Synthesis and NMR spectra of the hydroxyundecahydro-*closo*-dodecaborate $[B_{12}H_{11}OH]^{2-}$ and its acylated derivatives

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Tetrabutylammonium hydroxyundecahydro-*closo*-dodecaborate was obtained in high yield *via* $[B_{12}H_{11}NMP]^-$ (NMP = *N*-methylpyrrolidone) by the modified method. $[B_{12}H_{11}OH]^{2-}$ is easily acylated by aromatic acyl chlorides to give novel compounds $[B_{12}H_{11}OCOAr]^{2-}$ in high yields. All the compounds were characterized by standard and special NMR methods.

Key words: hydroxyundecahydro-*closo*-dodecaborate, *O*-acylated derivatives, NMR-spectra.

The chemistry of polyhedral boron hydrides, particularly the $[B_{12}H_{12}]^{2-}$ anion, has recently gained importance in the boron neutron capture therapy of cancer[1]. Thus the mercaptoundecahydro-*closo*-dodecaborate $[B_{12}H_{11}SH]^{2-}$ anion and its derivatives are now widely studied[2,3]. That is why it is also interesting to study the reactivity of hydroxyundeca-*closo*-dodecaborate $[B_{12}H_{11}OH]^{2-}$ anion. The optimum method of $[B_{12}H_{11}OH]^{2-}$ synthesis and its acylation by aromatic acylchlorides are the subjects of this article.

Results and Discussion

A number of methods for $[B_{12}H_{11}OH]^{2-}$ synthesis are known, but none can be considered preparative. One method is based on the reaction of sodium dodecahydro-*closo*-dodecaborate salt with acetylchloride[4,5];

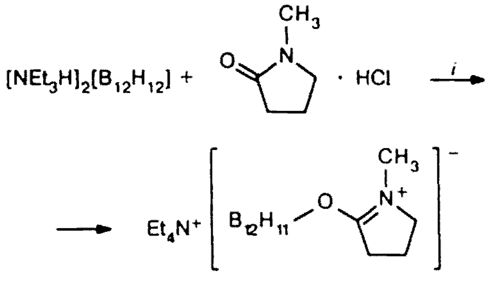
$$Na_2B_{12}H_{12} \xrightarrow{i} \underset{21\ \%}{[NR_4]_2[B_{12}H_{11}COCH_3]} + \underset{69\ \%}{[NR_4]_2[B_{12}H_{11}OH]}$$

i. 1. CH_3COCl, acetone; 2. H_2O/NR_4Br

The yield of the product is rather high, but it is difficult to separate it from the monoacylated derivative.

Alkaline hydrolysis of $[B_{12}H_{11}NMP]^-$ (NMP = *N*-methylpyrrolydone) is used in another method of synthesis[6]. However, the method for the synthesis of the initial product (heating of $Na_2[B_{12}H_{12}]$ in NMP/HCl_{aq} mixture) is apparently not satisfactory because it results in only 24 % yield.

We succeeded in modifing the latter method, and the yield of $[B_{12}H_{11}NMP]^-$ in the form of its tetraethylammonium salt (**1**) reached 86 %.



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i. 1. $NMP/-H_2$; 2. H_2O/Et_4NBr

Two features distinguish our method from the method described previously[6]: first, the initial dodecaborate was taken in the form of the anhydrous triethylammonium salt instead of the sodium salt, which is a dihydrate; second, anhydrous NMP hydrochloride was used as reagent instead of its aqueous solution in hydrochloric acid. Thus, the reaction was carried out in anhydrous conditions, which may be essential for increasing the product yield. Moreover, just as NMP does not react with $[B_{12}H_{12}]^{2-}$ and acts only as a solvent, so using NMP hydrochloride in a 1 : 1 ratio makes it possible to avoid the formation of disubstituted by-products (Knoth et al.[6] used about 1 : 20 $[B_{12}H_{12}]^{2-}/NMP \cdot HCl$ ratio).

