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*Received October 27, 1997;*
*in revised form January 26, 1998*

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# Synthesis of lithium octahydrotriborate solvates with dioxane

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A method for the synthesis of lithium octahydrotriborate in the form of solvates with dioxane containing one, two, and four dioxane molecules was developed.

**Key words**: octahydrotriborate, pentaborane(9), diborane, tetrahydrofuran, dioxane, solvate.

Salts of octahydrotriborates with alkali metal cations (Na, K, Rb, and Cs) are known in the nonsolvated state[1–3] and in the form of solvates with dioxane (Dx): $NaB_3H_8 \cdot 3$ Dx, $NaB_3H_8 \cdot$ Dx,[3–4] and $KB_3H_8 \cdot 2.5$ Dx.[5] The following solvated alkali-earth octahydrotriborates were synthesized: $Mg(B_3H_8)_2 \cdot 6\ NH_3$,[6] $Mg(B_3H_8)_2 \cdot 2$ DG, $Ca(BH_4)(B_3H_8) \cdot 2$ DG, and $Sr(B_3H_8)_2 \cdot 3$ DG,[7] where DG is diethylene glycol dimethyl ether (diglyme), and tetraalkylammonium octahydrotriborates $R_4NB_3H_8$ (R = Me, Et, and Bu).[8]

$LiB_3H_8$ (**1**) is known to exist only as an ethereal solution. Compound **1** was previously synthesized[1] by the exchange reaction of nonsolvated $NaB_3H_8$ with LiBr in ether and THF; however, it was not isolated in the solid state.

This work is devoted to the synthesis of lithium octahydrotriborate in the form of solid solvates $LiB_3H_8 \cdot n$Dx and to the study of conditions of their desolvation.

## Experimental

$NaB_3H_8 \cdot 3$Dx (**2**) and LiBr were the starting compounds for the synthesis of $LiB_3H_8 \cdot n$Dx. The reaction was performed in THF at 20 °C. Prior to use, the starting compound **2** was recrystallized from 2-propanol. The resulting material contained 98.5% of the main compound; the purity of LiBr was 99.0%. Before the synthesis, THF was dried by refluxing over KOH and distilled from $LiAlH_4$.

**Synthesis of solvates of lithium octahydrotriborate with dioxane $LiB_3H_8 \cdot n$Dx.** A solution of LiBr (1.93 g, 22.2 mmol) in THF (10 mL) was added dropwise to a solution of compound **2** (7.32 g, 22.3 mmol) in THF (60 mL). A precipitate of NaBr was immediately formed. The mixture was stirred for 2—3 h, the precipitate was filtered off, and the filtrate was concentrated approximately to half its original volume. Dioxane was added to the solution obtained, and the precipitation of crystals of tetrasolvate $LiB_3H_8 \cdot 4$ Dx (**1a**) (yield 7.4 g, 86%) occurred during concentration of its solution. Found (%): Li, 1.85; B, 8.11; $H_{hydr}$, 2.28. $LiB_3H_{8(hydr)} \cdot C_{16}H_{32}O_8$. Calculated (%): Li, 1.80; B, 8.45; $H_{hydr}$, 2.10. IR ν/cm$^{-1}$: 2470 s, 2440 s, 2400 s, 2370 sh, 2120, 2070, 1450, 1300, 1260, 1160, 1120, 1080, 1050, 1020, 890, 870, 640.

At 20 °C in vacuum, tetradioxanate is easily transformed into bisdioxanate $LiB_3H_8 \cdot 2$Dx (**1b**).

When the mixed solvent (THF and dioxane) was completely distilled off, **1b** with admixture of LiBr and **2** was isolated in the solid phase. To purify **1b**, a small amount of benzene was added to the concentrated solution, and the precipitate of **2** was separated by filtration. The solution obtained was concentrated to dryness, and compound **1b** was extracted with ether from the residue. After separation of ether-insoluble LiBr and removal of the ether, **1b** was obtained. Found (%): Li, 3.15; B, 13.51; $H_{hydr}$, 3.84. $LiB_3H_{8(hydr)} \cdot C_8H_{16}O_4$. Calculated (%): Li, 3.22; B, 15.04; $H_{hydr}$, 3.74. IR, ν/cm$^{-1}$: 2480 s, 2440 s, 2420 s, 2360 sh, 2160 w, 2100, 1450, 1300, 1260, 1160, 1120, 1080, 1050, 1020, 890, 870, 640.

