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Synthesis of $Bu_4NB_{11}H_{14}$ by the Reaction of Tetrabutylammonium Octahydrotriborate with Diborane in Diglyme

L. A. Gavrilova*, L. V. Titov*, and P. V. Petrovskii**

**Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

***Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
ul. Vavilova 28, Moscow, GSP-1, 117813 Russia

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Abstract—The method for synthesis of $Bu_4NB_{11}H_{14}$ by dehydrocondensation of $Bu_4NB_3H_8$ with diborane in diglyme in the temperature range of 70–90°C was developed. The product is formed in 75–85% yield. The conditions that ensure complete conversion of the anions, namely, initial $B_3H_8^-$ and intermediate *arachno*-$B_9H_{14}^-$, into *nido*-$B_{11}H_{14}^-$ and prevent further dehydrocondensation of $B_{11}H_{14}^-$ to *closo*-$B_{12}H_{12}^{2-}$ were established.

Development of methods for synthesis and study of the properties of salts with polyhedral boron hydride anions, including $B_{11}H_{14}^-$, are of interest for the preparation of coordination compounds containing these anions as ligands and of metalloboranes and carboranes.

Previously, we studied dehydrocondensation of tetraalkylammonium octahydrotriborates with B_2H_6 [1] and B_5H_9 [2]. Dehydrocondensation of $Bu_4NB_3H_8$ with these boranes yields a mixture of tetrabutylammonium salts with the *arachno*-$B_9H_{14}^-$ and *nido*-$B_{11}H_{14}^-$ anions. The quantitative ratio of the anions depends on the conditions of dehydrocondensation. Salts with the $B_9H_{14}^-$ and $B_{11}H_{14}^-$ anions have not been obtained in a pure state.

The purpose of this study was to select the optimal conditions for the formation of $Bu_4NB_{11}H_{14}$ in the dehydrocondensation reaction of $Bu_4NB_3H_8$ with diborane.

EXPERIMENTAL

The study was carried out using $Bu_4NB_3H_8$ prepared and purified by the known procedure [3]. Diborane was prepared by the reaction of $NaBH_4$ with boron trifluoride etherate in diglyme. Diglyme and pentane were dehydrated and distilled from $LiAlH_4$. All operations were carried out in an atmosphere of dry nitrogen.

The IR spectra of solutions in diglyme were measured on a UR-20 spectrophotometer. ^{11}B NMR spectra were recorded on a Bruker WP-200-SY instrument (64.2 MHz) using $BF_3 \cdot OEt_2$ as an external standard.

The reaction between $Bu_4NB_3H_8$ and diborane was carried out in the following way. The $Bu_4NB_3H_8$ salt was charged into a 600-ml glass vessel, and dyglime was added until octahydrotriborate completely dissolved. The solution was cooled to –196°C and the vessel was evacuated and filled with diborane. The $Bu_4NB_3H_8 : B_2H_6$ molar ratio was 1 : 8 and the initial B_2H_6 pressure in the vessel was 200–300 mmHg. The reaction mixture was kept at a specified temperature for 24 or 48 h. After completion of the exposure, transparent yellow-colored solutions were obtained. The final gas pressure in the reaction vessel was not higher than atmospheric pressure.

According to $^{11}B\{^1H\}$ NMR data, depending on the temperature and the exposure time, the reaction solutions contained anions with the following chemical shifts (ppm): $B_3H_8^-$ (–29.8) [4]; $B_9H_{14}^-$ (–8.4, –20.6, –23.9) [5]; and $B_{11}H_{14}^-$ (–14.2, –16.5) [6, 7]. The spectra also exhibited weak unidentified signals whose total intensity corresponded to not more than 3–5% of the overall amount of boron added to the solution. The relative contents of hydroborates in the solutions (mol %) were calculated from the integrated intensities of signals in the $^{11}B\{^1H\}$ NMR spectra. The unidentified signals were not taken into account. The compositions of the solutions determined on the basis of NMR data are summarized in table. The solid $Bu_4NB_{11}H_{14}$ was isolated from solutions that contained, according to NMR data, only $B_{11}H_{14}^-$.

