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Abstract

Full Text

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ORGANOBORON COMPOUNDS

SYNTHESIS AND SOME PROPERTIES OF TRI-(ETHYLMERCAPTO)-DIBORANE

(Presented by Academician B. A. Kazanskii, July 7, 1960)

When diborane is allowed to react with an excess of *n*-propyl mercaptan or *n*-butyl mercaptan, 4 hydrogen atoms are replaced by alkylmercapto groups and tetra-(alkylmercapto)-diborane is obtained ([1]). It turned out that ethyl mercaptan behaves differently toward diborane. As a result of the reaction between diborane and ethyl mercaptan, carried out in an ether solution at room temperature, irrespective of the ratio of the reagents, tri-(ethylmercapto)-diborane (I) is formed, yield 60–70%.

$$B_2H_6 + 3C_2H_5SH \rightarrow C_2H_5SBH_2BH(SC_2H_5)_2 + 3H_2.$$

(I)

Tri-(ethylmercapto)-diborane is a liquid that distills in vacuum without decomposition and, in contrast to tetra-(alkylmercapto)-diboranes, does not dissociate in solution. Replacement of the remaining 3 hydrogen atoms by ethylmercapto groups is possible only at 110–150°. In this case triethyl thioborate (II) is obtained in good yield.

$$(C_2H_5S)_3B_2H_3 + 3C_2H_5SH \rightarrow 2B(SC_2H_5)_3 + 3H_2.$$

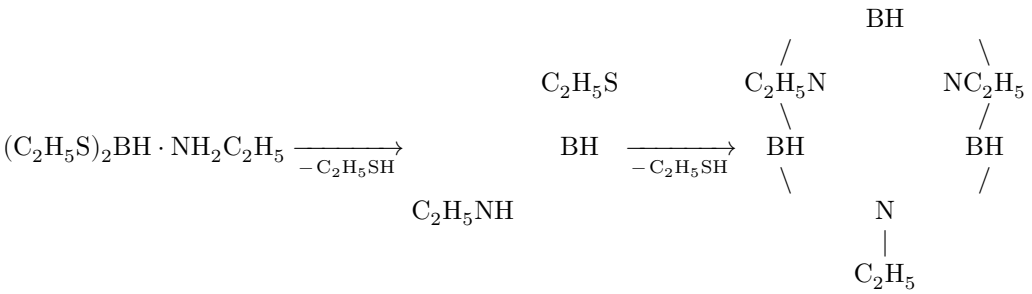
(II)

Under the action of ethylamine on tri-(ethylmercapto)-diborane, N-triethylborazole (VI) and ethylamine-borane (VII) are formed. In the first stage of the reaction, ethylamine complexes of di-(ethylmercapto)-borane (III) and ethylmercapto-borane (IV) arise.

$$(C_2H_5S)_2BHBH_2SC_2H_5 + 2C_2H_5NH_2 \rightarrow (C_2H_5S)_2BH \cdot NH_2C_2H_5 + C_2H_5SBH_2 \cdot NH_2C_2H_5.$$

(III) (IV)

Further, III, with elimination of mercaptan, is converted into ethylamino-ethylmercapto-borane (V), which condenses to N-triethylborazole (VI).



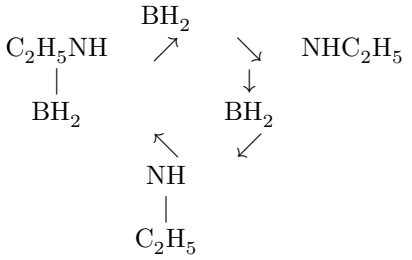
(V) (VI)

The ethylamine complex of ethylmercapto-borane (IV) also eliminates ethyl mercaptan and is converted into ethylamine-borane (VII). The latter is isolated from the reaction mixture chiefly in the form of the trimer.

$$C_2H_5SBH_2 \cdot NH_2C_2H_5 \rightarrow C_2H_5NHBH_2 + C_2H_5SH$$

(VII)

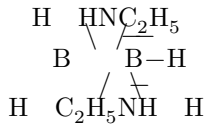
The trimer of ethylamine-borane (VIII)



(VIII)

is a solid substance, quite stable in air, which at room temperature does not react with water or alcohols. Hydrolysis of the trimer can be carried out only by boiling with 20% hydrochloric acid. In its chemical properties the compound obtained by us is analogous to the trimer of methylaminoborane [(2)].

