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Chemistry of Boranes. XII.[1] Structure of Alkylthioboranes

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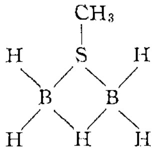
The alkylthio group is shown to occupy exclusively a bridging position in $CH_3SB_2H_5$, $[C_2H_5SBH_2]_3$, and $[n\text{-}C_4H_9SBH_2]_3$. Reaction of alkanethiols and diborane in approximately a 3:1 molar ratio yields polymeric alkylthioboranes that slowly depolymerize at 25° to a mixture of $(RS)_3B$ and $[RSBH_2]_3$. In these metastable polymers, B–S–B rather than B–H–B bonds serve as the associating units.

There are relatively few alkylthio derivatives of the simpler boron hydrides. The first to be reported was methylthiodiborane, $CH_3SB_2H_5$.[2] More recently a series of compounds was formulated as tris- and tetrakis-(alkylthio) derivatives of diborane,[3,4] but these reports were later corrected, and the compounds were described as trimers of $RSBH_2$.[5] We undertook an investigation of these various alkylthio derivatives and wish to report some definitive structural analyses.

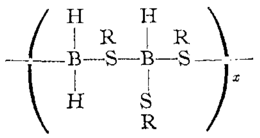
Results

The B^{11} n.m.r. spectrum of $CH_3SB_2H_5$ at −78° is a 1:2:1 triplet, showing that the boron atoms are equivalent and each is strongly coupled (135 c.p.s.) to two hydrogen atoms. Each component of the triplet is further split into a doublet of 35 c.p.s. separation; this magnitude of J_{BH} is in the range typical of the coupling of a boron atom to a bridge hydrogen atom.[6] These n.m.r. data uniquely establish the diborane structure 1 in which the sulfur atom is in a bridge position as originally proposed by Burg and Wagner.[2]



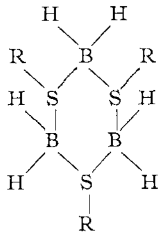
1

Reaction of diborane with ethanethiol in a 1:3 molar ratio at 25° yields a viscous composition that can be vacuum distilled at 90° to give a clear, colorless, viscous liquid that analyzes for $(C_2H_5S)_3B_2H_3$ as originally formulated by Shchegoleva and Belyazskaya.[4] This viscous liquid has a unique infrared spectrum and the composition is reproducible. This must be an associated species of the type shown as 2. The only basis for placing all hydrogen atoms in terminal positions is the absence of bridge BH stretching absorption in the infrared.



2

The viscous species, 2, disproportionates or depolymerizes on standing to give a clear mobile liquid that is a mixture of $(C_2H_5S)_3B$ and $[C_2H_5SBH_2]_3$. This point was established by the identity of the infrared and n.m.r. spectra of the mixture with an authentic mixture of these compounds and by the removal of $(C_2H_5S)_3B$ from the mixture by hydrolysis to ethanethiol and boric acid to leave the hydrolytically stable trimer. The identity of $[C_2H_5SBH_2]_3$ was established by analysis and molecular weight determinations. The B^{11} n.m.r. spectrum of the trimer is a broad peak (+31 p.p.m., ~500 c.p.s. wide at half height) at 25°. At 90° the trimer has a B^{11} resonance consisting of a 1:2:1 triplet (J_{BH} = 122 c.p.s.) establishing identity of boron atom environments and strong coupling of each boron atom with two hydrogen atoms.[7] Irradiation at 60 Mc. collapses the B^{11} triplet to a single peak. These data are consistent only with structure 3.



3

Reaction of diborane and ethanethiol in a 1:2 ratio followed by short-path distillation at 50° gives the

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[1] Paper XI: N. E. Miller, H. C. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 866 (1964).

[2] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

[3] B. M. Mikhailov and T. A. Shchegoleva, *Proc. Acad. Sci. USSR, Chem. Div.*, **131**, 321 (1960).

[4] T. A. Shchegoleva and E. M. Belyazskaya, *ibid.*, **136**, 123 (1961).

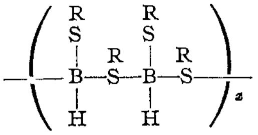
[5] B. M. Mikhailov, T. A. Shchegoleva, E. M. Shashkova, and V. D. Sheludyakov, *Bull. Acad. Sci. USSR, Chem. Div.*, 1143 (1962).

