exchange resin using acetonitrile as eluent. The acetonitrile was removed *in vacuo* and the residue sublimed at 40–45° to obtain 0.764 g (4.3 % yield, mp 145–146°).

The infrared spectrum (KBr phase) includes absorptions at λ_{max} 2545 (vs), 1570 (m), 1470 (s), 1435 (s), 1375 (m), 1320 (m), 1300 (w), 1260 (w), 1070 (m), 1060 (m), 1010 (s), 990 (s), 970 (s), 930 (m), 905 (m), 810 (m), 780 (m), 755 (m), 725 (s), 700 (m), 675 (s), 640 (w), 440 (m), and 390 (w) cm^{-1}.

The proton nmr spectrum ($CDCl_3$ solution) shows only a broadened resonance at τ 2.4 due to the C_6H_5 group. The boron nmr spectrum at 70.6 MHz (chloroform) exhibits resonances at (J_{BH} in parentheses) −4.4 (1 B, 140 Hz), 1.7 (2 B, 170 Hz), 5.6 (2 B, 165 Hz), 14.2 (2 B, 150 Hz), 17.7 (1 B, 155 Hz), and 23.3 ppm (2 B, 150 Hz), externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

$(CH_3)_4NB_{10}H_{11}AsR$ (R = CH_3 (VI) or C_6H_5 (VIII)). $B_{10}H_{12}AsR$ was dissolved in 4 *M* NH_3 and precipitated with tetramethylammonium chloride solution. The precipitate was crystallized under a nitrogen blanket from 95% ethyl alcohol (yield 90–95%).

The infrared spectrum of $(CH_3)_4NB_{10}H_{11}AsCH_3$ indicates absorption at λ_{max} 3025 (w), 2520 (vs), 1475 (s), 1410 (w), 1315 (w), 1280 (w), 1245 (m), 1010 (m), 985 (m), 945 (s), 445 (w), and 410 (w) cm^{-1}, while that of $(CH_3)_4NB_{10}H_{11}C_6H_5$ includes absorptions at λ_{max} 3020 (m), 2500 (vs), 1475 (vs), 1440 (m), 1430 (s), 1410 (w), 1290 (w), 1270 (w), 1050 (s), 1000 (s), 980 (s), 935 (s), 725 (s), 680 (s), 550 (w), 520 (w), 465 (m), 430 (m), and 415 (m) cm^{-1}.

The proton nmr spectrum of $(CH_3)_4NB_{10}H_{11}AsCH_3$ (acetone-d_6) consists of a very sharp singlet (12 H) at τ 6.62 ($(CH_3)_4N^+$) and a singlet (3 H) at τ 7.99 (CH_3), while that of the phenyl derivative (acetone-d_6) consists of a sharp singlet at τ 6.66 ($(CH_3)_4N^+$) and a multiplet (5 H) centered at τ 2.7 (C_6H_5). The boron nmr spectrum at 70.6 MHz of $(CH_3)_4NB_{10}H_{11}AsC_6H_5$ (acetone-d_6) includes resonances at (J_{BH} in parentheses) 10.5 (2 B, 145 Hz), 17.1 (2 B, 150 Hz), and 36.8 ppm (1 B, 140 Hz), externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

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Chemical and Nuclear Magnetic Resonance Studies of the $B_9H_{12}^-$ and $B_9H_{12}S^-$ Ions

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The 70.6-MHz ^{11}B nmr spectra of labeled $B_9H_{12}S^-$ derivatives indicate that a rearrangement process occurs during the formation of this thiaborane from decaborane(14). Treatment of $B_9H_{13} \cdot S(C_2H_5)_2$ or $B_9H_{12}^-$ with ammonium polysulfide forms $B_9H_{12}S^-$. Similar rearrangement of labeled molecules is also observed in these latter two chemical transformations. A unified mechanism which explains all the observed rearrangement reactions is proposed.

Introduction

Exclusive of the carboranes, the chemistry of nine-atom boranes and heteroatom boranes may be divided into three broad categories: (1) synthesis and reactions of the two neutral, isomeric B_9H_{15} hydrides,[2-7] (2) degradative reactions of decaborane to form $B_9H_{12}^-$,[8] $B_9H_{14}^-$,[9] and $B_9H_{13} \cdot$ligand species,[10,11] (3) insertion of heteroatoms into the B_9 framework to form $B_9H_{12}S^-$ and $B_9H_{12}NH^-$ [12] and metalloboranes such as $(R_3P)_2Pt(B_9H_{11} \cdot \text{ligand})$[13] and $(CO)_3Mn(B_9H_{13})^-$.[14] We have recently reported specific positional assignments of the ^{11}B nuclear magnetic resonance spectra of complex boron hydride species such as $B_{10}H_{13}^-$,[15] $B_{10}H_{15}^-$,[16] and $B_9H_{13} \cdot$ligand.[17] This paper reports the results of a 70.6-MHz ^{11}B nmr spectral study of $B_9H_{12}^-$, $B_9H_{12}S^-$, and their labeled derivatives.

