ISSN 1070-4272, Russian Journal of Applied Chemistry, 2017, Vol. 90, No. 11, pp. 1804−1809. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © P.P. Belov, P.A. Storozhenko, N.S. Voloshina, M.G. Kuznetsova, 2017, published in Zhurnal Prikladnoi Khimii, 2017, Vol. 90, No. 11, pp. 1498−1503.

SPECIFIC TECHNOLOGICAL PROCESSES

Synthesis of Decaborane by the Reaction of Sodium Undecaborate with Mild Organic Oxidants

P. P. Belov*, P. A. Storozhenko, N. S. Voloshina, and M. G. Kuznetsova

State Research Institute of Chemistry and Technology of Organoelement Compounds,
sh. Entuziastov 38, Moscow, 111123 Russia
**e-mail: ppbeloff@mail.ru*

Received November 17, 2017

Abstract—New organic oxidants (aldehydes and ketones) allowing efficient synthesis of decaborane in a high yield via intermediate alkali metal salt were found. The sodium undecaborate oxidation process was refined, and new reaction stoichiometry was suggested.

DOI: 10.1134/S107042721711012X

The ability of boron compounds to form stable framework structures that are similar to aromatic compounds and incorporate other elements is of much interest for different branches of chemistry. Diverse steric structure and strong chemical bonds of such derivatives of boron hydrides as carboranes and metallocarboranes not only determine their unique properties, but also allow their use in catalysis [1], in organometallic chemistry, and also in synthesis of luminescent materials [2], of polymers resistant to high temperatures, oxidation, and radiation [3, 4], of nanomaterials, and of liquid crystals.

Since recently, carboranes became particularly demanded by medicine, where they are used as absorbents of epithermal neutrons in boron neutron capture therapy (BNCT) [5–7].

Increased interest in framework boron derivatives stimulated the development of procedures for preparing the starting compound for their synthesis, decaborane. This framework boron hydride was synthesized for the first time by Alfred Stock in 1912 [8]. Since that time, the decaborane synthesis process underwent major changes. However, because of the synthesis complexity and relatively low yield of the target product, decaborane remains expensive and is in short supply. Therefore, the development of efficient, simple, and economically advantageous procedure for its synthesis is a topical problem.

Analysis of the published data shows that the route to decaborane via intermediate alkali metal tetradecahydroundecaborates (hereinafter, undecaborates) is the most promising for further development and improvement.

Previously reported procedures for decaborane synthesis are based on the reaction of sodium borohydride $NaBH_4$ with either boron trifluoride etherates [9, 10] or alkyl halides ($C_5H_{11}Br$ etc.) [11] as Lewis acids in diglyme at 100–110°C with the formation of a solution of sodium undecaborate $NaB_{11}H_{14}$ [Eqs. (1), (2)]:

$$17NaBH_4 + 20BF_3\cdot O(C_2H_5)_2 \rightarrow 2NaB_{11}H_{14} + 15NaBF_4 + 20H_2 + 20O(C_2H_5)_2, \quad (1)$$

$$11NaBH_4 + 10C_5H_{11}Br \rightarrow NaB_{11}H_{14} + 10C_5H_{12} + 10NaBr + 10H_2. \quad (2)$$

Then, diglyme was replaced by water, and the sodium undecaborate solution was oxidized with various oxidants in the presence of sulfuric acid. The following oxidants were used: potassium permanganate ($KMnO_4$), sodium bichromate ($Na_2Cr_2O_7$), hydrogen peroxide (H_2O_2) in the presence of a bivalent iron salt [12, 13], manganese dioxide (MnO_2), chromic anhydride (CrO_3), and a trivalent iron salt ($Fe_2(SO_4)_3\cdot 5H_2O$) [9]. The assumed reaction stoichiometry was described by Eq. (3) [13], according to which 1 mol of decaborane and 12 mol of boric acid are formed from 2 mol of sodium undecaborate:

$$2B_{11}H_{14}^{-} + 36H_2O \rightarrow B_{10}H_{14} \\ + 12B(OH)_3 + 18H_2 + 14H^+ + 16e-. \qquad (3)$$

