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RESEARCH ARTICLE

New approaches to the synthesis of substituted derivatives of the $[B_3H_8]^-$ anion

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Abstract

Objectives. To develop methods for the synthesis of substituted derivatives of the octahydrotriborate anion. Such compounds can be considered as hydrogen storage, components of ionic liquids, precursors for the production of boride coatings using the traditional chemical vapor deposition method, and also as a building material for the production of higher boron hydrogen clusters.

Methods. Since substitution reactions are sensitive to moisture and atmospheric oxygen, the syntheses were carried out in a direct flow of argon or in a dry, sealed SPEKS GB02M glove box with a double gas purification unit and two airlocks. The reaction was initiated by cooling to 0°C, in order to avoid the formation of by-products. All the results were characterized using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies.

Results. The study presents a detailed study of the known methods for preparing substituted derivatives of the octahydrotriborate(1−) anion using dry hydrogen chloride as an electrophilic inductor and makes recommendations for improvement. In this method it is advisable to use cesium octahydrotriborate which facilitates the yield of the target product. New methods were proposed to initiate the substitution reaction in the $[B_3H_8]^-$-anion using *N*-chlorosuccinimide and bromine. Using these inductors, new substituted derivatives of the octahydrotriborate anion with *N*-nucleophiles were obtained and defined by means of IR and NMR spectroscopies: $[B_3H_7NCR]$, (R = Et, *i*-Pr, Ph) and $[B_3H_7NH_2R]$, (R = C_9H_{19} (INA), Bn), $[B_3H_7NHEt_2]$, as well as $Bu_4N[B_3H_7Hal]$, $Bu_4N[B_3H_6Hal_2]$, where Hal = Cl, Br. It was also established that hydrogen bromide is released during the reaction with bromine and amines. This immediately protonates the amine which requires additional heating of the reaction mixture. The study also established that the reaction mechanism with *N*-chlorosuccinimide is not radical.

Conclusions. The main factors influencing the course of the substitution reaction are the possible occurrence of side interactions between the nucleophile and the inducer, steric possibilities, and subsequent isolation of the reactive reaction products.

Keywords

boron, borohydrides, octahydrotriborate(1−) anion, Lewis acids, nucleophilic substitution, succinimide, halogens

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НАУЧНАЯ СТАТЬЯ

Новые подходы к синтезу замещенных производных аниона $[B_3H_8]^-$

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Аннотация

Цели. Разработка методов синтеза замещенных производных октагидротриборатного аниона, потенциально рассматриваемых в качестве химических аккумуляторов водорода, компонентов ионных жидкостей, прекурсоров для получения боридных покрытий с уникальными свойствами методом Chemical Vapor Deposition (CDV), а также в качестве «строительного материала» для получения высших бороводородных кластеров.

Методы. Ввиду чувствительности реакций замещения к влаге и кислороду воздуха, синтезы проводили в постоянном токе аргона или в сухом герметичном перчаточном боксе СПЕКС ГБ02М с блоком двойной газоочистки и двумя шлюзами. Инициирование реакции проводили при охлаждении до 0°С во избежание образования побочных продуктов. Все результаты были охарактеризованы с помощью инфракравной (ИК) спектроскопии и спектроскопии ядерного магнитного резонанса (ЯРМ).

Результаты. Подробно изучены и усовершенствованы известные методики получения замещенных производных октагидротриборатного (1−) аниона с использованием сухого хлороводорода в качестве электрофильного индуктора. Установлено, что в данном методе целесообразно использовать октагидротриборат цезия, что позволяет облегчить выход целевого продукта. Предложены новые способы инициирования реакции замещения в анионе $[B_3H_8]^-$ с помощью *N*-хлорсукцинимида и брома. С помощью этих индукторов получены и охарактеризованы методами ИК и ЯМР-спектроскопии новые замещенные производные октагидротриборатного аниона с *N*-нуклеофилами: $[B_3H_7NCR]$, (R = Et, *i*-Pr, Ph) и $[B_3H_7NH_2R]$, (R = C_9H_{19} (INA), Bn), $[B_3H_7NHEt_2]$, а также $Bu_4N[B_3H_7Hal]$, $Bu_4N[B_3H_6Hal_2]$, где Hal = Cl, Br. Установлено, что в ходе реакции с бромом и аминами происходит выделение бромоводорода, который сразу протонирует амин, что требует дополнительного нагрева реакционной смеси. Также в ходе работы установлено, что механизм реакции с *N*-хлорсукцинимидом не является радикальным.

Выводы. Усовершенствованы и систематизированы известные методики получения замещенных производных октагидротриборатного аниона. Установлено, что основными факторами, влияющими на ход реакции замещения, являются возможное протекание побочных взаимодействий между нуклеофилом и индуктором, стерические возможности, последующая изоляция реакционноспособных продуктов реакции. В зависимости от нуклеофила выбор метода и условий может быть ограничен.