[6] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

[7] The temperature dependence of the n.m.r. spectra suggests that an intermediate rate of quadrupolar relaxation is responsible for the broad resonance at 25°. Viscosity has a significant effect. Solutions of the trimer in toluene or ether show the triplet structure as low as 0–25°. The B^{11} spectrum of such solutions sharpens on temperature increase and broadens progressively on temperature decrease. No signal was observed below about −60°. A referee pointed out an alternative explanation of the B^{11} n.m.r. temperature dependence. The B–S ring system is probably nonplanar and the hydrogen atoms on each boron atom would then be nonequivalent. "Fast" and "intermediate" rates of interconversion of axial and equatorial hydrogen atoms could be invoked to describe the triplet and the broad B^{11} spectrum observed at 90° and 25°, respectively. We were, however, unable to produce a B^{11} spectrum at low temperatures that would reflect a boron atom coupled to two nonequivalent hydrogen atoms.

trimer $[C_2H_5SBH_2]_3$. The trimer is decomposed by distillation at 90°. The distillate under these conditions is the viscous material $[(C_2H_5S)_3B_2H_3]_x$, which reverts on standing to a mixture of $(C_2H_5S)_3B$ and $[C_2H_5SBH_2]_3$.

Reaction of 1-butanethiol and diborane gives a viscous material that possesses a unique infrared spectrum and the empirical composition $(C_4H_9S)_2BH$. Reproducibility of the spectrum and composition indicates that this obviously associated material is a single species. Absence of a bridge BH stretching frequency in the infrared suggests an associated species like **4**. This compound, like the ethanethiol-diborane reaction product, disproportionates on standing to a mixture of $(n\text{-}C_4H_9S)_3B$ and $[n\text{-}C_4H_9SBH_2]_3$, a point which was established by a procedure as described above for the ethanethiol system. The B^{11} resonance of the trimer is a broad peak at room temperature at +31 p.p.m. (about 1000 c.p.s. wide at half-height). The resonance sharpens somewhat at 100° (half-height width of 600 c.p.s.) but not enough to show fine structure.



4

The infrared and n.m.r. data clearly establish that in all these alkylthioboranes of structures **1** through **4** the sulfur atom of the alkylthio group preferentially serves as a bridging element. This suggested to us the possibility that the tris(alkylthio)boranes are associated through sulfur bridges; however, we found the molecular weight of $(C_2H_5S)_3B$ to be precisely that of the monomer by ebullioscopic molecular weight determinations in benzene. Burg and Wagner[2] had earlier established the monomeric character of gaseous $(CH_3S)_3B$.

It should be noted that the later article by Mikhailov, *et al.*, is not correct in detail. They have revised their earlier data and concluded that the alkanethiol-diborane reaction produces polymeric $RSBH_2$ and that this polymer rearranges to the trimer. Our data clearly indicate the initial products from diborane and alkanethiol (~1:3 molar ratio) are associated species of specific compositions $[(C_2H_5S)_3B_2H_3]_x$ and $[(n\text{-}C_4H_9S)_4B_2H_2]_x$ which disproportionate on standing to mixtures of $(RS)_3B$ and $[RSBH_2]_3$. The polymers can be regenerated by thermal decomposition of the $RSBH_2$ trimers, and the regenerated polymer, on standing, gives not simply $[RSBH_2]_3$ but mixtures of $[RSBH_2]_3$ and $(RS)_3B$. The trimeric species, $[RSBH_2]_3$, can be *directly* obtained from the reaction of diborane and alkanethiol in 1:2 molar ratio; essentially no polymeric or viscous species is generated under these conditions.

Experimental

The reagents used are all commercially available and were used without purification. Diborane (98+%) was purchased in cylinders from the Callery Chemical Co.

The B^{11} n.m.r. spectra were obtained with a Varian high-resolution spectrometer using a 19.2-Mc. regulated temperature probe. An NMR Specialities Model SD 60 spin decoupler was used in the double irradiation experiments.[8] Trimethyl borate was employed as an external reference. Chemical shift data are considered approximate because the concentration dependence was not examined.

$CH_3SB_2H_5$.—Solid $(BH_2SCH_3)_x$ was prepared by the method of Burg and Wagner[2] from 92 mmoles (4.4 g.) of methanethiol and 46 mmoles (1.28 g.) of diborane. In 63 hr. at −78°, 60 mmoles of hydrogen had been released, an indication that a 67% yield of $(BH_2SCH_3)_x$ had been realized. The excess reactants were removed at room temperature to leave a white solid residue of $(BH_2SCH_3)_x$. The solid was heated to 90°, and diborane was recirculated over it and through a −95° trap at 500 mm. pressure. When the pressure decrease indicated that 30 mmoles (2.2 g.) of product had formed, the pyrolysis was stopped and the excess diborane removed. The contents of the trap were fractionated by passing through traps at −78, −95, and −196°. The material in the −95° trap was $CH_3SB_2H_5$, vapor pressure 2 mm. at −55° and m.p. −99 to −100° (lit.[2] vapor pressure 1.86 mm. at −57.4° and m.p. −101°).

