

ELECTROPHILIC ALKYLATION OF 1-SB₉H₉

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Summary

Reaction of *closo*-1-SB₉H₉ with either ethyl or methyl iodide in the presence of AlCl₃ produces alkylated derivatives of the type 1-SB₉H_(9-x)R_x (R = C₂H₅, CH₃; x = 1–5), which were identified by GC/MS, ¹¹B and ¹H NMR spectroscopy. The initial product is 6-R-1-SB₉H₈ rather than the 10-R-1-SB₉H₈ predicted on the basis of ground-state charge considerations. Thus, these results are as found for halogenation of 1-SB₉H₉, but differ from the precedent set by substitution reactions in *closo*-carboranes.

Introduction

The nature of Friedel–Crafts catalyzed proton exchange has been well documented by Hawthorne in the case of decaborane [1]. Under similar conditions, Williams and coworkers were able to prepare and identify various alkyl-substituted products of decaborane [2,3]. Several structural investigations indicate that the site of electrophilic substitution correlates with the site of highest electron density [4] in molecules such as B₁₀H₁₄ [5,6], 1,2- or 1,7-C₂B₁₀H₁₂ [7] and 2,4-C₂B₅H₇ [8]. In certain cases the initial electrophilic substitution in B₁₀H₁₀²⁻ has been shown to occur contrary to predicted axial placement [9–11]. Alkylation studies of 1-SB₉H₉ were undertaken to further elucidate directive effects in the substitution reactions of *closo* heteroboranes. Our previous work on the halogenation of 1-SB₉H₉ and SB₁₁H₁₁ [12] showed that the precedents of 1,2- and 1,7-C₂B₁₀H₁₂ and 2,4-C₂B₅H₇ were not followed with sulfur as the heteroatom.

Results and discussion

Several ethyl and methyl derivatives of 1-SB₉H₉ were synthesized by the reaction of 1-SB₉H₉ with either ethyl iodide or methyl iodide in the presence of aluminum chloride and hydrogen chloride in CS₂. It can be seen from Table 1 that the best results were obtained with a 1/1 ratio of AlCl₃ to thiaborane and an HCl pressure between 1.1 and 1.2 atmospheres.

In reactions using ethyl iodide overall yields of strictly ethylated products were lessened due to formation of several methylated derivatives. For instance, enough of the monomethyl product was isolated to be identified by means of ^{11}B NMR spectroscopy as the axially-substituted compound 10- CH_3 -1- SB_9H_8 . The formation of mixed methylethyl derivatives, as established by mass spectroscopy and ^{11}B NMR, also tends to lessen the percentage of strictly ethylated products. Apparently, these products arise from the decomposition of the ethyl

