Interaction of tetrabutylammonium octahydrotriborate with aluminum chloride. A new method for the preparation of tetraborane(10)

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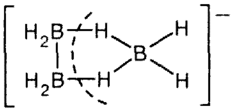
Interaction of $Bu_4NB_3H_8$ with $AlCl_3$ at 45—50 °C results in the formation of BH_4^- and unstable borane B_2H_4, which is converted into a mixture of B_4H_{10}, B_5H_9, and B_2H_6. This reaction can be used for the preparation of tetraborane(10).

Key words: octahydrotriborate, Lewis acids, tetrahydroborate, diborane(6), tetraborane(10), pentaborane(9).

Decomposition of the $B_3H_8^-$ anion with the formation of BH_4^- ion is the most characteristic property of octahydrotriborates. It is a result of cleavage of bridging B—H—B hydrogen bonds.



The reaction can be performed both under the action of Lewis acids and bases on octahydrotriborates and by heating the salts. It has been demonstrated[1] that the reaction of $R_4NB_3H_8$ with non-solvated $Al(BH_4)_3$ (**1**) results in the decomposition of the $B_3H_8^-$ anion with elimination of the BH_4^- ion and formation of the tetraalkylammonium salt with a complex anion $[Al(BH_4)_4]^-$. An analogous decomposition of the $B_3H_8^-$ anion in the reaction of Cp_2ZrCl_2 with NaB_3H_8 (**2**) gives a molecular compound $Cp_2ZrCl(BH_4)$.[2] The composition of gaseous products evolved has not been determined.[1,2]

Reactions of octahydrotriborates with Lewis acids usually occurs at 20—50 °C. For example, $Bu_4NB_3H_8$ (**3**) reacts with liquid **1** at -20 °C.

Decomposition of octahydrotriborates by bases, for instance the reaction of **3** with PPh_3 in a benzene—toluene mixture, occurs at 85 °C.[3] No gaseous products are formed. The final solid product is a mixture of the adduct $B_2H_4 \cdot 2PPh_3$ and tetrabutylammonium tetrahydroborate. It has been also demonstrated[3] that the reaction of **3** with PPh_3 is reversible.

In the absence of the second component, *viz*., Lewis acid or base, this process occurs at ~100 °C. When the reaction is performed under atmospheric pressure and at higher temperature (185 °C) the boranes formed react completely with BH_4^- to give[4] polyhedral anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. The liberated B_2H_4 instantaneously converts *in vacuo* into more stable boranes while BH_4^- remains bonded to the initial cation.

The thermal decomposition of alkaline and alkaline-earth octahydrotriborates *in vacuo*[5,6] at 100—140 °C is also accompanied by formation of tetrahydroborates. Pentaborane(9) was found in the gaseous phase upon thermal decomposition of octahydrotriboranes. Presumably, it results from dehydrocondensation of a rather unstable B_2H_4 which is liberated in the decomposition of $B_3H_8^-$ anion. We expected to isolate boranes less stable than pentaborane(9) by decomposition of octahydrotriborates at temperatures lower than 100 °C.

In the present work, the decomposition of $Bu_4NB_3H_8$ by a Lewis acid, $AlCl_3$, at 40—50 °C was studied.

Experimental

In the present work, we used complex **3**, which is poorly soluble in water and precipitated from an aqueous solution at 20 °C in the exchange reaction of $NaB_3H_8 \cdot 3C_4H_8O_2$[1] with Bu_4NBr. After successive recrystallizations from dichloromethane and isopropyl alcohol, compound **3** contained 99.5% of the main component. Aluminum chloride was purified by vacuum sublimation. Reaction was carried out in an apparatus, which consists of the reaction vessel, three traps, and a mercury manometer. The total volume of the apparatus was 360—400 cm^3.

Interaction of **3** with $AlCl_3$ (molar ratio 1 : 1.1) was carried out in the absence of a solvent. In a typical experiment a mixture of **3** (3.0 g, 10.7 mmol) ground in a mortar and $AlCl_3$ (1.6 g, 11.8 mmol) was placed in the reaction vessel. The system was evacuated, and the reaction mixture was heated to 45—50 °C. At this temperature the reaction mixture melted; simultaneously, gas evolution occurred, which was completed in one hour. When gas liberation ceased, the reaction mixture solidified. The liberated gas was passed through three traps (−196 °C), which were continuously evacuated. Boranes formed in the reaction condensed mainly in the first trap. The two other traps prevented passage of boranes and served as reserve vessels.