Ключевые слова

бор, бороводороды, октагидротриборатный (1−) анион, кислоты Льюиса, нуклеофильное замещение, сукцинимид, галогены

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INTRODUCTION

Substituted derivatives of octahydrotriborate anion act as promising components for chemical hydrogen accumulators [1–3]. They are also precursors for obtaining boride coatings with unique properties [4–6], and play the role of components for obtaining derivatives of higher borohydrates, ionic liquids and liquid crystals [7]. Due to the difficulty of their preparation, the applications of these compounds are still poorly studied.

The preparation of substituted derivatives of the $[B_3H_8]^-$ anion is based on methods using cleavage of the boron backbone of larger clusters, for example, by symmetric cleavage of tetraborane-10 [8]. However, interaction with certain nucleophiles does not lead to substitution, but provokes destruction of the boron backbone [9].

With the development of new and efficient methods for the synthesis of $[B_3H_8]^-$ [10, 11] anion, its substituted derivatives and the methods of their preparation based on

its direct interaction with nucleophiles are of increasing interest. The presence of an aromatic structure allows the octahydrotriborate anion to enter into reactions of electrophile-induced nucleophilic substitution of the hydrogen atom. They are similar to the higher cluster anions [12, 13], where various Lewis acids act as electrophilic inductor [14–16]. The preparation of substituted derivatives by the methods described above is a complex multifactorial process with a number of side reactions. As a result, the yield of the target product can be significantly reduced.

It has been shown that the interaction of $[B_3H_8]^-$ anion with metal halides in the presence of nucleophiles leads to the formation of a large variety of substituted products [14, 17]. By means of nuclear magnetic resonance (NMR) spectroscopy, it has been found that the reaction proceeds through the stage of formation of the transition complex $[B_3H_7–H–MHal_x]^-$. The rate of transformation of this complex is significantly affected by the nature of the Lewis acid. At the same time, the use of metal salts as inductors can significantly complicate the composition of the reaction mixture, complicating the purification of the target products. On the other hand, the use of gaseous hydrogen chloride in the preparation of substituted derivatives is of particular interest due to the almost complete absence of impurities, greatly facilitating the yield of the product. $(CH_3)_4N[B_3H_7Cl]$, $[B_3H_7NCCH_3]$, $[B_3H_7NCCH_3]$, $[B_3H_7DMF]$ (DMF = $(CH_3)_2NCH$) have already been obtained by this method [18], but this method also has a number of disadvantages. It requires a complex multi-component plant with a gas line, as well as cleaning, drying, and carrying out manipulations with gaseous hydrogen chloride gas.

The aim of this study is to improve and systematize the known methods, and develop new ones for the preparation of substituted derivatives of the $[B_3H_8]$ anion. These include: halogen-substituted $Bu_4N[B_3H_7Cl]$, $Bu_4N[B_3H_7Br]$, $Bu_4N[B_3H_6Cl_2]$, $Bu_4N[B_3H_6Br_2]$; nitrilium-substituted $[B_3H_7NCR]$, (R = CH_3, Et, *i*-Pr, Ph); amine-substituted derivatives of $[B_3H_7NH_2R]$, (R = C_9H_{19}, Bn), $[B_3H_7NHEt_2]$, $[B_3H_7NEt_3]$ by interaction of the octahydrotriborate(1−) anion with halogens (Br_2, I_2) and with *N*-chlorosuccinimide (NCS). The compounds $[B_3H_7NCR]$, (R = Et, *i*-Pr, Bn), $[B_3H_7NH_2R]$, (R = C_9H_{19}, Bn) were obtained for the first time using NCS. The use of NCS as an electrophilic inducer was proposed for the synthesis of chloro-substituted, nitrilic and amine-substituted derivatives.

EXPERIMENTAL

Salts of $[B_3H_8]^-$ anion were prepared according to the known method [10] by mild oxidation of sodium borohydride with benzyl chloride. Benzonitrile (99%, *Panreac Sintesis*, Spain), NCS (98%, *Sigma-Aldrich*, USA), bromine (98%, *Sigma-Aldrich*, USA), isononylamine (INA) (98%, *Sigma-Aldrich*, USA), benzylamine (99%, *Panreac Sintesis*, Spain), sulfuric acid (95%, *Chimmed*, Russia), NaCl (99%, *Ruschim*, Russia) were used without further purification.

Dichloromethane, acetonitrile, toluene, and petroleum ether were shaken with $CaCl_2$ and distilled over calcium hydride. The solvents were stored in a dark container over molecular sieves (4 Å) at ≈5°C.

Tetrahydrofuran, diethyl ether was passed through activated aluminum oxide and stored over molecular sieves (4 Å) at ≈5°C.

Triethylamine and diethylamine were purified by shaking with KOH until the darkening of potassium hydroxide stopped, then distilled at atmospheric pressure.

^{11}B and ^1H NMR spectra of solutions of the substances obtained in dichloromethane, deuterodichloromethane, tetrahydrofuran, toluene, and deuteroacetonitrile were recorded on an Avance II-300 NMR spectrometer (*Bruker*, Germany) at 96.32 MHz and 300.21 MHz, respectively, with internal deuterium stabilization. Tetramethylsilane and $BF_3{\cdot}OEt_2$ were used as external standards.

