

was used for the determination of nitrogen without any particular precautions, whereas carbon and hydrogen were determined by a modification<sup>9</sup> of the usual microdetermination method which was improved to prevent low carbon analyses.<sup>10</sup> Boron was determined by a flame spectrophotometric method<sup>11</sup> which had been developed for determining boron in boron-nitrogen compounds.

The proton magnetic resonance spectra were obtained at room temperature with a Varian A-60 high resolution n.m.r. spectrometer operating at 60 Mc. In these experiments, 10% carbon tetrachloride solutions were used with tetramethylsilane as an internal reference except for compound I and for amines,

(9) S. Mizukami and T. Ieki, *Microchem. J.*, **7**, 485 (1963).

(10) W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 113 (1962).

(11) T. Yoshizaki, *Anal. Chem.*, **35**, 2177 (1963).

for which saturated chloroform-*d*<sub>3</sub> solutions were employed. The <sup>11</sup>B n.m.r. spectrum of the ethyl derivative was recorded by Varian Associates, Palo Alto, Calif., using a Model HR-100 with the substitution of a 32.1 Mc. radiofrequency unit for the 100-Mc. unit.

The ultraviolet spectra were recorded in ether solution over a region of 220 to 500 mμ, using a Hitachi Model EPS-2 recording spectrophotometer.

The infrared spectra were recorded over a rock-salt region on a Type DS-201B spectrophotometer from the Optical Research Institute, Tokyo Kyoiku University. Polystyrene was the calibration standard. The spectra were taken in solutions, using both carbon disulfide and carbon tetrachloride as solvent. In Table III are listed the wave numbers in carbon disulfide, except in regions where the solvent showed its own absorptions. In these regions, the data in carbon tetrachloride solutions are given.

CONTRIBUTION NO. 1023 FROM THE CENTRAL RESEARCH DEPARTMENT,  
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON 98, DELAWARE

## Chemistry of Boranes. XXIII.<sup>1</sup> B<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup> and B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>

By W. H. KNOTH, W. R. HERTLER, AND E. L. MUETTERTIES

Received October 20, 1964

The reaction of B<sub>10</sub>H<sub>10</sub><sup>2-</sup> with dimethyl sulfoxide and hydrogen chloride has given B<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup> [(dimethyl sulfide)nonahydrodecaborate(1-)] and B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> [bis(dimethyl sulfide)decaborane(8)]. Although apical (1,10—see Figure 1) substitution predominates in this reaction, significant amounts of equatorial isomers are also formed. The carbon-sulfur bond in B<sub>10</sub>H<sub>9</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> is kinetically more labile than the boron-sulfur bond as shown by reaction with tributylphosphine to give (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>9</sub>SCH<sub>3</sub><sup>-</sup>. Thermal rearrangement of 1,10-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to 2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> has been observed at 230°. Halogenated derivatives of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and B<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup> have been prepared as well as diazonium, deuterio, hydroxy, benzoyl, and amine derivatives of the latter.

The polyhedral borane anions B<sub>10</sub>H<sub>10</sub><sup>2-</sup> and B<sub>12</sub>H<sub>12</sub><sup>2-</sup> are atypical boron hydride species as documented in previous publications.<sup>1-8</sup> The basic cage structure is kinetically very stable. However, the hydrogen atoms are susceptible to replacement by other atoms or groups. This has led to the development of a vast derivative chemistry which includes such varied substituents as halogen,<sup>4</sup> carboxyl,<sup>5</sup> azide,<sup>5</sup> isocyanate,<sup>5</sup> nitrile,<sup>5</sup> acyl,<sup>7</sup> hydroxy,<sup>7</sup> and nitrogen.<sup>5</sup> The subject of this paper is the chemistry of the two inner sulfonium salts, B<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup> and B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.<sup>2</sup>

### Results

Dimethyl sulfoxide and B<sub>10</sub>H<sub>10</sub><sup>2-</sup> react readily under acidic conditions to give good yields of B<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup> and B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> at 40–60°. With excess dimethyl sulfoxide as solvent, the ratio of these products

is dependent on reaction time; with acetic acid as solvent, preferential formation of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> occurs regardless of stoichiometry or reaction time.<sup>9</sup> The stereochemistry of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was initially reported<sup>2</sup> as bis-apical (1,10—see Figure 1) on the basis of 10-Mc. n.m.r. data. More sensitive spectral probes have since shown that significant, though minor, amounts of equatorially-substituted isomers are also formed. Crude CsB<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub> prepared in excess dimethyl sulfoxide was found to contain 77% of the apical isomer; separation of this from the equatorial isomer was readily accompanied by recrystallization from water. Apical substitution predominates to about the same extent in the second substitution with dimethyl sulfoxide, since crude B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> formed in excess dimethyl sulfoxide was found to contain 56% of the 1,10- isomer [(0.77)<sup>2</sup> = 0.59]. Virtually all of the remaining B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> is the 1,6- isomer. The two isomers can be separated by chromatography. Heating 1,10-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to 230° for 45 min. in Dowtherm A resulted in partial rearrangement to 2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.

The chemical stabilities of B<sub>10</sub>H<sub>9</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup> and B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> are comparable to that of B<sub>10</sub>H<sub>10</sub><sup>2-</sup>. Neither of the sulfonium salts is oxidized by silver nitrate. Oxi-

(1) Paper XXII: W. R. Hertler, W. H. Knuth, and E. L. Muetterties *J. Am. Chem. Soc.*, **86**, 5434 (1964).

(2) W. H. Knuth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *ibid.*, **84**, 1056 (1962).

(3) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knuth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(4) W. H. Knuth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *ibid.*, **3**, 159 (1964).

(5) W. H. Knuth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

(6) W. R. Hertler and M. S. Raasch, *ibid.*, **86**, 3661 (1964).

(7) W. H. Knuth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *ibid.*, **86**, 3973 (1964).

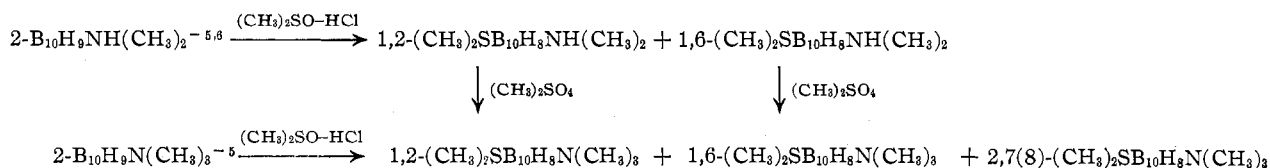
(8) W. R. Hertler, *ibid.*, **86**, 2949 (1964).

(9) This observation about the acetic acid system was first made by Dr. W. C. Drinkard.

dative coupling of  $B_{10}H_9S(CH_3)_2^-$  by ceric ion does occur<sup>10</sup> as reported<sup>11</sup> for  $B_{10}H_{10}^{2-}$  itself. Neither acid nor base degrades  $B_{10}H_9S(CH_3)_2^-$  or  $B_{10}H_8[S(CH_3)_2]_2$  under moderate conditions. For example, aqueous solutions of the hydronium salt of  $B_{10}H_9S(CH_3)_2^-$  are stable over a wide concentration range, and  $B_{10}H_8[S(CH_3)_2]_2$  is un-

hydrochloric acid. The latter species and the corresponding 1,6- isomer, available from earlier work,<sup>6</sup> have been allowed to react with dimethyl sulfate to give the corresponding isomers of  $(CH_3)_2SB_{10}H_8N(CH_3)_3$ . Alternative preparations of the 1,6- isomer as well as routes to the 1,2- and 2,7(8)- isomers are shown in Scheme I.

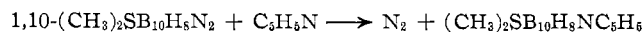
## SCHEME I



affected by 2% sodium hydroxide in refluxing 50% aqueous alcohol. However, treatment of  $B_{10}H_8[S(CH_3)_2]_2$  with tributylphosphine at 220° or with potassium phthalimide in refluxing dimethylformamide causes demethylation to give  $(CH_3)_2SB_{10}H_8SCH_3^-$ . This monoanion is readily methylated with methyl iodide to re-form the neutral derivative. Metallation of the methyl groups but not the boron atoms results from reaction with *n*-butyllithium.