Experimental Section

The ^{11}B nmr spectra were measured on equipment consisting of a pulsed nmr apparatus built in this department operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, and a 20K Nicolet 1080 series computer. Additional details have been reported elsewhere.[18] The ^{11}B nmr spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. Acetonitrile was the solvent for all ^{11}B nmr spectra except that of $B_9D_4H_{11} \cdot S(C_2H_5)_2$ where acetone was used. The proton nmr spectra were obtained with a Varian HR-220 spectrometer.

The method of Hertler and coworkers[12] was used to convert $B_{10}H_{14}$, 1,2,3,4-$B_{10}D_4H_{10}$, μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$, and 2-$BrB_{10}H_{13}$ to $CsB_9H_{12}S$, $CsB_9D_4H_8S$, $CsB_9D_8H_4S$, and $(C_2H_5)_4N[B_9BrH_{11}S]$, respectively.

Synthesis of $(C_2H_5)_4N[B_9BrH_{11}S]$ from $B_9BrH_{12} \cdot S(C_2H_5)_2$. To a solution of 0.3 g of $BrB_9H_{12} \cdot S(C_2H_5)_2$[17] in 10 ml of warm ethanol was added 1 ml of a 10% aqueous ammonium polysulfide solution. The mixture was warmed at 65° on a steam bath for 15 min, then cooled, and filtered. Saturated aqueous tetraethylammonium bromide, 5 ml, and acetonitrile, 5 ml, were added. Small amounts of

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sulfur were removed by filtration through Celite. Concentration of the filtrate under vacuum afforded the product as white crystals. An additional crystallization from aqueous acetonitrile gave 0.12 g (33%) of $(C_2H_5)_4NBrB_9H_{11}S$. *Anal.* Calcd for $C_8H_{31}B_9BrNS$: C, 27.43; H, 8.86; S, 9.14. Found: C, 27.62; H, 8.92; S, 8.92. Ir (KBr): strong absorptions occurred at 2525, 2500 sh, 1480, 1175, 1000, and 787 cm^{-1}. ^1H nmr (CD_3CN): in addition to peaks due to the cation, a broad singlet at +1.1 ppm appeared which is assigned to the bridge protons. This procedure was used to convert $B_9H_{13}\cdot S(C_2H_5)_2$ to $(C_2H_5)_4N[B_9H_{12}S]$ in 45% yield.

Salts of the $B_9H_{12}^-$ Ion. These were prepared by a slight modification of the method of Graybill, *et al.*[10] An excess of an aqueous solution of a quaternary ammonium hydroxide was added to an ethanol solution of $B_9H_{13}\cdot S(C_2H_5)_2$. The solution was concentrated on a rotary evaporator without heating until crystallization of the salt was complete. The product was isolated by filtration, vacuum dried, and stored in the cold under nitrogen. Yields of the $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ salts were typically 70–80%. The salts contained a trace of an impurity, observed as a shoulder on the +14.4-ppm peak in the ^{11}B nmr. Identification of this feature as due to an impurity is confirmed by its absence in the ^{11}B nmr spectrum of $(Ph_3PCH_3)B_9H_{12}$ prepared from $B_9H_{13}\cdot S(C_2H_5)_2$ and $Ph_3P{=}CH_2$. The infrared spectrum of $(CH_3)_4N[B_9H_{12}]$ (KBr) contained bands at 2990 (w), 2500 (s), 1470 (m), 1410 (m), 990 (w), 945 (m), 880 (w), 870 (w), and 680 (w) cm^{-1}. ^1H nmr (CD_3CN): in addition to a peak due to the cation, a broad peak was present at +1.64 ppm which is assigned to the bridge protons. Employing the previously reported method[17] 1,2,3,4-$B_{10}D_4H_{10}$ and 2-$BrB_{10}H_{13}$ were converted to $B_9D_4H_9\cdot S(C_2H_5)_2$ and $B_9BrH_{12}\cdot S(C_2H_5)$, respectively. Using the procedure described above, $(C_2H_5)_4N[B_9D_4H_8]$ and $(C_2H_5)_4N[B_9BrH_{11}]$ were prepared in 70 and 40% yields, respectively.