Thus, in the reaction with various inorganic oxidants more than a half of boron from the previously synthesized undecaborate ion is irretrievably lost. Furthermore, the process involves formation of a large amount of harmful waste (manganese, chromium, fluorine, boron compounds). Introduction of strong inorganic oxidants into the reaction mixture in the step of oxidation of undecaborate ion significantly restricts the choice of the extractant for decaborane, thus complicating its isolation. As for the solvent replacement step, each of the suggested procedures (azeotropic distillation of diglyme with water [13] or treatment with hexane [9]) implies an additional step of diglyme regeneration, which strongly complicates the process and makes it much more expensive.

To eliminate these drawbacks and increase the yield of the target product by finding an appropriate oxidant, we performed a thorough detailed chemical and technological analysis of the decaborane synthesis by oxidation of alkali metal undecaborates.

EXPERIMENTAL

All the steps of the decaborane synthesis were performed in one vessel: a 2-L flask with a jacket, equipped with a stirrer, a thermometer, and a descending condenser. The reactants were fed with a Masterflex L/S peristaltic pump (7524-55). The temperature was controlled with a Huber Unistat 125 thermostat. Synthesis of sodium undecaborate in diglyme solution was performed for 8 h at 100–105°C. The diborane vapor was trapped in a Drechsel bottle filled with triethylamine and in a U-shaped alcoholic trap. The synthesis was based on reaction (2); 3.8 mol of alkyl halide (30% excess) was taken per 3.2 mol of sodium borohydride. The diglyme volume was 800 mL. After the 8-h reaction, the mixture was cooled to room temperature with continuous stirring in an inert gas stream. Vacuum distillation of diglyme and unchanged Lewis acid was performed at 85°C/5–7 mm Hg. After cooling the residue to 20–25°C, 320 mL of toluene was added, and then 40% sulfuric acid (1600 g) was carefully added at a rate at which the gas evolution and foaming were controllable. To the resulting acidic solution of sodium undecaborate, 1.36 mol of acetone was added dropwise over a period of 105 min. Then, after the phase separation, the lower aqueous layer was discarded, and the upper organic layer was washed with distilled water (7 × 300 mL). The resulting toluene solution of decaborane was evaporated to the required concentration and analyzed by ^{11}B NMR spectroscopy.

To separate the impurity, a 20% solution of decaborane in toluene (321 g) was charged into a nitrogen-flushed four-necked flask equipped with a turbine stirrer, a thermometer, a dropping funnel, and a reflux condenser. After the temperature of 70°C was reached, dimethylaniline (140 g) was slowly added dropwise, with the subsequent gradual heating to 100°C. The reaction mixture was continuously stirred at this temperature until the gas evolution ceased. The cooled reaction mixture was transferred onto a glass frit and washed with three portions of pure toluene. In so doing, the impurity passed into the toluene solution. This solution was evaporated in a water-jet-pump vacuum. The dry residue was dissolved in n-hexane and analyzed by ^{11}B NMR spectroscopy.

The ^{11}B NMR spectra were recorded on a Bruker AM-360 spectrometer operating at 115.526 MHz. The chemical shifts are given relative to boron trifluoride etherate. Alkyl halides (n-bromobutane, -pentane, -hexane, 98+% purity) and diglyme (99% purity, water content <0.5%) were purchased from Alfa Aesar. Also, we used chemically pure grade toluene [TU (Technical Specification) 2631-020-44493179–98 with revisions 1, 2, 3], chemically pure grade sulfuric acid (TU 2631-020-44493179–98 with revisions 1, 2, 3), pure grade acetone [GOST (State Standard) 2603–79], analytically pure grade dimethylaniline (GOST 5855–78), and analytically pure grade hexane (TU 2631-003-05807999–98).