Ethylaminoborane exists not only in trimeric but also in dimeric form. On distillation of the reaction products, along with N-triethylborazole, there is obtained a liquid with b.p. 85-90° at 2 mm, the analysis of which corresponds to ethylaminoborane, while determination of the molecular weight gives values intermediate between the molecular weights of the dimer and the trimer. On standing, crystalline trimer (VIII) separates from this fraction. Apparently the indicated fraction is a mixture of the dimer (IX) and trimer (VIII) of ethylaminoborane. The dimer on standing passes into the trimer



(IX)

In its chemical properties the dimer (IX) differs from the trimer (VIII). It is considerably less stable toward oxygen and atmospheric moisture. Both forms on heating are converted into N-triethylborazole, but at different rates. If the trimer begins to evolve hydrogen only at 140-150° and for its complete conversion heating to 180° is necessary, then the dimer is already partially converted into N-triethylborazole during distillation in vacuo. On heating a mixture consisting approximately of 35% dimer and 65% trimer, hydrogen evolution begins at 100°. In the interval from 100° to 120°, after about one third of the theoretical amount of hydrogen has been evolved, further gas evolution ceases and begins again only when the temperature is raised to 150°.

We next investigated the behavior of tri-ethylmercapto-diborane toward unsaturated compounds. As was shown earlier [1], di-*n*-butylmercapto-diborane in ether solution reacts with olefinic hydrocarbons at room temperature with formation of *n*-butyl esters of dialkylthioboric acids, whereas tetra-*n*-butylmercapto-diborane adds to a double bond under more severe conditions.

Tri-(ethylmercapto)-diborane behaves similarly toward propylene, entering into an addition reaction at room temperature only with the more hydrogenated half of its molecule, with formation of the ethyl ester of di-*n*-propylthioboric acid (X). The second half of the tri-(ethylmercapto)-diborane molecule, which has not entered into the reaction, dimerizes to tetra-(ethylmercapto)-diborane (XI).

$$2C_2H_5SBH_2BH(SC_2H_5)_2+2CH_2{=}CH{-}CH_3 \rightarrow 2(C_3H_7)_2BSC_2H_5+(C_2H_5S)_2BHBH(SC_2H_5)_2$$

(X) (XI)

Tri-(ethylmercapto)-diborane does not react with ethylene or octene at room temperature. On boiling an ether solution of tri-(ethylmercapto)-diborane and octene, a mixture of esters of di-*n*-octylthioboric (XII) and *n*-octylthioboric

(XIII) acids is formed. In addition, in this case the addition reaction is accompanied by symmetrization, which leads to the formation, besides the indicated esters, of triethyl thioborate and tri-*n*-octylborane.

$$C_2H_5SBH_2BH(SC_2H_5)_2+3CH_2{=}CH{-}C_6H_{13} \rightarrow (C_8H_{17})_2BSC_2H_5+C_8H_{17}B(SC_2H_5)_2.$$

(XII) (X)

Experimental Part

Tri-(ethylmercapto)-diborane. 0.16 mole of diborane was passed over 5 hr at room temperature into a solution of 37.2 g (0.6 mole) of ethyl mercaptan in 100 ml of abs. ether, placed in a three-necked ···

flask equipped with a stirrer, a gas inlet, and a reflux condenser. Hydrogen was evolved, and the mixture became viscous.

On the following day the ether and excess ethyl mercaptan were removed in vacuo, and the residue (33.0 g) was distilled. 21.0 g of tri-(ethylmercapto)-diborane (63.5%) was obtained, b.p. 105–110° at 2 mm; d_4^{20} 0.9887; n_D^{20} 1.5360.

Found, %:	C 33.57; 33.60; H 9.25; 9.23; B 10.4; 10.8
$C_6H_{18}B_2S_3$. Calculated, %:	C 34.63; H 8.72; B 10.44;

Molecular weight* found 202.0, calculated 208.06.

In addition, during distillation, 4.3 g of a liquid condensed in a trap cooled to −70°, probably insufficiently pure di-(ethylmercapto)-diborane.

Triethyl thioborate. To tri-(ethylmercapto)-diborane (19.0 g; 0.09 mole) heated to 140°, 27.0 g (0.43 mole) of ethyl mercaptan was added over 3.5 hours. 6850 ml of hydrogen was evolved. Subsequent distillation of the reaction products gave 24.1 g of triethyl thioborate, b.p. 93–96° at 2 mm; d_4^{20} 1.0191; n_D^{20} 1.5465; MR_D** found 60.39, calculated 59.97.

Found, %:	C 37.59; 37.37; H 7.61; 7.79; B 5.88; 5.85
$C_6H_{15}BS_3$. Calculated, %:	C 37.11; H 7.79; B 5.57;

The yield of triethyl thioborate was 69% of theory.

Action of ethylamine on tri-(ethylmercapto)-diborane. To 39.0 g (0.188 mole) of tri-(ethylmercapto)-diborane placed in a two-necked flask with a dropping funnel and a reflux condenser, the end of which was connected to a gas pipette, 17.0 g (0.38 mole) of ethylamine was added at room temperature.

Warming of the reaction mixture was observed, but no hydrogen evolution occurred. Ethyl mercaptan (26.4 g; 75%) was distilled off in the vacuum of a water-jet pump, first at room temperature and then while heating the reaction mass on a water bath (bath temperature 30-40°).