Facile acid-catalyzed deuterium exchange has been reported<sup>3</sup> for  $B_{10}H_{10}^{2-}$ . In deuterium oxide solution, under conditions that cause about 25% deuteration of  $B_{10}H_{10}^{2-}$  in 2 min., no deuteration (B-D) of  $B_{10}H_9S(CH_3)_2^-$  was detected. Approximately 50% deuteration was achieved by heating an acidified deuterium oxide solution of  $B_{10}H_9S(CH_3)_2^-$  to 80° for 3 hr. No deuterium-hydrogen (B-H) exchange was observed for  $B_{10}H_8[S(CH_3)_2]_2$  under a variety of forcing conditions. Perhalogenation of  $B_{10}H_9S(CH_3)_2^-$  and  $B_{10}H_8[S(CH_3)_2]_2$  is also less facile than with  $B_{10}H_{10}^{2-}$ . Partial halogenation proceeds readily, however, and a monoiodo derivative (shown by n.m.r. to be mostly equatorially iodinated) of  $B_{10}H_9S(CH_3)_2^-$  as well as monoiodo, mono-, di-, and tribromo, and penta- and hexachloro derivatives of  $B_{10}H_8[S(CH_3)_2]_2$  have been prepared. Treatment of  $B_{10}H_2Cl_6[S(CH_3)_2]_2$  with tributylphosphine at 190° results in cleavage of two methyl groups to form  $B_{10}H_2Cl_6(SCH_3)_2^{2-}$ . The halogen atoms are unaffected in this reaction and in general appear to be as tightly bound in these derivatives as in the simple halogen derivatives of  $B_{10}H_{10}^{2-}$ .<sup>4</sup>

The reaction of  $1-B_{10}H_9S(CH_3)_2^-$  with nitrous acid yields a shock-sensitive species which can be converted to 1,10- $(CH_3)_2SB_{10}H_8N_2$  by reduction. The nitrogen in this inner diazonium salt, like that in 1,10- $B_{10}H_8(N_2)_2$ ,<sup>5</sup> is subject to displacement reactions, e.g.



Another product formed in the reaction of  $1-B_{10}H_9S(CH_3)_2^-$  with nitrous acid is 1,10- $(CH_3)_2SB_{10}H_8NO^-$ , which has been isolated as a shock-sensitive cesium salt and reduced to 1,10- $(CH_3)_2SB_{10}H_8NH_3$  with zinc and

The previously reported<sup>6</sup> preparations of 1,6- $(CH_3)_2SB_{10}H_8NH_3$  from both  $1-B_{10}H_9S(CH_3)_2^-$  and  $2-B_{10}H_9NH_3^-$  unequivocally established the apical position of the  $(CH_3)_2S$  group and the equatorial position of the  $NH_3$  group. The 1,6- assignment, as opposed to the only other possibility, 1,2-, was largely based on steric arguments. An X-ray determination of the structure of 1,2- $(CH_3)_2SB_{10}H_8NH(CH_3)_2$  has since been made.<sup>12</sup> Because of the interrelationships shown above, this has afforded confirmation of all the assignments for both the 1,6- and the 1,2- series. Aldehydes reacted with 1,6- $(CH_3)_2SB_{10}H_8NH_3$  to give protonated Schiff bases, e.g., 1,6- $(CH_3)_2SB_{10}H_8NH=CHC_6H_4Cl$  and 1,6- $(CH_3)_2SB_{10}H_8NH=CHC_6H_4N(CH_3)_2$ .

A number of other derivatives of  $B_{10}H_9S(CH_3)_2^-$  have been prepared by reaction of  $B_{10}H_{10}^{2-}$  derivatives with dimethyl sulfoxide and hydrochloric acid. For example,  $B_{10}H_9COC_6H_5^{2-}$ <sup>7</sup> and  $2-B_{10}H_9OCH=NH(CH_3)_2^-$ <sup>7</sup> have been converted to  $(CH_3)_2SB_{10}H_8COC_6H_5^-$  and 1,6- $(CH_3)_2SB_{10}H_8OCH=NH(CH_3)_2$ , respectively. The latter is cleaved to 1,6- $(CH_3)_2SB_{10}H_8OH^-$ <sup>13</sup> by aqueous sodium hydroxide. Certain oxygen deriva-

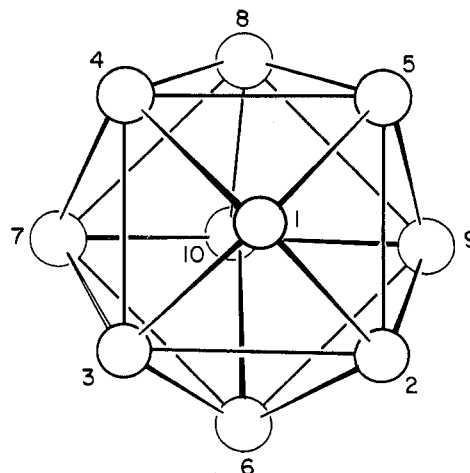


Figure 1.

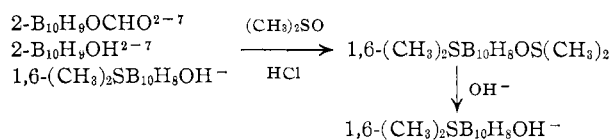
(12) We are indebted to Dr. J. F. Whitney for permission to use these results prior to publication.

(13) The 1,6- stereochemical assignment of this anion, and thereby of its precursors and derivatives, rests on an independent synthesis from 1,6- $(CH_3)_2SB_{10}H_8CO$  which has been related to the known 1,6- $(CH_3)_2SB_{10}H_8N(CH_3)_3$ . This is described in detail in the following paper of this series: W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *Inorg. Chem.*, **4**, 288 (1965).

(10) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

(11) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 729 (1962).

tives of  $B_{10}H_{10}^{2-}$  react with dimethyl sulfoxide and hydrogen chloride with formation of dimethyl sulfoxide derivatives.



### Discussion

The mechanism of the reaction of  $B_{10}H_{10}^{2-}$  with dimethyl sulfoxide and hydrochloric acid has not been determined. The fact that a B-S bond rather than a B-O bond is formed appears explicable only on the basis of attack by an electrophilic sulfur atom as in  $(CH_3)_2SOH^+$  or  $(CH_3)_2SCl^+$ . Characterization of the reaction as electrophilic is consistent with the failure of  $B_{12}H_{12}^{2-}$ , known to be less reactive toward electrophiles than  $B_{10}H_{10}^{2-}$ , to undergo an analogous reaction.

The 3:1 ratio of  $1-B_{10}H_9S(CH_3)_2^-$  to  $2-B_{10}H_9S(CH_3)_2^-$  is far greater than the 1:4 ratio expected on a statistical basis and is different from the stereochemical results observed with other electrophilic reagents (Table I). Clearly, the data assembled to date for

TABLE I

Reagent	Group introduced	Stereochemistry
HONO, NaBH <sub>4</sub>	-N <sub>2</sub> <sup>+</sup>	Exclusively apical <sup>1,5</sup>
NH <sub>2</sub> OSO <sub>3</sub> H	-NH <sub>3</sub> <sup>+</sup>	Predominantly equatorial <sup>6</sup>
(COCl) <sub>2</sub>	-CO <sup>+</sup>	Exclusively equatorial <sup>8,11</sup>
C <sub>6</sub> H <sub>5</sub> COCl	C <sub>6</sub> H <sub>5</sub> CO-	Predominantly equatorial <sup>7</sup>
D <sub>2</sub> O <sup>+</sup>	-D	Ratio of rates of ap. to eq. exchange is about 5:1

electrophilic substitution in  $B_{10}H_{10}^{2-}$  and its derivatives show no dependable correlation between ground-state electronic charge distribution and the stereochemistry of reaction.

The stereochemistry of the products from reaction of dimethyl sulfoxide with  $2-B_{10}H_9N(CH_3)_3^-$  and  $2-B_{10}H_9NH_3^-$  deserves comment since in the former reaction at least three isomers (*i.e.*, 1,6- (major product), 1,2-, and 2,7(8)-) of  $(CH_3)_2SB_{10}H_8N(CH_3)_3$  have been isolated, whereas in the latter reaction only 1,6- $(CH_3)_2SB_{10}H_8NH_3$  was isolated.<sup>6</sup> These results would appear to confer a special directive influence upon the NH<sub>3</sub> group. However, a more reasonable explanation is that 1,6- $(CH_3)_2SB_{10}H_8NH_3$  has a much lower solubility in water than do some of the unisolated isomers of this compound, resulting in the selective loss of the soluble isomers during work-up. It is interesting that in spite of the deactivation of position 1 in  $2-B_{10}H_9N(CH_3)_3^-$  by the bulky electronegative trimethylamino group, the reaction of this anion with dimethyl sulfoxide appears to give significantly more 1,2- than 2,7(8)- $(CH_3)_2SB_{10}H_8N(CH_3)_3$ . This further attests to the very decided preference for apical *vs.* equatorial substitution in the dimethyl sulfoxide reaction.