There are no references on $[B_{12}H_{11}NMP]^-$ spectral characteristics, and we report them here. The ^{11}B NMR spectrum (Table 1) consists of three signals with an intensity ratio of 1 : 10 : 1, which indicates monosubstitution of the product prepared. The signal at δ 4.39 ppm corresponds to *O*-substituted boron atom because this signal remains a singlet in the $^{11}B\{^1H\}$ NMR spectrum. The ^1H NMR spectrum data also satisfies the formula of compound **1** (see Experimental). The $^1H\{^{11}B\}$ NMR spectrum data on compound **1** is dis-

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Table 1. ^{11}B NMR spectra of the obtained compounds (δ, ppm)

Compound	Solvent	δ B(1)	δ B(2)—B(6)	J_{B-H}/Hz	δ B(7)—B(11)	J_{B-H}/Hz	δ B(12)	J_{B-H}/Hz
1	DMSO-d_6	4.39	−16.90	131.8	−16.90	131.8	−20.48	132.0
2	CD_3OD	5.01	−15.83	116.5	−17.98	121.6	−24.04	126.1
3a	D_2O/DMSO-d_6	3.41	−15.44	128.0	−17.29	128.4	−20.84	117.4
3b	D_2O/DMSO-d_6	3.46	−15.42	129.8	−17.26	129.5	−20.78	118.9
3c	D_2O/DMSO-d_6	3.57	−15.45	129.1	−17.36	127.9	−20.90	116.0

cussed below. In the ^{13}C NMR spectrum, the signal at δ 178 ppm corresponds to the C=N carbon atom. Finally, in the infrared spectrum the absorption band at 1645 cm^{-1} is related to the C=N bond.

Knoth et al.[6] reported earlier that alkaline hydrolysis of $[B_{12}H_{11}NMP]^-$ results in $[B_{12}H_{11}OH]^{2-}$, conversion being practically 100 %. It should be noted that it is nesessary to convert the triethylammonium salt (**1a**) to the cesium salt (**1b**) because the triethylammonium salt of $[B_{12}H_{11}NMP]^-$ is practicaly insoluble:

$$[NEt_3H]_2[B_{12}H_{12}] \xrightarrow[NMP,\ \Delta]{NMP\cdot HCl} \underset{\mathbf{1a}}{NEt_3H[B_{12}H_{11}NMP]} \xrightarrow[CsF]{CH_3OH} \underset{\mathbf{1b}}{Cs[B_{12}H_{11}NMP]} \xrightarrow[2.\ NBu_4Br]{1.\ H_2O/KOH} \underset{\mathbf{2}}{[NBu_4]_2[B_{12}H_{11}OH]}$$

Since the salt **1a** is incompletely soluble in methanol, its undissolved part on treatment of the reaction mixture was converted to $[B_{12}H_{11}OH]^{2-}$ as follows:

$$\underset{\mathbf{1a}}{NEt_3H[B_{12}H_{11}NMP]} \xrightarrow[-2.\ CsF;\ -NEt_3]{1.\ CH_3OH/KOH,\ \Delta} \underset{\mathbf{1b}}{Cs[B_{12}H_{11}NMP]} \xrightarrow[2.\ NBu_4Br]{1.\ H_2O/KOH} \underset{\mathbf{2}}{[NBu_4]_2[B_{12}H_{11}OH]}$$

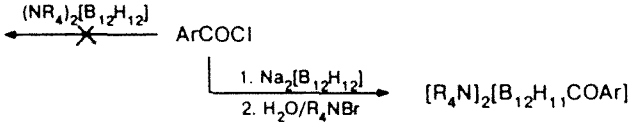
Since the tetrabutylammonium salt **2** was characterized earlier[5], it was identified by ^{11}B NMR (Table 1) and IR spectra. In the IR spectrum there are absorption bands at 3674 cm^{-1} (νOH) and 2473 cm^{-1} (νBH).

Acylation of the $[B_{12}H_{11}OH]^{2-}$ with benzoyl chloride was carried out earlier using microquantities of the reagents[5]. Here we present a new method of preparing $[B_{12}H_{11}OCOAr]^{2-}$ derivatives through $[B_{12}H_{11}OH]^{2-}$ acylation by aromatic acyl chlorides:

$$[NBu_4]_2[B_{12}H_{11}OH] \xrightarrow[2.\ CsF/CH_3OH]{1.\ ArCOCl/Et_3N,\ CH_3CN} Cs_2[B_{12}H_{11}OCOAr]$$