The infrared (IR) spectra of the compounds were recorded on an INFRALUM FT-02 IR Fourier spectrometer (*Lumex*, Russia) in the range 4000–400 cm^{-1} with a resolution of 1 cm^{-1}. Samples were prepared in the form of tablets pressed with KBr (*Sigma-Aldrich*, USA).

Elemental analysis for carbon, hydrogen and nitrogen was carried out on an automatic analyzer CHNS-3 FA 1108 Elemental Analyser (*Carlo Erba Reagents GmbH*, Germany).

Reactions requiring the absence of moisture and air were carried out in a sealed box model SPECS GB02M (*Spectroscopic Systems*, Russia) with a double gas purification unit and two airlocks.

Synthesis of $Bu_4N[B_3H_7Cl]$

$Bu_4N[B_3H_8]$ (100 mg, 0.35 mmol) was placed in a 25-mL flask and dissolved in 5 mL of dichloromethane. The mixture was cooled to −50°C and NCS (47 mg, 0.35 mmol) dissolved in 5 mL of dichloromethane was slowly added. The resulting succinimide was precipitated by addition of diethyl ether. The mixture was filtered off from the precipitate, the filtrate was evaporated at a rotary evaporator. ^{11}B NMR (CD_2Cl_2, 298 K, 96.32 MHz), δ, ppm: −16 (s, 2B), −22 (s, 1B). ^1H NMR (CD_2Cl_2, 298 K, 300 MHz), δ, ppm: 3.05 (m, 8H, Bu_4N), 1.57 (m, 8H, Bu_4N), 1.31 (m, 8H, Bu_4N), 0.93 (t, 12H, Bu_4N), 0.9–0.7 (broad, 7H, HB). IR (KBr), cm^{-1}: ν(BH): 2520, 2448, 2338, ν(BCl): 850.

Synthesis of $Bu_4N[B_3H_6Cl_2]$

$Bu_4N[B_3H_8]$ (100 mg, 0.35 mmol) was placed in a 25-mL flask and dissolved in 5 mL of dichloromethane.

The mixture was cooled to −50°C and NCS (93.1 mg, 0.70 mmol) dissolved in 5 mL of dichloromethane was slowly added. The resulting succinimide was precipitated by addition of diethyl ether. The mixture was filtered from the precipitate; the filtrate was evaporated at a rotary evaporator. ^{11}B NMR (CD_2Cl_2, 298 K, 96.32 MHz), δ, ppm: −5 (s, broad, 1B), −13 (s, 2B); ^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz), δ, ppm: 3.05 (m, 8H, Bu_4N), 1.57 (m, 8H, Bu_4N), 1.31 (m, 8H, Bu_4N), 0.93 (t, 12H, Bu_4N), 0.9–0.7 (broad, 6H, HB). IR (KBr), cm^{-1}: ν(BH): 2517, 2458, 2336, ν(BCl): 811.

Synthesis of $[B_3H_7NCCH_3]$

Method 1. $Cs[B_3H_8]$ (100 mg, 0.57 mmol) was placed in a 10-mL flask and dissolved in 100 μL of acetonitrile. Then 2 mL of toluene was added. The mixture was cooled to −50°C and NCS (75 mg, 0.57 mmol) dissolved in 100 μL of acetonitrile was slowly added. The mixture was stirred for 1 h. Then the precipitate was filtered off and the acetonitrile was distilled off at a rotary evaporator. The filtrate was left in the freezer at T = −5°C for three days until the crystallization of succinimide was complete. The crystals were filtered off. Then the solution was evaporated to a concentrated solution and $[B_3H_7NCCH_3]$ was precipitated with petroleum ether. ^{11}B NMR (CH_3CN, 298 K, 96.32 MHz), δ, ppm: −7.6 (2B), −35.2 (1B); ^{1}H (CD_2Cl_2, 298 K, 300 MHz), δ, ppm: 2.43 (c, 3H, CH_3), 1.68 (broad, 7H, HB). IR (KBr), cm^{-1}: ν(BH): 2516, 2446, 2372, 2340. Calculated/found, %: C (29.83/29.87), H (12.51/12.56), N (17.31/17.29), B (40.27/40.21).

Method 2. Synthesis was conducted using the new method and setup shown in Fig. 1. One gram of sodium chloride was added to the first 250-mL flask, and 1 mL of 95% sulfuric acid was added to a drop funnel with a pressure compensator. A Teflon tube filled with calcium chloride was incorporated for drying and additional purification. The dehydrated gaseous HCl flowed into a three-necked 250-mL flask through a bubbler. The three-necked flask was necessary for gradual sampling. 20 mL of CH_3CN and 0.5 g of dissolved $Cs[B_3H_8]$ were pre-poured into the flask. The interaction was carried out under conditions of slight cooling in an ice bath. The system was equipped with a glycerol bubbler to control the argon flow and two traps, one of which was empty and other contained Et_3N. It should be noted that Teflon hoses were used when working with gaseous HCl. The flasks were equipped with magnetic stirrers.

