Chemistry

1961

SovietRxiv

Abstract

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Chemistry

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Synthesis and Properties of Tetra-*n*-propyldiborane and Tetra-*n*-butyldiborane

(Presented by Academician B. A. Kazanskii, July 9, 1960)

When trimethylboron and diborane interact in the gas phase, mono-, di-, tri-, and tetramethyldiborane are formed (^1), the yield of the latter being 2.8%. From triethylboron and diborane (8 : 1), triethyldiborane and tetraethyldiborane are obtained (^2); from tri-*n*-propylboron, by this method, *n*-propyl- and unsymmetrical di-*n*-propyldiborane have been synthesized (^2). Tetra-*n*-propyldiborane was obtained by the action of lithium aluminum hydride on di-*n*-propylboron chloride (^3). All known alkyldiboranes were identified only by vapor pressure. According to the literature data, the stability of alkyldiboranes increases with an increase in the number of substituents, although all of them disproportionate at room temperature into an equilibrium mixture.

We investigated the reaction of diborane with trialkylborons (tri-*n*-propylboron and tri-*n*-butylboron) in ethereal solution and found that when 1 mole of diborane is passed into an ethereal solution of 4 moles of trialkylboron at room temperature, tetraalkyldiboranes—tetra-*n*-propyl- and tetra-*n*-butyldiborane—are obtained in 70–85% yield. If, however, an equimolecular amount of diborane is passed into an ethereal solution of tri-*n*-propylboron,

$$4R_3B + B_2H_6 \rightarrow 3R_2BH - HBR_2,$$

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

then, by distillation of the reaction products, it is possible to isolate, along with tetra-*n*-propyldiborane, unsymmetrical di-*n*-propyldiborane.

The second method of synthesis of tetraalkyldiboranes investigated by us is based on the reaction between diborane and olefinic hydrocarbons. This reaction, discovered by Hurd (^4), is catalyzed by simple ethers (^5) and until now has been used for obtaining trialkylborons.

We established that in an ethereal medium at −70 to −30° diborane and olefinic hydrocarbons (propylene or butene-1), taken in a ratio of 1 : 4, form tetraalkyldiboranes in 48% yield

$$4\mathrm{CH_2} = \mathrm{CH} - \mathrm{R} + \mathrm{B_2H_6} \rightarrow (\mathrm{RCH_2} - \mathrm{CH_2})_2\mathrm{BH} - \mathrm{HB}(\mathrm{CH_2} - \mathrm{CH_2R_2}),$$

$$\mathrm{R} = \mathrm{CH_3}; \quad \mathrm{C_2H_5}.$$

The tetraalkyldiboranes synthesized by us are quite stable compounds, withstanding heating to 100° and capable of being distilled in vacuum. Their refractive index, on standing after distillation, increases somewhat. However, upon heating or distillation of the product, the refractive index again decreases to the initial value. Determination of the molecular weight in benzene indicates their partial dissociation in solution to dialkylborane.

Tetraalkyldiboranes spontaneously ignite in air and possess high reactivity. They react with alcohols with formation of esters of dialkylborinic acids

$$(\mathrm{R_2BH})_2 + 2\mathrm{R'OH} \rightarrow 2\mathrm{R_2BOR'} + 2\mathrm{H_2},$$

with aniline they form dialkylphenylaminoboranes

$$(\mathrm{R_2BH})_2 + 2\mathrm{NH_2C_6H_5} \rightarrow 2\mathrm{R_2BNHC_6H_5} + 2\mathrm{H_2},$$

and under the action of mercaptans they are converted into esters of dialkylthioboric acids

$$(\mathrm{R_2BH})_2 + 2\mathrm{R'SH} \rightarrow 2\mathrm{R_2BSR'} + 2\mathrm{H_2}.$$

