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Rearrangements in the nona- and azanonaborane clusters*

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Abstract: In the conversion of nonaboranes $B_9H_{13}SMe_2$ to azanonaboranes B_8NH_{11}-NHR, one boron atom is lost. This boron atom was identified, and a pathway for the rearrangement of the cluster is proposed, based on the fate of covalently labeled boron atoms.

INTRODUCTION

Polyhedral boron-containing cage chemistry based on eight boron atoms is relatively sparsely developed because suitable eight-boron starting materials are generally only available via multistep reactions from commercially available decaborane(14). The eight-boron species $[(EtH_2N)B_8H_{11}NHEt]$ (1), available in high yield in two simple steps from *nido*-$B_{10}H_{14}$, has been shown to constitute a good entry into azacarbaborane [1,2] and azametallaborane chemistry [3]. Its structure is based on a cluster of *hypho*-type eight-vertex character that bears two amine-derived residues, viz. one amine ligand in an exo terminal position and one amino group in a bridging position (Fig. 1). The eight-boron species can be obtained from decaborane(14) via the nine-boron species $B_9H_{13}SMe_2$ with a total of 3 equiv of primary amines. The reaction proceeds step-wise, with the first amine forming the bridging position (Fig. 1).

In the transition from $(Me_2S)B_9H_{13}$ to $[(RH_2N)B_8H_{11}NHR]$, the cluster loses one boron atom and must undergo rearrangement. The topic of this paper is to determine which boron atom is eliminated, and what the nature of the cluster rearrangements is that might occur during the conversion of $(Me_2S)B_9H_{13}$ to the B_8N cluster. We have achieved this by investigating the conversion of B-substituted nonaboranes to the azanonaboranes.

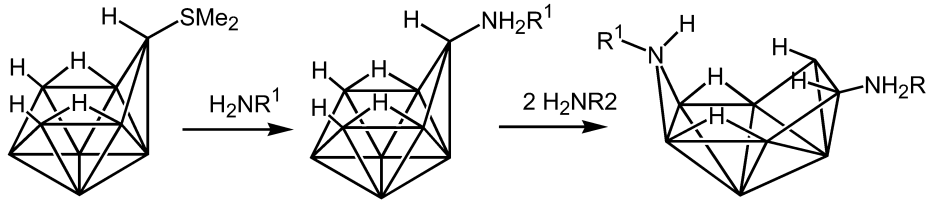

Fig. 1 Conversion of the nonaborane-SMe_2 via nonaborane-NH_2R to the azanonaborane.

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METHODS AND RESULTS

Preparation of precursors

A variety of B-substituted $B_{10}H_{14}$ derivatives are known [4–6]. We have prepared some of these compounds where R = Et, Br, and D, respectively. These compounds can readily be converted via the two-step procedure, with 6,9-$(Me_2S)_2B_{10}H_{12}$ derivatives as intermediates to the corresponding arachno-nonaborane system [7–9]. The labels were chosen because they are stable under the reaction conditions: Neither the bromine atom nor the ethyl group can be removed by Et_3N [7], and no deuterium exchange has been noted in refluxing the tetradeuterated $(Me_2S)B_9H_{13}$ with diethylamine in benzene [9].

Thus, the following $(Me_2S)B_9H_{13}$ compounds with labeled B-atoms could be prepared (Scheme 1): Et at B^2 (**2**) or B^7 (**3**), Br at B^2 (**4**) or B^6 (**5**) or B^1 (**6**) and D at B^1, B^2, B^3, and B^7 (**7**). The presence of the positions of the substituents could be identified unequivocally by NMR, IR, and MS spectra.

It was also attempted to prepare selectively labeled boron-10-labeled decaborane(14) through the introduction of a single boron-10 atom. The corresponding B_{11} cluster undergoes, however, rapid rearrangement [10], and total scrambling is observed.

Resulting compounds

After the reaction of the nonaborane derivatives with an excess of isopropylamine in benzene, the corresponding azanonaborane compounds could be obtained. The labels of the B_9 cluster appeared in the following positions of the B_8N cluster after reaction with isopropylamine (Scheme 1, Table 1): Et at B^2 of **2** was bonded to B^2 in the B_8N cluster **8**; Et located at B^7 of **3** was converted to the B^5-ethylated B_8N cluster **9**. The B^2-brominated B_9 cluster **4** yields the B^2-brominated B_8N cluster **10**, and the B^6-brominated B_9 cluster **5** yields the B^4-brominated cluster **11**. The B^1-brominated nonaborane **6** yields the non-brominated B_8N cluster **1**. The 1,2,3,7-tetradeuterated nonaborane **7** was transformed to the 2,5,7-trideuterated B_8N cluster **12**. The NMR results show clearly that one deuterium atom is lost (Table 1) while the positions of the other deuterium atoms could be identified unequivocally.

Table 1 Summary of the stereochemistry of the starting and resulting compounds.

Substituent	Compound start-final	Position in B_9 cluster	Position in B_8N cluster	Starting compound	Resulting compound
Ethyl	**3–9**	7	5 or 6	prochiral	one diastereomer
Ethyl	**2–8**	2	2	chiral	enantiomer
D	**7–12**	1,2,3,7	2,4,6 or 2,5,7	prochiral	??
Br	**6–1**	1	missing	prochiral	enantiomer
Br	**4–10**	2	2	chiral	enantiomer
Br	**5–11**	6	4 or 7	chiral	one diastereomer

Thus, the boron atoms B^3, B^6, and B^7 in B_9 cluster end up at the positions B^7, B^4, and B^5 in B_8N, respectively (Fig. 2); B^2 in the B_9 cluster remains B^2 in the B_8N cluster while B^1 of the B_9 cluster is lost during the conversion.

