic anhydride did not react with hexamethyldisiloxane as did boric oxide [2] to form an ester. Boric oxide, however, caused fission of ethoxytrimethylsilane to give a mixture of triethyl and tristrimethylsilyl borates, which are easily separated by distillation: $3EtO{\cdot}SiMe_3 + B_2O_3 \longrightarrow (EtO)_3B + (Me_3Si{\cdot}O)_3B$.

The tristrialkylsilyl borates are not hydrolysed rapidly, more than 50% being recovered after being shaken with water for long periods. This slow hydrolysis is presumably due to considerable steric hindrance by the three large trialkylsilyl groups. This steric effect on the rate of hydrolysis of borates has been extensively investigated.[7] The lower steric hindrance in the phenylboron esters explains the faster hydrolysis of these compounds than of the borates. The resistance of trialkylsilylboron esters to hydrolysis may be further enhanced by the powerful water-repelling properties of the silanols and disiloxanes formed on hydrolysis.

Hydrogen chloride and bromide reacted rapidly and completely with tristrimethylsilyl borate to produce boric acid and the corresponding trimethylhalogenosilanes: in this the borate closely resembles the tertiary alkyl esters of boron.[8]

Reaction of boric oxide with the tristrialkylsilyl borates produced the trialkylsilyl metaborates: $(R_3Si{\cdot}O)_3B + B_2O_3 \longrightarrow (R_3Si{\cdot}O{\cdot}BO)_3$. These compounds are trimeric like the corresponding alkyl metaborates,[9,10] and we believe them to have the cyclic boroxole structure [11] of the alkyl metaborates. This is supported by the presence of the doublet band at 720 and 735 cm.$^{-1}$ in the infrared spectrum, which has recently been assigned [10] to the out-of-plane vibrations of the boroxole skeleton. It is to be noted that tertiary alkyl metaborates of similar structure do not exist. Whereas the tristrialkylsilyl borates can be refluxed unchanged, the silyl metaborates decompose on attempted distillation to boric oxide and the corresponding orthoborate. The metaborates can, however, be heated for 50 hr. in a sealed tube at 250° without decomposition; the orthoborates have been recovered unchanged after being heated in sealed tubes at 275°.

The strongest bands in the infrared spectrum of all the compounds reported above are

[5] Lappert, *J.*, 1953, 667.
[6] Gerrard, Lappert, and Pearce, *J.*, 1957, 381.
[7] Steinburg and Hunter, *Ind. Eng. Chem.*, 1957, **49**, 174.
[8] Gerrard and Lappert, *J.*, 1951, 2545.
[9] Goubeau and Keller, *Z. anorg. Chem.*, 1951, **267**, 1.
[10] Lappert, *J.*, 1958, 2790.
[11] Goubeau and Keller, *Z. anorg. Chem.*, 1953, **272**, 303.

due to the B–O stretching modes [12,13] in the 1300—1400 cm.$^{-1}$ region, with a maximum absorption at 1334 ± 5 cm.$^{-1}$, except in the metaborates where the maximum occurs at 1380 cm.$^{-1}$.

Experimental

Analyses and molecular-weight measurements were made by the Microanalytical Laboratory, Imperial College.

Preparations.—Triethylsilanol,[14] ethoxytrimethylsilane,[15] trisdiethylaminoboron,[6] phenylboron dichloride,[16] and diphenylboron chloride [16] were prepared by established methods. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics.

Interaction of Boric Acid and Triethylsilanol.—The acid (0·51 g., 1 mol.), triethylsilanol (5·32 g., 5 mol.), and benzene (20 ml.) were heated slowly, and the water–benzene azeotrope allowed to distil off (2 hr.). Careful fractionation of the residue gave hexaethyldisiloxane (1·38 g.), b. p. 60°/1 mm., n_D^{20} 1·4340, and tristriethylsilyl borate (2·94 g., 89% on H_3BO_3 taken), b. p. 120°/1 mm., n_D^{20} 1·4370 (Found: B, 2·68. Calc. for $C_{18}H_{45}O_3BSi_3$: B, 2·73%).