RESULTS AND DISCUSSION

Comparative analysis of the above procedures for preparing sodium undecaborate shows that the reaction of sodium borohydride with alkyl bromide ($C_nH_{2n+1}Br$, where $n = 4–6$) in diglyme is preferable from the process viewpoint. We reached the best results with n-butyl bromide. In addition, this bromide is many times cheaper than other bromoalkanes. We decided to perform solvent replacement by vacuum distillation, which allowed us to recycle the distilled-off diglyme without any additional

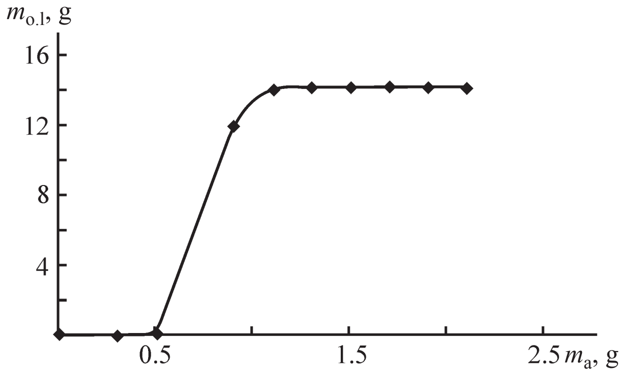

Fig. 1. Organic layer weight $m_{o.l}$ as a function of the amount of the acid added m_a.

regeneration. As a result, the sodium undecaborate synthesis was considerably simplified and was made appreciably less labor-consuming.

However, we paid particular attention to the search for new effective oxidants for the sodium undecaborate oxidation step. We have found in the course of our studies that some organic compounds containing carbonyl group, such as acetone, benzaldehyde, methyl ethyl ketone, acetylacetone, formaldehyde, etc., are capable to oxidize the $B_{11}H_{14}^-$ ion to decaborane with the formation of the corresponding alcohols [14]. The use of such oxidants also allowed us to use aromatic solvents.

However, in the course of developing the process for sodium undecaborate oxidation with acetone, we reached the decaborane yield higher than 100% relative to the stoichiometry of Eq. (3) (run nos. 3 and 4 in the table).

Therefore, we suggested refined stoichiometry of this redox reaction [Eq. (4)], according to which only one molecule of sodium undecaborate is required for the formation of one decaborane molecule:

$$2NaB_{11}H_{14} + 4CH_3COCH_3 + H_2SO_4 + 6H_2O$$
$$\rightarrow 2B_{10}H_{14} + 2H_3BO_3 + 4C_3H_7OH + Na_2SO_4. \quad (4)$$

In accordance with Eq. (4), the reaction occurs without hydrogen evolution. However, actually the decaborane synthesis is accompanied by the formation of a large amount of this gas, which contradicts the suggested stoichiometry. Therefore, to understand the reaction mechanism better, we divided the process into two steps: preparation of aqueous acid solution of $NaB_{11}H_{14}$ and the redox reaction proper.

We found that the major fraction of hydrogen is released specifically during preparation of the aqueous acid solution. Also, the reaction mixture underwent phase separation. The weight of the upper organic layer first increased with the addition of the acid and then reached a certain limit (Fig. 1).

In the ^{11}B NMR spectra (C_6D_6) of the diglyme solution, along with the signals (δ, ppm) at –14.1 (d, 1B), –16.0 (d, 5B), and –16.7 (d, 5B), belonging to the boron atoms in $NaB_{11}H_{14}$, we identified the signals at –8.19 (d, 3B), –20.5 (d, 3B), and –23.8 (d, 3B) (intensity ratio 1 : 1 : 1), corresponding to the boron atoms in $B_9H_{14}^-$, and a characteristic multiplet of $B_3H_8^-$ at –30.1 ppm (nonet, $^1J_{BH}$ = 33.3 Hz). The $^{11}B\{^1H\}$ NMR spectrum of the upper organic layer formed (Fig. 2b) contains virtually no signals apart from those of $B_{11}H_{14}^-$.