3a: Ar = Ph
3b: Ar = 4-ClC_6H_4
3c: Ar = 4-$CH_3OC_6H_4$

The yields of the products obtained were from 70 to 80 %. Note that in this case acylation affects the oxygen atom only, and acylation at the boron atom does not take place, although the sodium salt of $[B_{12}H_{12}]^{2-}$ is easily acylated by the action of ArCOCl[5]. However, the tetraalkylammonium salts of $[B_{12}H_{12}]^{2-}$ were found to be inert to the action of aromatic acyl chlorides. Therefore the acylation side reaction at boron was avoided without any difficulties:



The structures of the compounds **3a—c** were defined from IR and NMR spectra. In the IR spectra of **3a—c** there are absorption bands of the CO groups in the range 1670—1680 cm^{-1}. In the ^{11}B NMR spectra of **3a—c** (Table 1) four signals in 1 : 5 : 5 : 1 ratio are observed as in the case of $[B_{12}H_{11}OH]^{2-}$, which indicates monosubstitution of the products obtained. The signals in the spectra were assigned using the ^{11}B—^{11}B COSY NMR spectra. Comparison of the ^{11}B NMR spectra of compounds **3a—c** and the initial compound **2** reveals the following: the signal of the substituted boron atom of $[B_{12}]$—COAr shifts to lower field as compared with $[B_{12}]$—OH, and of the antipodal boron atom to the higher field (Table 1). This can be explained by the decreasing +M-effect of the oxygen atom on the boron cage as a result of introduction of the COR acceptor substituent.

In the ^1H NMR spectra of compounds 3(a—c), multiplets of the B—H protons and the signals of the corresponding aromatic systems are observed (see Experimental).

The signals of the C=O carbon atoms of about 170 ppm in the ^{13}C NMR spectra of **3a—c** are typical

Table 2. ^{13}C NMR spectra of the $[B_{12}H_{11}OCOAr]^{2-}$ derivatives (**3a—c**) (D_2O/DMSO-d_6 3 : 1, δ, ppm)

Compound	Ar	C=O	Found Calculated			
			C_{ipso}	C_o	C_m	C_p
3a	Ph	170.4	130.4	131.0	130.1	134.3
3b	4-ClC_6H_4	169.9	$\underline{132.9}$ 128.5	$\underline{132.6}$ 132.4	$\underline{130.5}$ 130.5	$\underline{139.6}$ 136.7
3c	4-$CH_3OC_6H_4$	170.1	$\underline{126.9}$ 122.7	$\underline{133.2}$ 132.0	$\underline{115.4}$ 115.7	$\underline{164.1}$ 170.1

Table 3. The B—H protons chemical shifts of the compounds **1**, **2**, **3c** (δ, ppm)

Compound	H(2)—H(6)	H(7)—H(11)	H(12)
1	2.41	2.01	1.85
2*	0.50	0.21	0.00
3c	1.40	0.94	0.77

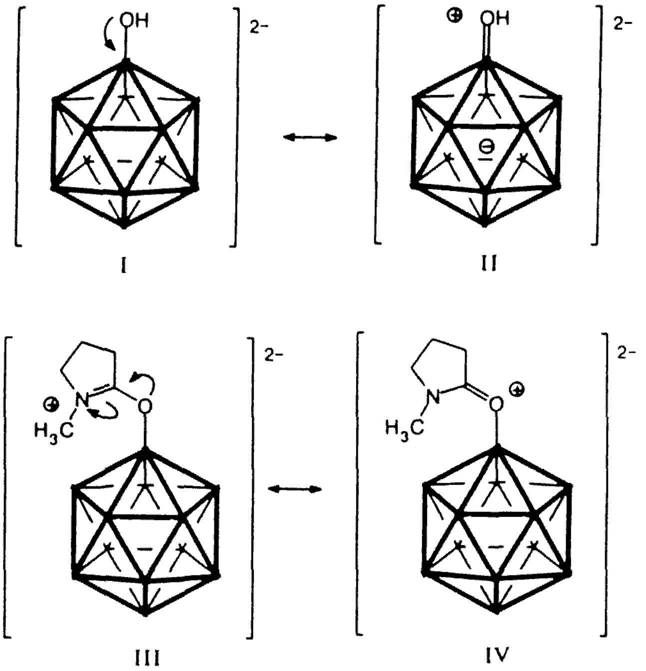
* See Ref. 3.

