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A new preparative method for the synthesis of oxonium derivatives of the decahydro-*closo*-decaborate anion

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A new method for the synthesis of oxonium derivatives of the *closo*-decaborate anion in high yields was described. Reactions of the anion $B_{10}H_{10}^{2-}$ with cyclic ethers (tetrahydrofuran (THF) and tetrahydropyran) in the presence of dry HCl are stepwise processes. Depending on the reaction temperature and time, either mono- or disubstituted products were obtained. Their structures were determined using ^{11}B, ^{13}C, and ^{1}H NMR and IR spectroscopy, ESI mass spectrometry, and elemental analysis for boron.

Key words: boranes, *closo*-decaborate anion, oxonium derivatives of the *closo*-decaborate anion, electrophile-induced nucleophilic substitution.

Oxonium derivatives of *closo*-decaborates are of considerable interest for the preparation of novel compounds and materials for various areas of medicine and engineering.[1,2]

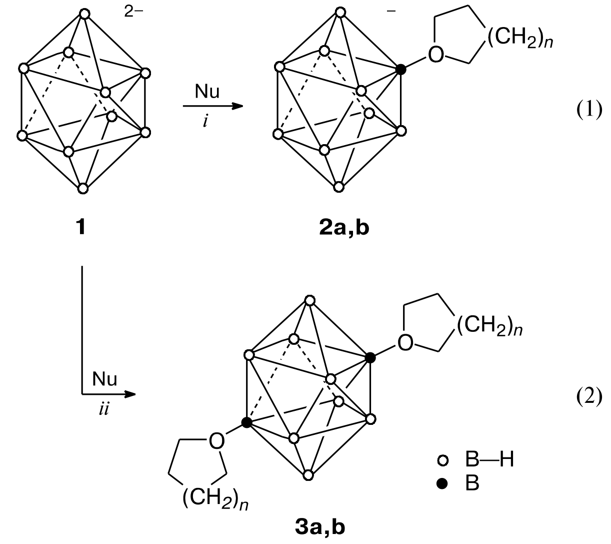
Oxonium *closo*-decaborates can be synthesized in different ways, *e.g.*, by reactions of the anion $B_{10}H_{11}^{-}$ with cyclic ethers,[3] by reactions of the *closo*-decaborate anion with appropriate nucleophiles in the presence of CF_3COOH,[3] and by using Lewis acids as initiators.[4,5] However, these methods involve expensive reagents and complicated procedures for isolation of the target products.

In the present work, we developed a new preparative method for the synthesis of oxonium derivatives by reactions of cyclic ethers with salts of the decahydro-*closo*-decaborate anion (**1**) in the presence of dry HCl. This method is distinguished from the previous ones by a simple procedure and high yields (up to 95%) and allows the synthesis of disubstituted derivatives.

Results and Discussion

We studied reactions of salts of the *closo*-decaborate anion (**1**) with cyclic ethers in the presence of dry HCl as an initiator. Depending on the reaction conditions (temperature and time), mono- (**2**) and disubstituted derivatives (**3**) were obtained (Scheme 1).

Scheme 1



n = 1 (**a**), 2 (**b**)
Nu is tetrahydrofuran (**a**), tetrahydropyran (**b**)

Conditions: *i.* HCl, 1 h, 50—88 °C; *ii.* HCl, 3 h, reflux.

The highest yields of monosubstituted products **2** (up to 95%) were achieved at 60 °C and a reaction time of 1 h. The course of the reactions was monitored by ^{11}B NMR spectroscopy. The ^{11}B NMR spectrum of product **2b** (see Scheme 1) shows a singlet at δ 5.1 for the substituted B atom (the singlet is not split into a doublet without broadband proton decoupling) and two singlets at δ −1.1 and −7.8 with equal integral intensities for two nonequivalent apical B atoms, which indicates the presence of one substituent in an equatorial position of the boron cluster. The spectrum also contains signals for the other B atoms at δ −23.2, −25.1, and −31.4 with an integral intensity ratio of

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2 : 2 : 3. A similar pattern is observed in the ^{11}B NMR spectrum of mono(tetrahydrofuranium) derivative **2a** (δ: 3.7 (s, B(2)), −2.8 (d, B(10)), −9.5 (d, B(1)), −25.0 (d, B(6,9)), −26.8 (d, B(3,5)), −33.2 (B(4,7,8))).