Analysis of the $^{11}B\{^1H\}$ NMR spectra (Figs. 2a, 2b) shows that treatment with sulfuric acid does not alter the boron framework of sodium undecaborate

Data on the theoretical [Eqs. (1)–(4)] and practically reached yield of decaborane synthesized by different procedures

Run no.	$NaBH_4$, g	Lewis acid	Oxidant	Theoretical yield of $B_{10}H_{14}$ according to Eq. (3), g	Theoretical yield of $B_{10}H_{14}$ according to Eq. (4), g	Actual yield of $B_{10}H_{14}$, g
1	60	$BF_3\cdot O(C_2H_5)_2$	H_2O_2/Fe(II)	11.4	–	8.9[a]
2	60	$BF_3\cdot O(C_2H_5)_2$	$KMnO_4$	11.4	–	9.1[a]
3	60	C_4H_9Br	$CO(CH_3)_2$	8.8	17.6	9.9
4	60	$C_5H_{11}Br$	$CO(CH_3)_2$	8.8	17.6	9.6
5	60	$C_6H_{13}Br$	$CO(CH_3)_2$	8.8	17.6	8.7

[a] Experimental data given in [13].

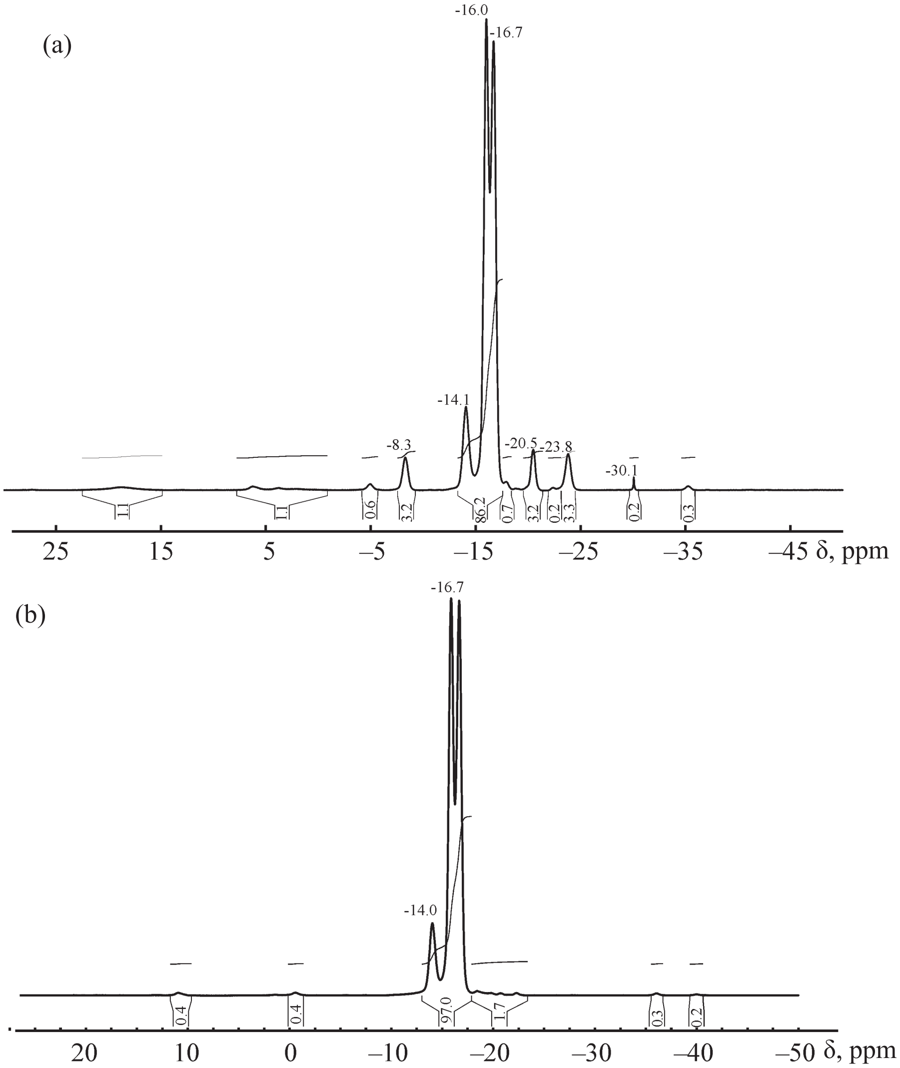

Fig. 2. $^{11}B\{^1H\}$ NMR spectra of the (a) diglyme solution of sodium undecaborate and (b) upper organic layer obtained after treatment of sodium undecaborate with an aqueous solution of sulfuric acid. (δ) Chemical shift.