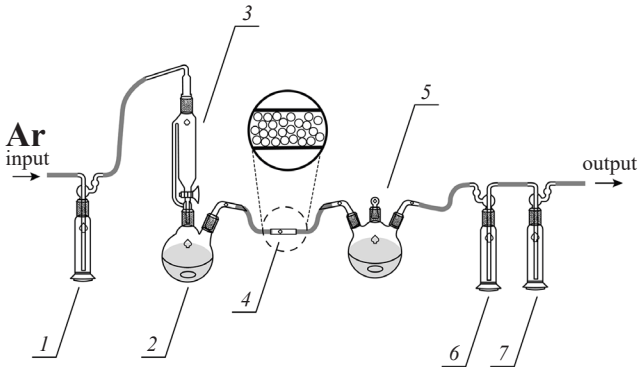

Fig. 1. Scheme of the setup for the synthesis of $[B_3H_7NCCH_3]$:
(*1*) bubbler with glycerin;
(*2*) two-necked flask 250 mL;
(*3*) dropping funnel with pressure compensator;
(*4*) Teflon tube with calcium chloride;
(*5*) three-necked flask 250 mL;
(*6*) empty trap;
(*7*) trap with Et_3N

Synthesis of $[B_3H_7NCPh]$

$Cs[B_3H_8]$ (100 mg, 0.57 mmol) was placed in a 25-mL flask and 5 mL of toluene was added. Benzonitrile (58.8 μL, 0.57 mmol) was added to the suspension and the mixture was cooled to −50°C. Next, NCS (75 mg, 0.57 mmol) dissolved in 1 mL of dichloromethane was added. The mixture was stirred under refrigeration for 1 h. The precipitate was filtered off and left in the refrigerator for three days until the crystallization of succinimide was completed. The crystals were filtered off, the solution was evaporated to a concentrated solution and $[B_3H_7NCBn]$ was precipitated with petroleum ether. ^{11}B NMR ($PhCH_3$, 298 K, 96.32 MHz), δ, ppm: −6.9 (2B), −35.0 (1B).

Synthesis of $[B_3H_7NHEt_2]$

$Cs[B_3H_8]$ (100 mg, 0.57 mmol) was placed in a 25-mL flask and 5 mL of toluene was added. Diethylamine (58.7 μL, 0.57 mmol) was added to the suspension and the mixture was cooled to −50°C. Next, NCS (75 mg, 0.57 mmol) dissolved in 1 mL dichloromethane was added. The mixture was stirred under cooling for 1 h. Then the precipitate was filtered off, kept in the refrigerator for three days, and evaporated under deep vacuum without heating. ^{11}B NMR ($PhCH_3$, 298 K, 96.32 MHz), δ, ppm: −14 (2B), −26 (1B). IR (thin film), cm^{-1}: ν(BH): 2502, 2425, ν(BN): 1455. Calculated/found, %: C, 42.65/42.5; H, 16.11/16.2; N, 12.43/12.4; B, 28.80/28.9.

Synthesis of $[B_3H_7NEt_3]$

Method 1. $Cs[B_3H_8]$ (100 mg, 0.57 mmol) was placed in a 25-mL flask and 5 mL of toluene was added. Triethylamine (79.2 μL, 0.57 mmol) was added to the suspension and the mixture was cooled to −50°C. Next, NCS (75 mg, 0.57 mmol) dissolved in 1 mL of dichloromethane was added. The mixture was stirred under cooling for 1 h. Then the precipitate was filtered off, kept in the refrigerator for three days, and evaporated under deep vacuum without heating. $^{11}B\{^1H\}$ (CD_2Cl_2, 298 K, 96.32 MHz), δ, ppm: −19.9 (2B), −22.4 (1B);

^1H (CD_2Cl_2, 298 K, 300 MHz), δ, ppm: 2.9 (m = 4, 6H, CH_2, J_{HH} = 7.2 Hz), 1.2 (t, 9H, CH_3, J_{HH} = 7.2 Hz), 1.1 (broad, 7H, HB). IR (thin film), cm^{-1}: ν(BH): 2501, 2448, 2424, ν(BN): 1450. Calculated/found, %: C, 51.23/51.4; H, 15.76/15.8; N, 9.96/9.79; B, 23.05/23.0.

Method 2. $Bu_4N[B_3H_8]$ (500 mg, 1.78 mmol) dissolved in 10 mL of dichloromethane was placed in a 50-mL flask, and triethylamine (245 μL, 1.78 mmol) was added. The mixture was cooled and Br_2 (91.7 μL, 1.78 mmol) dissolved in 5 mL of dichloromethane was added. The mixture was slowly warmed to room temperature (20°C), then the precipitate was filtered off and $[B_3H_7NEt_3]$ was separated by column chromatography on silica gel. The elution was carried out by hexane/dichloromethane mixture in the ratio 1 : 1.

