

Communication

Synthesis of the 1-hydroxy-*closo*-decaborate anion $[1-B_{10}H_9OH]^{2-}$

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Abstract

Reactions of the diazonium derivative of *closo*-decaborate anion with oxygen nucleophiles were studied. The reaction of $[1-B_{10}H_9N_2]^-$ with hydroxide ion gives the corresponding hydroxy derivative $[1-B_{10}H_9OH]^{2-}$ in high yield. The reactions with OR (R = Me, Et, *i*-Pr, Ph) result in mixture of $[1-B_{10}H_9OR]^{2-}$ and $[a^2-B_{20}H_{18}]^{4-}$.

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1. Introduction

The decahydro-*closo*-decaborate anion, $[B_{10}H_{10}]^{2-}$, and its derivatives have good prospects of use in nuclear medicine [1,2] and material science [3]. The last field requires synthesis of *closo*-decaborate derivatives with substituents situated at axial positions of the B_{10} cage. Practically, all known methods of introduction of substituents at axial position of the $[B_{10}H_{10}]^{2-}$ anion are based on its reactions with aryldiazonium salts producing 1-arylazoderivatives $[1-ArN=NH-B_{10}H_9]^-$ [4] followed their transformation to the amino $[1-B_{10}H_9NH_3]^-$ [4,5] or diazonium $[1-B_{10}H_9N_2]^-$ [6,7] derivatives.

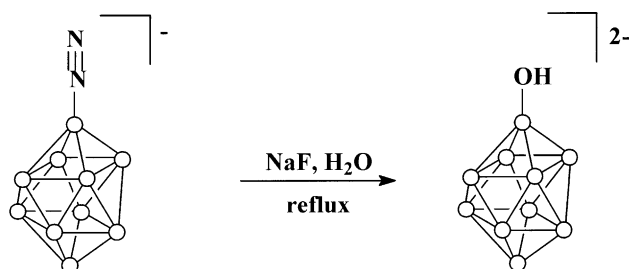
The diazonium function acting as a leaving group in apparent nucleophilic displacement reactions is one of the most useful substituents in organic synthesis. Despite the diazonium derivative of *closo*-decaborate anion $[1-B_{10}H_9N_2]^-$ was prepared for the first time more than 30 years ago [6] and demonstrates the extraordinary stability [8], nucleophilic substitution in this compound was investigated very limitedly. The reaction of

$[1-B_{10}H_9N_2]^-$ with pyridine results in the corresponding pyridinium derivative $[1-B_{10}H_9NC_5H_5]^-$ [7], the reactions with amines give the corresponding ammonium derivatives $[1-B_{10}H_9NH_nR_{3-n}]^-$ [9], and the reaction with *N,N*-dimethylthioformamide followed by alkaline hydrolysis of forming intermediate results in the mercapto derivative $[1-B_{10}H_9SH]^{2-}$ [10].

In continuation of our study of chemistry of the $[B_{10}H_{10}]^{2-}$ anion [11–13], we studied reactions of $[1-B_{10}H_9N_2]^-$ with different oxygen nucleophiles (hydroxy-, alkoxy- and aryloxy-anions). Heating $[1-B_{10}H_9N_2]^-$ in aqueous solution of sodium hydroxide results in formation of the corresponding hydroxy derivative $[1-B_{10}H_9OH]^{2-}$ and $B(OH)_4^-$ as a product of the boron cage destruction. The products ratio depends on the alkali strength – the stronger alkali the higher yield of $B(OH)_4^-$. The cage destruction can be depressed using mild alkaline conditions, i.e. aqueous solution of sodium fluoride. Heating $[1-B_{10}H_9N_2]^-$ with NaF in aqueous solution results in its practically quantitative conversion to the hydroxy derivative (Scheme 1). In some cases, trace amounts of the parent *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ were found. It should be noted that no formation of $[1-B_{10}H_9F]^{2-}$ [14] was observed under these conditions. The hydroxy derivative was

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Scheme 1.

isolated as the triphenylbenzylphosphonium salt and characterized by methods NMR and IR spectroscopy and chemical analysis.

In the ^{11}B NMR spectrum, substitution of diazonium by hydroxy group results in unprecedented large downfield shift of signal corresponding to the substituted boron atom (-13.7 ppm for $[1-B_{10}H_9N_2]^{2-}$ and 23.8 ppm for $[1-B_{10}H_9OH]^{2-}$, $\Delta = 37.5$ ppm), as well as unprecedented large upfield shift of signal corresponding to the antipodal axial boron atom (20.8 ppm for $[1-B_{10}H_9N_2]^{2-}$ and -15.8 ppm for $[1-B_{10}H_9OH]^{2-}$, $\Delta = -36.6$ ppm). The signals corresponding to the equatorial boron atoms also demonstrate upfield shift from -17.0 and -25.2 ppm for $[1-B_{10}H_9N_2]^{2-}$ to -32.2 and -33.9 ppm for $[1-B_{10}H_9OH]^{2-}$.