but leads to the disappearance of $B_9H_{14}^-$, $B_3H_8^-$, and other impurities formed in the step of synthesizing the diglyme solution of sodium undercaborate, as these impurities are readily broken down to boric acid with the evolution of hydrogen in the step of preparation of the acid solution. The gas evolution is also accompanied by the decomposition of the unchanged $NaBH_4$.

Thus, treatment of sodium undecaborate with an aqueous sulfuric acid solution leads to exchange reaction (5):

$$2NaB_{11}H_{14} + H_2SO_4 \rightarrow 2HB_{11}H_{14} + Na_2SO_4. \qquad (5)$$

In the second step, the species reacting with acetone is not sodium undecaborate but its acid form, "undecaboric" acid [Eq. (6)]:

$$HB_{11}H_{14} + CH_3COCH_3 + 3H_2O \rightarrow B_{10}H_{14} + H_3BO_3 + C_3H_7OH + H_2. \qquad (6)$$

In accordance with Eqs. (5) and (6), 1 mol of sodium undecaborate is still required for obtaining 1 mol of decaborane, but 1 mol of hydrogen is released in the process, which well agrees with the experimental data.

Thus, oxidation of sodium undecaborate can be described by overall Eq. (7):

$$2NaB_{11}H_{14} + H_2SO_4 + 2CH_3COCH_3 + 6H_2O \rightarrow 2B_{10}H_{14} + 2H_3BO_3 + 2C_3H_7OH + Na_2SO_4 + 2H_2. \qquad (7)$$

It should be noted that the decaborane thus obtained, irrespective of particular oxidant containing a carbonyl