Synthesis of $[B_3H_7NH_2Bn]$

$Cs[B_3H_8]$ (100 mg, 0.57 mmol) was placed in a 25-mL flask and 5 mL of toluene was added. Benzylamine (62 μL, 0.57 mmol) was added to the suspension and the mixture was cooled to −50°C. Next, NCS dissolved in 1 mL of dichloromethane was added. The mixture was stirred under cooling for 1 h. The precipitate was then filtered off and evaporated on a vacuum unit without heating. The filtrate was kept in a freezer at −5°C for three days, the succinimide was filtered off and evaporated on a vacuum unit without heating. ^{11}B ($PhCH_3$, 298 K, 96.32 MHz), δ, ppm: −8.1 (2B), −28.3 (1B); IR (thin film), cm^{-1}: ν(BH): 2502, 2429, 2320, ν(BN): 1372. Calculated/found, %: C, 57.33/57.26; H, 10.99/11.01; N, 9.55/9.53; B, 22.11/22.09.

Synthesis of $[B_3H_7INA]$

$Bu_4N[B_3H_8]$ (500 mg, 1.78 mmol) dissolved in 10 mL of tetrahydrofuran was placed in a 50-mL flask, and INA (322 μL, 1.78 mmol) was added. The mixture was cooled and Br_2 (91.7 μL, 1.78 mmol) dissolved in 5 mL of dichloromethane was added. The mixture was slowly warmed to room temperature (20°C) and then heated to the boiling point of tetrahydrofuran for 6 h. $^{11}B\{^1H\}$ (CD_2Cl_2, 298 K, 96.32 MHz), δ, ppm: −13.0 (2B), −30.1 (1B).

RESULTS AND DISCUSSION

Interaction of $Bu_4N[B_3H_8]$ with halogens in dichloromethane

The anion $[B_3H_8]^-$ reacts with Br_2 to form bromo-substituted derivatives $[B_3H_7Br]^-$ and $[B_3H_6Br_2]^-$. The reaction was carried out under conditions of cooling by slowly spiking a solution of Br_2 in dichloromethane; at a ratio of $Bu_4N[B_3H_8]$: Br_2 = 2 : 1. As a result, several signals were observed in the ^{11}B NMR spectrum (Fig. 2a): one signal at −31 ppm with a multiplicity of 9 from the initial octahydrotriborate; and two signals at −13 and −30 ppm with an integral intensity ratio of 2 : 1, related to $[B_3H_7Br]^-$. It can thus be concluded that the reaction is incomplete. At the same time, the formation of a presumably dibromo-substituted derivative was noted in the reaction mixture, as evidenced by the appearance of two signals at −16 and −22 ppm with an integral intensity ratio of 1 : 2. After 24 h, no changes were observed in the ^{11}B NMR spectrum of the reaction mixture (Fig. 2b). After addition of another 0.267 mmol of Br_2, a decrease in signal intensity at −31 ppm from the original octahydrotriborate and an increase in signal intensity at −13 and −30 ppm from the monobromo-substituted derivative were observed (Fig. 2c). Upon subsequent addition of another 0.267 mmol Br_2, the complete disappearance of the signal of the original $[B_3H_8]^-$ and an increase in the intensity of the signals from the mono- and dibromo-substituted products were observed (Fig. 2d).

The addition of acetonitrile to the reaction mixture in the ratio $TBA[B_3H_8]$: CH_3CN = 1 : 1, a stronger nucleophile when compared to bromine, leads to the exchange reaction and the formation of the nitrile mono-substituted product $[B_3H_7NCCH_3]$.

The addition of an equivalent amount of bromine to the mixture of triborate and amine (Et_2NH, Et_3N, $C_9H_{19}NH_2$ (INA)) in dichloromethane leads to a substitution reaction to form the corresponding amine-substituted products $[B_3H_7NHEt_2]$, $[B_3H_7NEt_3]$, $[B_3H_7INA]$. The reaction proceeds incompletely both at −50°C and at room temperature (20°C). HBr is formed during the reaction. Most of this is used for the protonation reaction of the amine which can also act as an inducer of the substitution reaction. However, this reaction requires additional heating. According to the method described in [19], we performed interaction of triborate and isononylamine in tetrahydrofuran at T = 66°C. Bu_4NBr which is insoluble under these conditions precipitated. Carrying out the reaction under the above conditions allowed the yield of the target product $[B_3H_7INA]$ to be significantly increased. However, complete conversion requires the addition of excess bromine. An attempt to carry out a similar interaction with benzylamine led to the formation of only a bromine-substituted derivative, indicating the stronger nucleophilicity of bromine compared to benzylamine.

The interaction of octahydrotriborate with iodine did not lead to the formation of iodine-substituted derivatives. However, when $[B_3H_8]^-$ interacted with triethylamine, diethylamine and isononylamine in the presence of iodine, the ^{11}B NMR spectra of the reaction mixtures in all cases showed two signals characteristic of mono-substituted derivatives with an integral intensity ratio of 2 : 1. From the amine-substituted products they were: −14 and −26 ppm for $[B_3H_7NHEt_2]$; −19.9 and −22.4 ppm for $[B_3H_7NEt_3]$; −13.0 and −30.1 ppm for $[B_3H_7INA]$.

