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Directive Effects in the Electrophilic Substitution of Deltahedral Boranes and Heteroboranes. Deuteration and Halogenation of $1\text{-}SB_9H_9$ and $SB_{11}H_{11}$

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Because of a moderate reaction rate, it is possible to determine the course of the sequential electrophilic halogenation of $1\text{-}SB_9H_9$. The directive effect of the sulfur heteroatom does not correlate with the ground-state charge distribution of $1\text{-}SB_9H_9$. It appears that initial attack is at the 6 position instead of the anticipated 10 position. In the case of monobromination and monoiodination there is a significant degree of rearrangement to also give the thermodynamically more stable 10 isomer in the reaction mixture ($\Delta H_{\text{isomerization}} = 6.8$ kcal/mol). Only the 6 isomer results from monochlorination. Rearrangement is also a significant factor as halogenation becomes more extensive. The initial halogenation of $SB_{11}H_{11}$ is analogous to that of $1\text{-}SB_9H_9$. The site of initial deuteration was not established clearly, but under forceful conditions deuteration was not complete and $6,7,8,9,10\text{-}D_5\text{-}1\text{-}SB_9H_4$ and $7,8,9,10,11,12\text{-}D_6\text{-}1\text{-}SB_{11}H_5$ were obtained.

Introduction

For closo (deltahedral) heteroboranes like 1,2- and 1,7-$C_2B_{10}H_{12}$ and $2,4\text{-}C_2B_5H_7$, ground-state charge distributions correlate nicely with the results of electrophilic halogenation.[2,3] In the case of the deltahedral borane anions $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ electrophilic halogenation[4] does not appear to correlate well with predictions for sequential substitution.[5] However, interpretation of the results was complicated somewhat by the ease of halogenation and the difficulty of isomer separation. No evidence for the rearrangement of these deltahedral dicarbaboranes or borane anions during the course of halogenation has been presented. We expand here our previous communication[6] on the halogenation of $1\text{-}SB_9H_9$ and $SB_{11}H_{11}$ which can be followed sequentially and thus provides a good probe for the theory of directive effects in substitution reactions in deltahedral boranes. The results suggest that intramolecular rearrangement plays a role in the ultimate stereochemistry of the products. Exhaustive deuteration appears to proceed in a manner similar to that which we found for the Friedel–Crafts alkylation of $1\text{-}SB_9H_9$.[7]

Experimental Section

Apparatus and Techniques. Gases and volatile materials were handled using standard vacuum line techniques.[8] Bromine and chlorine samples were measured by expansion of the vapors into a weighing bulb fitted with an all-Teflon valve.[9] The mercury manometer in this section was coated with Kel-F oil.

Solids were handled on the bench top, but all reaction tubes and handling tubes were evacuated and back-filled with dry nitrogen to minimize exposure to air and moisture. Samples were weighed in 6-mm o.d. tubes previously flushed with dry nitrogen.

All reactions were performed in sealed tubes. Iodination tubes were fitted with an extension to be opened with a modified "key" breaker; tubes for chlorination or bromination had a greaseless (Fischer-Porter) valve. After reaction, tubes were opened on the vacuum line. Noncondensable gases were collected via a Toepler pump. Condensable gases were fractionated through appropriate slush baths and identified by vapor pressure, IR, and gas density measurements. Volatile solids were purified by vacuum sublimination and gas chromatography. Product identification was by means of IR, mass, and ^{11}B NMR spectra. Yields are reported in terms of the initial amount of SB_9H_9. Melting points were determined in sealed capillaries and are uncorrected.

Infrared spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer. Gases were investigated in a 10-cm cell fitted with KBr windows. Solid spectra were obtained from KBr pellets. The ^{11}B NMR spectra were obtained in $CDCl_3$ on a JEOL JNM-PS-100 operating at 32.1 MHz using pulsed Fourier transform methods. Chemical shifts are reported relative to external $(C_2H_5)_2O \cdot BF_3$ with positive values downfield.[10] Mass spectra were determined on an Associated Electronics Industries MS-902. GC separations were obtained on a Varian Aerograph Series 2700 with thermal conductivity bridge detector using helium as the carrier gas. The column was 5 ft × $^1/_4$ in. stainless steel packed with 1.5% OV-101 on Chromosorb G (100/120 mesh). Electronic spectra over the 400–200-nm range were determined in 1.0-cm cells with a Cary 14 using spectroquality heptane (Eastman). Volumetric glassware was calibrated with water. Raman spectra were obtained from solid samples in melting point tubes on a Spex 1401 double spectrometer using the argon laser line at 4880 Å.