The ^{1}H NMR spectrum of mono(tetrahydropyranium) derivative **2b** shows a triplet at δ 5.05 and two quintets at δ 2.53 and 2.25 for the protons in the α-, β-, and γ-positions (in the order of moving away from the O atom) of the *exo*-polyhedral substituent.

The ^{13}C NMR spectra of product **2b** also contain signals for three types of the C atoms of the *exo*-polyhedral substituent. The signals at δ 82.9, 24.5, and 20.3 can be assigned to the C atoms in the α-, β-, and γ-positions, respectively.

The IR spectrum of product **2b** exhibits a new band at 944 cm^{-1}, which is absent from both the spectra of the starting salts of the anion $B_{10}H_{10}^{2-}$ and the spectrum of free tetrahydropyran ($\nu(CO)_{as}$ = 1100 cm^{-1}, $\nu(CO)_{s}$ = = 815 cm^{-1}). The band can be assigned to the C—O stretching vibrations in the oxonium ether fragment C—O—C. The absorption band ν(B—H) is shifted to the higher wavenumbers (2472 against 2448 cm^{-1} for the starting anion).

An increase in the reaction time leads to disubstituted derivatives. The highest yields of compounds **3a** (81%) and **3b** (85%) were obtained upon 3-h reflux in an appropriate solvent. At longer reaction times, the reaction mixture was strongly contaminated by oxidation products. The ^{11}B NMR spectrum of di(tetrahydropyranium) derivative **3b** contains a singlet at δ 2.2, which is not split into a doublet without broad-band proton decoupling. The singlet can be assigned to two equivalent B atoms bearing the tetrahydropyranium substituents. The spectrum also shows a signal at δ −11.6 for two equivalent apical B atoms and signals at δ −22.4, −31.4, and −38.5 for the other B atoms. Such a spectral pattern provides incontestable evidence for the formation of a disubstituted product with the substituents in the adjacent equatorial planes. However, the analytical techniques we used cannot identify precisely which of the geometrical (2,6 or 2,7) and optical isomers (2,6(9) or 2,7(8)) is formed in such reactions.

The ^{1}H and ^{13}C NMR spectra of products **3b** and **2b** are similar, except for a slight difference in the chemical shifts and the absence of the signals for the cation atoms in the spectra of disubstituted derivative **3b**.

The IR spectrum of compound **3b** retains the absorption band at 944 cm^{-1} (ν(C—O) in the fragment C—O—C of the oxonuim substituent). However, the absorption band due to the ν(B—H) stretching vibrations in the disubstituted product is shifted to the higher wavenumbers and split into two components (2486 and 2536 cm^{-1}) compared to this band for the monosubstituted product (2472 cm^{-1}).

Thus, we developed a new preparative method for the synthesis of oxonium derivatives in 81—95% yields.

Experimental

Materials. Tetrabutylammonium decahydro-*closo*-decaborate $[(n\text{-Bu})_4N]_2[B_{10}H_{10}]$ and tetraphenylphosphonium decahydro-*closo*-decaborate $(Ph_4P)_2[B_{10}H_{10}]$ were prepared according to known procedures.[6] Hydrogen chloride was prepared as described earlier.[7] Tetrahydropyran (99.5% purity) was used without additional purification. Tetrahydrofuran was purified according to a known procedure.[8]

Physicochemical analytical techniques. Elemental analysis for boron was carried out by atomic absorption spectroscopy (AAS) with electrothermal atomization on Perkin Elmer spectrometers (model 2100 with HGA-700 and model 403 with HGA-72). The probe was prepared as described earlier.[9] IR spectra were recorded on an INFRALUM FT-02 FTIR spectrometer (NPF AP Lumeks) in the 4000—400 cm^{-1} range (resolution 1 cm^{-1}). Samples were suspended in Nujol (Aldrich) or a Fluorolube fluorinated oil (Merck) in KBr cells. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker AVANCE II-300 spectrometer (300.13, 96.32, and 75.49 MHz, respectively) in CD_3CN with internal deuterium stabilization. Tetramethylsilane and boron trifluoride etherate were used as the external standards. Preparative column chromatography (columns 2×40 cm) was carried out on silica gel 40 (Aldrich) with dichloromethane as an eluent.