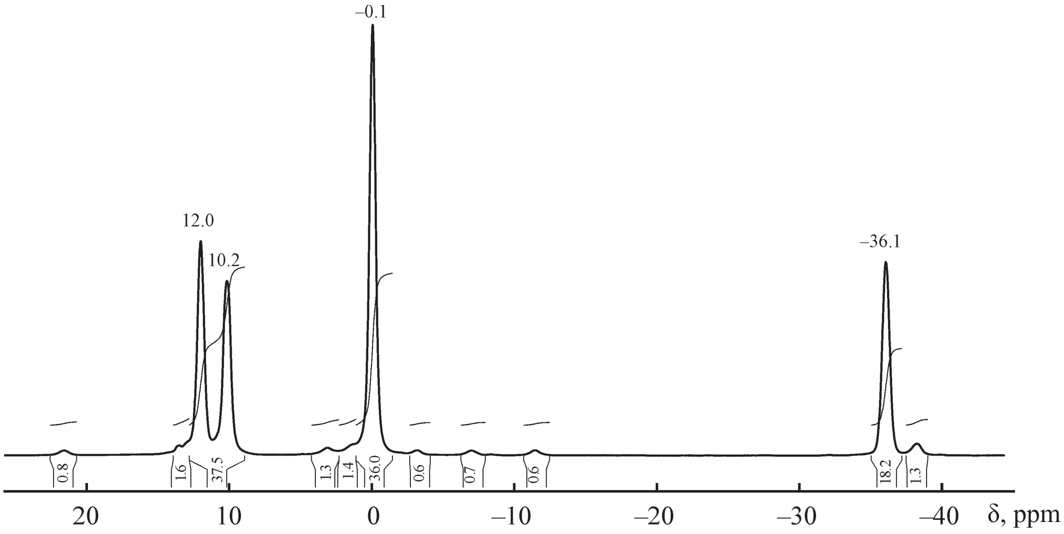

Fig. 3. $^{11}B\{^1H\}$ NMR spectrum of decaborane containing impurities.

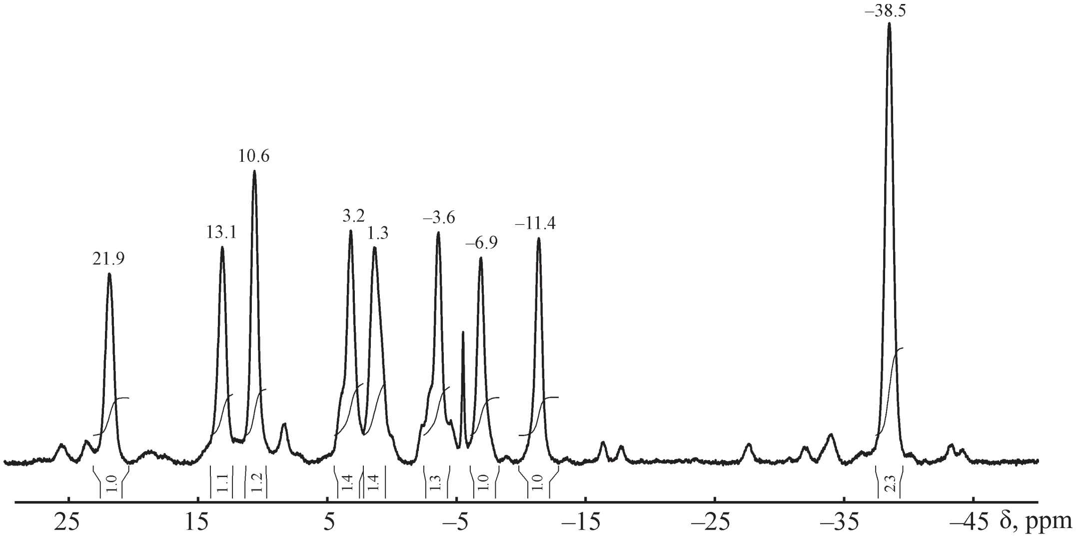

Fig. 4. $^{11}B\{^1H\}$ NMR spectrum of the boron impurity of type 5-$RB_{10}H_{13}$.

group, always contains similar boron impurity in an amount of 3–5% and more (Fig. 3).

The $^{11}B\{^1H\}$ NMR spectrum of the solution of the separated impurity (Fig. 4) contains nine signals (δ, ppm) at 21.9 (s, 1B), 13.1 (d, 1B), 10.6 (d, 1B), 3.2 (d, 1B), –3.6 (d, 1B), –6.9 (d, 1B), –11.4 (d, 1B), and –38.5 (d, 2B), which correspond to chemical shifts of boron atoms in decaborane with a substituent at the B^5 atom, 5-$RB_{10}H_{13}$ [15].

The results obtained allowed us to patent a new procedure for decaborane synthesis [14]. As compared to the known analogs, this procedure is not only more efficient, but also technologically and environmentally safer and less resource-consuming.

CONCLUSIONS

(1) A highly efficient procedure for oxidation of sodium undecaborate was developed. It allows the process to be performed with considerably lower loss of “hydride” boron, which led to a more than 25% increase in the yield of the target product.

(2) A comprehensive study of the sodium undecaborate oxidation process allowed suggesting a new reaction stoichiometry describing the process most adequately.

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