Materials. SB_9H_9 was prepared by vacuum pyrolysis of SB_9H_{11}.[11] $SB_{11}H_{11}$ was obtained from the pyrolysis of $SB_{10}H_{12}$[11] or the method of Hermanek.[12] Iodine (Mallinckrodt Analytical Grade) was ground with potassium iodide and sublimed in air. Bromine (Matheson Coleman and Bell) was used as received. Chlorine (Linde High Purity) was purified by fractionation through −78, −126, and −196 °C traps; the −126 °C fraction was used. Aluminum trichloride (Baker Analyzed Reagent Grade) was sublimed in vacuo before use.

I-1-SB_9H_8. Iodine and SB_9H_9 were mixed without solvent in a reaction tube to give I_2:SB_9H_9 ratios of 0.5:1 or 1:1. The tube was evacuated, sealed, and heated at 200 °C from 2 to 5 h. The intense purple color of I_2 vapors was dispersed after approximately 2 h; at room temperature the products were yellow or light brown solids. The reaction tube was opened on the vacuum line for analysis of volatile products before sublimation of the solid products.

In a typical reaction 0.294 g of SB_9H_9 (2.12 mmol) and 0.536 g of I_2 (2.12 mmol) were heated at 205 ± 5 °C for 2.5 h. Noncondensable gases (0.276 mmol) were assumed to be H_2, although the molecular weight by gas density was 4.0 g mol^{-1}. The only condensable gas was HI (1.79 mmol) identified by gas density molecular weight (observed 127.8 ± 0.4, calculated 127.9). A GC of the sublimate (0.396 g) showed in order of increasing retention time: 7.7% unreacted SB_9H_9, 51.3% 10-I-1-SB_9H_8, and 33.4% 6-I-1-SB_9H_8. This corresponds to a 59.5% yield of I-1-SB_9H_8 with a ratio of ax:lb (axial:lower belt) isomers of 1.6:1. The melting point of the lower belt isomer was 110–111 °C; that of the axial isomer, 84–86 °C. (See the beginning of the Discussion and Figure 1 for a definition of ub, lb, and ax.)

Molar ratios of I_2:SB_9H_9 of less than 1:1 led to incomplete reaction. If the reaction was stopped as soon as the I_2 had reacted, negligible amounts of noncondensables were observed; increasing reaction times led to increasing amounts of noncondensables. Addition of $AlCl_3$ to the reaction mixture gives approximately the same distribution of products.

Br-1-SB_9H_8. Bromine and SB_9H_9 were combined in 1:1 ratio in a reaction tube fitted with a greaseless valve and a small sidearm with constriction to permit vacuum transfer of the bromine sample. At room temperature (ca. 22 °C) the reaction was vigorous as evidenced by bubbling when solid and liquid came in contact. In ca. 0.5 h the bromine color was mostly dispelled. After removal of volatile products on the vacuum line, cyclohexene was used to destroy excess bromine and permit solution transfer of solids for sublimation.

In a typical reaction 0.385 g of SB_9H_9 (2.78 mmol) and 0.442 g of Br_2 (2.77 mmol) were reacted at 22 °C for 2 h followed by heating at 70 °C for 2 h. No noncondensable products were detected. Condensable gases (2.15 mmol) were identified as HBr by IR spectra, vapor pressure, and gas density. The sublimate (0.515 g) showed in order four major peaks by GC analysis: 4% unreacted SB_9H_9, 45% 6-Br-1-SB_9H_8, 45% 10-Br-1-SB_9H_8, 4% Br_2-1-SB_9H_7. This corresponds to a 77% yield of Br-1-SB_9H_8 with a ratio of ax:lb isomers of 1:1. The melting point of the lower belt isomer was 122.0 °C; the axial isomer melted at 121.5–122.0 °C.

The neat bromination proceeds with the same yield and product distribution when $AlCl_3$ is added or when light is excluded. However, attempts to brominate SB_9H_9 in CCl_4 solution give low yields of Br-1-SB_9H_8, even in the presence of aluminum chloride. For example, a room temperature reaction of Br_2 and SB_9H_9 in CCl_4 (ca. 1.3 M in each reagent) for 16 h with $AlCl_3$ present yields less than 2% Br-1-SB_9H_8. However, the ratio of lb:ax isomers is 5:1. Under similar conditions but in the absence of $AlCl_3$, negligible reaction occurs.

