Synthesis of 6-Aza-*nido*-decaborane(12) and its Derivatives

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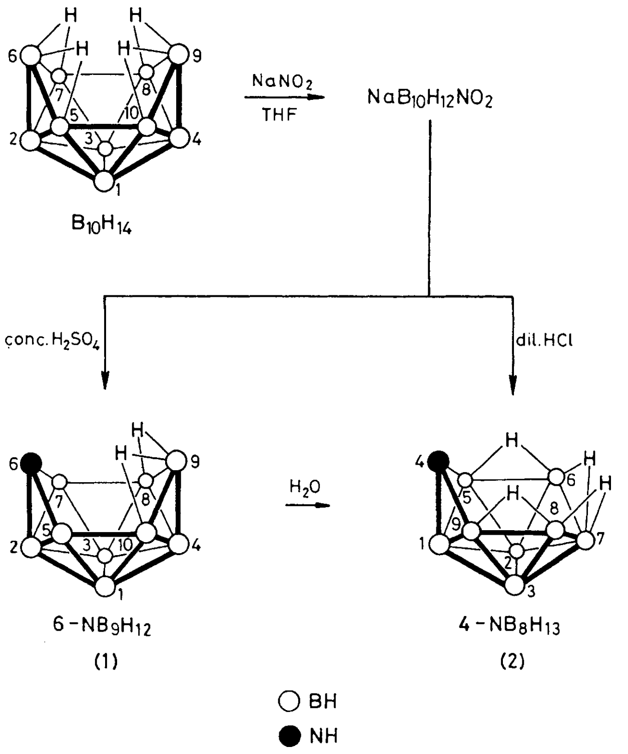
Summary The aza-*nido*-borane 6-NB_9H_{12} (**1**) has been prepared by treatment of the reaction intermediate formed in the reaction of $B_{10}H_{14}$ and $NaNO_2$ in tetrahydrofuran with concentrated H_2SO_4; hydrolysis of compound (**1**) afforded *arachno*-4-NB_8H_{13} (**2**) and the addition of Lewis bases produced the *arachno*-9-L-6-NB_9H_{12} (**3**) compounds [L = Me_2S (**3a**), MeCN (**3b**), and PPh_3 (**3c**)].

AZABORANES, namely $NMe_3NB_9H_{12}$, $NB_9H_{13}^-$, and MeCNN-B_9H_{12}, have been prepared by Muetterties *et al.*[1] from the $Me_2NNB_9H_{12}^-$ anion, produced in low yield in the reaction of $B_{10}H_{14}$ with $Me_2N{-}N{=}S$ in diethyl ether. In a previous communication[2] we reported the preparation of compound (**2**) which was produced by treatment of the reaction intermediate[3] formed in the reaction of $B_{10}H_{14}$ and $NaNO_2$ in tetrahydrofuran (THF) with hydrochloric acid.

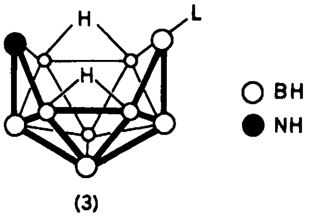
We report herein a high-yield synthesis of the parent 6-aza-*nido*-decaborane(12) (**1**) which is formed by concentrated H_2SO_4 degradation of the above-cited reaction intermediate, postulated[3] to have the $NaB_{10}H_{12}NO_2$ composition (see the Scheme). Both the reaction pathways in the Scheme can be rationalised in terms of a degradative insertion of the nitrogen atom into the $B_{10}H_{14}$ framework to produce the azaborane (**1**) which, as we have found, gives compound (**2**) in high yield on hydrolysis. The hydrolysis of compound (**1**) to compound (**2**) can be explained in terms of the hydrolytic degradation of the B(9) atom in compound (**1**) (see the Scheme). This type of hydrolysis almost parallels the degradation of the 6-OH-$B_{10}H_{13}^{2-}$ and 6-$CB_9H_{12}^-$ anions[4,5] to $B_9H_{14}^-$ and 4-CB_8H_{14}, respectively. The azaborane (**1**) is a white, crystalline, and air-sensitive compound; m.p. 79—80 °C (sublimes); M^+ 125; ν_{max} (CCl_4) 3340 (N-H_{free}), 3160 (N-H_{bond}), 2570 (B-H_t), and 1950 cm^{-1} (B-H-B); λ_{max} (CH_2Cl_2) 284 nm (ϵ 2105); ^1H n.m.r. (100 MHz, C_6D_6) δ −3·2 (2 H); ^{11}B n.m.r. (32·1 MHz, C_6D_6) δ_B 14·0 (1 B), 11·3 (2 B), −1·8 (2 B), −14·5 (2 B), −27·5



