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Abstract

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SYNTHESIS AND CERTAIN TRANSFORMATIONS OF ALKYLMERCAPTODIBORANES

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In a letter to the editor (^{1}) we reported on the reaction between diborane and mercaptans. We have studied the interaction of diborane with *n*-propyl mercaptan or *n*-butyl mercaptan in ether solution at room temperature, with various ratios of the reagents.

When an excess of mercaptan is used, the principal product of the reaction is tetraalkylmercaptodiborane

$$B_2H_6 + 4RSH \rightarrow (RS)_2BHBH(SR)_2 + 4H_2,$$

$$R = \text{n-}C_3H_7, \quad \text{n-}C_4H_9.$$

These compounds are distinguished by considerable stability. They do not change on prolonged storage and can be distilled in vacuo. It is interesting to note that tetraalkylmercaptodiboranes distil as extremely viscous liquids, which after several hours again become mobile. Determination of the molecular weight by the cryoscopic method gives a value approximately 1.5 times smaller than the molecular weight of the dimeric form of the dialkylmercaptoborane. Evidently, in benzene solution the alkylmercapto derivatives of diborane obtained undergo partial dissociation. When the reaction between diborane and *n*-butyl mercaptan is carried out with the reagents taken in a ratio of 1 : 2, considerably less tetra-*n*-butylmercaptodiborane is obtained, and the chief product formed is di-*n*-butylmercaptodiborane, $C_4H_9SBH_2BH_2SC_4H_9$. This compound is unstable and even on standing at room temperature symmetrizes into diborane and tetra-*n*-butylmercaptodiborane. To identify di-*n*-butylmercaptodiborane we used its ability to react with olefins at room temperature with formation of *n*-butyl esters of dialkylthioboric acids

$$[(C_4H_9S)BH_2]_2 + 4CH_2{=}CHR \rightarrow 2C_4H_9SB(CH_2CH_2R)_2.$$

When propylene was passed through the reaction mixture obtained from the interaction of diborane and *n*-butyl mercaptan (reagent ratio 1 : 2), tri-*n*-propylborane (8%) was obtained, formed from unreacted diborane, as well as the *n*-butyl ester of di-*n*-propylthioboric acid (40%) and tetra-*n*-butylmercaptodiborane (24%), which under these conditions does not react with propylene. If, however, propylene is passed through a reaction mixture that has stood overnight, more tri-*n*-propylborane (18%) and tetra-*n*-butylmercaptodiborane (37%) are obtained, while very little *n*-butyl ester of di-*n*-propylthioboric acid is formed (5%).

Di-*n*-butylmercaptodiborane can be obtained by the action of diborane on tetra-*n*-butylmercaptodiborane; however, its yield is very small,

since an equilibrium is established between the starting reagents and the reaction product, expressed by the following equation:

$$(C_4H_9S)_2BHBH(SC_4H_9)_2 + B_2H_6 \rightleftarrows 2C_4H_9SBH_2BH_2SC_4H_9.$$

It should be noted that Berg and Wagner, in the interaction of diborane and methyl mercaptan in the gas phase, obtained a polymer of composition $(CH_3SBH_2)_x$ (^{2}). Tetraalkylmercaptodiboranes possess very interesting chemical properties. The hydrogen atoms in these compounds are considerably less reactive than in diborane. This is indicated first of all by the fact that, under the conditions of synthesis of these compounds, in the presence of a large excess of mercaptan, no trialkylthioborate is formed. The reaction of tetraalkylmercaptodiborane with mercaptan begins only at 50–60° and proceeds fairly vigorously at the boiling temperature of the mercaptan. As a result, trialkylthioborate is obtained:

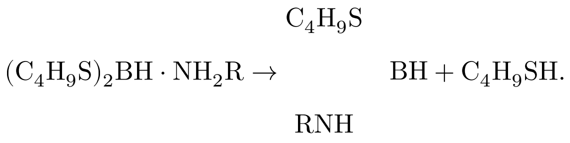
$$[(RS)_2BH]_2 + 2RSH \rightarrow 2(RS)_3B + 2H_2, \quad R = n\text{-}C_3H_7,\ n\text{-}C_4H_9.$$

When tetra-*n*-butylmercaptodiborane is treated with water or alcohol at room temperature, no evolution of hydrogen occurs. Under the same conditions, by the action of primary amines (ethylamine, *n*-butylamine) on tetra-*n*-butylmercaptodiborane, N-trialkylborazoles were obtained.