We have found no evidence of skeletal rearrangements in  $B_{10}H_{10}^{2-}$  chemistry during reactions occurring at either apical or equatorial<sup>8</sup> positions or in isolated

products under moderate conditions; this is further substantiated by the stereochemical integrity of 1,10- $B_{10}H_8[S(CH_3)_2]_2$  to 180°. These findings are critical to any rationale of observed stereochemistry since they preclude the possibility of skeletal rearrangements prior to stereochemical characterization. Rearrangement has been demonstrated<sup>1</sup> for some  $B_{10}H_{10}^{2-}$  derivatives at temperatures in excess of 200°. Another illustration of this is the rearrangement of 1,10- $B_{10}H_8[S(CH_3)_2]_2$  to 2,7(8)- $B_{10}H_8[S(CH_3)_2]_2$  at 230°. The observed course of this rearrangement is that predicted<sup>1</sup> from the simple model in which elongation of the B<sub>2</sub>-B<sub>3</sub> and B<sub>6</sub>-B<sub>7</sub> (or B<sub>7</sub>-B<sub>8</sub> to obtain the other member of an asymmetric pair) is the lowest energy pathway.

An interesting point with regard to the H<sup>1</sup> n.m.r. spectrum of 2,7(8)- $B_{10}H_8[S(CH_3)_2]_2$  is that the methyl hydrogen resonance appears as two equal peaks separated by about 3 c.p.s. (at 60 Mc.). At 100 Mc., the separation is about 5 c.p.s. The nonequivalence of the methyl groups may be attributed to the molecular asymmetry which characterizes this isomer. This phenomenon is not observed in 1,10- or 1,6- $B_{10}H_8[S(CH_3)_2]_2$  or in 1- and 2- $B_{10}H_9S(CH_3)_2^-$ . The two peaks coalesce with concomitant broadening at about 69° which may be due to inversion of the sulfur atoms. The H<sup>1</sup> n.m.r. spectrum of 2,7(8)- $(CH_3)_2SB_{10}H_8N(CH_3)_3$  likewise shows two peaks (separated by about 2 c.p.s. in chloroform) for the -S(CH<sub>3</sub>)<sub>2</sub> group asymmetry with the expected single peak for the -N(CH<sub>3</sub>)<sub>3</sub> group. The separation of the S-methyl resonances is solvent-dependent.

The empirical similarity of  $B_{10}H_8[S(CH_3)_2]_2$  to  $B_{10}H_{12}[S(CH_3)_2]_2$  and other  $B_{10}H_{12}(\text{base})_2$  species<sup>14-16</sup> which undergo facile ligand displacement reactions suggests that  $B_{10}H_8[S(CH_3)_2]_2$  should be an intermediate to a variety of  $B_{10}H_8(\text{base})_2$  species. That this is not the case is demonstrated by the reaction of  $B_{10}H_8[S(CH_3)_2]_2$  with tributylphosphine to give  $(CH_3)_2SB_{10}H_8S(CH_3)_2^-$  and not  $B_{10}H_8[P(C_4H_9)_3]_2$ . The only readily displaceable ligand yet observed in a  $B_{10}H_{10}^{2-}$  derivative is nitrogen, as in  $B_{10}H_8(N_2)^{2-}$  and  $(CH_3)_2SB_{10}H_8N_2$ . The difference in lability between the two ligands in the latter compound is demonstrated by its reaction with pyridine in which only the nitrogen is displaced.

A comparison of the spectral properties of 1,10- $(CH_3)_2SB_{10}H_8NO^-$  with those reported<sup>17</sup> for a series of nitroso derivatives of  $B_{20}H_{19}^{2-}$  is disappointing. A strong band at 8.45 μ (1180 cm.<sup>-1</sup>) was assigned to the NO absorption in the infrared spectrum of  $B_{20}H_{18}NO^{3-}$ . There is no significant absorption band near this frequency in the infrared spectrum of  $Cs(CH_3)_2SB_{10}H_8NO$ . Instead, there is an extra band in the CH<sub>3</sub> deformation region which we are tentatively assigning to the N=O stretching mode. In this region, there is a strong band at 1425 cm.<sup>-1</sup>, assignable to the asymmetric deformation of the CH<sub>3</sub> group, and a weaker band at 1330 cm.<sup>-1</sup>

(14) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

(15) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **80**, 6685 (1958).

(16) W. H. Knox and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(17) R. A. Wiesboeck, *J. Am. Chem. Soc.*, **85**, 2725 (1963).

for the symmetric mode.<sup>18a</sup> Both of these bands are also present in the spectra of  $\text{CsB}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$ ,  $\text{N}_2\text{B}_{10}\text{H}_8\text{S}(\text{CH}_3)_2$ , and  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ . In addition, there is a band of moderate intensity at  $1385\text{ cm}^{-1}$  in the spectrum of  $\text{Cs}(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NO}$  which is not in the spectrum of the other inner sulfonium salts, and we are assigning this as the  $\text{N}=\text{O}$  stretching frequency. The reported absorption range for NO groups on carbon is  $1495$  to  $1620\text{ cm}^{-1}$  and the comment is made that the NO absorption is particularly sensitive to the nature of its environment.<sup>18b</sup>

The introduction of positively charged substituents onto the  $\text{B}_{10}\text{H}_{10}^{2-}$  cage should decrease reactivity toward electrophilic reagents and this is consistent with the observed orders of decreasing ease of deuteration and halogenation:  $\text{B}_{10}\text{H}_{10}^{2-} > \text{B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2^- > \text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ . Previously, evidence was presented<sup>7</sup> which demonstrated that the net effect of halogen substitution on the  $\text{B}_{10}\text{H}_{10}^{2-}$  cage is one of inductive electron withdrawal. Such withdrawal should facilitate nucleophilic cleavage of C-S bonds in derivatives of  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ . This is observed in the reaction of  $\text{B}_{10}\text{H}_2\text{Cl}_6[\text{S}(\text{CH}_3)_2]_2$  with tributylphosphine at  $190^\circ$  in which two methyl groups are cleaved, compared with the cleavage of only one methyl group from  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$  by the same reagent at  $210^\circ$ .

### Experimental

The preparation of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  has been described previously.<sup>8</sup> Proton nuclear magnetic resonance spectra were determined at 60 Mc. on a Varian Model A60 spectrometer. Boron spectra were determined at 19.2 Mc. on a Varian Model V4300 spectrometer, except where otherwise noted, with methyl borate as reference. Double irradiation was effected with an NMR Specialties Model SD60 spin decoupler. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. Melting points are corrected unless noted otherwise. Silica gel thin-layer chromatography plates ( $2 \times 8$  in.) were purchased from Custom Service Chemicals, Inc., of Wilmington, Del.

**$\text{B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2^-$ .**—Hydrogen chloride was passed into a solution of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  (40 g., 260 mmoles) in 200 ml. of dimethyl sulfoxide for 5 min. at a rate such as to keep the temperature at about  $60^\circ$  with cooling in an ice-water bath. The solution was then poured with stirring into 500 ml. of water and filtered through Celite filter aid to remove a small amount of  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ . A solution of cesium fluoride (50 g., 0.33 mole) in 100 ml. of water was added to precipitate 38 g. (47%) of  $\text{CsB}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$ . The analytical sample was recrystallized from a large volume of water. *Anal.* Calcd. for  $\text{CsB}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$ : C, 7.7; H, 4.8; Cs, 42.6; B, 34.6; S, 10.3. Found: C, 7.7; H, 4.9; Cs, 43.0; B, 33.8; S, 10.4. A tetramethylammonium salt was also prepared and analyzed. *Anal.* Calcd. for  $(\text{CH}_3)_4\text{NB}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$ : C, 28.4; H, 10.7; B, 42.7; S, 12.6. Found: C, 28.2; H, 10.4; B, 42.0; S, 13.3.

A small aliquot of the crude cesium salt from a similar experiment at  $40^\circ$ , with 30 g. (195 mmoles) of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  in 300 ml. of dimethyl sulfoxide, was converted to a sodium salt by ion exchange. The  $\text{H}^1$  n.m.r. of this salt in  $\text{D}_2\text{O}$  had a peak at  $\tau$  6.9 (apical  $\text{S}(\text{CH}_3)_2$ , relative intensity 3.4) and one at  $\tau$  7.61 (equatorial  $\text{S}(\text{CH}_3)_2$ , relative intensity 1). The remainder of the crude cesium salt from this preparation was boiled with 1.2 l. of water, cooled, and filtered to give 32 g. (53%) of  $\text{Cs}[1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2]$ .

