REACTION OF TETRA-n-BUTYLMERCAPTODIBORANE WITH UNSATURATED COMPOUNDS

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As we established previously, in contrast to di-n-butylmercaptodiborane, tetra-n-butylmercaptodiborane does not react with olefins at room temperature in ether [1]. On further investigation it was found that olefins (1-hexene, 1-octene, and styrene) react with tetra-n-butylmercaptodiborane at 70-80° in the presence of pyridine with the formation of n-butyl esters of alkylthioboric acids according to the equation

$$[(C_4H_9S)_2BH]_2 + 2CH_2{=}CHR \longrightarrow 2(C_4H_9S)_2BCH_2CH_2R$$

$$R = n\text{-}C_4H_9,\quad n\text{-}C_6H_{13};\quad C_6H_5.$$

Cyclohexene and methyldiethylvinylsilane react with tetra-n-butylmercaptodiborane under analogous conditions to form n-butyl esters of cyclohexylthioboric and 2-methyldiethylsilylethylthioboric acids (1), respectively.

$$(C_2H_5)_2CH_3SiCH_2CH_2B\,(SC_4H_9)_2 \qquad (I)$$

The reactions between tetra-n-butylmercaptodiborane and propene or isobutene are complex. Heating a mixture of tetra-n-butylmercaptodiborane and propene in the presence of pyridine in an autoclave at 70-80° and 5-15 atm formed the n-butyl ester of n-propylthioboric acid and also the n-butyl ester of di-n-propylthioboric acid and tri-n-butyl thioborate. Tetra-n-butylmercaptodiborane reacted analogously with isobutene, giving a mixture of esters of isobutylthioboric and diisobutylthioboric acids and tri-n-butyl thioborate. The formation of esters of dialkylthioboric acids and the thioborate is explained by the fact that in these cases the tetra-n-butylmercaptodiborane was symmetrized to thioborate and di-n-butylmercaptodiborane. The latter reacted with olefins, giving the corresponding esters of dialkylthioboric acids.

$$(C_4H_9SBH_2)_2 + CH_2{=}CH{-}R \longrightarrow 2C_4H_9SB\,(CH_2CH_2R)_2$$

EXPERIMENTAL

All operations with organoboron compounds were carried out in a nitrogen atmosphere.

n-Butyl n-hexylthioborate. A mixture of 7 g (0.018 mole) of tetra-n-butylmercaptodiborane, 7 g (0.083 mole) of 1-hexene, and 0.5 ml of pyridine was placed in a two-necked flask with a nitrogen inlet and a reflux condenser and heated at 70° for 3 hr. The excess hexene was removed in a water-pump vacuum and then the residue distilled. We obtained 9.0 g (89%) of n-butyl n-hexylthioborate with b.p. 97-98° (0.06 mm); d_4^{20} 0.8860; n_D^{20} 1.4840. Found: C 61.47; 61.43; H 11.26, 11.36%. $C_{14}H_{31}BS_2$. Calculated: C 61.29; H 11.39%.

n-Butyl n-octylthioborate. A mixture of 7 g (0.0185 mole) of tetra-n-butylmercaptodiborane, 8.3 g (0.074 mole) of 1-octene, and 0.5 ml of pyridine was heated for 3 hr at 70°. After removal of the excess octene in vacuum, the residue was distilled. We obtained 9.3 g (83% of theoretical) of n-butyl n-octylthioborate with b.p. 134-136° (0.05 mm); d_4^{20}0.8770; n_D^{20} 1.4820. Found: C 63.75; 63.46; H 11.74; 11.80; B 3.40; 3.20%. $C_{16}H_{35}BS_2$. Calculated C 63.55; H 11.67; B 3.58%.

n-Butyl 2-phenylethylthioborate. A mixture of 6.8 g (0.018 mole) of tetra-n-butylmercaptodiborane, 4.0 g (0.038 mole) of styrene, and 0.5 ml of pyridine was heated for 3 hr at 70°. Subsequent fractionation yielded 3.1 g (30%) of n-butyl 2-phenylethylthioborate with b.p. 145-146° (0.02 mm); d_4^{20}0.9827; n_D^{20} 1.5419. Found: C 65.06; 65.34; H 9.12; 8.99; B 3.86; 3.96%. $C_{16}H_{27}BS_2$. Calculated: C 65.29; H 9.29; B 3.67%.