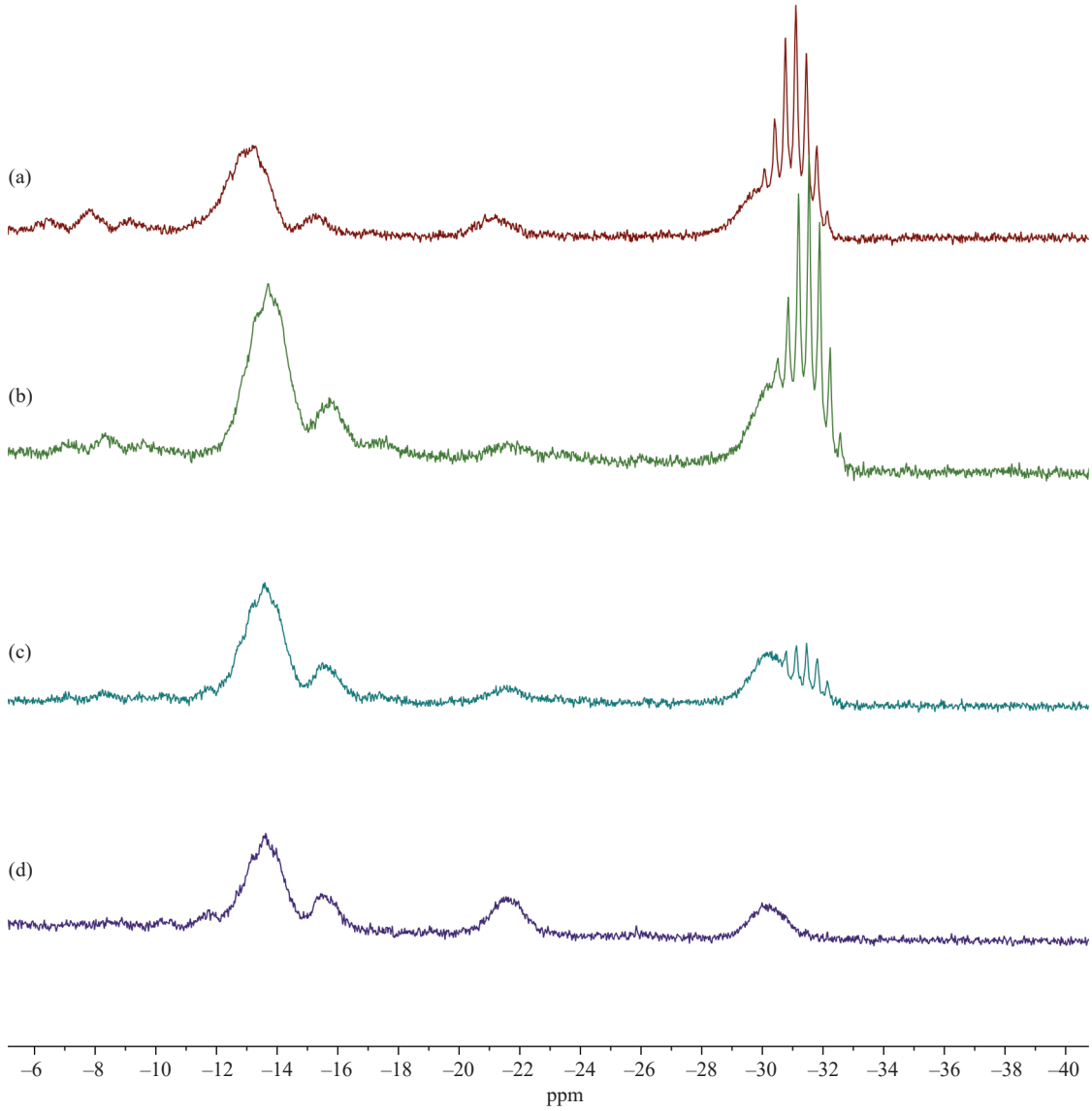

Fig. 2. ^{11}B NMR spectra of a mixture of $Bu_4N[B_3H_8]$ with Br_2:
(a) 1 h after the start of the reaction,
(b) after 24 h,
(c) after adding 0.267 mmol of Br_2,
(d) after adding another 0.267 mmol of Br_2

The highest yield was observed with isonononylamine. In the preparation of substituted derivatives using iodine, excess iodine in the reaction mixture interacts with the substituted derivatives of the $[B_3H_8]^-$ anion to form by-products. Column chromatography helps to get rid of unwanted impurities but reduces the final yield of the target product.

Interaction of $[B_3H_8]^-$ with HCl in acetonitrile

Earlier in [18], a method for the preparation of nitrilium-substituted derivative $[B_3H_7NCCH_3]$ using dry hydrogen chloride was described. The authors used tetramethylammonium salt of octahydrotriborate as a starting substance. The interaction of $(Me_4N)[B_3H_8]$ with HCl in acetonitrile yielded pure acetonitrile-substituted derivative in solution.

This study used the cesium salt of octahydrotriborate, resulting in the relatively fast formation of CsCl precipitate. This simplified the purification and increased the yield of the target product $[B_3H_7NCCH_3]$.