The  $\text{H}^1$  n.m.r. spectrum of this product (as sodium salt in  $\text{D}_2\text{O}$ ) has a single peak at  $\tau$  6.92 consistent with  $1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2^-$ . The  $\text{B}^{11}$  n.m.r. spectrum of the same anion (as potassium salt in water) shows an incompletely resolved doublet at low field which apparently consists of a doublet at 14 p.p.m. ( $J \sim 97$  c.p.s.), representing one unsubstituted apical boron atom, superimposed on a single peak at  $\sim 14$  p.p.m., representing one substituted apical boron atom. These peaks decouple to a single peak on irradiation at 60 Mc. There is a larger doublet at 47.6 p.p.m. ( $J = 128$  c.p.s.) which represents eight unsubstituted equatorial boron atoms. This doublet decouples to a single peak on irradiation at 60 Mc.

Evaporation of the aqueous extract of the crude product gave 10 g. (16.4%) of  $\text{CsB}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$  which consisted of a mixture of 1- and 2- isomers in the ratio of 1:5.7 as determined by  $\text{H}^1$  n.m.r. Three recrystallizations of this from water gave 3.16 g. of  $\text{Cs}[2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2]$ . *Anal.* Calcd. for  $\text{CsB}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$ : C, 7.69; H, 4.8; B, 34.6; S, 10.3. Found: C, 7.54; H, 4.9; B, 34.7; S, 10.0. The  $\text{H}^1$  n.m.r. spectrum of this isomer (as sodium salt in  $\text{D}_2\text{O}$ ) shows two peaks at  $\tau$  7.63 (equatorial  $\text{S}(\text{CH}_3)_2$ ) and 6.92 (apical  $\text{S}(\text{CH}_3)_2$ ). The intensity ratio of the peaks indicates that the product consists of 93%  $2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2^-$  and 7%  $1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2^-$ . The  $\text{B}^{11}$  n.m.r. spectrum (19.2 Mc.) of the product (as sodium salt in water) shows two overlapping doublets at 19.6 p.p.m. ( $J = 138$  c.p.s.) and 22.6 p.p.m. ( $J = 137$  c.p.s.) which can be decoupled to two single peaks on irradiation at 60 Mc. These doublets represent two unsubstituted apical boron atoms which experience different chemical shifts. The seven unsubstituted equatorial boron atoms are represented by a larger doublet at 46 p.p.m. ( $J = 104$  c.p.s.) which can be decoupled to a single peak on irradiation at 60 Mc. In addition, there is a peak at 36.2 p.p.m. which represents one substituted equatorial boron atom and is unaffected by irradiation at 60 Mc.

**1,10- and 1,6- $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ .** (A).—Hydrogen chloride was passed into a solution of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  (20 g., 130 mmoles) in 100 ml. of dimethyl sulfoxide with cooling in an ice-water bath for 1 hr. at a rate such that the temperature was maintained at  $50\text{--}60^\circ$ . A solid formed, and the mixture became very thick. It was added with stirring to 600 ml. of water. Crude  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$  precipitated and was washed with five 50-ml. portions of water. The residue was dissolved in 300 ml. of acetone and filtered, and the acetone solution was added with stirring to 400 ml. of water to reprecipitate 29 g. (93%) of crude  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ , m.p.  $249\text{--}251^\circ$ . The  $\text{H}^1$  n.m.r. spectrum of the crude product in chloroform-*d* showed peaks at  $\tau$  6.8 (relative intensity 3.58, apical  $\text{S}(\text{CH}_3)_2$ ) and 7.52 (relative intensity 1, equatorial  $\text{S}(\text{CH}_3)_2$ ) consistent with a mixture of 56% of the 1,10- and 44% of the 1,6- isomer. The analytical sample was recrystallized from aqueous alcohol, m.p.  $242\text{--}242.5^\circ$ . *Anal.* Calcd. for  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ : C, 20.0; H, 8.4; B, 45.0; mol. wt., 244. Found: C, 19.3; H, 8.5; B, 44.8; mol. wt., 247 (cryoscopic in  $(\text{CH}_3)_2\text{SO}$ ).

(B).—A stream of gaseous hydrogen chloride was passed through a mixture of 20 g. (0.13 mole) of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ , 23 ml. of dimethyl sulfoxide, and 100 ml. of glacial acetic acid for 1 hr. The temperature was prevented from rising above  $60^\circ$  by occasional use of an ice bath. The resulting mixture was filtered, and the filter cake was washed well with water to give 22.5 g. (72%) of  $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$  as a mixture of 1,10- and 1,6- isomers. Thin-layer chromatography of the crude product on silica gel using ethylene chloride showed two spots at  $R_f$  0.55 (1,6- isomer) and  $R_f$  0.63 (1,10- isomer). The  $\text{H}^1$  n.m.r. spectrum of the crude product in chloroform-*d* showed peaks at  $\tau$  7.0 (relative intensity 3.86, apical  $\text{S}(\text{CH}_3)_2$ ) and 7.7 (relative intensity 1, equatorial  $\text{S}(\text{CH}_3)_2$ ), with a high-field shoulder (relative intensity 0.107) consistent with an isomeric mixture consisting of 64.7% 1,10- and 33.5% 1,6- $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$  with 1.8% of diequatorial isomer(s).

A 10-g. portion of the crude product was chromatographed on 1000 g. of acid-washed alumina (Woelm). Elution with 23 100-ml. portions of 1:1 benzene-ethylene chloride gave 6.22 g. of  $1,10\text{-B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$  followed by a small fraction (0.54 g.) con-

(18) The symmetrical deformation frequency for  $\text{CH}_3\text{-S}$  groups is at  $1323\text{ cm}^{-1}$ ; see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958: (a) p. 25; (b) pp. 303-306.

taining a mixture of isomers, and finally, by eluting with 1:1 acetonitrile-ethylene chloride, 2.85 g. of 1,6-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was obtained.

A sample of 1,10-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was prepared for analysis by recrystallization from benzene-cyclohexane to give crystals with m.p. 257-258°. *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 20.0; H, 8.4; B, 45.0; S, 26.6. Found: C, 19.7; H, 8.11; B, 44.5; S, 26.4.

Thin-layer chromatography of the product on silica gel (ethylene chloride) showed a single spot (*R<sub>f</sub>* 0.63). The H<sup>1</sup> n.m.r. spectrum of 1,10-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in chloroform-*d* has a single peak, at  $\tau$  6.95. The B<sup>11</sup> n.m.r. spectrum (19.2 Mc.) in acetonitrile shows a peak at 8.15 p.p.m. (relative intensity 1.8) which can be assigned to the two substituted apical boron atoms and a doublet at 43 p.p.m. (*J* = 135 c.p.s., relative intensity 8.2) which can be assigned to the eight unsubstituted equatorial boron atoms (can be decoupled to a single peak by irradiating at 60 Mc.).

A sample of 1,6-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was prepared for analysis by recrystallization from benzene-cyclohexane to give feathery crystals with m.p. 235-236°. *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 20.0; H, 8.4; B, 45.0; S, 26.6. Found: C, 20.3; H, 8.4; B, 44.8; S, 27.1.

Thin-layer chromatography of the product on silica gel showed a single spot (*R<sub>f</sub>* 0.55). The H<sup>1</sup> n.m.r. spectrum of 1,6-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in chloroform-*d* has two equal peaks at  $\tau$  6.95 (apical S(CH<sub>3</sub>)<sub>2</sub>) and 7.65 (equatorial S(CH<sub>3</sub>)<sub>2</sub>). The B<sup>11</sup> n.m.r. spectrum (19.2 Mc.) in acetonitrile shows a peak at 12.3 p.p.m. with a distinct shoulder at  $\sim$ 17.3 p.p.m. which can be assigned to a substituted apical boron atom ( $\sim$ 12.3 p.p.m.) and an unsubstituted apical boron atom (doublet  $\sim$ 14.7 p.p.m., *J*  $\sim$  95 c.p.s.), and a doublet at 45.1 p.p.m. (*J* = 146 c.p.s., seven equatorial boron atoms) with a low-field shoulder (one substituted equatorial boron atom). On irradiating at 60 Mc. the peaks at 12.3 and 14.7 p.p.m. collapse to a broad peak, and at a slightly different irradiating frequency the doublet at 45.1 p.p.m. collapses to a single sharp peak and the low-field shoulder becomes discernible as a distinct peak of relative intensity  $\sim$ 1.3 compared to 1.9 for the 12.3 and 14.7 p.p.m. peaks and 6.8 for the 45.1 p.p.m. doublet.