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The composition of the boranes was determined according to the following procedure. The trap containing the boranes was heated to −125 °C. At this temperature, only diborane passed in the gas phase. The amount of B_2H_6 was calculated from the pressure in the system; it was identified by IR spectroscopy, ν/cm^{-1}: 2640 s, 2600 s, 2550 s, 2530 s, 2510 s, 1880 m, 1870 m, 1850 m, 1630 s, 1600 s, 1590 s, 1200 s, 1180 s, 1160 s, and 980 m. The yield of B_2H_6 eliminated in the reaction was 0.85 mmol, which amounted to 5.3% of the initial boron content.

Following removal of diborane from the system, the temperature of the trap was elevated to −20 °C, the amount of the gas was calculated from the pressure in the system, and its composition was established using IR spectroscopy. The gas was shown to consist of a mixture of pentaborane(9) (**4**), ν/cm^{-1}: 2620 s, 1820 m, 1630 w, 1500 m, 1450 s, 1430 s, 1415 s, 1060 m, 900 s, 810 w, 620 s, 605 s.sh, and 570 m, and tetraborane(10) (**5**), ν/cm^{-1}: 2610 s, 2590 s, 2580 s, 2500 s, 2300 w, 2160 s, 1400 m, 1280 w, 1180 m, 1150 m, 1080 w, 980 m, 905 w, 860 m, 560 m, and 465 m. In order to quantify **4** and **5** in the mixture, the gas was condensed again in the trap at −196 °C and then the temperature was elevated to −55 °C. This led to the separation of the components of the mixture. Tetraborane passed into the gas phase, while solid pentaborane remained in the trap. The measured quantity of C_4H_{10} reached 2.0 mmol (yield 24.9%). After removal of **5** from the calibrated system, the quantity of **4** was measured by heating the trap to −20 °C. The yield of **4** was 0.24 mmol (3.7% with respect to boron). The overall yield of di-, tetra-, and pentaboranes was 33.9%.

The solid residue after completion of the reaction contained tetrabutylammonium aluminate with different ligands of the composition $Bu_4N[AlCl_3BH_4]$. In the IR spectrum of the residue, the bands corresponding to the covalently bonded BH_4 groups were clearly pronounced, ν/cm^{-1}: 2480, 2425 ($B-H_{term}$), 2220 sh and 2175 ($B-H_{bridg}$)[7]. Neither the initial **3** nor tetrabutylammonium tetrahydroborate (**6**) was found in the residue.

Results and Discussion

The reaction of **3** with $AlCl_3$ studied in the present work begins with the melting of the mixture at 50 °C and proceeds at this temperature for one hour. As in reaction with **1**, the liberated BH_4^- ion coordinates with $AlCl_3$ to form a complex anion $[AlCl_3BH_4]^-$, while unstable B_2H_4 decomposes and converts into more stable boranes with evolution of hydrogen. B_2H_6, B_5H_9, and B_4H_{10} were isolated by low-temperature fractionation and identified. Reaction of **3** with $AlCl_3$ is irreversible and proceeds until **3** is completely consumed. The yield of **5** is 25%; other boranes (B_2H_6, B_5H_9) are present in the reaction mixture in smaller quantities (yields 5.3 and 3.7%, respectively).

Decomposition of **3** by aluminum chloride can serve as a simple and convenient synthesis route to tetraborane(10) **5**. The known methods for its preparation involve decomposition of $Me_4NB_3H_8$ with polyphosphoric acid[8] or reaction of **2** with hydrogen chloride in the presence of diborane.[9] The latter method is inconvenient, as it requires the use of aggressive gaseous products and of hardly accessible non-solvated **2**. Compound **5** is obtained in a higher yield in reaction of **3** with BBr_3 at 0 °C in the absence of solvent.[10] The reaction studied by us seems to be a promising route for the laboratory preparation of compound **5**.

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