Cl-1-SB_9H_8. Gas–solid reactions at room temperature and liquid–solid reactions at reduced temperatures between chlorine and SB_9H_9 proceed very slowly. In BCl_3 or CH_2Cl_2 solution, yields of 15–20% $ClSB_9H_8$ were obtained with $AlCl_3$ showing a marked catalytic effect. Light did not noticeably affect yield or product distribution.

In a typical reaction 0.143 g of SB_9H_9 (1.03 mmol) and 0.070 g of Cl_2 (0.985 mmol) were reacted in ca. 2 mL of CH_2Cl_2 at −45 °C for 2 h and at room temperature for 6 h. The solution remained a pale yellow after the reaction. No noncondensables were detected. The material that passed through a −126 °C trap (0.985 mmol) was identified as HCl by IR and gas density. The sublimate (0.134 g) showed three major peaks by GC analysis: 65% unreacted SB_9H_9, 26% $ClSB_9H_8$, 9% $Cl_2SB_9H_7$. This corresponds to a 20% yield of $ClSB_9H_8$, which was exclusively the lower belt isomer. In a similar experiment (0.999 mmol of Cl_2 and 0.974 mmol of SB_9H_9 in ca. 2 mL of CH_2Cl_2) but with a trace of $AlCl_3$ (87 mg) and a reaction time with stirring of 1 h at room temperature, the yield of $ClSB_9H_8$ was 19%. The 0.102 g of sublimate showed four major peaks by GC analysis: 40% SB_9H_9, 32% $ClSB_9H_8$, 15% $Cl_2SB_9H_7$, 5% $Cl_3SB_9H_6$. Again only the lower belt monochloro derivative was obtained. The melting point was 171.0 °C. The axial isomer was obtained by heating the lower belt isomer in a sealed tube at 200 ± 10 °C for 20 h. It was separated from the lower belt isomer by preparative GC. This experiment also produced a trace of a third isomer of SB_9H_8Cl (by GC/MS analysis) of shorter retention time than the lower belt and axial isomers. It must be the upper belt isomer, but it was not isolated.

Isomerization of 5 mg of 6-Cl-1-SB_9H_8 in both a melting point capillary and a 7-cm^3 vial gave the same distribution of isomers after 20 h at 200 °C by GC analysis.

Preparation of X_n-1-SB_9H_{9-n} (n = 2–9). So as to limit polyhalogenation in the above syntheses, mole ratios of halogen to SB_9H_9 were kept near 1:1. If the ratio were less than 1:1, little reaction occurred; with the ratio greater than 1:1, polysubstitution occurred. The degree of halogenation was established readily by GC/MS and some compounds were isolated by preparative GC. Their spectral characteristics and structures are described in the Discussion.

I_2-1-SB_9H_7 and trace amounts of I_3-1-SB_9H_6 were obtained in 3–4% yield as a by-product from the iodination reactions described above. Yields of 1–4% of Br_2-1-SB_9H_7 were obtained from the sealed-tube bromination reactions described above.

Polychlorination of SB_9H_9 proceeded easily under the conditions described above. With reactant ratios of 1:1 the distribution of $ClSB_9H_8$, $Cl_2SB_9H_7$, and $Cl_3SB_9H_6$ was approximately 5:3:1. With reactant ratios of $2Cl_2$:$1SB_9H_9$, the ratio of mono- to di- to trichloro derivatives was approximately 3:3:2 with trace amounts of $Cl_4SB_9H_5$ observed. Even higher ratios give evidence for all degrees of chlorination up to SB_9Cl_9 when the reaction mixture is examined by mass spectra. The melting points of $Cl_2SB_9H_7$ and $Cl_3SB_9H_6$ were 155.0–155.5 and 161–163 °C, respectively.

Halogenation of $SB_{11}H_{11}$. Typical experiments were conducted similarly to those for 1-SB_9H_9. Iodination of 58 mg (0.35 mmol) of $SB_{11}H_{11}$ with 0.35 mmol of I_2 in a sealed tube required 7 days at 200 °C for the color to dissipate. GC/MS analysis showed that the 91 mg of sublimable product was 16% unreacted $SB_{11}H_{11}$, 57% I-$SB_{11}H_{10}$, 26% I_2-$SB_{11}H_9$, and 1% I_3-$SB_{11}H_8$. NMR indicated that the ax:lb ratio was 4:1 for I-$SB_{11}H_{10}$.