**2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. (C).**—A mixture of 3 g. (12.4 mmoles) of 1,10-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and Dowtherm A was heated in an oil bath at 230° for 45 min. The resulting solution was treated with pentane, and the precipitate was collected by filtration. The filter cake was extracted with warm benzene-cyclohexane, and the extract was evaporated. The residue was recrystallized twice from chloroform-carbon tetrachloride to give 125 mg. (2.8%) of crystalline 2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·CHCl<sub>3</sub>, m.p. 226-227.5°. *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·CHCl<sub>3</sub>: C, 16.7; H, 5.9; B, 30.1; S, 17.8; Cl, 29.6. Found: C, 16.9; H, 6.3; B, 31.4; S, 19.0; Cl, 26.7. The analysis indicates less than one chloroform of solvation. Recrystallization from ethanol gave 2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 20.0; H, 8.4; S, 26.6. Found: C, 19.2; H, 8.2; S, 26.5. The H<sup>1</sup> n.m.r. spectrum of 2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in chloroform-*d* has two equal peaks at  $\tau$  7.62 and 7.67, presumably due to the molecular asymmetry. At 100 Mc., the separation of the two peaks is 5 c.p.s. On heating a solution of 2,7(8)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in Dowtherm A to 77°, the two peaks collapse to a single peak. The B<sup>11</sup> n.m.r. spectrum (32.1 Mc.) in chloroform-*d* shows a doublet at low field (used as arbitrary reference point, 0 p.p.m.) with *J* = 154 c.p.s. which has a relative intensity of 2. This peak is assigned to two unsubstituted apical boron atoms. A single, slightly broad, peak at 13.8 p.p.m. is assigned to two substituted equatorial boron atoms. Three peaks at high field can be attributed to two overlapping doublets at 23.3 p.p.m. (*J* = 145 c.p.s.) and 27.7 p.p.m. (*J* = 135 c.p.s.) with relative intensities 2:4 which can be assigned to six unsubstituted equatorial boron atoms. Since there is a single resonance doublet for both apical boron atoms, the substituents must be located on different equatorial belts, *i.e.*, 2,7(8)- or 2,6(9)- substitution. In 2,6(9)-B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> the six unsubstituted equatorial boron atoms consist of two equivalent boron atoms which are adjacent to two

sites of substitution, two equivalent boron atoms which are adjacent to one site of substitution, and two equivalent boron atoms which are not adjacent to sites of substitution. In the 2,7(8)-isomer, two equatorial boron atoms are adjacent to two sites of substitution and four equatorial boron atoms are adjacent to one site of substitution. Thus, the unsubstituted equatorial boron atoms in the 2,6(9)-isomer would probably produce three equal doublets while the unsubstituted equatorial boron atoms in the 2,7(8)-isomer would probably produce two doublets in the observed ratio of 1:2.

**Metallation of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—A solution of *n*-butyllithium in heptane-pentane (71 mmoles in 40 ml.) was added slowly to a slurry of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (6.0 g., 25 mmoles) in 150 ml. of ether in a nitrogen atmosphere. The B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> dissolved. D<sub>2</sub>O (2.5 g., 125 mmoles) was added slowly, precipitating a solid. This was removed by filtration, dissolved in acetone, reprecipitated in water, dried, and then put through the same procedure again. The final product was recrystallized from aqueous ethanol, m.p. 260-261° (uncor.). *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 20.0; H, 8.4; B, 45.0; S, 26.6. Found: C, 19.8; H, 8.4; B, 42.8; S, 27.1. The infrared spectrum had a weak band at 2250 cm.<sup>-1</sup> for C-D stretching but had no B-D absorption bands.

**B<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub><sup>-</sup>. (A).**—A mixture of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (2.0 g., 8.4 mmoles) and tributylphosphine (6 ml.) was heated at 210° for 3 min. in a nitrogen atmosphere to form a clear colorless solution. The tributylphosphine was removed by distillation under vacuum, and the residue was washed thoroughly with benzene. It was then dissolved in 25 ml. of methanol and filtered into an ethanolic solution of tetramethylammonium chloride to give (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub> in 67% yield. The analytical sample was recrystallized from water. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>: C, 28.1; H, 9.8; B, 36.2; N, 4.6; S, 21.4. Found: C, 27.7; H, 9.5; B, 36.4; N, 4.4; S, 21.5.

**(B).**—A solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (4.0 g., 16.4 mmoles) and potassium phthalimide (4.0 g., 23 mmoles) in 75 ml. of dimethylformamide was refluxed for 20 min., cooled, and filtered. The filtrate was concentrated under vacuum until a sludge formed, and this was stirred with water and filtered. The water-insoluble portions were found, by infrared analysis, to be a mixture of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, phthalimide, and *N*-methylphthalimide. The addition of tetramethylammonium chloride to the filtrate precipitated (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub> (0.4 g., 8%), identical by infrared analysis with that prepared above. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>: B, 36.2; S, 21.4. Found: B, 35.7; S, 21.8.

A solution of (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub> (1.4 g., 4.7 mmoles) in hot water was passed through an ion-exchange column packed with Amberlite IR 120(H) resin. The effluent was evaporated to dryness leaving a benzene-soluble solid. This was recrystallized from benzene-petroleum ether to obtain 0.6 g., 56% of B<sub>10</sub>H<sub>8</sub>S-(H)CH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>, dec. pt. 190-195° (uncor.). *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>S(H)CH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>: B, 47.8; S, 28.3. Found: B, 47.8; S, 28.4. Treatment of an aqueous solution of B<sub>10</sub>H<sub>8</sub>S-(H)CH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub> with tetramethylammonium hydroxide reformed (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>.

The addition of methyl iodide to a solution of (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>SCH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub> in dimethylformamide gave a nearly instantaneous precipitation of tetramethylammonium iodide with accompanying formation of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> which was precipitated by dilution of the solution with water, recrystallized from aqueous acetone, and identified by infrared analysis.

**B<sub>10</sub>H<sub>8</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—Chlorine was passed into a solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (4.0 g., 16.5 mmoles) in 40 ml. of acetonitrile. The reaction temperature rose to 71°, and chlorination was continued until the temperature fell to 30°. The solution was poured into 200 ml. of water causing the separation of a grease. This was removed and solidified by brief trituration in boiling water. Extraction of the solid with three 50-ml. portions of boiling ethanol gave three crops of crystals, total weight 1.7 g. The last crop, 0.8 g. (14%), m.p. 314-317° (uncor.), was B<sub>10</sub>H<sub>8</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. *Anal.* Calcd. for B<sub>10</sub>H<sub>8</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 11.6;

H, 3.6; B, 26.3; Cl, 42.9; S, 15.5. Found: C, 11.8; H, 3.8; B, 25.7; Cl, 43.9; S, 14.7.

**B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—Chlorine was passed into a solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (10 g., 41.7 mmoles) in 75 ml. of acetonitrile. The solution refluxed spontaneously. When it began to cool, heat was applied to maintain reflux, and chlorination was continued an additional 7 hr. A crystalline solid (A, m.p. 359° (uncor.), 0.5 g.) separated during the chlorination. This was removed by filtration; the filtrate was concentrated to 30 ml. and then poured into 200 ml. of water. A white solid precipitated and was separated into three crystalline fractions (B, m.p. 340–359° (uncor.), 1.0 g.; C, m.p. 368–369° (uncor.), 4.5 g.; D, m.p. 360–361° (uncor.), 1.6 g.) by successive extractions with ethanol–water, with ethanol–water–acetonitrile, and, finally, with hot acetonitrile to which ethanol–water was added at the boiling point until the cloud point was reached. Fractions A and D (the least soluble fractions) had identical infrared spectra, different from those of fractions B and C. Fractions C and D both analyzed for B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and are assumed to be isomers. *Anal.* Calcd. for B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 10.7; H, 3.14; B, 24.2; Cl, 47.6; S, 14.5. Found: (C) C, 12.0; H, 3.3; B, 24.3; S, 13.8; (D) C, 11.2; H, 3.2; B, 25.0; Cl, 47.9; S, 14.0.

**B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub><sup>2-</sup>.**—A solution of B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1 g., 2.2 mmoles) in tributylphosphine (8 ml.) was heated to 195° under nitrogen for 20 min. The mixture was cooled and the supernatant tributylphosphine was decanted. The residue was washed with benzene and dissolved in methanol. Addition of this solution to alcoholic tetramethylammonium hydroxide precipitated [(CH<sub>3</sub>)<sub>4</sub>N]<sub>2</sub>B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub>, which was recrystallized from water. *Anal.* Calcd. for [(CH<sub>3</sub>)<sub>4</sub>N]<sub>2</sub>B<sub>10</sub>H<sub>2</sub>Cl<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub>: B, 19.1; S, 11.3; N, 5.0. Found: B, 18.8; S, 11.3; N, 5.4.