Anal. Calcd. for hydrolysis of $CH_3SB_2H_5$ (in mmoles/g.): boric acid, 271; H_2, 678; CH_3SH, 136. Found: boric acid, 265; H_2, 667; CH_3SH, 131.

$(C_2H_5S)_3B_2H_3$ and $(C_2H_5SBH_2)_3$.—Following the directions of Shchegoleva and Belyazskaya,[4] 5.4 g. (0.2 mole) of diborane was introduced as a gas into a solution of 44 ml. (37.2 g., 0.6 mole) of ethanethiol in 100 ml. of ether over a 5–8-hr. period at room temperature. Hydrogen was evolved steadily during this time. The mixture stood overnight at room temperature. The solvent was removed and the viscous residue (13 g.) distilled through a fractionating column. The very viscous distillate, b.p. 90–100° (1 mm.), 9.1 g. (22%), became mobile on standing.

Anal. Calcd. for $B_2H_3(SC_2H_5)_3$: C, 34.6; H, 8.7; B, 10.4; S, 46.2. Found: C, 34.7; H, 9.1; B, 10.5; S, 46.1.

The infrared spectrum of the viscous distillate had absorption in the B–H stretching region at 2480–2420 (s) and 2250 (w) cm.$^{-1}$. The spectrum was best characterized by bands at 990 (s), 860 (w), and 705 (w and broad) cm.$^{-1}$ not shown by $(C_2H_5SBH_2)_3$ or $(C_2H_5S)_3B$.

The viscosity of the distillate decreased over several days. The infrared bands at 705, 860, and 990 cm.$^{-1}$ disappeared. New bands appeared at 765, 920, and 955 cm.$^{-1}$, characteristic of $(C_2H_5S)_3B$, and at 975 cm.$^{-1}$, characteristic of $(C_2H_5SBH_2)_3$.

When a 0.4394-g. portion of the product which had become mobile upon standing at room temperature for several days was treated with water in a vessel attached to a vacuum line, only about 1.6 mmoles of hydrogen and about the same amount of ethyl mercaptan were formed. This amounts to less than one-fourth the 14.4 mmoles/g. expected according to eq. 1.

$$B_2H_3(SC_2H_5)_3 + 6H_2O \longrightarrow 2B(OH)_3 + 3HSC_2H_5 + 3H_2 \quad (1)$$

Considerable water-insoluble liquid was left. Further hydrolysis was not apparent, even when concentrated sulfuric acid was added and the mixture heated to 40–50° in the absence of oxygen.

The infrared spectrum of the water-treated phase no longer exhibited the bands characteristic of $(C_2H_5S)_3B$ at 765, 920, and 955 cm.$^{-1}$ which were present in the starting material.

A large sample of distilled product which had aged several days at room temperature was stirred with water for 1 day at room temperature and the organic phase was separated and dried over calcium sulfate for 1 week. Vacuum distillation (~1 mm.) through a fractionating column (pot temperature ~100°) gave a viscous distillate having an infrared spectrum like that of $(C_2H_5S)_3B_2H_3$. However, vacuum distillation (<1 μ) in a short-path still at a temperature somewhat above 50° gave a fluid distillate of the $C_2H_5SBH_2$ trimer.

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[8] We are grateful to Mr. C. B. Matthews for his assistance in obtaining the B^{11} spectra.

Anal. Calcd. for $B_3H_6(SC_2H_5)_3$: C, 32.5; H, 9.5; B, 14.6; S, 43.4; mol. wt., 222. Found: C, 33.0; H. 9.4; B, 14.5; S, 44.1; mol. wt., 223 (cryoscopic, benzene).

The infrared spectrum of $B_3H_6(SC_2H_5)_3$ had the following absorptions: 3000 (w), 2480 (s), 2420 (s), 2250 (w), 1450 (m), 1375 (m), 1265 (m), 1130 (m), 1110 (w), 1070/1040/1025 (s), 975 (m), 920 (w), 775 (w) cm.$^{-1}$.

$(C_2H_5SBH_2)_3$ was easily prepared in larger amounts as follows. The $C_2H_5SH–B_2H_6$ reaction was carried out in ether as described above using a 2:1 ratio of reactants. The product was then distilled in a molecular still at 1 μ or less at a pot temperature of less than 60° to give a 70% yield of the fluid trimer.