for esters ($\delta_{C=O}$ ($PhCOOCH_3$) = 166.8 ppm)[7]. The $B_{12}H_{11}OCO$ group increments were calculated based on the chemical shifts of the $[B_{12}H_{11}OCOPh]^{2-}$ aromatic rings carbon atoms. Using these values (δC_{ipso} +1.9, δC_o +2.5, δC_m +1.6, δC_p+5.8)), the ^{13}C-chemical shifts of the aromatic rings of the compounds **3b** and **3c** were calculated. The calculated and measured shifts (Table 2) match perfectly are for the *ortho* and *meta* carbon atoms, and for the *ipso* and *para* atoms they are slightly different.

The $^1H\{^{11}B\}$ NMR spectra of the compounds **1** and **3c** were measured. The **3c** proton signals are shifted strongly downfield compared to $[B_{12}H_{11}OH]^{2-}$ (**2**) (Table 3) because of the decreasing oxygen atom +M-effect. The proton signals of the $[B_{12}H_{11}NMP]^-$ are in the lower field due to the positive charge on the oxygen atom.

The analysis of the NMR data of the obtained products allows one to make some conclusions about the electron density distribution in the compounds. In the $[B_{12}H_{11}OH]^{2-}$ the lone electron pair of oxygen is shifted to the boron cage (resonance form II), enhancing the electron density in it. In the acylated derivatives this effect decreases due to the acceptor effect of the COAr group. In the NMP derivative this lone electron pair interacts with the NMP fragment and not with the boron cage (resonance form III).

Scheme 1



Experimental

Materials and equipment. The materials used were reagent grade and were used as received from standard commercial vendors (Bayer AG, Aldrich). N-methylpyrrolidone was vacuum distilled prior to use. Anhydrous NMP · HCl was obtained by passing dry HCl through a solution of NMP in benzene. In this case NMP · HCl precipitated. Acetonitrile was distilled from P_2O_5 and immediately prior to use, from CaH_2. Carboxylic acid chlorides were vacuum distilled from PCl_5. The ^1H, ^{11}B and ^{13}C NMR spectra were recorded at 400.13, 128.335, and 100.61 MHz respectively on a Bruker AMX-400 spectrometer. Chemical shifts (δ-scale) were referenced to external standards ($BF_3 \cdot Et_2O$, TMS, DMSO-d_6).

Tetraethylammonium (1-methyl-1-pyrrolinio-2-yloxy)undecahydro-*closo*-dodecaborate (1). A mixture of $(Et_3NH)_2[B_{12}H_{12}]$ (7 g, 20 mmol) and N-methylpyrrolydone hydrochoride (6 g, 20 mmol) in 50 ml of NMP was heated at 140—150 °C untill the evolution of hydrogen was completed. Then the temperature was increased to 180 °C and the solution heated for 5 hours. After that the solution was cooled to room temperature and solvent was evaporated *in vacuo*. The residue was dissolved in 300 ml of water, and Et_4NBr (4.2 g, 20 mmol) in 50 ml of water was added. The precipitate of the product **1** was filtered off and washed twice with water and once with ether and vacuum dried. Yield 6.37 g (86 %). Found (%): C, 41.95; H, 10.87; N, 7.62. $C_{13}H_{40}N_2B_{12}O$. Calculated (%): C, 42.18; H, 10.89; N, 7.57. ^{11}B NMR (DMSO-d_6, δ, ppm): 4.39 (s, 1 B, B(1)); −16.90 (d, 10 B, B(2—11): J_{B-H} −131.8 Hz): −20.48 (d, 1 B, B(12); J_{B-H} −132.0 Hz. ^1H NMR (DMSO-d_6, δ, ppm): 3.62 (t, 2 H, $N-CH_2$); 3.34 (s, 3 H, $N-CH_3$); 3.21 (q, 8 H, $N-C\underline{H}_2-CH_3$); 3.11 (t, 2 H, $=C-CH_2$); 2.07 (m, 2 H, $-CH_2-C\underline{H}_2-CH_2$); 1.17 (t, 12 H, $N-CH_2-C\underline{H}_3$). ^{13}C NMR (DMSO-d_6, δ, ppm): 178.0 (C=N); 51.4 ($N-\underline{C}H_2-CH_3$); 51.1 ($N-CH_2$); 31.2 ($N-CH_3$); 29.5 ($=C-CH_2$); 17.3 ($-CH_2-C\underline{H}_2-CH_2$); 7.1 ($N-CH_2-\underline{C}H_3$).