**B<sub>10</sub>H<sub>7</sub>Br[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—Bromine (6.7 g., 42 mmoles) was added to a solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (10 g., 41.7 mmoles) in 40 ml. of dichloromethane. The bromine reacted rapidly. Evaporation of the solution left an almost white solid which was extracted with five successive portions of propanol to obtain the following crystalline fractions: A, m.p. 205–208° (uncor.), 1.0 g.; B, m.p. 215–217° (uncor.), 1.2 g.; C, m.p. 222–224° (uncor.), 6.8 g.; D, m.p. 225–227° (uncor.), 3.18 g.; E, m.p. 230–233° (uncor.), 1.45 g. The infrared spectra of all these fractions were similar. Fractions D and E (total yield 4.6 g., 34%) were found by analysis to be B<sub>10</sub>H<sub>7</sub>Br[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. *Anal.* Calcd. for B<sub>10</sub>H<sub>7</sub>Br[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 15.1; H, 6.0; B, 33.8; Br, 25.0; S, 20.0. Found: (D) C, 15.4; H, 6.2; B, 34.5; Br, 25.2; S, 20.2; (E) B, 33.3; Br, 24.4.

**B<sub>10</sub>H<sub>6</sub>Br<sub>2</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—A solution of bromine (15 g., 94 mmoles) in 75 ml. of acetonitrile was added to a solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (10 g., 41.7 mmoles) in 75 ml. of acetonitrile. The solution was refluxed for 30 min., added to 300 ml. of methanol, and filtered. The filtrate was chilled in Dry Ice, precipitating 7.7 g. of B<sub>10</sub>H<sub>6</sub>Br<sub>2</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>; an additional 4 g. was obtained by concentration of the mother liquors to 30 ml. After recrystallization from aqueous methanol it had m.p. 193–195° (uncor.). *Anal.* Calcd. for B<sub>10</sub>H<sub>6</sub>Br<sub>2</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: B, 27.1; Br, 40.2; S, 16.1. Found: B, 27.2; Br, 41.3; S, 16.2. There was no ultraviolet absorption maximum in acetonitrile solution.

**B<sub>10</sub>H<sub>5</sub>Br<sub>3</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—A solution of bromine (15 g., 94 mmoles) in 75 ml. of acetonitrile was added to a solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (10 g., 41.7 mmoles) in 75 ml. of acetonitrile. The reaction solution was refluxed 30 min.; an additional 13 g. (81 mmoles) of bromine in 50 ml. of acetonitrile was added and refluxing was resumed for 16 hr. The solution was concentrated to 100 ml. and filtered to obtain a tan solid which was extracted with two 20-ml. portions of hot acetonitrile. A small amount of crystals, m.p. 277° (uncor.), separated upon cooling. The extraction residue was recrystallized from 100 ml. of hot acetonitrile to obtain a second crop of crystals, m.p. 282° (uncor.). A third crop, m.p. 281° (uncor.), was obtained by the addition of water to the mother liquors at the boiling point until the cloud point was reached and then allowing the solution to cool. The total yield was 1.5 g. (8%). The crystals with m.p. 282° were ana-

lyzed. *Anal.* Calcd. for B<sub>10</sub>H<sub>5</sub>Br<sub>3</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 10.0; H, 3.6; B, 22.7; S, 13.4. Found: C, 10.8; H, 3.8; B, 23.1; S, 13.2. Ultraviolet λ<sub>max</sub><sup>CH<sub>3</sub>CN</sup> 220 mμ (ε 10,000), shoulder at 255 mμ (ε 1050).

**B<sub>10</sub>H<sub>7</sub>I[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.**—Iodine monochloride (6.8 g., 41 mmoles) in 75 ml. of dichloromethane was added to a solution of B<sub>10</sub>H<sub>8</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (10 g., 41.7 mmoles) in 100 ml. of dichloromethane. The solution was stirred for 3 hr., concentrated to 20 ml., and added to 250 ml. of ethanol with stirring. A gummy solid separated. Two recrystallizations of this solid from ethanol gave 1.6 g. (10.5%) of B<sub>10</sub>H<sub>7</sub>I[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, m.p. 195–198° (uncor.). *Anal.* Calcd. for B<sub>10</sub>H<sub>7</sub>I[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: C, 13.1; H, 5.2; B, 29.5; I, 34.7; S, 17.5. Found: C, 13.9; H, 5.5; B, 29.9; I, 33.6; S, 17.8.

**B<sub>10</sub>H<sub>8</sub>IS(CH<sub>3</sub>)<sub>2</sub><sup>-</sup>.**—A solution of iodine (8.1 g., 32 mmoles) in 25 ml. of dimethylformamide was added to a solution of CsB<sub>10</sub>H<sub>8</sub>S(CH<sub>3</sub>)<sub>2</sub> (10 g., 32 mmoles) in 110 ml. of dimethylformamide. The iodine color disappeared after 5 min. stirring, and the solution was added with stirring to 500 ml. of aqueous tetramethylammonium hydroxide. The resulting precipitate of (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>I·S(CH<sub>3</sub>)<sub>2</sub> was recrystallized from water to obtain a final yield of 7.3 g. (61%). *Anal.* Calcd. for (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>I·S(CH<sub>3</sub>)<sub>2</sub>: C, 19.0; H, 6.9; B, 28.5; S, 8.5; I, 33.5. Found: C, 19.3; H, 6.9; B, 27.8; S, 8.5; I, 34.5.

There was no ultraviolet absorption maximum in acetonitrile. The B<sup>11</sup> n.m.r. in water solution (after conversion to a sodium salt by ion exchange) had poorly resolved irregular broad peaks in the apical and equatorial regions. Proton decoupling affected the apical (as well as the equatorial) peak considerably, showing the presence of apical B–H in at least a large portion of the product. The iodine must, therefore, be largely on equatorial boron atoms.

**1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OH<sup>-</sup>.**—Cs[2-B<sub>10</sub>H<sub>9</sub>OCH=N(CH<sub>3</sub>)<sub>2</sub>] (12.5 g., 38.8 mmoles) was dissolved in 50 ml. of dimethyl sulfoxide. Concentrated hydrochloric acid (18 ml.) was added, and the solution was warmed on a steam bath for 5 min. and poured into 250 ml. of water. Five grams of a solid, presumably 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OCH=N(CH<sub>3</sub>)<sub>2</sub>, precipitated. This was separated and then dissolved in 50 ml. of 10% aqueous sodium hydroxide with stirring. This solution was filtered; the addition of excess cesium hydroxide solution to the filtrate precipitated a low yield of Cs-1,6-B<sub>10</sub>H<sub>8</sub>OH·S(CH<sub>3</sub>)<sub>2</sub> which was recrystallized from water before analysis. *Anal.* Calcd. for CsB<sub>10</sub>H<sub>8</sub>OH·S(CH<sub>3</sub>)<sub>2</sub>: C, 7.3; H, 4.6; B, 32.9; S, 9.8. Found: C, 6.5; H, 4.3; B, 32.6; S, 9.5. The use of Cs<sub>2</sub>[2-B<sub>10</sub>H<sub>9</sub>OCHO] in place of Cs[2-B<sub>10</sub>H<sub>9</sub>OCH=N(CH<sub>3</sub>)<sub>2</sub>] in the above reaction led to the same product. The anion was also characterized as a tetramethylammonium salt. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>8</sub>OH·S(CH<sub>3</sub>)<sub>2</sub>: C, 26.7; H, 10.0; B, 40.1; N, 5.2; S, 11.9. Found: C, 26.8; H, 9.9; B, 39.7; N, 5.2; S, 11.8. The presence of the hydroxyl group was established by a sharp O–H stretching absorption at 3600 cm.<sup>-1</sup>.

**1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OS(CH<sub>3</sub>)<sub>2</sub>.**—Cs<sub>2</sub>[2-B<sub>10</sub>H<sub>9</sub>OH] (9.4 g., 23.5 mmoles), dimethyl sulfoxide (50 ml.), and 12 ml. of concentrated hydrochloric acid were mixed and heated on a steam bath for 40 min. The mixture was filtered, and the filtrate was poured into 200 ml. of water to precipitate 1.0 g. (16%) of 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OS(CH<sub>3</sub>)<sub>2</sub>. The analytical sample was recrystallized from 50% aqueous ethanol. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OS(CH<sub>3</sub>)<sub>2</sub>: C, 18.8; H, 7.8; B, 42.1; S, 25.0. Found: C, 19.3; H, 8.2; B, 42.0; S, 25.4. This compound can also be prepared under the same reaction conditions using Cs<sub>2</sub>[2-B<sub>10</sub>H<sub>9</sub>OCHO] or Cs[1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OH] in place of Cs<sub>2</sub>[2-B<sub>10</sub>H<sub>9</sub>OH]. Refluxing a mixture of 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OS(CH<sub>3</sub>)<sub>2</sub> and aqueous sodium hydroxide until a clear solution was formed, followed by addition of cesium chloride, gave Cs[1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OH], identified by infrared analysis. The position of attachment of the labile methyl sulfide is shown by the absence of O–H stretching absorption in the infrared spectrum of 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>OS(CH<sub>3</sub>)<sub>2</sub>.