The reactions of tetraalkyldiboranes with various reagents are convenient preparative methods for the synthesis of organoboron compounds. In most cases they are accompanied by the formation of only small amounts of by-products. Thus, when *n*-butyl mercaptan acts on tetra-*n*-propyldiborane, besides the ester of di-*n*-propylthioboric acid, a little ester of *n*-propylthioboric acid is also obtained. The reaction of tetra-*n*-butyldiborane with glycol proceeds with greater complications; as a result, glycol esters of di-*n*-butylboric and *n*-butylboric acids were obtained in approximately equal amounts, and, in addition, tri-*n*-butylboron. The formation of the latter indicates that, under the action of nucleophilic reagents, tetraalkyldiboranes not only replace hydrogen atoms but also undergo disproportionation into trialkylborons and alkylboranes. In general form the process should be represented by the scheme:

$$\begin{tikzcd}
(\mathrm{R_2BH})_2 \arrow[r, "\mathrm{R'YH}"] \arrow[dr] & \mathrm{R_2BYR'} + \mathrm{H_2} & \\
 & \mathrm{R_3B} + [\mathrm{RBH_2}] \arrow[r, "\mathrm{R'YH}"] & \mathrm{RB(YR')_2} + 2\mathrm{H_2}
\end{tikzcd}$$

The alkylborane formed under the action of the nucleophilic reagent either gives an organoboron compound with one radical at the boron atom, while the trialkylboron remains unchanged (for example, in the reaction with glycol), or enters into reaction, forming, for example, with a mercaptan an ester of dialkylthioboric acid (^{6}). As a result of the latter reaction, in the gaseous products of the conversion of tetra-*n*-propyldiborane under the action of a mercaptan, not only hydrogen but also a small amount of propane is detected.

Tetraalkyldiboranes are capable of reacting with olefinic hydrocarbons with formation of trialkylborons; in particular, unsymmetrical trialkylborons can be obtained in this way.

Experimental Part

All operations were carried out in an atmosphere of dry nitrogen. Diborane was obtained in 65–75% yield by adding an ethereal solution of boron trifluoride etherate to a suspension of sodium borohydride in ether.

Synthesis of tetraalkyldiboranes

Tetra-*n*-butyldiborane. a) In 45 ml of dry diethyl ether, 18.2 g (0.1 mole) of tri-*n*-butylboron (b.p. 109°/20 mm, n_D^{20} 1.4260; d_4^{20} 0.7556) were dissolved, and, with continuous stirring, 0.0275 mole of diborane was passed through the solution over 2–3 hr. The ether was then distilled off under vacuum from a water-jet pump, and the residue was subjected to fractional distillation. There were obtained 17 g of tetra-*n*-butyldiborane, b.p. 40–41°/0.25 mm; n_D^{20} 1.4375; d_4^{20} 0.7647. Yield 86.8% of theory.

Found, %: C 76.26; H 15.04; B 8.75; H_{act} 0.82
$C_8H_{19}B$. Calculated, %: C 76.22; H 15.19; B 3.58; H_{act} 0.791

Mol. wt.: found 216, calculated 252.

b) In 100 ml of dry diethyl ether, 0.375 mole of butene-1 was dissolved, and into the solution cooled to −30°, with continuous stirring, 0.075 mole of diborane was passed over 4 hr. The solvent was removed,

and the residue was fractionated in vacuo. Tetra-*n*-butyldiborane was obtained, b.p. 40–42° at 0.25 mm; n_D^{20} 1.4352. Yield 45% of theory.

Tetra-*n*-propyldiborane. a) Diborane (0.055 mole) was passed into an ethereal solution of 28.4 g (0.203 mole) of tri-*n*-propylborane (b.p. 48°/13 mm, n_D^{20} 1.4148). After distillation of the ether the reaction products were distilled. This gave 20.4 g of tetra-*n*-propyldiborane, b.p. 33–34° at 1 mm, n_D^{20} 1.4327; d_4^{20} 0.7388. Yield 70% of theory.

Found, %: C 73.13; H 15.40; B 11.11; H_{act} 0.729
$C_6H_{15}B$. Calculated, %: C 73.53; H 15.43; B 11.04; H_{act} 0.736

b) 0.375 mole of propylene was dissolved in 100 ml of ether, and 0.075 mole of diborane was passed into the solution cooled to −50°. After removal of the ether the residue was fractionated in vacuo. The following fractions were obtained: 1) 20-34°/1.2 mm—4.7 g; n_D^{20} 1.4180; 2) 34-36°/1.2 mm—7.4 g; n_D^{20} 1.4311; 3) in a trap cooled to −70°, 4.6 g of a substance with n_D^{20} 1.4175 was collected. The second fraction is tetra-*n*-propyldiborane, yield 45%.