$(C_4H_9S)_2B_2H_4$.—A 500-ml. flask with side arm and magnetic stirrer was connected through a reflux condenser to a mercury leg and flushed with nitrogen. A solution of 49 ml. (0.45 mole) of 1-butanethiol in 50 ml. of absolute ether was stirred in the flask under nitrogen as 3.4 g. (0.126 mole) of diborane was introduced by a gas inlet just under the surface of the liquid. The addition took 2 hr., and a viscous solution resulted. After 16 hr., the volatiles were removed, and the viscous residue was distilled in a 24-in. spinning-band column. A viscous distillate (12–13 g.) was collected, b.p. 98° (1 mm.), $n^{24}\text{D}$ 1.5153 (lit.[3] 98–102° (1 mm.), $n^{20}\text{D}$ 1.5170). The viscous distillate became mobile after several hours.

Anal. Calcd. for $[BH(SC_4H_9)_2]_x$: C, 50.5; H, 10.1; B, 5.7; S, 33.7. Found: C, 50.4; H, 10.5; B, 6.7; S, 33.5.

A sample of this product was stirred with water for several hours. The white solid which formed (boric acid) was filtered off, and the filtrate was extracted with petroleum ether. The organic layer was dried and distilled under vacuum in a molecular-type still. Solvent was removed and a fluid liquid distilling at 90–100° at 3 μ was collected.

Anal. Calcd. for $(BH_2SC_4H_9)_3$: C, 47.1; H, 10.9; B, 10.6; S, 31.4; mol. wt., 305. Found: C, 47.8; H, 10.7; B, 10.9; S, 31.7; mol. wt., 301 (cryoscopic, benzene).

The infrared spectrum of this compound showed the following absorptions: 2960 (s), 2860 (s), 2470 (s), 2410 (s), 2245 (w), 1460 (m), 1428 (m), 1379 (m), 1275 (m) triplet, 1227 (w), 1130 (m), 1105 (m), 1040 (s), 980 (m), 910 (w), 875 (w), 785 (w), 745 (m), shoulder at 725 cm.$^{-1}$.

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The Crystal Structure of Lithium Aluminum Tetraethyl[1a]

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The crystal structure of $LiAl(C_2H_5)_4$ has been determined by X-ray diffraction methods. The structure of the compound is analogous to that of dimethylberyllium and consists of linear chains of alternating lithium and aluminum. The locations of the ethyl groups are such that the structure can be largely accounted for in terms of Li^+ and $Al(C_2H_5)_4^-$ ions, although there is some evidence of weak covalent interaction involving lithium. The proton and lithium n.m.r. spectra in ether demonstrate that extensive dissociation into ethyllithium and triethylaluminum does not occur.

The concept of electron-deficient, or multi-center, bonding in covalent alkyl and hydride compounds of group I, II, and III elements is widely recognized.[2-6] For the most part, however, examples of such bonding are restricted to symmetrical cases of the form $A–M_n$, where A is the bridging atom (hydrogen or carbon) and M are the atoms joined by the multi-center bond (B, Be, Mg, Al, Li, etc.). Some asymmetry in the bridge bond may occur where M atoms, although of the same element, are in slightly different environments, as in the B–H–B bridge bonds in tetraborane-10.[3]

Lithium aluminum tetraethyl, $LiAl(C_2H_5)_4$, provides an example in which asymmetric bridge bonding joining two different elements may occur. As a naïve but suggestive way of viewing the compound, it may be compared with beryllium dialkyls. Dimethylberyllium in the solid state consists of linear chains of beryllium atoms joined by bridging carbon atoms. The arrangement of four carbon atoms about each beryllium is roughly tetrahedral. A similar structure may be predicted for lithium aluminum tetraethyl, with alternate atoms replaced by aluminum and the remainder by lithium. The bridge bonding in such a structure should be quite asymmetric, since aluminum possesses much greater bond-forming capacity than lithium. The structure may in fact approach a limiting ionic form of alternating Li^+ and AlR_4^- ions.

We report here the results of a study of lithium aluminum tetraethyl, undertaken with the above considerations in mind. Preparative procedures have been reported for both $LiAl(CH_3)_4$[8] and $LiAl(C_2H_5)_4$.[9] The ethyl derivative is more conveniently worked with and is more desirable also in that location of the β-carbon atom of the alkyl group provides very useful information.

Experimental

All preparative work involving metal alkyls and their solutions was carried out in an inert atmosphere glove box, under a

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(1) (a) Presented at the International Conference on Organometallic Chemistry, Cincinnati, Ohio, June, 1963; (b) Alfred P. Sloan Foundation Fellow. Address correspondence and requests for reprints to T. L. Brown.

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