$SB_{11}H_{11}$ (33 mg, 0.205 mmol), Cl_2 (14 mg, 0.203 mmol), and 24 mg of $AlCl_3$ were reacted in ca. 0.5 mL of CH_2Cl_2 in a sealed tube for 2 h at room temperature. The volatile product (0.139 mmol) that passed through a −126 °C trap was identified as HCl by IR spectra. The solid sublimate (30 mg) showed three major peaks on GC/MS analysis: 70% unreacted $SB_{11}H_{11}$, 22% $ClSB_{11}H_{10}$, 8% $Cl_2SB_{11}H_9$. This corresponds to a 17% yield of $ClSB_{11}H_{10}$. The ^{11}B NMR spectrum of the monochloro derivative was consistent with exclusively lower belt substitution, i.e., 7-Cl-1-$SB_{11}H_{10}$.

Since the SB_9H_9 used here contains 1% $SB_{11}H_{11}$ as an impurity, bromination of $SB_{11}H_{11}$ was investigated by GC separation of the trace amounts of $SB_{11}H_{10}Br$ formed during the bromination of SB_9H_9. The ^{11}B NMR indicated only axial substitution as previously reported.[12]

Deuteration of 1-SB_9H_9 and $SB_{11}H_{11}$. 1-SB_9H_9 and $SB_{11}H_{11}$ were deuterated under Friedel–Crafts conditions using DCl (80% deuteration by IR and mass spectra) generated from BCl_3 and D_2O. The reactor, consisting of a 1-L flask attached by an O-ring joint to a one-piece condenser and flask apparatus, was charged with 250 mg (1.81 mmol) of 1-SB_9H_9, 600 mg of sublimed $AlCl_3$, and about 20 mL of CS_2 which had been distilled in vacuo from a mercury/magnesium sulfate reservoir. The flask containing about 57 mmol of DCl(g) was attached to the condenser apparatus and stirred at room temperature for 170 h. The solution was evaporated leaving a white solid which was sublimed at 25–30 °C giving 6,7,8,9,10-D_5-1-SB_9H_4 as confirmed by IR, ^{11}B NMR, and mass spectra (Table I). IR bands (cm^{-1}) for 6,7,8,9,10-D_5-1-SB_9H_4 (KBr): 2582 (sh), 2548 (vs), 1960 (sh), 1914 (s), 995 (m), 937 (m), 860 (w), 772 (w), 724 (m), 615 (m), 598 (w), 570 (w), 473 (m).

Table I. ^{11}B NMR Spectra of Thiadecaboranes and Thiadodecaboranes[a]