The IR spectrum of $(PhCH_2PPh_3)_2[1-B_{10}H_9OH]$ contains the ν_{OH} band at 3650 cm^{-1} (3644 cm^{-1} in $[2-B_{10}H_9OH]^{2-}$ [15], 3674 cm^{-1} in $[B_{12}H_{11}OH]^{2-}$ [16]) and the ν_{BH} bands at 2458 and 2422 cm^{-1} .

In the case of alkoxy (OMe, OEt, O^{*i*}Pr) and aryloxy (PhO) anions, the reaction is more complicated and gives mixture of the desired alkoxy(aryloxy) derivative $[1-B_{10}H_9OR]^{2-}$ and $[a^2-B_{20}H_{18}]^{4-}$ [17] as well as trace amounts of the parent anion $[B_{10}H_{10}]^{2-}$ identified by ^{11}B NMR spectroscopy (Scheme 2). Optimization of these reactions for synthesis of $[1-B_{10}H_9OR]^{2-}$ derivatives is in a progress.

2. Experimental

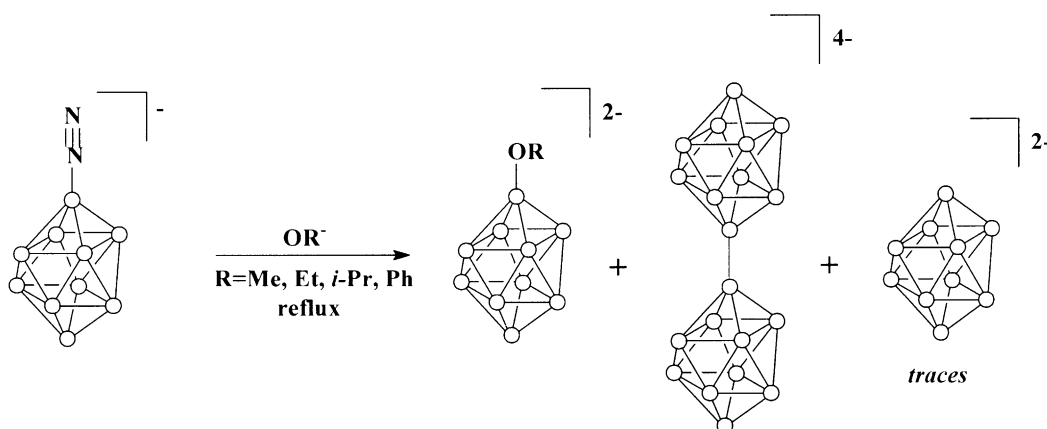
$(Et_3NH)[1-B_{10}H_9N_2]$ was prepared as described in the literature [18]. The ^{11}B NMR spectra were collected using a Bruker AM 360 spectrometer with $BF_3 \cdot Et_2O$ as the external standard. The IR spectra were obtained on a Specord M82 spectrometer as suspensions in Nujol mull. Elemental analysis was performed in the Laboratory of Microanalysis of the Institute of Organoelement Compounds (Moscow).

2.1. Synthesis of bis(benzyltriphenylphosphonium)1-hydroxy-*n*onahydro-*c*-closo-decaborate

To 0.49 g (2.0 mmol) $(Et_3NH)[1-B_{10}H_9N_2]$ in 20 ml of water 0.17 g (4.0 mmol) sodium fluoride was added. The solution was heated under reflux for 70 h , cooled to room temperature and treated with 0.97 g (3.0 mmol) $[Bu_4N]Br$ in 5 ml of water. The dulled precipitate formed was filtered off and filtrate was treated with 1.17 g (3.0 mmol) $[Ph_3PCH_2Ph]Cl$ in 10 ml of water. The formed light yellow precipitate was filtered, washed with 20 ml of water and 10 ml of acetonitrile, and dried in air to give 1.38 g (82%) of the product. ^{11}B NMR ($dms\text{-}d_6$, ppm): 23.8 (IB, s), -15.8 (IB, d, $J = 141\text{ Hz}$), -32.2 (4B, d, $J = 129\text{ Hz}$), -33.9 (4B, d, $J = 130\text{ Hz}$). IR (Nujol, cm^{-1}): 3650 (ν_{OH}), 2458 (ν_{BH}), 2422 (ν_{BH}). Anal. Calc. for $C_{50}H_{54}B_{10}P_2O$: C, 71.41 ; H, 6.47 ; P, 7.37 ; B, 12.85 . Found: C, 71.47 ; H, 6.60 ; P, 7.13 ; B, 12.76% .

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Scheme 2.

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