SCHEME

(1 B), and −32·9 (1 B) p.p.m. (relative to BF_3–OEt_2). The n.m.r. data show striking similarity to those obtained for the isoelectronic 6-SB_9H_{11} and 6-$CB_9H_{12}^-$ species[6,5] and are consistent with the symmetrical structure for (**1**) shown in the Scheme.

One molecule of Lewis base may be added to the azaborane (**1**) to obtain the 9-L-6-NB_9H_{12} derivatives (**3a**)—(**3c**), in almost quantitative yield, as white or yellowish crystals which are stable under nitrogen. Mass spectra of compounds (**3a**)—(**3c**) exhibit only the peaks which correspond to L^+ and $(^{14}N^{11}B_9{}^1H_{12})^+$. Similarly, the ^{11}B n.m.r. spectra of compounds (**3a**)—(**3c**) consist of signals attributable to a mixture of compound (**1**) and compounds (**3a**)—(**3c**), which indicates a remarkable dissociation in solution.



(3)

9-L-6-NB_9H_{12}

a; L = Me_2S

b; L = MeCN

c; L = PPh_3

Such dissociation also occurs at higher temperatures, which enabled the preparation of pure compound (**1**) by simple sublimation of compound (**3a**) at 50—60 °C/10^{-2} Torr.

In CH_2Cl_2 solutions the cleavage of the B(9)–L bond of compound (**3a**) [λ_{max} 281 nm, corresponding to compound (**1**), and λ_{max} 234 nm, corresponding to compound (**3a**)] and of compound (**3b**) [λ_{max} 287 nm (ϵ 2103), corresponding to compound (**1**)] was also confirmed by the u.v. spectra. The u.v. spectrum of compound (**3b**) in MeCN showed, however, λ_{max} 239 nm (ϵ 7535), corresponding to compound (**3b**), and no maximum attributable to compound (**1**). The presence of a strong CN vibration in the Raman spectrum, but a weak CN vibration in the i.r. spectrum indicates that the CN group is situated in the plane of symmetry intersecting the N(6)–B(2,4,9) atoms. The u.v. spectrum of compound (**3c**) is more complex due to the PPh_3 absorptions.

Reaction of compound (**3b**) with $LiAlH_4$ in THF produced the *arachno*-6-$NB_9H_{13}^-$ anion[1] which was isolated as the tetramethylammonium salt in high yield and identified by comparing the ^{11}B n.m.r. data with literature values.[1] The line narrowing in the ^{11}B n.m.r. spectrum (64·18 MHz) of this anion showed[7] that the high field doublet of intensity 4, found at δ_B −31·3 p.p.m. by Muetterties *et al.*,[1] consisted of one triplet of area 1 and two doublets of area 2 : 1. This result is consistent with the proposed *arachno*-structure for the anion.

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[1] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 1967, **6**, 1696.

[2] K. Baše, J. Plešek, S. Heřmánek, J. Huffman, P. Ragatz, and R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 1975, 934.

[3] E. L. Muetterties and C. Ford, U.S. P. 3,050,361, 1962.

[4] L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Am. Chem. Soc.*, 1963, **85**, 2674.

[5] B. Štíbr, K. Baše, S. Heřmánek, and J. Plešek, *J. Chem. Soc., Chem. Commun.*, 1976, 150.

[6] W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.*, 1976, **98**, 1441.

[7] S. Heřmánek, personal communication.