n-Butyl cyclohexylthioborate. Similarly, from 7.4 g (0.019 mole) of tetra-n-butylmercaptodiborane, 3.2 g (0.039 mole) of cyclohexene, and 0.5 ml of pyridine we obtained 8.3 g of n-butyl cyclohexylthioborate (79% of theoretical) with b.p. 180-185° (4 mm). After redistillation, the ester had b.p. 155-156° (1 mm); d_4^{20} 0.9516; n_D^{20} 1.5737. Found: C 62.40; 62.26; H 10.87; 10.71; B 4.33; 4.38%. $C_{14}H_{29}BS_2$. Calculated: C 61.76; H 10.74; B 3.97%.

n-Butyl 2-methyldiethylsilylethylthioborate. 6.4 g (0.017 mole) of tetra-n-butylmercaptodiborane was mixed with a solution of 2-methyldiethylvinylsilane (5.3 g, 0.041 mole) in ether (10 ml) and 0.3 ml of pyridine and the mixture heated to boiling (50-55° in the reaction flask). Two fractionations yielded 3.7 g (37%) of n-butyl 2-methyldiethylsilylethylthioborate with b.p. 150-160° (0.5 mm). After redistillation, the ester had b.p. 156-158° (1 mm); n_D^{20} 1.5013; d_4^{20}0.9224. Found: C 56.27; 55.96; H 11.16; 10.52; B 3.44; 3.48%. $C_{15}H_{35}BS_2Si$. Calculated: C 56.60; H 11.09; B 3.40%.

Action of propene on tetra-n-butylmercaptodiborane. 5 g (0.11 mole) of propene condensed at -40° was added to a cooled mixture of 7 g (0.018 mole) of tetra-n-butylmercaptodiborane and 0.3 ml of pyridine in a small autoclave. The reaction mixture was heated for 2 hr at 85° under a pressure of 15 atm. Three fractionations yielded: 1) 1.1 g (16.7%) of n-butyl di-n-propylthioborate with b.p. 97-105° (9 mm); n_D^{20} 1.4545 [literature data [2]: b.p. 98° (11 mm) n_D^{20} 1.4598]; 2) 1.5 g (17.8%) of n-butyl n-propylthioborate with b.p. 147-155° (9 mm) n_D^{20} 1.4919 [literature data [3]: b.p. 149-150° (13 mm); n_D^{20} 1.4956]; 3) 2 g (20%) of tri-n-butyl thioborate with b.p. 160-164° (2 mm); n_D^{20} 1.5205 (literature data [1]: b.p. 150° (1 mm); n_D^{20} 1.5265).

Action of isobutene on tetra-n-butylmercaptodiborane. Into a small autoclave were placed 8 g (0.021 mole) of tetra-n-butylmercaptodiborane and 0.3 ml of pyridine and then to the cooled mixture was added 10 g (0.17 mole) of isobutene, condensed at -30°. The reaction mixture was heated for 2 hr at 85° and a pressure of 5 atm. Three fractionations of the liquid reaction products yielded: 1) 2.3 g (25.6%) of n-butyl diisobutylthioborate with b.p. 112-113° (8 mm); n_D^{20} 1.4550 [literature data [2]; b.p. 107° (9.5 mm); n_D^{20} 1.4572]; 2) 2.8 g (27.4% of n-butyl isobutylthioborate with b.p. 141-142° (3.5 mm); d_4^{20}0.9020; n_D^{20} 1.4919. Found: C 58.79; 58.79; H 10.96; 11.19%. $C_{12}H_{27}BS_2$. Calculated: C 58.51, H 10.85%; 3) 2.4 g (20.6%) of tri-n-butyl thioborate with b.p. 170-175° (4.5 mm).

SUMMARY

Tetra-n-butylmercaptodiborane reacts with unsaturated compounds at 70-80° in the presence of pyridine to form esters of alkylthioboric acids.

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*Original Russian pagination. See C.B. translation.