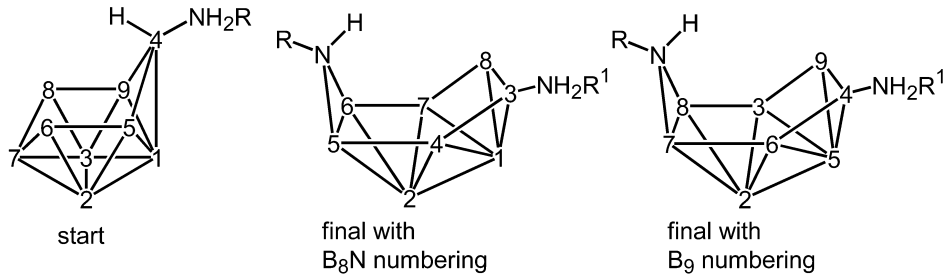

Fig. 2 Numbering of the boron atoms in the nonaborane, the resulting azanonaborane with IUPAC numbering of the atoms, and numbering according to the numbers of the starting nonaborane.

Note on stereochemistry

The compounds prepared are stereochemically well defined. Some of the starting nonaborane clusters are chiral, others are prochiral. The resulting azanonaboranes are either enantiomers (for which the absolute configuration was not elucidated), or only a single diastereomer was obtained. For the deuterated product, the position of the deuterium atoms could not be identified unambiguously, as a mixture of two compounds would be expected with very similar chemical shifts, and mixtures of substitutions with D resp. H.

For compounds **9** and **11**, the NMR spectra did not allow a final conclusion as to which atom bears the label in the final product.

PROPOSED MECHANISM

Figure 3 shows the proposed pathway for the reaction from nonaborane to the azanonaborane.

The first RNH_2 molecule attacks the cluster $(RH_2N)B_9H_{13}$ on B^5. For an attack on this atom, support is found by the reaction of $(Me_2S)B_9H_{13}$ with RNH_2 [7], where the molecule 5-$RH_2NB_9H_{13}$ can be isolated as intermediate. When 5-OMe(*i*PrH_2N)B_9H_{12} is refluxed with excess *i*PrNH_2 in benzene, no reaction occurs.

The RNH_2 moiety exchanges its position from exo to endo as described in the literature [12,13]. This is possibly aided by a weakened bond between B^5 and B^4.

The RNH_2 moiety migrates to boron atoms B^7 and B^8 followed by bond cleavage between B^8 and B^9. This assumption is supported by the observation of the reaction rate of **3** with Et on B^7, which is slow compared to the reaction rate of **2** with Et on B^2. At the same time, the second R^1NH_2 moiety migrates from B^5 to the exo position of B^4 [11]. An analogous migration is described in the literature [8].

With a diamond-square-diamond (DSD) rearrangement [14], the bond between B^3 and B^7 is broken and a new bond between B^2 and B^8 is formed.

An additional R^1NH_2 molecule attacks the cluster (perhaps again on B^5) and migrates from B^5 to B^1. The B^1 and two additional H atoms leave the molecule together with the most recently introduced amin, as indicated by reactions of 1,2,3,7-D_4 and 1-Br nonaboranes, respectively.

The bonds close between B^5–B^3, B^5–B^9, and B^6–B^4 to complete the formation of the azanonaborane cluster.

Depending on the final stereochemistry of the product, the attack of the initial amine (and probably the second and third amine as well), might also take place on atom B^9 (Fig. 3), which is equivalent to B^4. With the resulting compounds being diastereomers, the attack might matter. When the final product is an enantiomer, only the determination of the absolute stereochemistry might be able to determine the atom which is initially attacked.

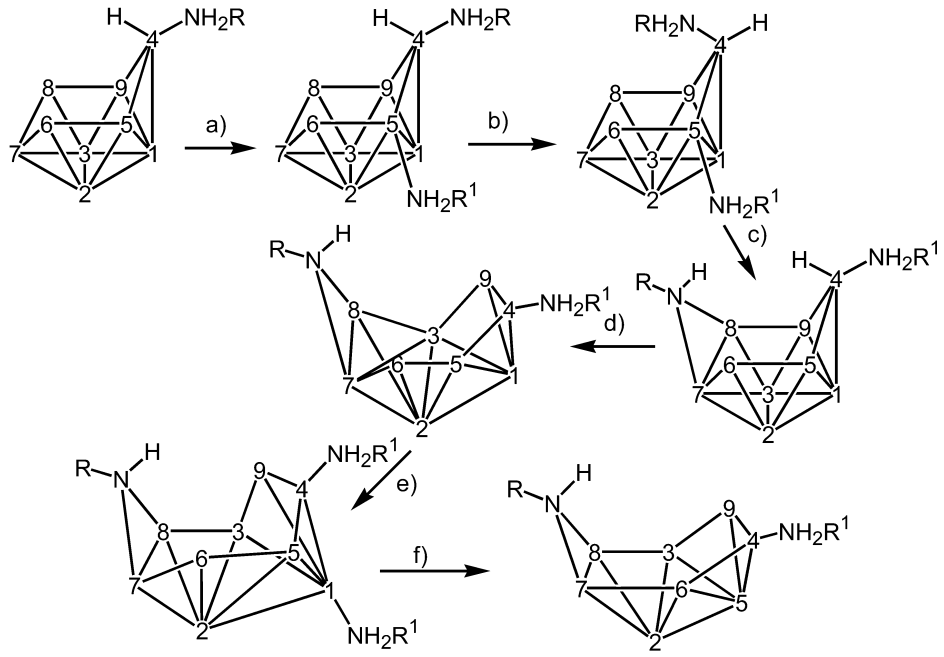

Fig. 3 Proposed mechanism for the rearrangement.

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