

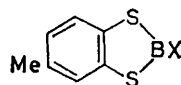
## 5-Methyl-1,3,2-benzodithiaborole and Related Compounds

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Reactions of 2-chloro-5-methyl-1,3,2-benzodithiaborole (I), obtained from toluene-3,4-dithiol and trichloroborane, with bis(trimethylsilyl)amine and tris(trimethylsilyl)amine have been studied. Tris-(5-methyl-1,3,2-benzodithiaborol-2-yl)amine, bis-(5-methyl-1,3,2-benzodithiaborol-2-yl)amine, and bis-(5-methyl-1,3,2-benzodithiaborol-2-yl)(trimethylsilyl)amine have been prepared. Tributyltin hydride converts (I) into 5-methyl-1,3,2-benzodithiaborole, which forms a stable complex with diethylamine.

1,3-DITHIA-2-BORACARBOCYCLES are little known.<sup>1</sup> Only a few such derivatives of ethane-1,2-dithiol and propane-1,3-dithiol have been described,<sup>2</sup> and a brief mention of 2-phenyl-1,3,2-benzodithiaborole has been made.<sup>3</sup> Boron heterocycles derived from toluene-3,4-dithiol are described in the present paper.

Toluene-3,4-dithiol reacted sluggishly with trichloroborane, and 2-chloro-5-methyl-1,3,2-benzodithiaborole (I) was obtained as a volatile colourless liquid. The dithiaborole (I) could be converted quantitatively into 5-methyl-1,3,2-benzodithiaborole (II) by reduction with



(I) X = Cl

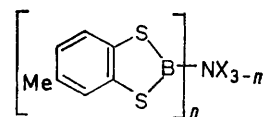
(II) X = H

tributyltin hydride. Unlike bis(alkylthio)boranes, which tend to disproportionate readily, compound (II) is thermally stable and can be distilled unchanged under reduced pressure. It readily forms a solid 1 : 1 complex with diethylamine which sublimes unchanged at 160—180° and 0.5 mmHg.

Chloroboranes have been shown to cleave the Si-N bond readily to give aminoboranes.<sup>4</sup> The 2-chloroborole (I) reacted with an equimolar amount of bis(trimethylsilyl)amine giving bis-(5-methyl-1,3,2-benzodithiaborole-2-yl)amine (III) as a sublimable solid. A similar

<sup>1</sup> H. Steinberg, 'Organoboron Chemistry,' vol. 1, Interscience, New York, 1964, pp. 187—239; R. H. Cragg and M. F. Lappert, *Organometallic Chem. Rev.*, 1966, **1**, 43; B. M. Mikhailov, *Progr. Boron Chem.*, 1970, **3**, ch. 5.

reaction with tris(trimethylsilyl)amine afforded bis-(5-methyl-1,3,2-benzodithiaborol-2-yl)(trimethylsilyl)amine (IV) as a distillable low-melting solid.



(III) n = 2, X = H

(IV) n = 2, X = SiMe<sub>3</sub>

(V) n = 3

Treatment of the mixed borylsilylamine with methanol (1 mol equiv.) resulted in preferential cleavage of the Si-N bond with the formation of the diborylamine (III). However, with an excess of methanol, toluene-3,4-dithiol was finally obtained.

Tris(trimethylsilyl)amine, even with an excess of the 2-chloroborole (I), gave (IV) as the final product. Tris-(5-methyl-1,3,2-benzodithiaborol-2-yl)amine (V), however, could be obtained easily from the diborylamine (III) and the 2-chloroborole (I) in the presence of triethylamine. It is a stable, white, sublimable solid.

### EXPERIMENTAL

*2-Chloro-5-methyl-1,3,2-benzodithiaborole* (I).—Hydrogen chloride was evolved slowly (5 h) from a mixture of tri-

<sup>2</sup> M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 1345; A. Finch and J. Pearn, *Tetrahedron*, 1964, **20**, 173; B. Z. Egan, S. G. Shore, and J. E. Bonnell, *Inorg. Chem.*, 1964, **3**, 1024.

<sup>3</sup> M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 1958, 3076.

<sup>4</sup> O. J. Scherer, *Organometallic Chem. Rev. (A)*, 1968, **3**, 281.

chloroborane (10.0 g, 85 mmol) and toluene-3,4-dithiol (10.0 g, 64 mmol). Removal of the excess of trichloroborane *in vacuo* and distillation of the residue yielded the 2-chloroborole (I) (10.93 g, 85%) as a liquid, b.p. 103–105° at 1.0 mmHg;  $\nu_{\max}$  3050w, 1595m, 1465s, 1155w, 1050m, 1020vs, 980vs, 920vs, 870m, and 810s  $\text{cm}^{-1}$  (Found: C, 41.7; H, 3.1; B, 5.5.  $\text{C}_7\text{H}_6\text{BClS}_2$  requires C, 41.9; H, 3.0; B, 5.4%).