TABLE 1
FRIEDEL-CRAFTS ALKYLATION PRODUCTS OF 1- SB_9H_9 ^a

| Reaction | Ratio 1- SB_9H_9 /RI | R | Distribution(%) | Conversion(%) |
|-----------------|---|------------------------|--|---------------|
| 1 | 1/1 | C_2H_5 | 1- SB_9H_9 (15) 1- $\text{SB}_9\text{H}_8\text{R}$ (23) 1- $\text{SB}_9\text{H}_7\text{R}_2$ (24) 1- $\text{SB}_9\text{H}_6\text{R}_3$ (14) 1- $\text{SB}_9\text{H}_5\text{R}_4$ (4) Mixed products(10) ^b | 86 |
| 2 | 1/2 | C_2H_5 | 1- SB_9H_9 (10) 1- $\text{SB}_9\text{H}_8\text{R}$ (10) 1- $\text{SB}_9\text{H}_7\text{R}_2$ (11) 1- $\text{SB}_9\text{H}_6\text{R}_3$ (22) 1- $\text{SB}_9\text{H}_5\text{R}_4$ (30) 1- $\text{SB}_9\text{H}_4\text{R}_5$ (7) Mixed products(10) ^b | 76 |
| 3 | 1/75 | C_2H_5 | 1- SB_9H_9 (5) 1- $\text{SB}_9\text{H}_5\text{R}_4$ (36) 1- $\text{SB}_9\text{H}_4\text{R}_5$ (54) Unidentified(5) | 71 |
| 4 | 1/1 | CH_3 | 1- SB_9H_9 (78) 1- $\text{SB}_9\text{H}_8\text{R}$ (10) 1- $\text{SB}_9\text{H}_7\text{R}_2$ (7) 1- $\text{SB}_9\text{H}_6\text{R}_3$ (5) | 80 |
| 5 | 1/2 | CH_3 | 1- SB_9H_9 (33) 1- $\text{SB}_9\text{H}_8\text{R}$ (26) 1- $\text{SB}_9\text{H}_7\text{R}_2$ (17) 1- $\text{SB}_9\text{H}_6\text{R}_3$ (7) 1- $\text{SB}_9\text{H}_5\text{R}_4$ (4) 1- $\text{SB}_9\text{H}_4\text{R}_5$ (13) | 95 |
| 6 | 1/10 | — | 1- SB_9H_9 (76) | |
| 7 ^c | 1/10 | C_2H_5 | 1- SB_9H_9 (78) 1- $\text{SB}_9\text{H}_8\text{R}$ (1) | 1 |
| 8 ^d | 1/1 | C_2H_5 | 1- SB_9H_9 (88) 1- $\text{SB}_9\text{H}_8\text{R}$ (1) | 1 |
| 9 ^e | 1/1 | C_2H_5 | 1- SB_9H_9 (15) 1- $\text{SB}_9\text{H}_8\text{R}$ (40) 1- $\text{SB}_9\text{H}_7\text{R}_2$ (22) 1- $\text{SB}_9\text{H}_6\text{R}_3$ (10) 1- $\text{SB}_9\text{H}_5\text{R}_4$ (3) Mixed products(10) ^b | 78 |
| 10 ^f | 1/1 | C_2H_5 | 1- SB_9H_9 (77) 1- $\text{SB}_9\text{H}_8\text{R}$ (1) | 1 |
| 11 ^g | 1/1 | C_2H_5 | 1- SB_9H_9 (85) 1- $\text{SB}_9\text{H}_8\text{R}$ (1) | 1 |

^a Unless otherwise stated the following conditions were used for all reactions: 3 days at refluxing temperature CS_2 under 1.1–1.2 atm HCl, ratio of AlCl_3 /1- SB_9H_9 = 1/1. ^b These mixed products were identified as being methylethyl derivatives by GC/MS. ^c Run in the absence of HCl. ^d Run in the absence of AlCl_3 . ^e Ratio of AlCl_3 /1- SB_9H_9 = 2/1. ^f 0.16 atm HCl. ^g Ratio of AlCl_3 /1- SB_9H_9 = 1/10.

iodide under the reaction conditions. This decomposition is facile since the above-mentioned products were observed both when the reaction was run at 25°C and at reflux. Recent results indicate that somewhat similar reactions involving alkyl-free radicals may occur during the methylation of 2,4-C₂B₄H₈ [8].

A comparison of alkylations run under different conditions as shown in Table 1 reveals the nature of the reaction. Run 6 shows best that SB₉H₉ is consumed slowly by the catalyst. Onak has observed a similar degradation of carboranes in a modified Friedel–Crafts reaction [13]. Runs 7 and 8 indicate that both HCl and AlCl₃ are required for effective catalysis. Similar comparisons indicate that practical amounts of alkylthiaboranes are obtained with a large excess of alkyl halide, but this leads predominantly to pentaalkylation. Monoalkylation is favored by a stoichiometric amount of RI but this results in lower total conversion. With small amounts of AlCl₃ (run 11) the reaction is very slow; a change of the AlCl₃/SB₉H₉ ratio from 1/1 to 2/1 leads to greater loss of SB₉H₉, but the same product distribution (runs 9 and 1).