Silanolysis Reactions.—(a) *Triethylborate with triethylsilanol.* The borate (1·60 g., 1 mol.) and silanol (4·32 g., 3 mol.) were slowly fractionated (3 hr.) to yield ethanol (1·19 g., 77%), b. p. 75—80°, n_D^{20} 1·3640. Distillation of the residue produced bistriethylsilyl ether (2·03 g.), b. p. 120°/25 mm., n_D^{20} 1·4260, and tristriethylsilyl borate (1·67 g., 38%), b. p. 184°/20 mm., n_D^{20} 1·4370 (Found: B, 2·74%).

(b) *Tristrimethylsilyl borate with triethylsilanol.* The borate (2·94 g., 1 mol.) and the silanol were kept at 150° and trimethylsilanol was allowed to distil off; this underwent rapid change to bistrimethylsilyl ether (2·38 g., 91·2%), b. p. 100°, n_D^{20} 1·3779, and water (0·25 g., 80%). Distillation of the residual liquid gave tristriethylsilyl borate (3·60 g., 85%), b. p. 184°/20 mm., n_D^{20} 1·4370 (Found: B, 2·71%).

Interaction of Boron Trichloride (1 mol.) and Triethylsilanol (3 mol.) in the Presence of Pyridine (3 mol.).—The chloride (3·46 g.) in light petroleum (15 c.c.) was added (30 min.) to the silanol (11·65 g.) and pyridine (6·97 g.) in light petroleum (30 c.c.) at −80°, with constant shaking. After 24 hr. at 20°, the precipitate was filtered off and washed with light petroleum, and excess of solvent removed (20°/0·5 mm.). Pyridinium chloride (2·35 g.) was washed from the precipitate with water (3 × 20 c.c.) to leave (after being dried at 20°/0·01 mm.) pyridine–boron trichloride (3·70 g.), m. p. 114° (Found: N, 7·3%. Calc. for C_5H_5N,BCl_3: N, 7·1%). Removal of solvent from the filtrate (0°/20 mm.) and subsequent distillation gave a forerun (7·0 g.) (unchanged pyridine and hexaethyldisiloxane) and then tristriethylsilylborate (4·0 g., 34%), b. p. 185°/20 mm., n_D^{20} 1·4378 (Found: B, 2·72%).

Interaction of Sodium Triethylsiloxide and Boron Trichloride.—The siloxide (from 6·18 g. of silanol and 1·10 g. of sodium) in light petroleum (30 c.c.) was treated with boron trichloride (1·84 g.) in light petroleum (10 c.c.) at −70°. After being warmed to 20° the mixture was set aside (2 hr.), and sodium chloride filtered off. Removal of solvent from the filtrate (20°/0·1 mm.) and subsequent distillation of the residue gave tristriethylsilyl borate (4·62 g., 73%), b. p. 183°/17 mm., n_D^{20} 1·4370 (Found: B, 2·69%).

Interaction of Diphenylboron Chloride and Sodium Triethylsiloxide.—The chloride (6·45 g., 1 mol.) in benzene (20 c.c.) was added with constant shaking to sodium triethylsiloxide (4·96 g., 1 mol.) in benzene (25 c.c.), heat was evolved during addition (15 min.), and shaking was continued for 2 hr. Removal of benzene (20°/20 mm.), and subsequent distillation gave *triethylsilyl diphenylborinate* (9·20 g., 97%), b. p. 135°/0·5 mm., d_4^{20} 0·974, n_D^{20} 1·5270 (Found: C, 72·7; H, 8·3; B, 3·6. $C_{18}H_{25}OBSi$ requires C, 73·0; H, 8·8; B, 3·7%).

Interaction of Phenylboron Dichloride and Sodium Triethylsiloxide.—In the same manner we obtained *bistriethylsilyl phenylboronate* (6·30 g., 56%), b. p. 120°/0·2 mm., d_4^{20} 0·928, n_D^{20} 1·4730 (Found: C, 62·0; H, 10·4; B, 3·2. $C_{18}H_{35}O_2BSi_2$ requires C, 61·7; H, 10·0; B, 3·1%).