Apparently, in the first stage of the process a complex of dialkylmercaptoborane with the amine (I) is formed, which, with elimination of mercaptan, is converted into alkylmercapto-alkylaminoborane (II). From the latter, with elimination of mercaptan, an N-alkyl derivative of borazole is obtained

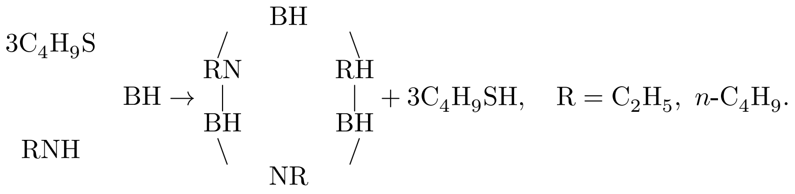
$$[(C_4H_9S)_2BH]_2 + 2RNH_2 \rightarrow 2(C_4H_9S)_2BH \cdot NH_2R,$$

I



$$(C_4H_9S)_2BH \cdot NH_2R \rightarrow \begin{matrix} C_4H_9S & \\ & BH \\ RNH & \end{matrix} + C_4H_9SH.$$

II



$$3\begin{matrix} C_4H_9S & \\ & BH \\ RNH & \end{matrix} \rightarrow \begin{array}{ccccc} & & BH & & \\ & / & & \backslash & \\ & RN & & RH & \\ & | & & | & \\ & BH & & BH & \\ & \backslash & & / & \\ & & NR & & \end{array} + 3C_4H_9SH, \quad R = C_2H_5,\ n\text{-}C_4H_9.$$

The great strength of the B—H bond in tetraalkylmercaptodiboranes is also manifested in reactions with olefins. We were able to carry out the addition of tetra-*n*-butylmercaptodiborane to olefin hydrocarbons by heating the reagents at 70° in the presence of pyridine.

Experimental Part

All operations with organoboron compounds were carried out in an atmosphere of nitrogen. Diborane was synthesized in 80–85% yield from boron trifluoride etherate and lithium aluminum hydride (^{3}).

1. **Tetra-*n*-butylmercaptodiborane.** A solution of 40.5 g (0.45 mole) of *n*-butyl mercaptan in 50 ml of absolute ether was placed in a three-necked flask equipped with a stirrer with a mercury seal, a gas inlet, and a reflux condenser. Diborane (0.055 mole) was passed in at room temperature for 2 hours; during this time the reaction mixture became warm and viscous. On the following day, the ether was removed in vacuo with a water-jet pump, and the residue was distilled. 15.7 g of tetra-*n*-butylmercaptodiborane was obtained, b.p. 98–103° at 2 mm. Yield 75%. After additional

on distillation the substance had b.p. 89–90° at 1 mm, d_4^{20} 0.9561; n_D^{20} 1.5170.

Found, %:	C 50.58; 50.45;	H 10.30; 10.38;	B 5.81, 5.54
$C_{16}H_{38}B_2S_4$. Calculated, %:	C 50.52;	H 10.07;	B 5.68

Mol. wt. 256, 258*; calculated 380.

On distillation of tetra-*n*-butylmercaptodiborane, 2.1 g of liquid (boron content 9.29%) condensed in a trap cooled to −70°, which is probably a mixture of boron hydrides with a lower degree of substitution.

2. Tetra-*n*-propylmercaptodiborane. In analogous fashion, from 34.3 g (0.45 mole) of *n*-propyl mercaptan and 0.055 mole of diborane, 10.0 g (56%) of tetra-*n*-propylmercaptodiborane was obtained, b.p. 93-95° at 4 mm, d_4^{20} 0.9809; n_D^{20} 1.5265.

Found, %:	C 44.37; 44.67;	H 9.52; 9.54;	B 6.24; 6.50
$C_{12}H_{30}B_2S_4$. Calculated, %:	C 44.45;	H 9.33;	B 6.67

Mol. wt. found 239, 237; calculated 324.

3. Reaction of diborane and *n*-butyl mercaptan at a reagent ratio of 1:2. The experiment was carried out analogously to the preparation of tetra-*n*-butylmercaptodiborane. 0.07 mole of diborane was passed over 4 hr into a solution of 12.6 g (0.14 mole) of *n*-butyl mercaptan in 75 ml of abs. ether. After the gaseous diborane that had not entered into reaction was displaced with nitrogen, a slow stream of propylene was passed through the reaction mixture for 2 hr. The reaction with propylene was accompanied by heating. The ether was distilled off in a water-pump vacuum, and the residue was subjected to fractional distillation. The following fractions were obtained: 1) 48-50° at 11 mm −1.5 g; 2) 64-70° at 2 mm −10.4 g; 3) 98-105° at 2 mm −6.4 g. During distillation of the last fraction, 0.6 g of substance (B content 10.11%) was collected in a trap cooled to −70°.