**(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>COC<sub>6</sub>H<sub>5</sub><sup>-</sup>.**—[(CH<sub>3</sub>)<sub>4</sub>N]<sub>2</sub>B<sub>10</sub>H<sub>9</sub>COC<sub>6</sub>H<sub>5</sub> (5 g., 13.5 mmoles) was slurried in 50 ml. of glacial acetic acid. Dimethyl sulfoxide (2.1 g., 28 mmoles) was added. The mixture was placed in an ice–water bath and hydrogen chloride was passed into it for 5 min. at 12–23° during which a clear, dark red solu-

tion formed. Pouring this solution into 400 ml. of water precipitated 3.5 g. of an orange solid. This was dissolved in a small amount of acetone, and the solution was poured into aqueous potassium hydroxide. The resulting cloudy solution was filtered, and the addition of aqueous thallium nitrate to the filtrate precipitated  $\text{TlB}_{10}\text{H}_5\text{COC}_6\text{H}_5\cdot\text{S}(\text{CH}_3)_2$  as a light yellow solid. This was recrystallized from water on a steam bath; it appeared to decompose in boiling water. *Anal.* Calcd. for  $\text{TlB}_{10}\text{H}_5\text{COC}_6\text{H}_5\cdot\text{S}(\text{CH}_3)_2$ : C, 22.2; H, 3.9; B, 22.0; S, 6.5. Found: C, 23.0; H, 4.4; B, 22.7; S, 7.4.

**1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N<sub>2</sub>.**—A solution of  $\text{Na}[1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2]$  (26 g., 130 mmoles) and sodium nitrite (45 g., 650 mmoles) in 100 ml. of water was prepared and cooled in an ice-water bath. Hydrochloric acid (130 ml. of 3.6 M) was added slowly with stirring. The mixture foamed, became dark brown, and a solid separated. *This solid is explosive and is extremely sensitive. It should be kept moist at all times and, if allowed to dry, should not be scraped or handled in amounts larger than a few milligrams.* The mixture was filtered. The filter cake was dissolved in methanol and sodium borohydride was added slowly with stirring to the dark methanol solution until the color became very light yellow. The methanol solution was concentrated to 100 ml. and added to 400 ml. of water to precipitate 8 g. (30%) of 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N<sub>2</sub>. The analytical sample was recrystallized from ethanol, dec. pt. 165–172°. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N<sub>2</sub>: C, 11.6; H, 6.8; B, 52.5; N, 13.6; mol. wt., 206. Found: C, 12.2; H, 7.3; B, 52.4; N, 14.0; mol. wt., 201 (b.p. in ethylene chloride). Ultraviolet  $\lambda_{\text{max}}$  252 m $\mu$  ( $\epsilon$  20,600).

The infrared spectrum includes absorptions for B–H at 2515 cm.<sup>-1</sup> and for N≡N at 2240 cm.<sup>-1</sup>. The H<sup>1</sup> n.m.r. spectrum in deuterioacetone consists of a single sharp peak at  $\tau$  7.28.

The B<sup>11</sup> resonance spectrum in acetone-*d* consists of a peak at approximately 0 p.p.m. and a very broad one at 1.3 p.p.m. overlapping an apparent 1:2:1 triplet at 33.3, 39.2, and 44.2 p.p.m. Decoupling affects the triplet but not the two low-field peaks. Integration is obscured by overlapping, but approximate intensity ratios for the two low-field peaks and the triplet are 1.2:1.3:7.5. The 0 p.p.m. peak is assigned to an apical boron attached to sulfur, the 1.3 p.p.m. peak, because of its very broad character, is assigned to a boron (apical) attached to nitrogen, and the triplet to two overlapping doublets each representing four equatorial hydrogen-bonded boron atoms. The addition of excess aqueous cesium fluoride to the filtrate from the crude reaction mixture precipitated 3.5 g. (18%) of Cs[1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NO] as a yellow solid. The analytical sample was recrystallized from water. *Anal.* Calcd. for Cs(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NO: C, 7.0; H, 4.1; B, 31.7; Cs, 39.0; N, 4.1. Found: C, 7.6; H, 4.5; B, 31.0; Cs, 37.6; N, 4.5. Ultraviolet  $\lambda_{\text{max}}$  257 m $\mu$  ( $\epsilon$  6900). Cs[1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NO] is impact sensitive.

The proton resonance of this salt in (CD<sub>3</sub>)<sub>2</sub>SO shows a single sharp resonance at  $\tau$  7.27. The B<sup>11</sup> resonance spectrum of the corresponding sodium salt in D<sub>2</sub>O has single peaks, which do not decouple, at 0.36 and 8.6 p.p.m. and a doublet, which does decouple, at 43.8 p.p.m. ( $J$  = 132 c.p.s.). The intensity ratio of the two low-field peaks to the high-field doublet is 1.8 to 8.2, establishing the apical positions of the substituents.

An increased yield of 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N<sub>2</sub> was obtained by using acetic acid in place of hydrochloric acid. A solution of  $\text{Na}[1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2]$  (3.5 g., 17.3 mmoles), sodium nitrite (10 g., 145 mmoles), and 60 ml. of water was prepared. Glacial acetic acid (5 ml., 87 mmoles) was added over a period of 1–2 min.; the solution was stirred 10 min. and then filtered. The filter cake (the cautions above regarding this explosive intermediate also apply here) was extracted several times with alcohol. An alcohol-insoluble residue was dissolved in glyme. The alcohol and glyme solutions were each stirred with zinc dust and a small amount of hydrochloric acid until they were light green in color. They were then filtered into an excess of water to precipitate a total of 2.3 g. (64%) of 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N<sub>2</sub>. This yield was reproducible. In control runs with hydrochloric acid, the yields of the diazonium product were 25–30%. Thin-layer chromatog-

raphy of the crude product on silica gel (ethylene chloride) showed the presence of only one isomer.

**(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NC<sub>5</sub>H<sub>5</sub>.**—A solution of 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N<sub>2</sub> (2.4 g., 11.6 mmoles) in 75 ml. of pyridine was refluxed for 16 hr. Nitrogen (260 ml., 92%) was evolved. The solution was stirred into 400 ml. of water. The addition of 75 ml. of 12 M hydrochloric acid to the solution precipitated 1.9 g. (64%) of (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NC<sub>5</sub>H<sub>5</sub>. The analytical sample was recrystallized from aqueous glyme, m.p. 266–268°. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>S-B<sub>10</sub>H<sub>5</sub>NC<sub>5</sub>H<sub>5</sub>: C, 32.7; H, 7.4; B, 42.0; N, 5.4. Found: C, 33.6; H, 7.4; B, 41.4; N, 5.5. Ultraviolet  $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$  318 m $\mu$  ( $\epsilon$  8700), 232 m $\mu$  ( $\epsilon$  9300).

**1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH<sub>3</sub>.**—A mixture of Cs[1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NO] (0.5 g., 1.5 mmoles), zinc dust, and dilute hydrochloric acid was heated on a steam bath for 30 min. and filtered while still hot. Crystalline 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH<sub>3</sub> separated from the filtrate on cooling. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH<sub>3</sub>: C, 12.3; H, 8.7; N, 7.2. Found: C, 11.9; H, 9.1; N, 7.1.

**1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>3</sub>.**—To a refluxing solution of 120 mg. of 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH<sub>3</sub> in 30 ml. of water was added 5 ml. of 10% sodium hydroxide solution and 0.6 ml. of dimethyl sulfate. Tetrahydrofuran (15 ml.) was added to retard precipitation of incompletely methylated products, and three more additions of 5 ml. of 10% sodium hydroxide and 0.6 ml. of dimethyl sulfate were made. The mixture was concentrated *in vacuo*, and the resulting slurry was filtered to give 120 mg. of 1,10-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>3</sub> as a tan solid. Recrystallization from ethanol-acetone gave off-white crystals with m.p. 268.5–269.5° (cor.). *Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>3</sub>: C, 25.3; H, 9.8; S, 13.5. Found: C, 25.0; H, 9.7; S, 13.3.

The infrared spectrum of the product shows no absorption attributable to N–H and differs markedly from the spectra of 1,2-, 1,6-, and 2,7(8)-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>3</sub>.