Tetraphenylphosphonium 2-(tetrahydropyran-1-ium)nonahydro-*closo*-decaborate(1−) (2b), $(Ph_4P)[2\text{-}B_{10}H_9(OC_5H_{10})]$. A 100-mL two-neck flask fitted with a magnetic stirring bar, a reflux condenser, and a bubbler was charged with $(Ph_4P)_2[B_{10}H_{10}]$ (2.0 g, 2.5 mmol) and tetrahydropyran (50 mL). The system was purged with dry argon and the mixture was heated with stirring to 88 °C. Then dry HCl prepared by a parallel reaction of cold conc. H_2SO_4 with anhydrous NaCl was bubbled through the reaction mixture for 1 h. The resulting yellow solution slowly produced white transparent crystals, which were filtered off and dried on filter paper. The yield of compound **2b** was 1.3 g (95%). Found (%): B, 19.83. $C_{29}H_{39}OPB_{10}$. Calculated (%): B, 19.92. MS (ESI/MS, anionic part): found *m/z* 203.43 ($[2\text{-}B_{10}H_9OC_5H_{10}]^-$), calculated *m/z* 203.31. $C_5H_{19}{}^{10}B_2{}^{11}B_8O$. ^{1}H NMR, δ: 0.60—2.10 (m, 9 H, $B_{10}H_9$); 2.25 (m, 2 H, γ-C$\underline{\mathrm{H}}_2$); 2.53 (m, 4 H, β-C$\underline{\mathrm{H}}_2$); 5.05 (t, 4 H, α-C$\underline{\mathrm{H}}_2$, J = 5 Hz). ^{13}C{^{1}H} NMR, δ: 20.3 (1 C, γ-$\underline{\mathrm{C}}$H$_2$); 24.5 (2 C, β-$\underline{\mathrm{C}}$H$_2$); 82.9 (2 C, α-$\underline{\mathrm{C}}$H$_2$). ^{11}B NMR, δ: 5.1 (s, 1 B, B(2)); −1.1 (d, 1 B, B(10), J = 141.6 Hz); −7.8 (d, 1 B, B(1), J = 141.6 Hz); −23.2 (d, 2 B, B(6,9), J = 122.1 Hz); −25.1 (d, 2 B, B(3,5), J = 127.0 Hz); −31.4 (d, 3 B, B(4,7,8), J = 117.2 Hz). IR (KBr), cm^{-1}: 2472 (ν(B—H)); 1102 (δ(B—B—H)); 699 (δ(B—B—B)); 944 (ν(C—O)).

Bis(tetrahydropyran-1-ium)octahydro-*closo*-decaborane (3b), $[eq\text{-}B_{10}H_8(OC_5H_{10})_2]$. The starting salt $(Ph_4P)_2[B_{10}H_{10}]$ (3.0 g, 3.8 mmol) was placed in a two-neck flask fitted with a bubbler and a reflux condenser. Tetrahydropyran (50 mL) was added, the system was purged with argon, and the mixture was heated to boiling. Then HCl was bubbled through the system for 3 h. The resulting dark orange solution was concentrated on a rotary evaporator to a waxy substance, which was chromatographed on silica gel 40 (column 2×40 cm) with CH_2Cl_2 as an eluent. The collected fraction (180—320 mL) was dried up in a desiccator over paraffin chips to give a white powdery solid. The yield of compound **3b** was 0.90 g (85%). Found (%): B, 37.39. $C_{10}H_{28}O_2B_{10}$. Calculated (%): B, 37.48. ^{1}H NMR, δ: 0.60—2.10 (m, 9 H, $B_{10}H_9$); 2.76 (m, 4 H, γ-C$\underline{\mathrm{H}}_2$); 2.87 (m, 8 H, β-C$\underline{\mathrm{H}}_2$); 5.40 (t, 8 H, α-C$\underline{\mathrm{H}}_2$, J = 5 Hz). ^{13}C{^{1}H} NMR, δ: 20.2 (2 C, γ-$\underline{\mathrm{C}}$H$_2$); 24.6

(4 C, β-$\underline{C}H_2$); 84.2 (4 C, β-$\underline{C}H_2$). ^{11}B NMR, δ: 2.2 (s, 2 B, B(2,6(7))); −11.6 (d, 2 B, B(10,1), *J* = 151 Hz); −22.4 (d, 2 B, B_{eq}, *J* = 137 Hz); −31.4 (d, 2 B, B_{eq}, *J* = 132 Hz); −38.5 (d, 2 B, B_{eq}, *J* = 137 Hz). IR (KBr), cm^{-1}: 2486, 2536 (ν(B—H)); 1104 (δ(B—B—H)); 698 (δ(B—B—B)); 944 (ν(C—O)).

