Degradative Insertion Reactions of *nido*-7,9-$C_2B_9H_{12}^-$. Synthesis and Properties of 4-Thia-6,8-dicarba-*arachno*-nonaborane(10), 4,6,8-$SC_2B_6H_{10}$

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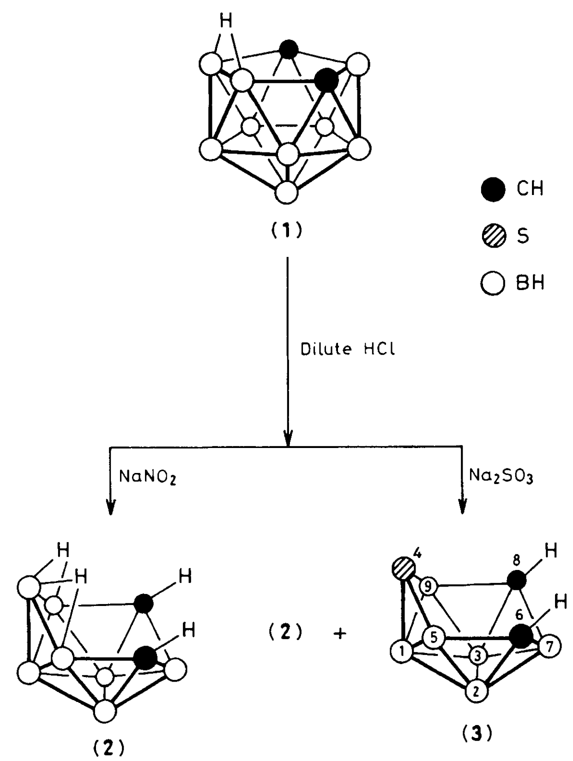
The reaction of 7,9-$C_2B_9H_{12}^-$ (**1**) with $NaNO_2$ and Na_2SO_3 in dilute hydrochloric acid affords 6,8-$C_2B_7H_{13}$ (**2**) and the new thiacarbaborane 4,6,8-$SC_2B_6H_{10}$ (**3**) the structure of which is proposed on the basis of ^1H and ^{11}B n.m.r. spectra.

Degradative insertion reactions of decaborane(14) with inorganic salts as a method for the synthesis of heteroboranes have been described.[1] In the corresponding *nido*-dicarbaborane series, these reactions have been systematically studied only for *nido*-7,8-$C_2B_9H_{12}^-$.[2—4] We now report a comparative study on the degradative insertion reactions of the *nido*-7,9-$C_2B_9H_{12}^-$ anion (**1**).[5] Treatment of anion (**1**) with $NaNO_2$ in dilute hydrochloric acid under the reaction conditions described[3] for *nido*-7,8-$C_2B_9H_{12}^-$ afforded the known *arachno*-6,8-$C_2B_7H_{13}$ carbaborane (**2**)[6] only. In contrast, the reaction of anion (**1**) with Na_2SO_3 under these reaction conditions afforded in low yield a new thiadicarbaborane (**3**) together with (**2**) (see Scheme 1). Compound (**3**) was isolated from the reaction mixture by column chromatography on silica gel (benzene–hexane 1 : 1). The solvents were evaporated *in vacuo* (product volatilizes with solvents) and the crude product was purified by sublimation at 25—30 °C/10^{-2} Torr.

The thiadicarbaborane (**3**) is a white, crystalline, volatile, air sensitive compound, which is readily soluble in organic solvents; m.p. 104—105 °C; M^+ 132 (corresponding to $^{32}S^{12}C_2{}^{11}B_6{}^1H_{10}$). The structure of compound (**3**) was deduced from its ^1H and ^{11}B n.m.r. spectra. The ^1H n.m.r. spectrum (200 MHz) in $CDCl_3$ showed only one signal at δ 0.219 (4 H; C–H) and overlapping signals in the area δ 3.8 to −0.5 (6 H; B–H_t). The ^1H n.m.r. spectrum in C_6D_6 exhibited two signals at δ −0.317 (2 H; C–H_{eq} of lower acidity: δ C_6D_6 − δ $CDCl_3$ = −0.536) and δ −0.775 (2 H; C–H_{axial} of higher acidity: δ C_6D_6 − δ $CDCl_3$ = −0.994), and overlapping signals in the area δ 3.8 to −1.00 (6 H; B–H_t) (relative to tetramethylsilane). The ^{11}B n.m.r. spectrum (64.18 MHz, $CDCl_3$) exhib-



Scheme 1

ited four signals of relative intensities 1:2:2:1 at δ [J_{BH} in Hz; width at half height ($w_{1/2}$) of the ^{1}H decoupled signal in Hz]: 7.60 (156; 26), 5.70 (168; 31), −21.68 (160; 54), and −35.60 (175; 65) p.p.m. (relative to $BF_3{\cdot}OEt_2$), which indicated the existence of a plane of symmetry bisecting the nonaborane framework in the 1, 4, and 7 positions. The location of the heteroatoms from the n.m.r. spectra was based on the empirical rule[7] that the signal of a B-atom located in the open face between two heteroatoms is distinctly narrow, indicated by its low $w_{1/2}$ value in the $^{11}B\{^{1}H\}$ n.m.r. spectrum. The best agreement with this empirical rule is given by the 4,6,8-$SC_2B_6H_{10}$ structure which is also consistent with Rule 3 of the Williams' Co-ordination Number Pattern Recognition concept,[8] according to which the incorporation of an electron rich element (*e.g.* sulphur) at a low-co-ordinate site is preferred (4 *vs.* 7).

However, the low-intensity B–S and C–S valence vibrations in the i.r. spectrum and a very strong signal at ν 688 cm^{-1} in the Raman spectrum attributable to symmetrical C–S–C valence vibration[9] suggest that the 7,6,8-$SC_2B_6H_{10}$ arrangement may be possible. The final structure should be confirmed by *X*-ray analysis.

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