Synthesis of $B_9D_4H_9\cdot S(C_2H_5)_2$ from $(C_2H_5)_4N[B_9D_4H_8]$. A stream of dry hydrogen chloride was passed into a suspension of 0.2 g of $(C_2H_5)_4N[B_9D_4H_8]$ in 5 ml of diethyl sulfide. An exothermic reaction occurred and the solid dissolved. The solvent was removed under reduced pressure and the residue extracted with 30 ml of diethyl ether. The extract was filtered and the filtrate evaporated. The residue was crystallized from dichloromethane–hexane to give crystalline $B_9D_4H_9\cdot S(C_2H_5)_2$.

Results and Discussion

^{11}B Nmr Studies of $B_9H_{12}S^-$. Treatment of decaborane with aqueous ammonium polysulfide results in partial degradation of the decaborane framework and sulfur atom insertion by an unknown mechanism to form $B_9H_{12}S^-$ in high yield.[12] The 70.6-MHz ^{11}B nmr spectrum of $CsB_9H_{12}S$ in acetonitrile (Figure 1) consists of six resonances of relative areas 1:2:1:1:2:2 reading upfield. The pattern of the nmr spectrum is consistent with the solid-state structure of $B_9H_{12}S^-$ found in an X-ray crystallographic study of $(PPh_3)_3Au[B_9H_{12}S]$ which is shown in Figure 2.[19] The numbering system employed in Figure 2 and for $B_9H_{12}^-$ departs from that used previously[17] and is essentially the same as in decaborane. This allows easy reference to the labeled decaborane derivatives used in this work.

The triplet of unit area at +15.0 ppm (J_{BH} = 110 Hz) can be assigned by inspection to B(9) to which two terminal hydrogens are bonded. Upon irradiation at the bridge proton frequency (+1.85 ppm at 220 MHz), the doublets of relative area 2 at +7.9 and +33.4 ppm in the ^{11}B nmr spectrum undergo a reduction in line width and an increase in signal amplitude. These two resonances must then be due to B(5,7) and B(8,10) which are directly bonded to the two bridge hydrogens and which would be expected to be weakly spin coupled to these nuclei. The remaining doublet of area 2 at +36.6 ppm must therefore be due to B(1,3).

The ^{11}B nmr spectrum of $CsB_9D_4H_8S$ prepared from 1,2,3,4-$B_{10}D_4H_{10}$ is shown in Figure 3. The doublet resonances at +36.6 and −4.0 ppm in the spectrum of $B_9H_{12}S^-$ appear to be almost completely collapsed to singlets in Figure 3. In addition the resonances at +33.4 and +11.3 ppm show partial collapse to singlets and those at +14.9 and +7.9 ppm appear unaffected. Thus, there is some but not complete scrambling of the deuterium label during the formation of $B_9D_4H_8S^-$.

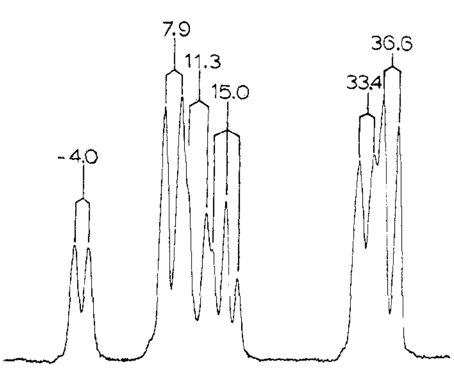

Figure 1. The 70.6-MHz ^{11}B nmr spectrum of $CsB_9H_{12}S$.

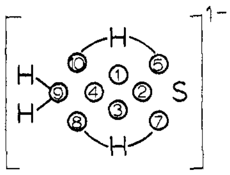

Figure 2. Structure and numbering system for the $B_9H_{12}S^-$ ion.

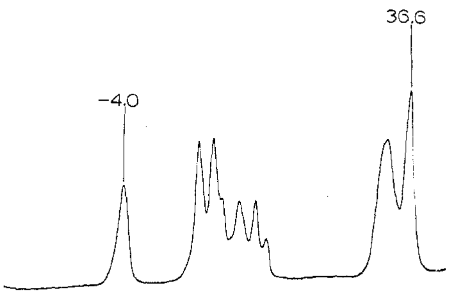

Figure 3. The 70.6-MHz ^{11}B nmr spectrum of $CsB_9D_4H_8S$ obtained from 1,2,3,4-$B_{10}D_4H_{10}$.

The ^{11}B nmr spectrum of $CsB_9D_8H_4S$ prepared from μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$ is shown in Figure 4. Barring rearrangement or H-D exchange, it was anticipated that this spectrum would contain singlets at +7.9 and +33.4 ppm due to B-D groups at B(5,7) and B(8,10) and a singlet at +15 ppm due to a BD_2 group at position B(9). Exchange of terminal hydrogens with the water used for crystallization of the labeled compounds was excluded by the observation that recrystallization of $CsB_9H_{12}S$ from hot D_2O resulted in no incorporation of terminal deuterium by infrared analysis. However, reference to Figure 4 shows that, again, some redistribution of the deuterium label has occurred but that the process is not random.