6-I-1-SB_9H_8: +71.2, d (1), J_{BH} = 175; −5.1, d (4), J_{BH} = 180; −16.8, d (2), J_{BH} = 135; −19.9, d (1), J_{BH} = 135; −24.1, s (1)
10-I-1-SB_9H_8: +50.1, s (1); −6.7, d (4), J_{BH} = 185; −16.2, d (4), J_{BH} = 165
6-Br-1-SB_9H_8: +69.3, d (1), J_{BH} = 175; −3.0, d (2), J_{BH} = 175; −6.9, d (2), J_{BH} = 190; −10.0, s (1); −15.4, d (2), J_{BH} = 180; −21.3, d (1), J_{BH} = 195
10-Br-1-SB_9H_8: +65.6, s (1); −8.3, d (4), J_{BH} = 175; −18.4, d (4), J_{BH} = 150
6-Cl-1-SB_9H_8: +68.7, d (1), J_{BH} = 175; −2.0, d (2), J_{BH} = 145; −4.2, s (1); −7.0, d (2), J_{BH} = 180; −14.6, d (2), J_{BH} = 170; −23.2, d (1), J_{BH} = 160
10-Cl-1-SB_9H_8: +73.4, s (1); −3.3, d (4), J_{BH} = 185; −17.3, d (4), J_{BH} = 160
6,10-I_2-1-SB_9H_7: +48.8, s (1); −5.5, d (4), J_{BH} = 180; −13.6, d (2), J_{BH} = 155; −15.7, d (1), J_{BH} = 180; −23.5, s (1)
6,10-Br_2-1-SB_9H_7: +64, s (1); −5.3, d (2), J_{BH} = 190; −7.6, d (2), J_{BH} = 175; −10.4, s (1); −14.8, d (2), J_{BH} = 180; −20.6, d (1), J_{BH} = 185
6,7,8-Cl_3-1-SB_9H_6: +61.9, d (1), J_{BH} = 170; +1.5, s (1); +0.6, d (2), J_{BH} = 180; −2.8, d (2), J_{BH} = 160; −3.5, s (2); −13.9, d (1), J_{BH} = 165
1-SB_9H_9:[b] +74.5, d (1), J_{BH} = 180; −4.8, d (4), J_{BH} = 170; −17.6, d (4), J_{BH} = 150
12-I-1-$SB_{11}H_{10}$: +0.8, s (1); −1.8, d (5), J_{BH} = 160; −5.0, d (5), J_{BH} = 180
7-I-1-$SB_{11}H_{10}$: +21.5, d (1), J_{BH} = 135; ca. −1 to −5 (9);[d] −17.0, s (1)
12-Br-1-$SB_{11}H_{10}$: +16.8, s (1); −2.8, d (5), J_{B-H} = 140; −6.1 d (5), J_{B-H} = 160
7-Cl-1-$SB_{11}H_{10}$: +20.4, d (1), J_{B-H} = 145; +8.1, s (1); −3.6, d (4), J_{B-H} = 150; −5.9, d (4), J_{B-H} = 160; −11.7, d (1), J_{B-H} = 170
1-$SB_{11}H_{11}$:[b] +19.2, d (1), J_{B-H} = 145; −3.8, d (5), J_{B-H} = 140; −5.8, d (5), J_{B-H} = 160
6,7,8,9,10-D_5-1-SB_9H_4:[b] +74.1, s (1); −4.9, d (4), J_{BH} = 175; −17.9, s (4)
7,8,9,10,11,12-D_6-1-$SB_{11}H_5$:[c] +20.0, s (1); −2.2, s (5); −5.0, d (5), J_{BH} = 170

[a] The chemical shift data are given in ppm relative to external $Et_2O\cdot BF_3$ (+ values downfield)[10] followed by a description of the signal (d = doublet, s = singlet), its relative intensity (in parentheses), and observed coupling constant given in Hz. Spectra were determined at 32.1 MHz in $CDCl_3$ solution unless otherwise noted. [b] In benzene-d_6. [c] In CS_2. [d] Peaks in this region could not be resolved because the spectrum was obtained on a mixture of 80% 12 isomer and 20% 7 isomer.

For $SB_{11}H_{11}$ the reaction was allowed to proceed 240 h using only 25 mg (0.15 mmol) of the thiaborane, 30 mmol of DCl, and 600 mg of $AlCl_3$ in 25 mL of CS_2. Sublimation gave 7,8,9,10,11,12-D_6-1-$SB_{11}H_5$ as shown by the ^{11}B NMR spectrum (Table I).

Equilibrium Studies. Pure samples (ca. 6 mg) of 6- and 10-Br-1-SB_9H_8 were held at temperatures ranging from 167 to 270 °C for periods of 1–28 days in sealed evacuated tubes (0.6 cm^3). In order to observe the establishment of equilibrium from both sides, both isomers were observed at every temperature except at 167 °C. The temperature was regulated to ±2 °C over the period of heating. The relative amount of each isomer present after heating was determined by integration of GC traces. Neither isomer was isomerized by the GC conditions or by standing at 25 °C. The following values of Q (6 isomer:10 isomer) were obtained by averaging the values obtained from each direction (temperature K in parentheses): 0.42 ± 0.04 (541), 0.33 ± 0.04 (522), 0.25 ± 0.04 (492), 0.12 (440). A least-squares fit of these data gives $\Delta H_{\text{isomerization}}$ = 6.8 kcal/mol.