Tetrabutylammonium hydroxyundecahydro-*closo*-dodecaborate (2). A mixture of $(Et_3NH)_2[B_{12}H_{12}]$ (51.9 g, 150 mmol) and NMP · HCl (21.9 g, 160 mmol) was heated at 170 °C with vigorous stirring in 150 ml of NMP for 20 h until the evolution of hydrogen stopped. The solution was cooled and the solvent was evaporated *in vacuo*. Methanol (150 ml) was added to the residue and the insoluble material was filtered off. CsF (22.8 g, 150 mmol) in 50 ml of methanol was added to the filtrate, and the precipitated first portion of **1b** was filtered off and air-dried. Triethylammonium salt **1a** undissolved in methanol was suspended in 100 ml of methanol and refluxed with KOH until the solution became clear. This solution was added to the filtrate from **1b** isolation, and the second portion of **1b** was filtered off and air-dried. The obtained cesium salts were combined and heated in a solution of KOH (8.41 g) in 200 ml of water at 80 °C until the solution became clear. Then the solution was brought to pH 6—7 and added to the solution NBu_4Br (96.7 g, 300 mmol) in 100 ml of water. The product **2** was filtered off, washed twice with water and once with ether, and dried over P_2O_5 *in vacuo*. Yield 75.2 g (78 %), m.p. 117 °C.

Acylation of $[B_{12}H_{11}OH]^{2-}$ with aromatic acyl chlorides. A solution of **2** (1.6 g, 2.5 mmol), triethylamine (0.35 mL, 3 mmol), and ArCOCl (3 mmol) in 50 ml of acetone was stirred for 12 h (in the case where Ar = $4\text{-}CH_3OC_6H_4$, refluxing for 12 h is required). Then the solvent was removed *in vacuo* and the residue was dissolved in 80 ml of methanol. The addition of CsF (0.67 g, 5 mmol) in 20 ml of MeOH causes the precipitation of the desired products. They were filtered off, air-dried, and reprecipitated from a small amount of hot water by methanol.

Cesium benzoyloxyundecahydro-*closo*-dodecaborate (3a). Yield 1.09 g (82 %), m.p. > 380 C. Found (%): C, 15.88; H, 3.09; B, 24.49. $C_7H_{16}B_{12}Cs_2O_2$. Calculated (%): C, 15.93; H, 3.06; B, 24.58. IR (ν cm^{-1}): 2501 (B—H), 1676 (C=O). ^{1}H NMR (D_2O/DMSO-d_6, δ, ppm): 8.16÷7.37 (m, 5 H, Ph), 1.96÷–1.11 (m, 11 H, BH).

Cesium 4-chlorobenzoyloxyundecahydro-*closo*-dodecaborate (3b). Yield 1.01 g (72 %), m.p. > 380° C. Found (%): C, 14.81; H, 2.71; B, 23.12. $C_7H_{15}B_{12}ClCs_2O_2$. Calculated (%): C, 14.96; H, 2.69; B, 23.07. IR (ν, cm^{-1}): 2506 (B—H), 1679 (C=O). ^{1}H NMR (D_2O/DMSO-d_6, δ, ppm): 7.75 and 7.35 (AX-system, 4 H, Ar); 2.24÷–1.14 (m, 11 H, BH).

Cesium 4-metoxybenzoyloxyundecahydro-*closo*-dodecaborate (3b). Yield 1.16 g (80 %), m.p. > 380° C. Found (%): C, 17.15; H, 3.26; B, 23.12. $C_8H_{17}B_{12}Cs_2O_3$. Calculated (%): C, 17.23; H, 3.25; B, 23.26. IR (ν, sm^{-1}): 2497 (B—H), 1681 (C=O). ^{1}H NMR (D_2O/DMSO-d_6, δ, ppm): 7.65 и 6.87 (AX-system, 4H, Ar); 3.72 (s, 3 H, OCH_3), 2.05÷–1.02 (m, 11 H, BH).

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