Synthesis using the tetrabutylammonium salt of octahydrotriborate in acetonitrile leads to the formation of a mixture of acetonitrile-substituted derivative and chlorine-substituted derivative. This can be confirmed by the appearance in the ^{11}B NMR spectrum of two pairs of signals with an integral ratio of 2 : 1 at −7.6 and

−35.2 ppm from $[B_3H_7NCCH_3]$ and at –16 and −22 ppm from $[B_3H_7Cl]^-$. Signals from the latter decrease over time. Increasing the amount of added HCl or increasing the synthesis time leads to degradation of the obtained products.

Interaction of $[B_3H_8]^-$ with NCS

Preparation of $Bu_4N[B_3H_7Cl]$ and $Bu_4N[B_3H_6Cl_2]$

NCS is a well-known chlorinating agent in organic chemistry. The interaction of NCS with octahydrotriborate anion leads to the formation of $[B_3H_7Cl]^-$ at the ratio $Bu_4N[B_3H_8]$: NCS = = 1 : 1, and to the formation of $[B_3H_6Cl_2]^-$ at the ratio $Bu_4N[B_3H_8]$: NCS = 1 : 2 (Fig. 3). A subsequent increase in the amount of NCS leads only to the destruction of the boron backbone.

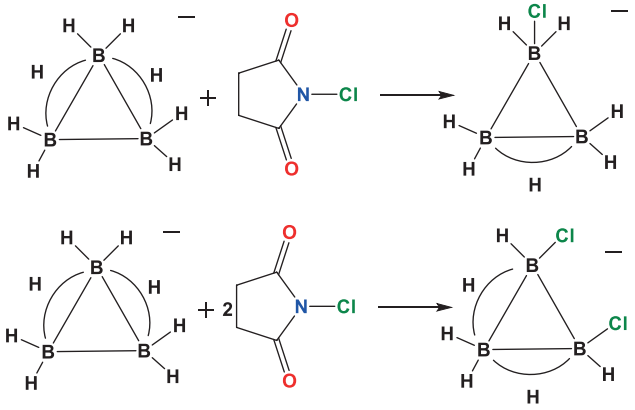

Fig. 3. Scheme of the interaction of NCS with octahydrotriborate anion

The succinimide formed in the reaction interacts with chloro-substituted derivatives to form by-products. This significantly complicates the purification process and reduces the yields of the target compounds. Carrying out the reaction and purification of chloro-substituted derivatives of $[B_3H_8]^-$ anion at cooling to −50°C reduces the solubility of succinimide and, together with its salting with diethyl ether, prevents the occurrence of side processes.

Preparation of nitrile and amine-substituted derivatives

The interaction of the cesium salt of octahydrotriborate with NCS in acetonitrile leads to $[B_3H_7NCCH_3]$. The reaction proceeds through the stage of formation of the monochloro-substituted derivative and is an exchange reaction, in which chlorine is displaced by the nucleophilic stronger acetonitrile. The exchange process of the nucleophilic fragment is equilibrium. The precipitation of cesium chloride shifts the equilibrium towards the formation of the acetonitrile-substituted product (Fig. 4).

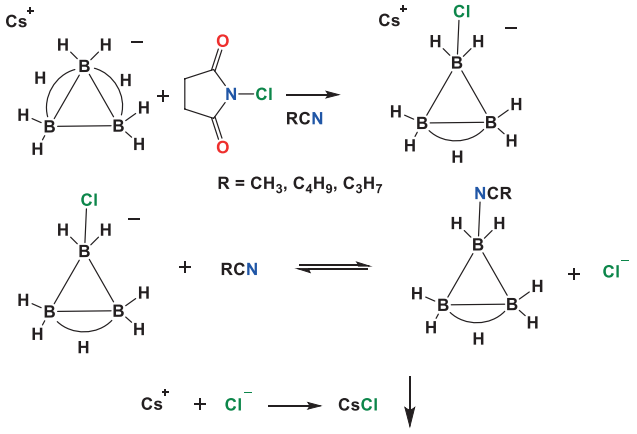

Fig. 4. Scheme of the interaction of the cesium salt of octahydrotriborate with NCS in acetonitrile

Thus, carrying out a similar reaction with the tetrabutylammonium salt of octahydrotriborate in acetonitrile leads to the formation of only chloro-substituted derivatives $[B_3H_7Cl]^-$ and $[B_3H_6Cl_2]^-$. The results of the study are confirmed by ^{11}B NMR spectroscopy data. Two signals were observed in the spectra of the reaction mixture (Fig. 5a) at the first stages: at −7 and −35 ppm with the ratio of integral intensities 2 : 1, belonging to the acetonitrile-substituted derivative. Two signals observed at −16 and −22 ppm correspond to $[B_3H_7Cl]^-$. After 1 h after the beginning of the reaction there was a decrease in the intensity of signals from the chloro-substituted derivative, until their complete disappearance and an increase in the intensity of signals of the acetonitrile-substituted product (Fig. 5b).

The addition of NCS to the mixture of octahydrotriborate with various amines in toluene also leads to the formation of substituted derivatives. However, it significantly increases the reaction time due to the low solubility of the reagents in toluene, while preventing interaction of substituted products with the formed succinimide. In contrast to the neutral substituted derivatives thus formed, succinimide is practically insoluble in toluene, especially at low temperature. For this reason, the synthesis and subsequent isolation of products were carried out at low temperatures, not exceeding 0°C.