Compound **1b** is a white crystalline product, which is stable in vacuum up to 65 °C, well soluble in water without decomposition, soluble in THF, ether, and 2-propanol, and poorly soluble in benzene.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1446—1447, July, 1998.

1066-5285/98/4707-1408 $20.00 © 1998 Plenum Publishing Corporation

Compound **1b** was desolvated at 70—75 °C *in vacuo* to the constant weight. According to the weight loss, the solid precipitate was monodioxanate $LiB_3H_8 \cdot Dx$ (**1c**). No hydrogen release was observed. Exposure of the monosolvate at 85—100 °C for 8 h leads to its further desolvation accompanied by a weak gas release. We obtained the solvate $LiB_3H_8 \cdot 0.9\ Dx$, which decomposed completely at ~150 °C. The solid residue obtained after the decomposition is nonsolvated $LiBH_4$. The gas phase consisted of hydrogen, dioxane, and gaseous boron hydrides: pentaborane(9) and diborane. No tetraborane(10) was observed. The yield of pentaborane(9) with respect to the boron content in **1c** is 56%.

## Results and Discussion

The use of accessible starting compounds (LiBr and **2**) in the synthesis of compound **1**, the possibility of performing the reaction in THF, and a comparatively high yield of the product (up to 86%) make the procedure developed a promising and reliable method for the preparative synthesis of **1**. In this method, lithium octahydrotriborate is isolated in the form of dioxanate. Unlike other donor solvents, such as THF and ether, dioxane solvates **1** to form a crystalline solvate **1a**. Lithium octahydrotriborate tetradioxanate is an unstable compound. This solvate is easily transformed into **1b** at 20 °C in vacuum. Like tetradioxanate, a sufficiently stable disolvate is soluble in THF, ether, and 2-propanol, and we believe that it is the most promising starting compound, along with **2**, in the synthesis of other octahydrotriborates. Monodioxanate, which is formed upon desolvation of **1b**, is more hygroscopic and less convenient for the synthesis. Attempts to obtain nonsolvated **1** failed. Desolvation of **1c** is accompanied by the decomposition of the $B_3H_8^-$ anion. The general sequence of the desolvation of **1a** can be presented by the scheme:

$$\underset{\mathbf{1a}}{LiB_3H_8 \cdot 4\ Dx} \xrightarrow[0.1\ \text{Torr}]{20\ ^\circ\text{C}} \underset{\mathbf{1b}}{LiB_3H_8 \cdot 2\ Dx} \xrightarrow[0.1\ \text{Torr}]{70\text{—}75\ ^\circ\text{C}}$$

$$\longrightarrow \underset{\mathbf{1c}}{LiB_3H_8 \cdot Dx} \xrightarrow[0.1\ \text{Torr}]{85\text{—}100\ ^\circ\text{C}} LiB_3H_8 \cdot 0.9\ Dx \xrightarrow[0.1\ \text{Torr}]{140\text{—}150\ ^\circ\text{C}}$$

$$\longrightarrow LiBH_4 + B_5H_9 + B_2H_6 + H_2 + C_4H_8O_2$$

We have previously established that the composition of the boron hydrides that are formed in the decomposition of the $B_3H_8^-$ anion depends substantially on the temperature. For example, the cleavage of octahydrotriborates with Lewis acids at temperatures not higher than 50 °C is accompanied by the predominant release of tetraborane(10) with admixtures of diborane and pentaborane(9) to the gas phase.[9] At 100—150 °C, the pyrolysis of octahydrotriborates gives pentaborane(9) and diborane, while tetraborane(10) is absent.[1,4,7] Thermolysis at 150 °C of monodioxanate **1c** obtained in this work also affords pentaborane(9) and an admixture of diborane.

The primary act of the decomposition of octahydrotriborates is the elimination of the unstable group $B_2H_4$. At low temperatures (20 °C), $B_2H_4$ is predominantly transformed into tetraborane(10), whereas at higher temperatures (~50 °C), a mixture of tetraborane(10) and pentaborane(9) is formed;[9] finally, only pentaborane(9) is formed at ~150 °C.[5,7]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34095).

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*Received November 21, 1997;*
*in revised form January 8, 1998*