These results may be accounted for by postulating the existence of a boron hydride intermediate prior to sulfur atom insertion which has *effective C_{3v} symmetry.* Such a tautomerizing structure has been postulated for $B_9H_{14}^-$ on the basis of its ^{11}B nmr spectrum.[20,21] The gross geometry of our proposed intermediate is shown in Figure 5. The sets of boron atoms in the B_9 fragment which are equivalently related by the C_3 axis are B(1,3,4), B(5,7,9), and B(2,8,10). Sulfur atom insertion can occur at any of three equivalent

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(21) The 70.6-MHz ^{11}B nmr spectrum of $CsB_9H_{14}\cdot H_2O$ in tetrahydrofuran contains three doublets of equal area at +7.9, +20.7, and +23.6 ppm.

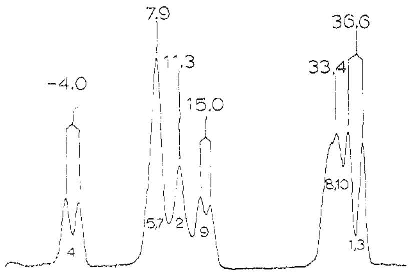

Figure 4. The 70.6-MHz ^{11}B nmr spectrum of $CsB_9D_8H_4S$ obtained from μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$.

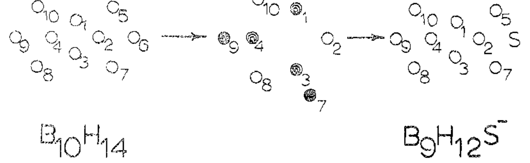

Figure 5. The proposed effective C_{3v} intermediate and its relationship to starting material and product.

positions to form $B_9H_{12}S^-$. Thus, when $B_9D_8H_4S^-$ is formed from μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$, B(4) and B(1,3) would not interchange with any positions which contain deuterium and should give rise to the doublets at −4.0 ppm (area 1) and +36.6 ppm (area 2), respectively (see Figure 4). The B(8,10) and B(2) positions would be interchanged so that each contained $^1/_3$ H and $^2/_3$ D, giving rise to the partially collapsed doublets at +33.4 ppm (area 2) and +11.3 ppm (area 1), respectively. The B(5,7) and B(9) positions should not lose deuterium in the proposed process and should give rise to singlets in the ^{11}B nmr spectrum. On this basis, the singlet at +7.9 ppm in Figure 4 may be assigned to B(5,7). The B(9) resonance at +15 ppm in Figure 4 appears as a doublet (J_{BH} = 100 Hz). This resonance appears to be due to a B(D)H unit. This unusual result can be explained by the following observations. Treatment of a tetrahydrofuran solution of $CsB_9H_{12}S$ with NaOD and D_2O results in incorporation of deuterium at only one terminal BH position [*i.e.*, B(9)] as indicated by the ^{11}B nmr spectrum in Figure 6. In addition, the bridge hydrogen atoms have exchanged as well since the proton nmr spectrum of this sample contained no bridge hydrogen resonance at +1.85 ppm. We therefore conclude that during the formation of $B_9D_8H_4S^-$ in alkaline H_2O, H for D exchange of one deuterium atom at B(9) occurred to give a B(D)H unit. The ^{11}B nmr spectrum of $CsB_9D_4H_8S$, Figure 3, may also be assigned on the basis of the postulated effective C_{3v} intermediate just described.

The spectrum of $(C_2H_5)_4N[BrB_9H_{11}S]$, prepared from 2-$BrB_{10}H_{13}$, is shown in Figure 7. The singlet of unit area at +24.6 ppm may be assigned to the bromine-substituted boron atom. However, the presence of eight discernible resonances in this spectrum reveals that the bromine must be located off the mirror plane of symmetry passing through the sulfur, B(2), B(4) and B(9). Sulfur atom insertion into a bromine-containing C_{3v} intermediate[22,23] would in principle form 1-$BrB_9H_{11}S^-$ (or the enantiomeric 3-$BrB_9H_{11}S^-$) and 4-$BrB_9H_{11}S^-$ in a 2:1 ratio. Careful examination of the reaction products failed to disclose the presence of a second isomer in addition to the isolated isomer which we believe to be 1-$BrB_9H_{11}S^-$. Thus, the 4-bromo derivative either is not formed at all, possibly due to the steric or electronic effects of the halogen substituent, or, once formed, is rapidly destroyed in the reaction mixture.