In organic chemistry, chlorination reactions using NCS are described as a radical process initiated by a quantum of light. An attempt to carry out two parallel syntheses of monochloro-substituted octahydrotriborate derivative using a red laboratory lamp and under UV irradiation was proposed. According to NMR spectroscopy, absolutely no differences were observed in the reaction masses. Thus, it can be said that the reaction mechanism is still not radical.

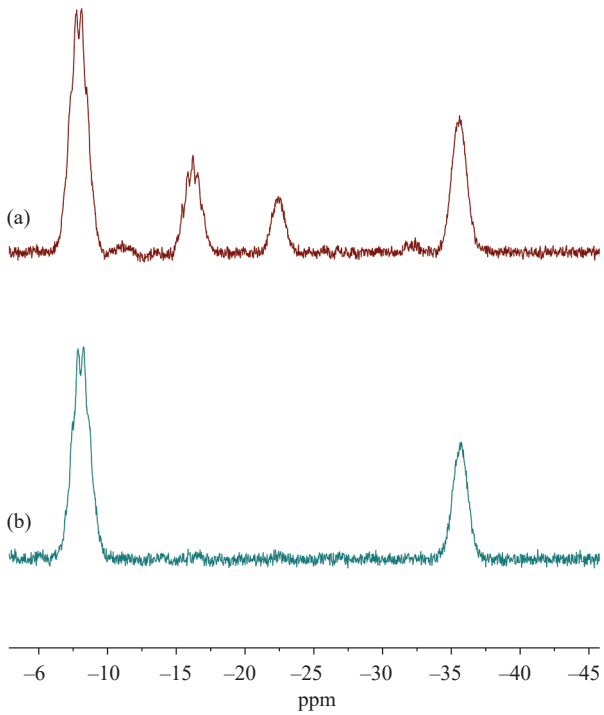

Fig. 5. ^{11}B NMR spectra of a mixture of $Bu_4N[B_3H_8]$ with NCS:
(a) immediately after the start of the reaction,
(b) after 1 h.

Therefore, NCS can act as a chlorinating agent both for the preparation of chloro-substituted derivatives of octahydrotriborate anion by direct interaction with salts of $[B_3H_8]^-$ anion, and for the preparation of other substituted derivatives through the substitution of a nucleophilic fragment.

CONCLUSIONS

All the methods mentioned above are suitable for the preparation of substituted derivatives of the $[B_3H_8]^-$ anion. Depending on the nucleophile, the choice of method and conditions may be limited. The main factors influencing the course of the substitution reaction are the possible occurrence of side interactions between the nucleophile and the inducer, steric possibilities, and the subsequent isolation of reactive reaction products.

This study for this first time proposed the use of NCS as an electrophilic inducer for the synthesis of chloro-substituted, nitrilic and amine-substituted derivatives. Also for the first time, new substituted derivatives of $[B_3H_7NCR]$, (R = Et, *i*-Pr, Bn), $[B_3H_7NH_2R]$, ($R = C_9H_{19}$, Bn) were obtained by this method.

This study also systematizes and improves the known methods for the preparation of substituted octahydrotriborate anion derivatives. For the preparation of nitrilium-substituted derivatives using dry hydrogen chloride, the use of cesium salt enables the product to be isolated.

New methods have been developed for the preparation of halogen-substituted $Bu_4N[B_3H_7Cl]$, $Bu_4N[B_3H_7Br]$, $Bu_4N[B_3H_6Cl_2]$, $Bu4N[B_3H_6Br_2]$; nitrilium-substituted $[B_3H_7NCR]$, (R = CH_3, Et, *i*-Pr, Ph); and amine-substituted derivatives of $[B_3H_7NH_2R]$, ($R = C_9H_{19}$, Bn), $[B_3H_7NHEt_2]$, $[B_3H_7NEt_3]$ by interaction of octahydrotriborate(1−) anion with halogens (Br_2, I_2) and with NCS. The study also found that protonation of the amine occurs during the preparation of amine-substituted derivatives using bromine. In order to avoid this, the synthesis temperature must be increased to 66°C.

When iodine is used as an inducer, its excess can lead to a degradation of the target compound. Thus the isolation of the target product should be carried out immediately after complete conversion of the initial anion $[B_3H_8]^-$.

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Authors' contributions

A.A. Lukoshkova – conducting the experiments, analysis of the results, and writing the text of the manuscript.

A.T. Shulyak – conducting the experiments, analysis of the results, and writing the text of the manuscript.

E.E. Posypayko – conducting the experiments, analysis of the results, and writing the text of the manuscript.

N.A. Selivanov – conducting NMR analysis.

A.V. Golubev – conducting NMR analysis.

A.S. Kubasov – conducting X-ray diffraction analysis.

A.Yu. Bykov – project supervision, development of the research concept, and editing the text of the article.

A.P. Zhdanov – resources.

K.Yu. Zhizhin – project supervision, development of the research concept, and editing the text of the article.

N.T. Kuznetsov – project manager.

The authors declare no conflicts of interest.

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