The ¹¹B NMR spectra of the mono-, di-, tri-, and tetra-ethylated products show the presence of at least two isomers for each stoichiometry. (The following conventions are used throughout this paper: lb = lower belt = B(6, 7, 8, 9); ub = upper belt = B(2, 3, 4, 5); ax = axial = B(10). Refer to Fig. 1 for the numbering convention.) In the case of the monoethyl isomer, the substitution is predominantly on one of the four equivalent lb borons. The spectrum for the diethyl compound shows a mixture of lb-lb and lb-ax substitution, with the lb-lb isomer being more predominant by 3/1. The ¹¹B NMR spectra for the tri- and tetra-ethyl compounds indicate that the major isomers present are 6,7,10-(CH₃CH₂)₃-1-SB₉H₉ or 6,7,8,10-(CH₃CH₂)₄-1-SB₉H₉, respectively. The minor isomers seen in these two spectra are 6,7,8-(CH₃CH₂)₃-1-SB₉H₉ and 6,7,8,9-(CH₃CH₂)₄-1-SB₉H₉.

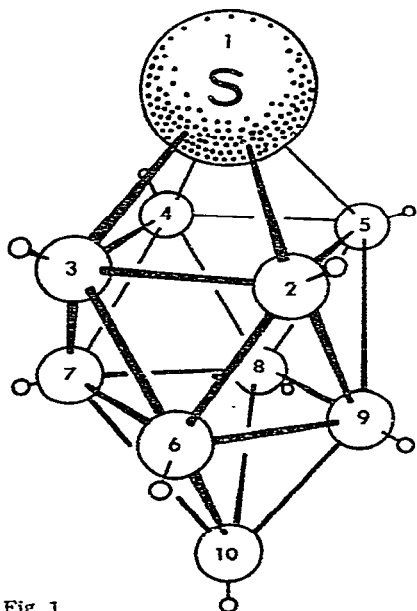


Fig. 1.

In contrast, however, in the methyl series only the dimethyl compound showed an appreciable amount of a second isomer. All the NMR data are presented in Table 2 and discussed later.

One of the arguments which favors axial over lower belt substitution is that which relates to coordination number. It has been suggested [8] that in Friedel-Crafts reactions an unstable positively charged species is formed as an intermediate due to attack of a carbonium ion at a site of high electron density. The lower-belt boron atoms in 1-SB₉H₉ would increase their coordination number from 5 to 6 upon formation of the complex intermediate. On the other hand, the axial position would increase in coordination to 5 and thus might be favored if the substitution rate were enhanced by a lower coordination number.

In addition, Extended Hückel Molecular Orbital calculations on 1-SB₉H₉ indicate that the B site antipodal to the sulfur atom is the most negative (electron-rich) site and thus should be susceptible to electrophilic attack if ground-state charge considerations dominate. The following charges are from a Mulliken population analysis *ub* = 0.2524; *lb* = 0.0733; *ax* = -0.0734. The method of calculation and parameterization for this analysis has been discussed by Rudolph and Pretzer [14]. The bond distances and angles used in the calculations were average values obtained from the crystal structure of 2,2'-(1-SB₉H₈)₂ [15].

Similar to alkylation, the halogenation of 1-SB₉H₉ has been shown to produce both *lb* and *ax* isomers of Cl, Br, and I [12a]. The ratio of *ax*/*lb* does not agree with a statistical distribution, but rather favors *ax* substitution under the conditions employed. In the case of alkyl derivatives, heating the monoethyl deriva-