Synthesis of 1,1′-di-*n*-propyldiborane. 15.5 g (0.111 mole) of tri-*n*-propylborane was dissolved in 100 ml of ether, and 0.12 mole of diborane was passed into the solution over 3 h. After removal of the solvent in vacuo, the residue was subjected to fractional distillation. The following were obtained: 1) 2.9 g of a substance, b.p. 33-34°/32 mm, n_D^{20} 1.4088, corresponding, according to analytical data and chemical properties, to unsymmetrical di-*n*-propyldiborane, yield 16%; 2) 6.5 g of tetra-*n*-propyldiborane, b.p. 33-34°/1 mm, n_D^{20} 1.4327.

Action of *n*-butanol on 1,1-di-*n*-propyldiborane. 9.5 ml of *n*-butanol was added dropwise to 2.8 g of 1,1-di-*n*-propyldiborane. Vigorous evolution of hydrogen occurred (2.15 l). After distillation of the reaction products, the following were obtained: 1) 3.8 g of the *n*-butyl ester of di-*n*-propylboric acid, b.p. 72-76°/7 mm, n_D^{20} 1.4130 (literature data: b.p. 66.5°/5 mm, n_D^{20} 1.4133 (7)); 2) 3.8 g of tri-*n*-butyl borate, b.p. 72-74°/2 mm, n_D^{20} 1.4088; d_4^{20} 0.8572 (literature data: b.p. 105-106°/8 mm, n_D^{20} 1.4080; d_4^{20} 0.8567 (8)).

Reactions of tetraalkyldiboranes with alcohols. 5.8 g of *n*-butanol was added dropwise to 7.3 g of tetra-*n*-propyldiborane. Fractional distillation gave: 1) 8.1 g of the *n*-butyl ester of di-*n*-propylboric acid (63%), b.p. 59-63°/4.5 mm, n_D^{20} 1.4140 (literature data: b.p. 76-76.5°/15 mm, n_D^{20} 1.4133 (7)); 2) 2.1 g of the di-*n*-butyl ester of *n*-propylboric acid, b.p. 64-72°/4.5 mm; n_D^{20} 1.4130 (literature data: b.p. 83°/7 mm, n_D^{20} 1.4120 (9)). In the experiment, 1.58 l of hydrogen was obtained. In an analogous manner, from 10.5 g of tetra-*n*-butyldiborane and methanol, 8.45 g (65%) of the methyl ester of di-*n*-butylboric acid was obtained, b.p. 90-91°/42 mm, n_D^{20} 1.4180; d_4^{20} 0.7845; *MR* found 50.11; calculated 49.57.

Found, %: C 69.26; H 13.51; B 7.00
$C_9H_{21}BO$. Calculated, %: C 69.23; H 13.46; B 7.05

Reaction of tetra-*n*-butyldiborane with ethylene glycol. To 10.5 g of tetra-*n*-butyldiborane, 2.8 g of ethylene glycol was added at room temperature. The reaction, accompanied by evolution of hydrogen, continued for 7 h. After fractional distillation the following were obtained: 1) 3.25 g of the glycol ester of *n*-butylboric acid, b.p. 80-81°/66 mm, n_D^{20} 1.4140 (literature data: b.p. 78-79°/66 mm, n_D^{20} 1.4129 (10)); 2) 4.4 g of tri-*n*-butylborane, b.p. 64-67°/3 mm, n_D^{20} 1.4260, and 3) 4.67 g of the glycol ester of di-*n*-butylboric acid, b.p. 155-156°/3 mm, n_D^{20} 1.4350 (literature data: b.p. 133-134°/1 mm, n_D^{20} 1.4340 (10)).