The first fraction is tri-*n*-propylborane, yield 7.9%, calculated on the diborane taken into the reaction, n_D^{20} 1.4100 (lit. b.p. 62°/20 mm, $n_D^{22.6}$ 1.4135 (4)). The second fraction is the *n*-butyl ester of di-*n*-propylthioboric acid, yield 0.056 mole (40%), n_D^{20} 1.4563 (lit. b.p. 98°/11 mm, n_D^{20} 1.4598 (5)). The third fraction is tetra-*n*-butylmercaptodiborane, yield 0.017 mole (24%), n_D^{20} 1.5150.

4. Reaction of diborane and tetra-*n*-butylmercaptodiborane. A solution of 10.1 g (0.053 mole) of tetra-*n*-butylmercaptodiborane in 30 ml of ether was placed in a two-necked flask with a gas inlet and a reflux condenser, and saturated with diborane for 2 hr. On the following day, propylene was passed through the solution for 2 hr until heating of the reaction mixture ceased. The solvent was removed in a water-pump vacuum, and the residue was fractionated. This gave 2.8 g (0.020 mole) of tri-*n*-propylborane, b.p. 48-53°/13 mm, n_D^{20} 1.4195; 2.4 g (0.013 mole) of the *n*-butyl ester of di-*n*-propylthioboric acid, b.p. 65-70°/2 mm, n_D^{20} 1.4570; 5.7 g (0.030 mole) of tetra-*n*-butylmercaptodiborane, b.p. 105-110°/3 mm, n_D^{20} 1.5140.

During distillation of the last fraction, 1.6 g of a substance containing 10.89% boron condensed in a trap cooled to −70°.

5. Tri-*n*-butyl thioborate. A mixture of 7.4 g (0.020 mole) of tetra-*n*-butylmercaptodiborane and 4.2 g (0.046 mole) of *n*-butyl mercaptan, placed in a two-necked flask with a thermometer and a reflux condenser, the end of which was connected to a gasometer, was heated for 4 hr. Gas evolution begins at 60°; by the end of the reaction the temperature of the mixture was raised to 150°. In the experiment, 870 ml of hydrogen was obtained.

* The molecular weight was determined cryoscopically in benzene.

The liquid reaction products were distilled in vacuum. This gave 7.9 g (70%) of tri-*n*-butyl thioborate, b.p. 150–152° at 1 mm; d_4^{20} 0.9684; n_D^{20} 1.5205.

$C_{12}H_{27}BS_3$. Found, %: C 51.89; 52.05; H 10.03; 9.78; B 3.88; 3.87
Calculated, %: C 51.77; H 9.79; B 3.89

6. Tri-*n*-propyl thioborate. In an analogous manner, from 5.3 g (0.016 mole) of tetra-*n*-propylmercaptodiborane and 5.0 g (0.066 mole) of *n*-propyl mercaptan there was obtained 6.1 g (78%) of tri-*n*-propyl thioborate, b.p. 135–135.5°/4 mm; d_4^{20} 0.9952; n_D^{20} 1.5312.

$C_9H_{21}BS_3$. Found, %: C 46.01; 45.76; H 8.90; 8.76; B 4.62; 4.66
Calculated, %: C 45.75; H 8.96; B 4.58

7. N-Triethylborazole. To 16.5 g (0.043 mole) of tetra-*n*-butylmercaptodiborane, placed in a two-necked flask with a dropping funnel and reflux condenser, 4.8 g (0.107 mole) of ethylamine was added. Warming of the reaction mixture was observed. After holding for 1 hour at room temperature, the mercaptan was distilled off in the vacuum of a water-jet pump, heating the mixture first at 30–40°, and toward the end to 90–100°. The mercaptan evolved (18 ml) condensed in a receiver cooled to −70°. The residue was distilled twice in vacuum. This gave 3.7 g of N-triethylborazole, b.p. 66–68° at 20 mm, n_D^{20} 1.4373 (lit. n_D^{20} 1.4344 (6)). The yield is 77% of theory.

8. N-Tri-*n*-butylborazole. The reaction between 11.6 g (0.03 mole) of tetra-*n*-butylmercaptodiborane and 4.4 g (0.06 mole) of *n*-butylamine was carried out analogously to the preceding procedure. From the residue after removal of the mercaptan, 3.3 g (66%) of N-tri-*n*-butylborazole was isolated, b.p. 78–80° at 0.25 mm; d_4^{20} 0.8426; n_D^{20} 1.4515.

$C_{12}H_{30}N_3B_3$. Found, %: C 57.41; 57.51; H 12.26; 12.22; B 13.52; 13.45
Calculated, %: C 57.91; H 12.15; B 13.04

In addition, 1.0 g of a crystalline substance was obtained, which was not investigated in greater detail.

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Note: Figure translations are in progress. See original paper for figures.