From the residue, as a result of fractional distillation, 10.1 g of N-triethylborazole was isolated (yield 50% of theory), b.p. 68-70° at 23 mm; n_D^{20} 1.4380 (lit. b.p. 66-68° at 20 mm, n_D^{20} 1.4370) ([1]); 4.6 g of trimeric ethylamino-borane (yield 21% of theory), m.p. 171-173° (recrystallized from benzene).

Found, %:	C 42.18; 42.38; H 13.95; 13.89; B 19.29; 19.31; H_{act} 3.48; 3.61
$(C_2H_7NB)_3$. Calculated, %:	C 42.21; H 14.16; B 19.01; H_{act} 3.55

Molecular weight found 181.4, calculated 170.73.

Also isolated was 3.3 g of a liquid with b.p. 85-90° at 2 mm; n_D^{20} 1.4593, representing a mixture of the dimer and trimer of ethylamino-borane.

Found, %:	B 17.59; 17.94; H_{act} 3.39; 3.82
C_2H_7BN. Calculated, %:	B 19.01; H_{act} 3.55;

Determination of the molecular weight gives values of 153.3, 147.6, which corresponds to a content in the mixture of 35% dimer and 65% trimer. 3.2 g of the mixture was heated with a reflux condenser. Gas evolution begins at 100°; in the range 100-120°, 450 ml of hydrogen was evolved

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* The molecular weight was determined cryoscopically in benzene.
** The molecular refraction was calculated as the sum of the bond refractions. For values of bond refractions C–C, C–H, C–S, C–N, N–H see ([3]); for the B–C bond see ([4]). The refraction of the B–S bond, from a comparison of the molecular refractions of various boron-sulfur-containing compounds, was taken as 5.70; the refraction of the B–H bond was calculated analogously as 1.57.

(35% of theoretical), and then gas evolution ceased; only when the temperature was raised to 150° did hydrogen again begin to be evolved. To complete the reaction, the mixture was heated to 180-200°. In all, 1100 ml of gas was evolved (87% of theoretical). The remaining liquid was distilled. 1.7 g of N-triethylborazole was obtained, b.p. 68-70° at 23 mm, n_D^{20} 1.4365. Yield 53%.

Action of propylene on tri(ethylmercapto)diborane. Propylene was passed into a solution of 44.7 g (0.22 mole) of tri(ethylmercapto)diborane in 200 ml of abs. ether until self-heating of the reaction mixture ceased. After removal of the solvent, the residue was subjected to fractional distillation in

vacuo. 17.4 g (25% of theoretical) of ethyl ether of di-*n*-propylthioboric acid was obtained, b.p. 40–50° at 1 mm; on redistillation the ether had b.p. 61–65° at 8 mm; d_4^{20} 0.8214; n_D^{20} 1.4576; MR_D found 52.49, calculated 52.13.

Found, %: C 62.03; 61.96; H 12.41; 12.35
$C_8H_{19}BS$. Calculated, %: C 60.76; H 12.11

19.4 g (33% of theoretical) of tetra(ethylmercapto)diborane, b.p. 75–85° at 1 mm; d_4^{20} 0.9755; n_D^{20} 1.5206; MR found 83.66, calculated 83.14.

Found, %: B 7.84; 7.50
$C_8H_{22}B_2S_4$. Calculated, %: B 8.07

4.1 g (10% of that taken into the reaction) of starting tri(ethylmercapto)diborane, b.p. 102–110° at 1 mm.

Action of octene on tri(ethylmercapto)diborane. A mixture of 17.4 g (0.08 mole) of tri(ethylmercapto)diborane, 33.6 g (0.3 mole) of octene, and 25 ml of abs. ether was boiled for 50 h (temperature of the reaction mixture 55–60°). After removal of the ether and excess octene, the residue was subjected to fractional distillation in vacuo. Obtained: 1) 3.2 g (10% of theoretical) of triethyl thioborate, b.p. 51–58° at 0.1 mm, n_D^{20} 1.5376; 2) 1.8 g (10% of that taken into the reaction) of starting tri(ethylmercapto)diborane, b.p. 68–75° at 0.07 mm, n_D^{20} 1.5322; 3) 7.8 g (20% of theoretical) of ethyl ether of *n*-octylthioboric acid, b.p. 85–95° at 0.05 mm; d_4^{20} 0.8888; n_D^{20} 1.4804; MR_D found 78.78, calculated 79.29.

Found, %: B 4.03; 4.05
$C_{12}H_{27}BS_2$. Calculated, %: B 4.39

4) 7.2 g (15% of theoretical) of ethyl ether of di-*n*-octylthioboric acid, b.p. 116–125° at 0.08 mm; d_4^{20} 0.8435; n_D^{20} 1.4663; MR_D found 98.00, calculated 98.66.

Found, %: B 3.27; 3.26
$C_{18}H_{39}BS$. Calculated, %: B 3.63

5) 13.9 g (25% of theoretical) of tri-*n*-octylboron, b.p. 140–150° at 0.06 mm; n_D^{20} 1.4459.

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