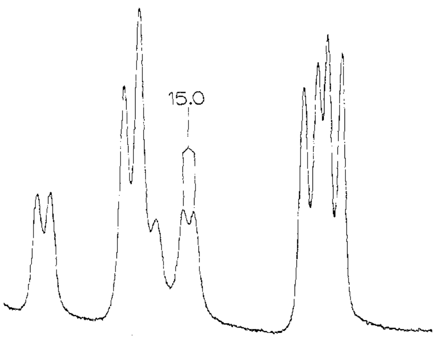

Figure 6. The 70.6-MHz ^{11}B nmr spectrum of $CsB_9D_3H_9S$ obtained from D_2O-OD^- exchange of $CsB_9H_{12}S$.

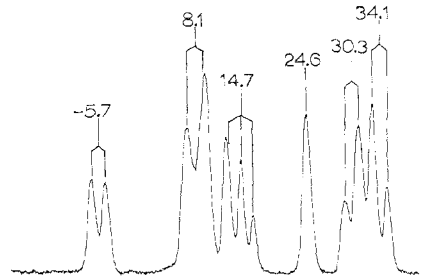

Figure 7. The 70.6-MHz ^{11}B nmr spectrum of $(C_2H_5)_4N[BrB_9H_{11}S]$ obtained from 2-$BrB_{10}H_{13}$.

Possible Intermediates in the Formation of $B_9H_{12}S^-$. The labeling experiments described above led to the expectation that $B_9H_{14}^-$, which has the required effective C_{3v} symmetry of the postulated intermediate,[18] was an intermediate in the formation of $B_9H_{12}S^-$. This also seemed reasonable since $B_9H_{14}^-$ is formed by degradation of $B_{10}H_{14}$ in aqueous alkaline solution.[7] It was surprising to find, therefore, that $CsB_9H_{14}\cdot H_2O$ did not react with aqueous ammonium polysulfide under the conditions used to prepare $B_9H_{12}S^-$. Other B_9 intermediates were then considered which could plausibly form under the reaction conditions, namely, $B_9H_{13}\cdot$ligand species and $B_9H_{12}^-$ which is derived from the former by deprotonation and loss of the ligand.[10] Treatment of either $B_9H_{13}\cdot S(C_2H_5)_2$ or $(CH_3)_4NB_9H_{12}$ in acetonitrile with aqueous ammonium polysulfide formed $B_9H_{12}S^-$ in about 45% yield. A similar reaction between 4-$BrB_9H_{12}\cdot S(C_2H_5)_2$, in which the position of substitution is known from previous nmr studies,[17] formed $BrB_9H_{11}S^-$ which had a ^{11}B nmr spectrum identical with the $BrB_9H_{11}S^-$ derivative synthesized from 2-$BrB_{10}H_{13}$.[23]

Based upon these experiments we suggest that $B_{10}H_{14}$ might be transformed to $B_9H_{12}S^-$ through a series of reactions like

$$B_{10}H_{14} + OH^- \rightarrow B_{10}H_{13}^- + H_2O$$

$$B_{10}H_{13}^- + S_x^{2-} \rightarrow [B_{10}H_{13}(S_x)]^{3-}$$

$$[B_{10}H_{13}(S_x)]^{3-} \xrightarrow[H_2O]{OH^-} [B_9H_{13}(S_x)]^{2-}$$

$$[B_9H_{13}(S_x)]^{2-} + OH^- \rightarrow B_9H_{12}^- + H_2O + S_x^{2-}$$

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(22) There is also a second possible bromine-containing intermediate which after sulfur atom insertion would result in the formation of 8-$BrB_9H_{11}S^-$ (or the enantiomeric 10-$BrB_9H_{11}S^-$) and 2-$BrB_9H_{11}S^-$. The reasons for rejecting this second possibility are given in the next section (see ref 23).

(23) This experimental result strongly suggests that only one of the two possible BrB_9 intermediates (see ref 22) is formed in this reaction. Based on the known structure of 4-$BrB_9H_{12}\cdot S(C_2H_5)_2$ and our postulated mechanism (*vide supra*), we propose that the product of this reaction is 1-$BrB_9H_{11}S^-$. More definitive evidence concerning the structure of this compound must await a single-crystal X-ray investigation.

$$B_9H_{12}^- + S_x^{2-} \rightarrow B_9H_{12}S^-$$

The intermediate $[B_{10}H_{13}(S_x)]^{3-}$ may be considered as a member of the $B_{10}H_{12}\cdot 2$(ligand) class of molecules as are the anions $B_{10}H_{14}^{2-}$ and $B_{10}H_{13}(CN)^{2-}$. The $[B_9H_{13}(S_x)]^{2-}$ intermediate may be viewed as a member of the $B_9H_{13}\cdot$ligand class of which $B_9H_{13}(SCN)^-$ [11] is an example. It is pertinent to note that decaborane in aqueous sodium hydroxide solution at room temperature is relatively stable with regard to further degradation to B_9 species. In contrast, the reaction of decaborane with aqueous polysulfide is quite brisk. This suggests that the polysulfide ion plays an active, nucleophilic role in the degradation process leading to the elision of one boron atom and labilizes the boron framework to further attack.