TABLE 2

¹¹B NMR DATA FOR ALKYLTHIADECABORANES ^{a,b}

| | |
|---|---|
| 10-Me-1-SB ₉ H ₈ | +85(1), -7.7(4)176, -20.4(4)161. |
| 6-Me-1-SB ₉ H ₈ | +73.5(1)171, -3.6(2)176, -6.2(2)195, -6.2(1), -16.5(2)146, -20.7(1)142. |
| Me ₂ -1-SB ₉ H ₇ ^c | 6,10-isomer (30%), +84(1); 6,7-isomer (70%), +74(1)171, -18.3(2)151; unresolved triplet centered at -5.7. |
| 6,7,8-Me ₃ -1-SB ₉ H ₆ | +74(1)156, -1.0(2)150, -2.83(2)150, -2.9(1), -6.6(2), -15.5(1)151. |
| 6,7,8,9-Me ₄ -1-SB ₉ H ₅ | +74.6(1)151, -0.8(4)166, -4.5(4). |
| 6,7,8,10-Me ₄ -1-SB ₉ H ₅ | +82.7(1), -3.0(2)150, -4.8(2)150, -6.1(1), -9.5(2), -17.0(1)146. |
| 6,7,8,9,10-Me ₅ -1-SB ₉ H ₄ | +82.7(1), -2.17(4)166, -7.22(4). |
| 6-Et-1-SB ₉ H ₈ | +73.2(1)162, -3.3(2)160, -5.7(1), -6.4(2)160, -16.6(2)142, -21.0(1)142. |
| Et ₂ -1-SB ₉ H ₇ ^c | 6,10-isomer (30%), +87(1); 6,7-isomer (70%) +73(1)181, -18.4(2)- 151; unresolved doublet centered at -4.8. |
| Et ₃ -1-SB ₉ H ₆ ^d | 6,7,8-isomer (30%), +72(1); 6,9,10-isomer (70%), +85.6(1), -20.4(2)147; broad unresolved peak at -5.7. |
| 6,7,8,10-Et ₄ -1-SB ₉ H ₅ | +84.1(1), -3.15(2)156, -4.3(1), -4.3(2)156, -6.9(2), -18.2(1)156. |
| 6,7,8,9,10-Et ₅ -1-SB ₉ H ₄ ^e | +79.9(1), -5.0(4)190, -5.9(4). |

^a The data for each signal are presented as follows: chemical shift (ppm relative to external BF₃ · OEt₂; + values downfield), intensity (in parentheses), coupling constant in Hz (if applicable). All spectra were taken in CDCl₃ solutions. If an assignment is found to be ambiguous, the spectrum is further explained by means of a footnote. ^b Chemical shifts downfield from BF₃ · OEt₂ are reported as positive(+) and upfield as negative (-). This change in sign convention was agreed upon at IMEBORON III, Munich-Ettal, Germany, July, 1976. ^c Mixture of isomers; features discernible at 32 MHz are mentioned above. There also may be a small amount of the 6,8-isomer present. ^d Mixture of isomers; features discernible at 32 MHz are mentioned above. There also may be a small amount of the 6,7,10-isomer present. ^e Determined at 86.7 MHz.

tive for 24 h at 200°C in a sealed tube changes the ax/lb ratio from 1/6 to 1/2.5. The monomethyl complex, when isolated at a GC detector temperature of 250°C, is substituted totally on the unique ax position. However, isolation of this derivative at a detector temperature of 125°C gives 95% of the lb isomer, as evidence through ^{11}B NMR. This indicates that the ax isomer is thermodynamically favored at the higher temperature, but that initial attack is on the lb with rearrangement taking place during the reaction or isolation of the products. A simple diamond-square-diamond (dsd) mechanism [16] has been suggested to account for intramolecular polyhedral rearrangements in polyhedra having 5 to 12 cage atoms [17]. This process requires little atomic motion and the GC collection temperature may well supply the energy to overcome the barrier to intermolecular rearrangement. The results of halogenation experiments on 1-SB₉H₉ also indicate that the axially-substituted isomer is thermodynamically more stable [12a]. Therefore, in *closo*-thiaboranes the site of substitution does not agree with the ground-state charge distribution and rearrangement is important in determining the substitution site. The site of electrophilic substitution on B₁₀H₁₀²⁻ also has been shown [9,10] to be contradictory to the predicted position of substitution [11], but no evidence for rearrangement was found. Moreover, this situation is realized for 1-SB₉H₉, even though lb substitution necessarily suggests a less favorable, sterically encumbered transition-state than for ax-substitution.