Reactions of tetraalkyldiboranes with aniline. 12 g of aniline was added dropwise to 12 g of tetra-*n*-propyldiborane. Observ—

the formation of a white complex was observed, which gradually decomposed with evolution of hydrogen. After distillation, 18.5 g (80%) of di-*n*-propylphenylaminoborane was obtained, b.p. 120-123°/11.5 mm, n_D^{20} 1.5049 (literature data: b.p. 117.5°/11 mm, n_D^{20} 1.5050 (6)) and 1.3 g of a fraction with b.p. 90-174°/1 mm. Similarly, from 7 g of tetra-*n*-butyldiborane and 5.6 g of aniline, 9.14 g (76%) of di-*n*-butylphenylaminoborane was obtained, b.p. 142-144°/8.5 mm, n_D^{20} 1.5003. Literature data: b.p. 139°/7.5 mm, n_D^{20} 1.5001 (11). In the experiment, 1155 ml of hydrogen was obtained.

Reactions of tetraalkyldiboranes with mercaptans. To 7.1 g of tetra-*n*-propyldiborane, 6.8 g of *n*-butyl mercaptan was added. As the reaction proceeded, gaseous substances were evolved. A total of 1.59 l of H_2 and 95 ml of propane was obtained. On distillation, 11.2 g (83%) of the *n*-butyl ester of di-*n*-propylthioboric acid was obtained, b.p. 98.5-102°/11.5 mm, n_D^{20} 1.4580 (literature data: b.p. 98.2°/11 mm, n_D^{20} 1.4590 (10)) and 1.4 g of the di-*n*-butyl ester of *n*-propylthioboric acid, b.p. 109-110°/2 mm, n_D^{20} 1.4895 (literature data: b.p. 150°/13 mm, n_D^{20} 1.4956 (12)).

In an analogous manner, from 8.05 g of tetra-*n*-butyldiborane and 8 g of *n*-butyl mercaptan, 10.13 g (75%) of the *n*-butyl ester of di-*n*-butylthioboric acid was obtained, b.p. 137-141°/18 mm, n_D^{20} 1.4604 (literature data: b.p. 118.5°/8 mm, n_D^{20} 1.4548 (11)).

By the action of 7 g of *n*-propyl mercaptan on 10 g of tetra-*n*-butyldiborane, 11.7 g (74%) of the *n*-propyl ester of di-*n*-butylthioboric acid was obtained, b.p. 122-126°/18 mm, n_D^{20} 1.4600; d_4^{20} 0.8310, MR found 65.79; calculated 65.98.

$C_{11}H_{25}BS$. Found, %: C 66.35; 66.16; H 12.64; 12.46; B 5.56; 5.70
Calculated, %: C 66.00; H 12.50; B 5.50

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Received
6 VII 1960

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1. H. Schlesinger, A. Wolker, *J. Am. Chem. Soc.*, **57**, 621 (1935).
2. H. Schlesinger, L. Horwitz, A. Burg, *J. Am. Chem. Soc.*, **58**, 407 (1936).
3. L. Long, M. Wallbridge, *Chem. and Ind.*, 1959, 295.
4. D. Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948).

5. H. Brown, B. Subba-Rao, *J. Org. Chem.*, **22**, 1136 (1957).
6. B. M. Mikhailov, V. A. Vaver, Yu. N. Bubnov, *DAN*, **126**, 575 (1959).
7. B. M. Mikhailov, T. A. Shchegoleva, *ZhOKh*, **29**, 3130 (1959).
8. B. A. Arbuzov, V. S. Vinogradova, *DAN*, **55**, 417 (1947).
9. B. M. Mikhailov, T. A. Shchegoleva, *Izv. AN SSSR, OKhN*, 1956, 508.
10. R. L. Letsinger, S. Skoog, *J. Am. Chem. Soc.*, **76**, 4174 (1954).
11. B. M. Mikhailov, Yu. N. Bubnov, *Izv. AN SSSR, OKhN*, 1959, 172.
12. B. M. Mikhailov, T. K. Kozminskaya, N. S. Fedotov, V. A. Dorokhov, *DAN*, **127**, 1023 (1959).

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