Discussion

The structure of 2,2′-(1-SB_9H_8)$_2$ is known[13] and allows the two doublets of relative intensity 4 in the ^{11}B NMR spectrum of 1-SB_9H_9[14] to be assigned. The lower field doublet is due to the belt of four borons adjacent to the sulfur (ub-B2,3,4,5) and the higher field doublet to the other belt of four borons (lb-B6,7,8,9). The signal for the unique boron (ax-B10) is well separated at very low field. See Figure 1 for the numbering convention. These assignments allow the site of substitution to be ascertained. The NMR data are given in Table I. A linear correlation between the Pauling electronegativity of X and the chemical shift of the substituted boron is observed for both axial and lower belt regions (Figure 2). In general for lower belt monosubstitution, the signals for the unsubstituted upper belt borons displayed relatively little change from the corresponding region for 1-SB_9H_9, but major shifts were evident in the lower belt region. In all cases, the barycenter for the upper belt and lower belt regions was maintained within ±1 and ±3 ppm, respectively, of the corresponding signal for 1-SB_9H_9. For the axial isomers, the ^{11}B NMR spectra were quite simple and showed the expected downfield singlet[15] and two upfield doublets of relative intensity 1:4:4. However, as previously reported,[6] the singlet was easily saturated and unusually hard to detect.

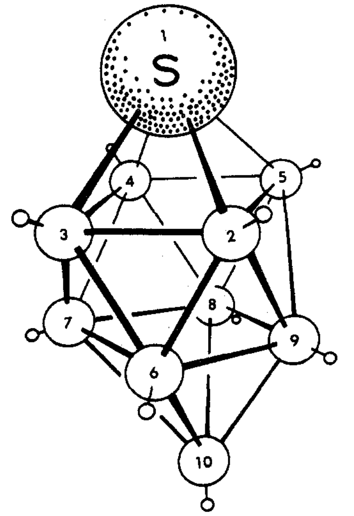

Figure 1. Structure and numbering convention for the thiadecaborane framework. The upper belt (ub) is B2,3,4,5; the lower belt (lb) is B6,7,8,9; the axial position (ax) is B10.

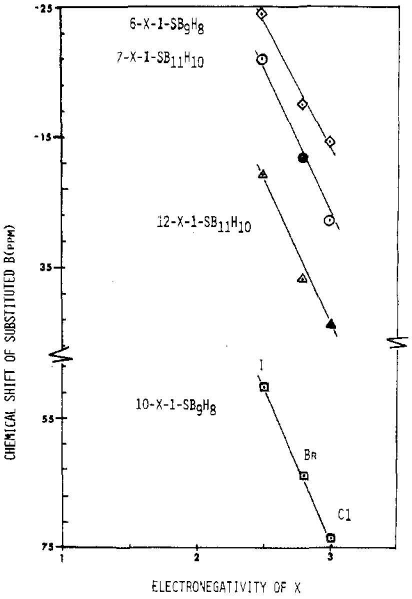

Figure 2. Chemical shift vs. Pauling electronegativity. The symbols ◇, □, ○, and △ give the values for 6-X-1-SB_9H_8, 10-X-1-SB_9H_8, 7-X-1-$SB_{11}H_{10}$, and 12-X-1-$SB_{11}H_{10}$, respectively. Shaded symbols are predicted values.

All the halothiadecaboranes described here were characterized additionally by mass spectrometry. They showed the expected parent ion m/e cutoffs with the correct intensity ratio for $^{34}S/^{32}S$ peaks at the cutoff region. IR spectra for most of the molecules and certain Raman spectra are given in Table

Table II

IR and Raman Spectra of X_n-1-SB_9H_{9-n} (cm^{-1})

6-I-1-SB_9H_8		6-Br-1-SB_9H_8		10-I-1-SB_9H_8		10-Br-1-SB_9H_8	
IR	Raman	IR	Raman	IR	Raman	IR	Raman
	2627 s		2633 s		2627 m		2634 m
	2617 vs		2624 vs		2615 vs	2616 s	2623 vs
2605 vs	2603 s	2605 vs	2609 w	2600 s	2604 vs	2602 s	2608 vs
	2577 m		2588 w		2580 w		2585 w
	2566 s		2576 s		2569 s		2574 s
2558 vs	2557 m		2568 s		2557 vs	2560 vs	2565 vs
2540 vs	2550 s	2562 vs	2560 s	2550 vs	2550 m	2545 s	2551 m
1152 m		2552 vs	2552 w	1070 m		1084 m	
960 m	959 vw	1010 w	1014 vw	1055 m	1059 s	1055 vs	
948 m		968 s	974 w	1038 s	1046 m	991 vs	995 vw
855 s	854 w	953 m	959 w	984 vs	990 w	972 m	
810 m	820 m	864 s	854 m	844 s	850 m	851 vs	853 w
783 s		842 m			707 m	717 w	722 vw
754 w	753 w	816 m	814 vw	695 m	701 m		712 w
704 s	703 m	791 s			674 m	706 m	705 w
	674 m	758 w	754 w	604 m	603 w	608 m	601 vw
604 w	603 w	710 m	715 m	476 vw	484 m	580 vw	588 vw
	484 m	691 w	703 m			534 w	536 vw
	467 s		687 m			498 w	498 vw
	211 vs		674 m			482 w	486 w
	136 s	606 w	599 w				
	130 s	580 vw	586 w				
		532 w	538 w				
			517 m				
			468 vs				
			250 vs				
			151 s				
			148 s				