Nuclear magnetic resonance

The ^{11}B NMR, spectrum of the parent 1-SB₉H₉, has been previously assigned [12,15]. Substitution of an alkyl group at the axial boron, B(10), shifts the resonance 5–10 ppm downfield from that of the unsubstituted 1-SB₉H₉ (Table 2). This downfield shift of the substituted position compares favorably with results for other thiaboranes [12,18,19] and with those of alkyl-substituted borons in pentaborane and several carboranes [8,13,20,21]. Lower belt alkyl substitution does not shift the unsubstituted axial signal appreciably. However, major shifts can be seen within the lower belt region, especially with respect to the unsubstituted positions. As the degree of alkyl substitution increases, the perturbation of the lower belt signals becomes more noticeable. In the tetramethyl derivative (all lower belt substitution), the signal for the lower belt borons can be found within 1 ppm of the upper belt signal for the parent 1-SB₉H₉.

In the case of the methylated derivatives, the ^1H NMR signals for methyl groups which are substituted on lower belt borons fall in the range τ 10.1–9.8 ppm. The signal for the axially-substituted boron varies from τ 8.19 ppm for 10-CH₃-1-SB₉H₈ to τ 8.73 ppm for 6,7,8,9,10-(CH₃)₅-1-SB₉H₄. The ^1H NMR spectrum also showed the presence of distinct quartets characteristic of unsubstituted BH sites. A comparison of 10-CH₃-1-SB₉H₈ and 6,7,8,9,10-(CH₃)₅-1-SB₉H₄ showed the order of these quartets to be (intensity in parentheses, τ value in ppm and coupling constant in Hz): axial (1), 4.45, $J(\text{BH})$ 162; upper belt (4), 7.53, $J(\text{BH})$ 173; lower belt (4), 8.70, $J(\text{BH})$ 158. These coupling constants and assignments agree with previous assignments for the ^{11}B NMR spectrum of 1-SB₉H₉, both in order (high to low field) and in magnitude. The results presented here indicate the possibility of using ^1H NMR spectroscopy to make substitution-site assignments for 1-SB₉H₉.

Experimental

Reagents

Reagent grade CS₂ was freshly distilled just prior to each reaction from triply-distilled mercury and MgSO₄. Hydrogen chloride gas (Linde) was purified before use by passage through successive -78°C and 126°C traps. Reagent grade aluminum chloride used in the reactions was stored in a dry glove box under a nitrogen atmosphere. Alkyl halides were used without further purification. Thiaborane was prepared as previously described [18].

Reactions were run using a pressure bulb attached to a reflux condenser by means of an O-ring. In a typical alkylation reaction, the reaction vessel was charged with approximately 1.2 atm of prepurified hydrogen chloride gas, 420 mg (3 mmol) of 1-SB₃H₈, 400 mg (3 mmol) of anhydrous aluminum chloride, 3 mmol of alkyl halide and 25 ml of carbon disulfide. The reaction was then stirred at reflux temperature for 3 days. The color of the reaction gradually changed from yellow to red-orange. The final reaction product was washed with carbon disulfide and cyclohexane and filtered to remove all insoluble material. The remaining material was subjected to GC/MS analysis in order to confirm the presence of alkylated products.

Nuclear magnetic resonance

¹¹B (32.1 MHz) and ¹H (100 MHz) NMR spectra were recorded using a JEOL EC-100 spectrometer operating at ambient conditions. Higher field (86.7 MHz) ¹¹B NMR spectra were recorded at the University of Wisconsin.

Vapor phase chromatography

All alkylated compounds were collected using a Varian Series 2700 gas chromatograph. Methyl derivatives were isolated using a 5' × 3/8" stainless steel column filled with 2% OV-101 on Chromosorb G support. The flow rate was 75 ml/min with a column temperature of 110°C and the detector temperature at 125°C. The axially-substituted monomethyl derivative 10-CH₃-1-SB₃H₈ was isolated under the same conditions except that the detector was set at 250°C. All ethyl derivatives were collected from a 5' × 1/4" stainless steel column filled with 1.5% OV-101 Chromosorb G support. The flow rate was 75 ml/min and the detector set at 250°C. The column was programmed from 120–220°C at 6°/min.

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