Previous studies of the ^{11}B nmr spectra of labeled derivatives of $B_{10}H_{12}\cdot 2$ligand[24] and $B_9H_{13}\cdot$ligand[17] compounds did not reveal any label interchanges or scrambling. We have therefore investigated the ^{11}B nmr spectra of $B_9H_{12}^-$ derivatives obtained from labeled $B_9H_{13}\cdot S(C_2H_5)_2$ molecules in search of the point where labeled position interchange might occur.

^{11}B Nmr Studies of the $B_9H_{12}^-$ Ion. The ^{11}B nmr spectrum of $B_9H_{12}^-$, obtained at an unspecified but low field strength, has been reported previously.[25] An ethanol solution of $B_9H_{13}\cdot S(C_2H_5)_2$ was mixed with an aqueous solution of tetraethylammonium hydroxide to form $(C_2H_5)_4N[B_9H_{12}]$. The 70.6-MHz ^{11}B nmr spectrum of this salt is illustrated in Figure 8. The spectrum consists of four doublets at +10.0, +14.4, +34.2, and +52.0 ppm of relative areas 3:3:2:1, respectively. The spectrum of $B_9D_4H_8^-$ prepared in the same manner starting from 1,2,3,4-$B_{10}D_4H_{10}$ is shown in Figure 9A along with a line-narrowed[26] spectrum of the sample (Figure 9B). Comparison of the spectra in Figures 8 and 9 indicates that doublets at +10.0, +14.4, and +52.0 ppm have collapsed to singlets as a result of deuteration. Thus two resonances are observed within each of the two low-field multiplets of area 3. This information suggests that the ^{11}B nmr spectrum of $B_9H_{12}^-$ contains at least six doublets in a 1:2:2:1:2:1 ratio reading upfield.[27] Attempts to determine the solid-state structure of $B_9H_{12}^-$ by X-ray methods have been frustrated by disorder problems.[28] Based on the crystal structure of $B_9H_{13}(CH_3CN)$,[29] the facile interconversion of $B_9H_{13}\cdot S(C_2H_5)_2$ and $B_9H_{12}^-$, and the observed pattern of resonances in the ^{11}B nmr spectrum of $B_9H_{12}^-$, it is reasonable to assume that $B_9H_{12}^-$ has the same overall arrangement of boron atoms as was found in $B_9H_{13}(CH_3CN)$. In an earlier study it was observed that $B_9H_{12}^-$ could be converted back to the $B_9H_{13}\cdot$(Lewis base) derivative with hydrogen chloride and a Lewis base.[10] We therefore treated the $(C_2H_5)_4N[B_9D_4H_8]$ described above with HCl in diethyl sulfide to form $B_9D_4H_9\cdot S(C_2H_5)_2$. The ^{11}B nmr spectrum of this product is presented in Figure 10. Comparison of this spectrum with the 80.2-MHz ^{11}B nmr spectrum of $B_9H_{13}\cdot S(C_2H_5)_2$ published earlier[17] also shows that partial interchange of deuterium-labeled positions has

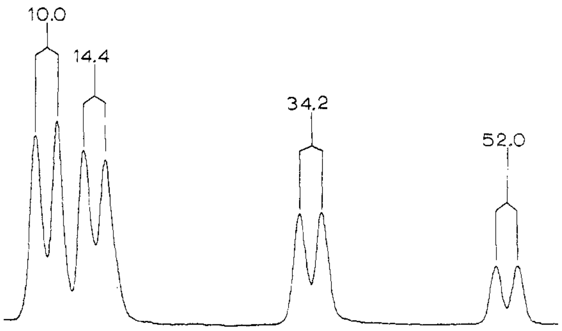

Figure 8. The 70.6-MHz ^{11}B nmr spectrum of $(C_2H_5)_4N[B_9H_{12}]$.