[12] Webster and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355.
[13] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.
[14] Di Giorgio, Strong, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 1380.
[15] Sauer, *ibid.*, 1944, **66**, 1707.
[16] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

Interaction of Trisdiethylaminoboron and Triethylsilanol.—Triethylsilanol (4·46 g., 3 mol.) was added to trisdiethylaminoboron (2·56 g., 1 mol.); during the addition heat was evolved, and the vessel was kept at 0°. After 30 min., diethylamine (1·84 g., 75%), b. p. 55°, n_D^{20} 1·3860, was removed (20°/15 mm.). The remaining tristriethylsilyl borate (4·45 g., 98%), b. p. 182°/15 mm., n_D^{20} 1·4370 (Found: B, 2·70%), distilled unchanged (n_D^{20} 1·4371).

Attempted Fission of Hexamethyldisiloxane with Phenylboronic Anhydride.—After the compounds had been heated in a sealed tube at 250° (40 hr.) and then cooled, the siloxane (96%) and anhydride (94%) were recovered unchanged.

Interaction of Boric Oxide and Ethoxytrimethylsilane.—The silane (18·67 g.) was refluxed (5 hr.) with boric oxide (7·40 g.). After removal of unchanged boric oxide by filtration, distillation gave triethyl borate (7·87 g., 99%), b. p. 118—120°, n_D^{20} 1·3741 (Found: B, 7·3. Calc. for $C_6H_{15}O_3B$: B, 7·4%), and tristrimethylsilyl borate (11·0 g., 75%), b. p. 186°, n_D^{20} 1·3840 (Found: B, 3·97%. Calc. for $C_9H_{27}O_3BSi_3$: B, 3·89%); a glass-like residue (3·83 g.) remained.

Hydrolysis of Tristrimethylsilyl Borate.—The borate (4·5 g., 1 mol.) was shaken violently (2 hr.) with water (3·0 g., >10 mol.), and the mixture then extracted with ether. Unchanged tristrimethylsilyl borate (2·74 g., 61%), b. p. 84°/20 mm., n_D^{20} 1·3680 (Found: B, 3·8%), was obtained. After similar treatment tristriethylsilyl borate (67%) was also recovered.

Action of Hydrogen Halides on Tristrimethylsilyl Borate.—(a) *Hydrogen chloride.* The gas was passed through the ester in a very slow stream at 0°. There was an immediate evolution of heat and the products set to a solid white mass. Passage of the gas was continued for a further 10 min., then volatile matter was removed (20°/20 mm.). The residue was boric acid (0·497 g., 98%) (Found: B, 17·6. Calc. for H_3BO_3: B, 17·7%). Distillation of the condensate gave trimethylchlorosilane (2·47 g., 95%), b. p. 57°, n_D^{22} 1·3874 (Found: Cl, 31·9. Calc. for C_3H_9ClSi: Cl, 32·7%).

(b) *Hydrogen bromide.* In a similar manner we obtained boric acid (0·768 g., 88%) (Found: B, 17·9%), and trimethylbromosilane (6·28 g., 98%), b. p. 81°, n_D^{19} 1·4132 (Found: Br, 51·7. Calc. for C_3H_9BrSi: Br, 52·3%).

Formation of the Silyl Metaborates.—(a) *Trimethylsilyl metaborate.* Tristrimethylsilyl borate (5·16 g., 1 mol.) and boric oxide (1·41 g., 1·1 mol.) were heated (30 hr.) in a sealed tube at 225°. Only small traces of solid boric oxide then remained, and the mixture was poured into ether (20 c.c.) and stored (24 hr.) in a stoppered flask. After filtration, solvent was removed (20°/0·1 mm.) to leave *trimethylsilyl metaborate* (5·63 g., 87%), d_4^{20} 0·988, n_D^{20} 1·4101 (Found: C, 30·4; H, 7·4; B, 9·5%; *M*, 331. $C_9H_{27}O_6B_3Si_3$ requires C, 31·0; H, 7·8; B, 9·3%; *M*, 348), as a slightly viscous liquid.

(b) *Triethylsilyl metaborate.* Tristriethylsilyl borate and boric oxide reacted as described in (a) to produce *triethylsilyl metaborate* (7·65 g., 84%), d_4^{20} 0·955, n_D^{20} 1·4360 (Found: C, 46·2; H, 8·9; B, 6·9%; *M*, 450. $C_{18}H_{45}O_6B_3Si_3$ requires C, 45·5; H, 9·5; B, 6·8%; *M*, 474).

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