IR Spectra of X_n-1-SB_9H_{9-n} (cm^{-1})

6-Cl-1-SB_9H_8	10-Cl-1-SB_9H_8	6,10-I_2-1-SB_9H_7	Cl_2-1-SB_9H_7	6,7,8-Cl_3-1-SB_9H_6
2610 vs	2605 s	2602 s	2612 vs	2610 vs
2560 vs	2565 vs	2593 s	2570 vs	2570 s
1155 vw	2550 vs	2563 vs	1156 w	1155 w
1033 m	1610 vw	1150 w	1094 w	1095 w
1020 m	1150 m	1051 w	1047 s	1052 m
981 s	1116 s	1036 s	1043 m	1040 m
956 m	1081 vs	978 vs	1003 s	1018 s
904 m	995 s	883 vw	979 vs	1007 vs
884 vs	954 w	848 w	959 m	978 s
849 w	901 vw	814 w	905 m	968 s
821 m	867 s	769 m	883 vs	912 w
800 s	796 vw	734 w	869 m	893 m
763 vw	760 m	599 vw	847 m	879 m
717 m	712 m	535 vw	820 m	862 m
693 w	610 m	493 vw	795 s	849 m
680 w	536 vw		750 vs	832 m
665 w	499 w		719 w	810 m
625 w	332 vw		698 m	801 m
604 w			614 m	790 m
589 vw			585 w	772 s
501 vw			540 w	750 w
			525 w	740 w
			500 vw	618 w
			487 w	495 w
			465 vw	465 vw
			365 w	390 vw
			335 vw	373 vw
				352 vw
				338 vw
				318 vw

II. The spectra of a given isomer regardless of halogen might be expected to be very similar except for shifts in halogen-associated vibrations. However, since halogen-associated motions are not clearly evident from the data, they probably are coupled strongly to cage vibrations.

The UV spectra of various X-1-SB_9H_8 molecules and 1-SB_9H_9 are compared in Table III. The value of λ_{max} decreases monotonically with increasing electronegativity of X, but it does not appear to depend significantly on the position of substitution. Therefore, the λ_{max} transition is not likely associated with the sulfur lone pair but with the halogen.

In keeping with previous observations for carboranes,[2,3] one would expect that those B sites furthest removed from the sulfur heteroatom would be most negative and most susceptible to electrophilic substitution. This assumes that the course of substitution is controlled by ground-state charge distribution and is also not subject to rearrangement of the framework. Our EHMO calculations corroborate this expectation and give the following atom charges from a Mulliken population analysis:[16] ub = 0.2524; lb = 0.0733; ax = −0.0734. Deu-

Table III. UV-Visible Spectra of X-1-SB_9H_8

Compd	λ, nm	$10^3\epsilon$, L mol^{-1} cm^{-1}
6-I-1-SB_9H_8	320	0.81
	278	3.82
	259	9.26
	220	6.37
6-Br-1-SB_9H_8	270	1.47
	239	8.49
	213	5.65
6-Cl-1-SB_9H_8	275	1.01
	229	5.17
	209	5.87
10-I-1-SB_9H_8	276	7.59
	258	22.2
	200	15.7
10-Br-1-SB_9H_8	270	3.34
	238	31.6
	205	8.15
1-SB_9H_9	214	8.1

teration experiments appear to be in accord since the belt of boron atoms adjacent to the S (ub = upper belt) in both 1-SB_9H_9 and $SB_{11}H_{11}$ remains undeuterated even under forceful electrophilic reaction conditions. However, the site of initial deuteration was not determined. For iodination and bromination monosubstitution was observed and found to give a ratio of ax:lb between about 2:1 and 1:1 depending on the run even though there is a four times greater statistical chance for lower belt vs. axial substitution. At first glance these deuteration and halogenation results appear to be in accord with ground-state charge distributions; however, we suspect differently in view of the results of chlorination and isomerization experiments.