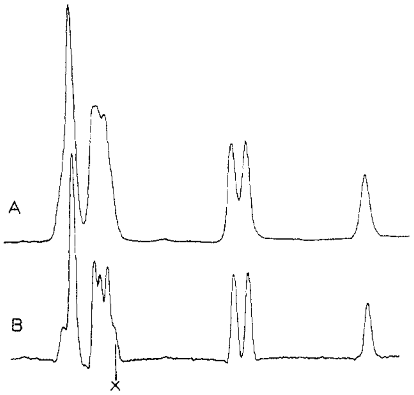

Figure 9. The 70.6-MHz ^{11}B nmr spectrum of $(C_2H_5)_4N[B_9D_4H_8]$ obtained from 1,2,3,4-$B_{10}D_4H_{10}$ and a line-narrowed spectrum of the sample.

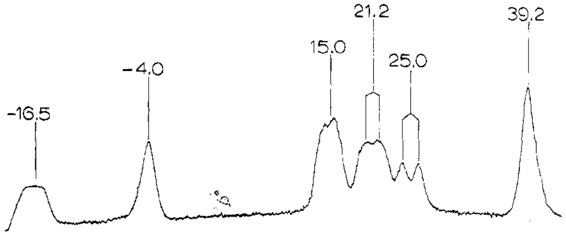

Figure 10. The 70.6-MHz ^{11}B nmr spectrum of $B_9D_4H_9\cdot S(C_2H_5)_2$ obtained from $(C_2H_5)_4N[B_9D_4H_8]$ by reaction with HCl in diethyl sulfide.

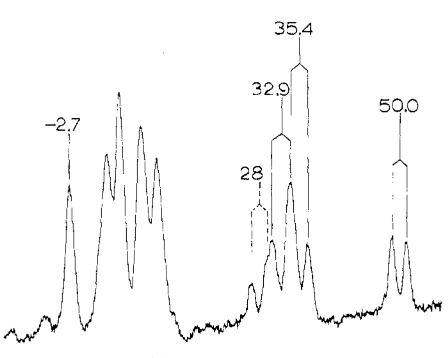

Figure 11. The 70.6-MHz ^{11}B nmr spectrum of $(C_2H_5)_4N[BrB_9H_{11}]$.

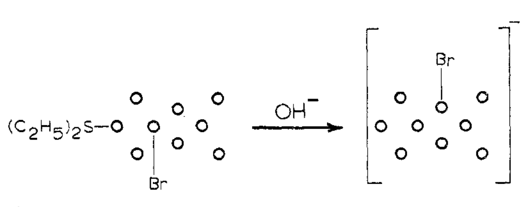

Figure 12. Proposed interchange of bromine-labeled positions during formation of 1-$BrB_9H_{11}^-$ from 4-$BrB_9H_{12}\cdot S(C_2H_5)_2$.

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(24) D. E. Hyatt, F. R. Scholer, and L. J. Todd, *Inorg. Chem.*, 6, 630 (1967).

(25) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 138.

(26) A. O. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, 95, 2496 (1973).

(27) In Figure 9B, the peak marked with an X is due to an impurity in the sample as was determined by alternate synthesis of the compound. See the Experimental Section.

(28) Reference 25, p 187.

(29) F. E. Wang and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 83, 491 (1961).

occurred. The doublet resonances centered at −4 and +39.2 ppm due to B(4) and B(1,3) appear completely collapsed. The resonances at −16.5 and +15 ppm due to B(2) and B(8,10) appear partially collapsed and the other two doublets due to B(5,7) and B(9) are unchanged. These results are consistent with the existence of a C_{3v} intermediate which is causing the partial scrambling of the labeled boron atoms.

Treatment of $4\text{-BrB}_9H_{12}\cdot S(C_2H_5)_2$[17] with aqueous ethanolic tetraethylammonium hydroxide at room temperature produced $(C_2H_5)_4N[BrB_9H_{11}]$ and the ^{11}B nmr spectrum of this product is presented in Figure 11.[30] The appearance of at least seven resonances in this spectrum suggests that the bromine atom in the product is located at a position which is not on the mirror plane passing through B(2), B(4), and B(9). Therefore rearrangement of the bromine label (possibly as shown in Figure 12) has occurred in this case also.

While these observations do not serve as proof concerning our proposed mechanism for the formation of $B_9H_{12}S^-$ from decaborane, the generation of similarly "rearranged" labeled molecules in these transformations strongly suggests the existence of a common reaction intermediate with effective C_{3v} symmetry (possibly a B_9H_{13} species) in these processes. Further studies concerning the mechanism of formation of $B_9H_{12}S^-$ are in progress.

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Registry No. $(C_2H_5)_4N[B_9BrH_{11}S]$, 51292-99-0; $B_9BrH_{12}\cdot S(C_2H_5)_2$, 51292-00-6; $(C_2H_5)_4N[B_9H_{12}S]$, 51293-01-7; $CsB_9H_{12}S$, 51358-27-1; $(C_2H_5)_4N[B_9H_{12}]$, 51464-40-5; $(C_2H_5)_4N[BrB_9H_{11}]$, 51668-01-0; ^{11}B, 14798-13-1.