Synthesis of $Bu_4NB_{11}H_{14}$. The reaction vessel containing $Bu_4NB_3H_8$ (0.35 g, 1.24 mmol), diglyme (17 ml), and B_2H_6 (9.95 mol) was kept at 80°C for 24 h. The solid product was precipitated by pentane, Composition of the products formed in dehydrocondensation of $Bu_4NB_3H_8$ with diborane

T, °C	Time, h	Content, mol %		
		$B_3H_8^-$	$B_9H_{14}^-$	$B_{11}H_{14}^-$
60	24	59.9	16.9	23.2
60	48	27.7	9.1	63.2
60	96	0.0	3.5	96.3
75	24	2.6	5.6	91.8
75	48	0.0	0.0	100
90	24	0.0	0.0	100
90	48	0.0	0.0	100

washed, and dried in a vacuum. The product was recrystallized from isopropyl alcohol. The yield was 75–85%. On heating in an atmosphere of argon at 220–240°C, the salt $Bu_4NB_{11}H_{14}$ decomposes with vigorous gas evolution.

For $C_{16}H_{40}NB_{11}$

anal. calcd. (%):	C, 51.18;	H, 13.42;	B, 31.67.
Found (%):	C, 49.57;	H, 13.02;	B, 30.69.

The $^{11}B\{^1H\}$ NMR spectrum of a dyglime solution of the salt exhibits only signals with chemical shifts of –14.2 and –16.2 ppm, typical of the $B^{11}H_{14}^-$ anion [6, 7].

RESULTS AND DISCUSSION

The known method [8] used for the preparation of salts with the $B_{11}H_{14}^-$ anion is based on the reaction of tetrahydroborates with decaborane. Our study of dehydrocondensation of octahydrotriborates with diborane and pentaborane also revealed the formation of the $B_{11}H_{14}^-$ anion whose amount depended appreciably on the reaction conditions, in particular, the nature of the solvent, the temperature, the reactant ratio, and the exposure time. Thus, the reaction carried out at 60°C for 5 days in a number of solvents (toluene, dioxane, and diglyme) yields a mixture containing 60, 88, and 95 mol % of $B_{11}H_{14}^-$, respectively [1].

Our study of the reaction of $Bu_4NB_3H_8$ with diborane in diglyme showed that at 60°C and at an exposure time of 24 h, 40.1 mol % of the $B_3H_8^-$ anion added enters the reaction to give 23.2 mol % of $B_{11}H_{14}^-$ and 16.9 mol. % of $B_9H_{14}^-$. An increase in the exposure time increases the reaction efficiency, in particular, the starting octahydrotriborate is wholly consumed, and the reaction products contain lower amount of $B_9H_{14}^-$ and higher amount of $B_{11}H_{14}^-$ as compared to the previous case (table). When the temperature is elevated to 75°C, both the initial $B_3H_8^-$ anion and the intermediate $B_9H_{14}^-$ anion are fully consumed. After 48 h, the solution contains only $B_{11}H_{14}^-$.

The IR spectra of the solutions exhibit an intense absorption band at 2540 cm^{-1} that corresponds to the stretching vibrations of the B–H bonds in $B_{11}H_{14}^-$. The ν(B–H) modes typical of the $B_9H_{14}^-$ anion cannot be seen, as they are overlapped by the intense ν(B–H) mode for $B_{11}H_{14}^-$. Irrespective of the exposure time, no $B_3H_8^-$ or $B_9H_{14}^-$ anions are found in the reaction products obtained at 90°C. In the temperature range from 60 to 90°C, a minor impurity of unidentified boronhydrides can be detected in solutions; at 105°C, the proportion of these compounds increases to 20% of the total boron taken for the reaction.

Thus, a temperature of 75–90°C and an exposure time of 24 to 48 h are considered to be the optimal conditions for the synthesis of $Bu_4NB_{11}H_{14}$. Under these conditions, the $B_{11}H_{14}^-$ anion does not undergo further dehydrocondensation to $B_{12}H_{12}^-$. The reaction can be represented by the following overall equation

$$Bu_4NB_3H_8 + 4B_2H_6 \longrightarrow Bu_4NB_{11}H_{14} + 9H_2. \quad (1)$$

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