When 1-SB_9H_9 is treated with Cl_2 in the manner used for bromination and iodination, only the lower belt isomer of chloro-1-thiadecaborane is observed (6-Cl-1-SB_9H_8) *not* the axial isomer predicted on the basis of charge distribution! Furthermore, when heated to 200 °C, a mixture of axial, lower belt, and upper belt (trace) Cl-1-SB_9H_8 isomers results. The latter distribution is independent of concentration.

We have also observed that after 20 h in a sealed tube at 200 °C the ratio of axial to lower belt Br-1-SB_9H_8 changes from 1:1 to 2:1,[17] indicating that the reaction mixture is not an equilibrium mixture. A plot of log (lb:ax ratio) vs. $1/T$ for equilibrated mixtures between 167 and 270 °C gave a ΔH = 6.8 kcal/mol in favor of axial Br-1-SB_9H_8 as the thermodynamically more stable isomer.

These observations suggest that initial attack is at the lower belt and that cage rearrangement occurs during the course of iodination and bromination. Certainly, the reaction temperature was high enough for intramolecular rearrangement in the case of iodination and apparently either the vigor of attack of bromine or the nature of the transition state results in the formation of considerable axial isomer during bromination. Light was excluded from certain bromination and chlorination reactions, but this did not alter yield or product distribution.

The course of sequential halogenation also appears to be complicated by rearrangement. Our EHMO calculations[16,18] suggest that both axial and lower belt isomers of Cl-1-SB_9H_8 should yield 6,10-Cl_2-1-SB_9H_7 exclusively since for 6-Cl-1-SB_9H_8 the axial site is most negative. Indeed, the only dibromo and diodo isomer observed in the reaction mixtures is the 6,10 isomer. However, no axial substitution has been detected in the case of the Cl_2-1-SB_9H_8 which appears to be a mixture of lower belt isomers as isolated from the reaction mixture.

While the halogenation and deuteration of $SB_{11}H_{11}$ have not been studied thoroughly, our experiments indicate that again the lower belt is the site of initial substitution. Assignments were made on the basis of ^{11}B NMR data. It is important to note that for $SB_{11}H_{11}$ the belt regions are assigned on the basis of relaxation times[20] in the opposite order from 1-SB_9H_9, i.e., lower belt at lower field and upper belt at higher field for $SB_{11}H_{11}$.

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Registry No. 1-SB_9H_9, 41646-56-4; $SB_{11}H_{11}$, 56464-75-6; 6-Cl-1-SB_9H_8, 58568-93-7; 6-I-1-SB_9H_8, 58575-41-0; 10-I-1-SB_9H_8, 58575-42-1; 6-Br-1-SB_9H_8, 58575-43-2; 10-Br-1-SB_9H_8, 58568-92-6; 10-Cl-1-SB_9H_8, 58568-94-8; 6,10-I_2-1-SB_9H_7, 58568-95-9; 6,10-Br_2-1-SB_9H_7, 58604-83-4; 6,7,8-Cl_3-1-SB_9H_6, 64200-77-7; 12-I-1-$SB_{11}H_{10}$, 64200-76-6; 7-I-1-$SB_{11}H_{10}$, 64200-75-5; 12-Br-1-$SB_{11}H_{10}$, 56464-76-7; 7-Cl-1-$SB_{11}H_{10}$, 64200-74-4; 6,7,8,9,10-D_5-1-SB_9H_4, 64200-73-3; 7,8,9,10,11,12-D_6-1-$SB_{11}H_5$, 64200-72-2; Cl_2-1-SB_9H_7, 64215-85-6.

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(16) The method of calculation and parameterization is discussed by R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972). Bond distances and angles were average values obtained from the crystal structure of 2,2′-(1-$SB_9H_8)_2$ (ref 13).

(17) In our original communication,[6] this single observation was incorrectly stated as evidence for the thermodynamic stability of the axial isomer. Similarly, although in ref 7 we infer that the axial isomer of 1-$SB_9H_8(CH_3)$ is more stable than the lower belt isomer, the available data do not show this conclusively.

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