Tetrabutylammonium 2-(tetrahydrofuran-1-ium)nonahydro-*closo*-decaborate(1−) (2a), $(Bu_4N)[2\text{-}B_{10}H_9(OC_4H_8)]$. The starting salt $(Bu_4N)_2[B_{10}H_{10}]$ (2.0 g, 3.3 mmol) was placed in a two-neck flask fitted with a bubbler and a reflux condenser. Tetrahydrofuran (50 mL) was added, the system was purged with dry argon, and the mixture was heated to 60 °C. Then dry HCl was bubbled for 1 h. The resulting light yellow solution produced white crystals, which were filtered off and dried on filter paper. The yield of compound **2a** was 1.3 g (94%). Found (%): B, 20.31. $C_{20}H_{53}ONB_{10}$. Calculated (%): B, 20.45. MS (ESI/MS, anionic part): found *m/z* 189.39 ($[2\text{-}B_{10}H_9OC_4H_8]^-$), calculated *m/z* 189.28. $C_4H_{17}{}^{10}B_2{}^{11}B_8O$. ^{1}H NMR, δ: 0.60—2.10 (m, 9 H, $B_{10}H_9$); 1.87 (m, 4 H, β-$C\underline{H}_2$); 4.01 (t, 4 H, α-$C\underline{H}_2$, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR, δ: 25.3 (2 C, β-$\underline{C}H_2$); 82.2 (2 C, α-$\underline{C}H_2$). ^{11}B NMR, δ: 3.7 (s, B(2)); −2.8 (d, 1 B, B(10), *J* = 141 Hz); −9.5 (d, 1 B, B(1), *J* = 145 Hz); −25.0 (d, 2 B, B(6,9), *J* = 151 Hz); −26.8 (d, 2 B, B(3,5) *J* = 151 Hz); −33.2 (d, 3 B, B(4,7,8), *J* = 121 Hz). IR (KBr), cm^{-1}: 2521, 2480, 2452 (ν(B—H)); 1103 (δ(B—B—H)); 697 (δ(B—B—B)); 968 (ν(C—O)).

Bis(tetrahydrofuran-1-ium)octahydro-*closo*-decaborane (3a), $[eq\text{-}B_{10}H_8(OC_4H_8)_2]$. A 100-mL two-neck flask fitted with a magnetic stirring bar, a reflux condenser, and a bubbler was charged with $(Bu_4N)_2[B_{10}H_{10}]$ (3 g, 4.9 mmol) and THF (50 mL). The mixture was heated with stirring to 60 °C and HCl was bubbled for 2.5 h. The resulting light yellow transparent solution was concentrated on a rotary evaporator. The residue was chromatographed on silica gel 40 (column 2×40 cm) with CH_2Cl_2 as an eluent. The collected fraction (200—350 mL) was dried up in a desiccator over paraffin chips to give a white powdery solid. The yield of compound **3a** was 1.0 g (81%). Found (%): B, 41.39. $C_8H_{24}O_2B_{10}$. Calculated (%): B, 41.52. ^{1}H NMR, δ: 0.60—2.10 (m, 9 H, $B_{10}H_9$); 2.15 (m, 4 H, β-$C\underline{H}_2$); 4.32 (t, 4 H, α-$C\underline{H}_2$, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR, δ: 25.5 (4 C, β-$\underline{C}H_2$); 83.6 (4 C, α-$\underline{C}H_2$). ^{11}B NMR, δ: 5.1 (s, 2 B, B(2,6(7))); −8.0 (d, 2 B, B(10,1), *J* = 151 Hz); −18.7 (d, 2 B, B_{eq}, *J* = 137 Hz); −25.5 (d, 2 B, B_{eq}, *J* = 132 Hz); −33.9 (d, 2 B, B_{eq}, *J* = 137 Hz). IR (KBr), cm^{-1}: 2486 (ν(B—H)); 1102 (δ(B—B—H)); 696 (δ(B—B—B)); 968 (ν(C—O)).

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