[30] The small doublet at +28 ppm is due to an impurity. This product could not be purified further due to its instability.

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Some By-Products of the Oxidative Coupling of Decahydrodecaborate(2−), $B_{10}H_{10}^{2-}$

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The involvement of ions other than the primary oxidizing agents in the oxidation of $B_{10}H_{10}^{2-}$ produces a variety of substituted species in addition to $B_{20}H_{19}^{3-}$ and $B_{20}H_{18}^{2-}$. $Fe(NO_3)_3$ yields $B_{20}H_{18}NO^{3-}$; $FeCl_3$ yields $1,6,8\text{-}B_{10}H_7Cl_3^{2-}$ and 1,6- (or 2,4) $\text{-}B_{10}H_8Cl_2^{2-}$; $KClO_3$ yields $B_{10}H_4Cl_6^{2-}$ and a free radical. The effects of temperature, reagent concentration, solvent, acidity, and reaction time on the yields of the principal by-products were explored.

Introduction

Over the years, we and other researchers investigating the oxidative coupling of $B_{10}H_{10}^{2-}$ have observed extraneous bands in the infrared spectra of the expected products, blue and purple colors, and other evidence of side reactions. Wiesboeck[2] assumed that the blue color produced by $Fe(NO_3)_3$ is due to the same nitroso derivative as the one made with gaseous oxides of nitrogen. He did not isolate the colored material, and since the free radicals formed by $B_{10}H_{10}^{2-}$ absorb in the same region of the visible spectrum,[3] we decided to isolate and characterize the colored species in our reactions. In one system the colored species turned out to be the $B_{20}H_{18}NO^{3-}$ ion;[2,4] in another it was a free radical.[3] The extraneous infrared bands were found to belong to partially halogenated decahydrodecaborates. Since the published halogenation methods[5] are unsuitable for the synthesis of specific ions having fewer than eight chlorines, due to the very rapid substitution rate, it seemed worthwhile to explore conditions under which the yield of such chlorinated species is optimized. Moreover, as the molecular structure of one of our products ($B_{10}H_7Cl_3^{2-}$) had already been determined by X-ray crystallography,[6] it seemed only appropriate that the synthesis be published too.

Experimental Part

Reagents and Techniques. Salts of $B_{10}H_{10}^{2-}$ were prepared in this laboratory from decaborane;[7] all other chemicals were reagent grade. The infrared spectra of samples pressed into KBr pellets were recorded on a Perkin-Elmer Model 337 spectrophotometer. The visible spectra were recorded on a Cary 14 spectrophotometer. The ^{11}B nmr spectra were obtained at a frequency of 19.25 MHz on a Varian DA-60 spectrometer. Samples were considered free of $B_{20}H_{18}^{2-}$ when the uv spectrum showed no traces of the intense bands at 2320 and 2930 Å and free of $B_{20}H_{19}^{3-}$ in the absence of the hydrogen-bridge ir band at 1870 cm^{-1}.[8] Overall purity was also ascertained with the aid of tlc. For the halogenated species the best results were obtained on basic alumina with eluents consisting of acetonitrile–2-propanol–water (5:4:1) or acetonitrile–acetone (2:1).

$B_{20}H_{18}NO^{3-}$. Procedure A. To solutions of $(Et_3NH)_2B_{10}H_{10}$ in 15 ml of water weighed samples of $Fe(NO_3)_3\cdot 9H_2O$ (uncrushed lumps) were added *without stirring* and the mixtures were left standing at room temperature. Filtration removed a purple solid which was washed with four 25-ml aliquots of water and dried for 24 hr over P_2O_5. The dry solid was washed repeatedly with dry acetone until only the creamy $(Et_3NH)_3B_{20}H_{19}$ remained undissolved. The washings were evaporated to near dryness, and the residue was recrystallized from acetone–ethanol mixtures till no $B_{20}H_{18}^{2-}$ was detectable. The infrared and visible spectra of the products were indistinguishable from those of $(Et_3NH)_2B_{20}H_{18}NO$ made with NO_2.[2,4] When heated above 170° the salt turns colorless before it melts with decomposition. The melting point is a poor criterion of purity since even traces of impurities shift it by as much as 20°. Our purest samples ranged from 175 to 185°. The visible spectrum in CH_2Cl_2 consisted of bands at 6000 and 4000 Å.

Anal. Calcd for $[(C_2H_5)_3NH]_3B_{20}H_{18}NO$: C, 37.8; H, 11.6; B, 37.9; N, 9.81. Found: C, 37.2; H, 11.9; B, 37.6; N, 9.54.

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