*5-Methyl-1,3,2-benzodithiaborole* (II).—An exothermic reaction occurred on adding tributyltin hydride (4.55 ml, 18.0 mmol) to 2-chloro-5-methyl-1,3,2-benzodithiaborole (3.45 g, 17.2 mmol) under nitrogen. The mixture was heated at 90° for 2 h and then fractionated to give the borole (II) (2.58 g, 90%) as the lower boiling fraction (b.p. 75–77° at 0.8 mmHg);  $\tau$  (neat) 7.9 (3H, s) and 2.55–3.4 (3H, m);  $\nu_{\max}$  3050w, 2605vs (B–H), 1595m, 1465s, 1155w, 1120w, 1080m, 1070s, 1020w, 1010s, 870m, and 810s  $\text{cm}^{-1}$  (Found: C, 50.3; H, 4.2; B, 6.4.  $\text{C}_7\text{H}_7\text{BS}_2$  requires C, 50.6; H, 4.25; B, 6.5%).

*5-Methyl-1,3,2-benzodithiaborole-Diethylamine Adduct*.—The borole (1.10 g, 6.6 mmol) was added to diethylamine (1.4 g, 19.1 mmol) at 0°. After the mixture had attained room temperature, the excess of diethylamine was removed *in vacuo* leaving a solid adduct (1.5 g), which sublimed unchanged at 160–180° and 0.5 mmHg;  $\tau$  ( $\text{CS}_2$ ) 8.98 (6H, t,  $J$  7.0 Hz), 7.86 (3H, s), 6.98 (4H, q,  $J$  7.0 Hz), and 2.75–3.45 (3H, m);  $\nu_{\max}$  3080s, 2470s (B–H), 1585w, 865m, and 805s  $\text{cm}^{-1}$  (Found: C, 55.4; H, 7.6; B, 4.4; N, 5.6.  $\text{C}_{11}\text{H}_{18}\text{BNS}_2$  requires C, 55.2; H, 7.6; B, 4.5; N, 5.85%).

*Bis-(5-methyl-1,3,2-benzodithiaborol-2-yl)amine* (III).—An exothermic reaction occurred between bis(trimethylsilyl)amine (0.95 g, 5.9 mmol) and the 2-chloroborole (I) (2.34 g, 11.7 mmol) in benzene (15 ml). On removing trimethylchlorosilane and solvent, the diborylamine was obtained as a solid residue (1.94 g, 95%) which sublimed at 180° and 0.6 mmHg;  $\nu_{\max}$  3350m, 1590w, 1150m, 1120m, 1050m, 970m, 950s, 865w, 855w, 810s, and 800s  $\text{cm}^{-1}$  (Found: C, 48.5; H, 3.9; B, 6.1.  $\text{C}_{14}\text{H}_{13}\text{B}_2\text{NS}_4$  requires C, 48.7; H, 3.8; B, 6.3%).

*Bis-(5-methyl-1,3,2-benzodithiaborol-2-yl)(trimethylsilyl)amine* (IV).—A mixture of tris(trimethylsilyl)amine (1.64 g, 7.0 mmol) and the 2-chloroborole (I) (4.20 g, 21.0 mmol) was heated at 120–130° for 3 h and the liberated chlorotrimethylsilane was removed *in vacuo*. The process was repeated but no chlorotrimethylsilane appeared to be formed. Distillation of the residue (4.3 g) gave unchanged (I) (1.2 g) (b.p. 80° at 1 mmHg) and the trimethylsilyl-diborylamine (2.2 g, 75%), b.p. 230° at 0.1 mmHg, as a low melting, waxy solid,  $\tau$  ( $\text{CCl}_4$ ) 9.57 (9H, s), 7.70 (6H, s), and 2.6–3.3 (6H, m),  $\nu_{\max}$  3050w, 1595m, 1465s, 1415s, 1250s, 880s, 840s, 810s, and 770m  $\text{cm}^{-1}$  (Found: C, 49.2; H, 5.2; B, 5.1.  $\text{C}_{17}\text{H}_{21}\text{B}_2\text{NS}_4\text{Si}$  requires C, 48.9; H, 5.1; B, 5.2%).

*Methanolysis of the Borylsilylamine* (IV).—(a) Methanol (0.11 g, 3.4 mmol) in benzene (2 ml) was added dropwise to the trimethylsilyldiborylamine (IV) (1.30 g, 3.1 mmol) in benzene (5 ml). The mixture was stirred for 0.5 h and dried *in vacuo*, leaving the diborylamine (III) (1.03 g), which sublimed at 180° and 0.6 mmHg (authentic i.r. spectrum).

(b) A mixture of (IV) (0.5 g) and methanol (20 ml) was refluxed and distilled. Toluene-3,4-dithiol (0.35 g; authentic i.r. spectrum) was obtained on drying the residue, *in vacuo*.

*Tris-(5-methyl-1,3,2-benzodithiaborol-2-yl)amine* (V).—A mixture of the diborylamine (III) (1.38 g, 4.0 mmol), the 2-chloroborole (I) (0.81 g, 4.0 mmol), and triethylamine (0.76 g, 7.5 mmol) in benzene (25 ml) was refluxed for 4 h. Benzene was removed and the residue was repeatedly washed with hot chloroform until the product (1.9 g) gave a negative test for chloride ion. The triborylamine was purified by sublimation at 230° and 0.5 mmHg;  $\nu_{\max}$  1595w, 1275s, 1235s, 1150m, 1120m, 1050w, 970w, 950w, 940w, 920m, 865m, and 805s  $\text{cm}^{-1}$  (Found: C, 49.8; H, 3.5; B, 6.2.  $\text{C}_{21}\text{H}_{18}\text{B}_3\text{NS}_6$  requires C, 49.55; H, 3.6; B, 6.4%).

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