The H<sup>1</sup> n.m.r. spectrum of the product in chloroform-*d* shows two peaks at  $\tau$  6.38 (relative intensity 1.5) and 6.92 (relative intensity 1) which can be assigned to apical N(CH<sub>3</sub>)<sub>3</sub> and apical S(CH<sub>3</sub>)<sub>2</sub>, respectively.

The B<sup>11</sup> n.m.r. spectrum (19.2 Mc.) of the product shows two single peaks at –4.9 and +14.2 p.p.m. (unaffected by double irradiation) and a large doublet at 45.4 p.p.m. ( $J$  = 134 c.p.s.) which collapses to a single peak on irradiation at 60 Mc. The –4.9 p.p.m. peak can be assigned to one N(CH<sub>3</sub>)<sub>3</sub>-substituted apical boron atom, and the +14.2 p.p.m. peak can be assigned to one S(CH<sub>3</sub>)<sub>2</sub>-substituted apical boron atom. The 45.4 p.p.m. doublet can be assigned to the eight unsubstituted equatorial boron atoms.

Thin-layer chromatography of 1,10-, 2,7(8)-, 1,6-, and 1,2-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>3</sub> on silica gel using 2% acetonitrile in ethylene chloride gave  $R_f$  values of 0.62, 0.61, 0.56, and 0.21, respectively.

**1,2- and 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub>.**—A mixture of 1.67 g. (7.1 mmoles) of (CH<sub>3</sub>)<sub>2</sub>N[2-B<sub>10</sub>H<sub>9</sub>NH(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>2,6,7</sup> 9.5 ml. of dimethyl sulfoxide, and 3.1 ml. of concentrated aqueous hydrochloric acid was heated on a steam bath for 45 min., cooled, and poured into ice-water. Filtration gave 1.34 g. of (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub>. The crude solid was extracted with warm ethylene chloride, leaving 160 mg. (10%) of undissolved 1,2-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub>. Recrystallization from acetonitrile-ethanol gave crystals with m.p. 286–288°. The X-ray powder pattern of the product agrees well with the calculated values from a single crystal study of 1,2-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub>.<sup>16</sup>

The ethylene chloride extract was chromatographed on 150 g. of acid-washed alumina (Woelm). Elution with ethylene chloride gave 810 mg. (51%) of 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub>. Later fractions gave oils. Recrystallization from acetone-ethanol gave crystals with m.p. 221–222.5°. *Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub>: C, 21.5; H, 9.5; B, 48.5; N, 6.3; S, 14.4. Found: C, 21.2; H, 10.0; B, 48.8; N, 6.3; S, 14.4.

The B<sup>11</sup> n.m.r. spectrum (19.2 Mc.) of 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>5</sub>NH(CH<sub>3</sub>)<sub>2</sub> in acetonitrile solution shows a multiplet at 17 p.p.m. which can be assigned to a (CH<sub>3</sub>)<sub>2</sub>S-substituted apical boron atom (single peak) and an unsubstituted apical boron atom (doublet).

This multiplet can be decoupled by irradiating at 60 Mc. to give a single peak at 17 p.p.m. A peak at 27.3 p.p.m. represents a  $(\text{CH}_3)_2\text{NH}$ -substituted equatorial boron atom and cannot be decoupled. A multiplet at 42 and 47.6 p.p.m. which can be decoupled to a single peak represents the seven remaining equatorial boron atoms. The intensity ratios of the 17:27.3:47.6 p.p.m. peaks are 2:0.93:7.1 (theory requires 2:1:7).

**1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ . Method A.**—A mixture of 1 g. (5.13 mmoles) of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}_3$ ,<sup>6</sup> 50 ml. of water, and 15 ml. of tetrahydrofuran was stirred at reflux and treated eight times with 5 ml. of 10% sodium hydroxide solution and 0.6 ml. of dimethyl sulfate. The mixture was concentrated under reduced pressure, and the resulting slurry was filtered to give 1.19 g. (98%) of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ . Two recrystallizations from methanol gave needles with m.p. 203.5–204.5°. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ : C, 25.3; H, 9.8; B, 45.6; N, 6.0; S, 13.5. Found: C, 25.2; H, 9.8; B, 46.3; N, 6.0; S, 13.5. The  $\text{H}^1$  n.m.r. spectrum of the product in acetonitrile- $d_3$  (external TMSi) shows two sharp peaks at  $\tau$  7.19 (relative intensity 1) and 7.52 (relative intensity 1.5) due, respectively, to apical  $\text{S}(\text{CH}_3)_2$  and equatorial  $\text{N}(\text{CH}_3)_3$ .

The  $\text{B}^{11}$  n.m.r. spectrum (19.2 Mc.) of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  shows a multiplet at 16.3 and 21.1 p.p.m. which can be assigned to one  $(\text{CH}_3)_2\text{S}$ -substituted apical boron atom, one unsubstituted apical boron atom (doublet), and one  $(\text{CH}_3)_2\text{N}$ -substituted equatorial boron atom. A 43.6 p.p.m. multiplet can be assigned to the remaining seven unsubstituted equatorial boron atoms. The intensity ratio of the 16.3 + 21.1 p.p.m. multiplet: 43.6 p.p.m. multiplet is 2.9:7.1 (theory requires 3:7). On irradiation at 60 Mc. the 43.6 p.p.m. multiplet collapses to a single sharp peak, and the low-field multiplet gives a peak at 18.5 p.p.m., which may be assigned to the two apical boron atoms, and a peak at 24.7 p.p.m., which then represents the substituted equatorial boron atom.

**Method B.**—A mixture of 160 mg. of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}(\text{CH}_3)_2$ , 30 ml. of water, 10 ml. of tetrahydrofuran, and 2 pellets of sodium hydroxide was stirred at reflux and treated three times with 10 ml. of 10% sodium hydroxide and 1.2 ml. of dimethyl sulfate. The mixture was concentrated under reduced pressure, and the resulting slurry was filtered to give 177 mg. of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ . Recrystallization from methanol-benzene gave needles with m.p. 201.5–202.5°, mixture melting point with sample prepared above 202–203°. The X-ray powder patterns of the two samples are identical.

**1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ .**—A mixture of 80 mg. of 1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}(\text{CH}_3)_2$ , 15 ml. of water, and 5 ml. of tetrahydrofuran was stirred at reflux and treated three times with 5 ml. of 10% sodium hydroxide solution and 0.6 ml. of dimethyl sulfate. The solution was concentrated under reduced pressure, and the resulting slurry was filtered to give 65 mg. of 1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ . Recrystallization from acetonitrile-ethanol gave crystals with m.p. 267.5–268°.

Thin-layer chromatography on silica gel (2% acetonitrile in ethylene chloride) showed that the 1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  ( $R_f$  0.22) thus obtained was free of the 1,6- isomer ( $R_f$  0.64).

**$(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  from 2- $\text{B}_{10}\text{H}_8\text{N}(\text{CH}_3)_3^-$ .**—A solution of 21 g. of  $(\text{CH}_3)_4\text{N}[2-\text{B}_{10}\text{H}_8\text{N}(\text{CH}_3)_3]$  in 120 ml. of dimethyl sulfoxide and 40 ml. of 12 *N* hydrochloric acid was heated on a steam bath for 45 min. The solution was cooled and poured into a large volume of cold water, and the precipitate was collected by filtration to give 16.1 g. of crude  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ . A portion (12 g.) of the crude product was chromatographed on 1000 g. of acid-washed alumina (Woelm, activit ygrade I). Elution with 2:1 benzene-ethylene chloride gave in the first 10 250-ml. fractions 185 mg. of 2,7(8)- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ , then in 15 250-ml. fractions 2.69

g. of a mixture of isomers, then in 69 250-ml. fractions 5.99 g. of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ . Elution with four 250-ml. portions of ethylene chloride gave 710 mg. of an isomeric mixture, then six 250-ml. portions gave 438 mg. of 1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ .

2,7(8)- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  was recrystallized twice from ethanol to give crystals with m.p. 251–253°. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ : C, 25.3; H, 9.8; B, 45.6. Found: C, 24.9; H, 9.8; B, 45.5.

The  $\text{H}^1$  n.m.r. spectrum of the product in acetonitrile- $d_3$  (external TMSi) shows two peaks at  $\tau$  7.52 (relative intensity 1.5) and 7.87 (relative intensity 1) corresponding, respectively, to equatorial  $\text{N}(\text{CH}_3)_3$  and equatorial  $\text{S}(\text{CH}_3)_2$ . No splitting of the  $\tau$  7.87 peak occurred at temperatures as low as  $-25^\circ$ .

The  $\text{H}^1$  n.m.r. spectrum of the product in chloroform- $d$  shows three peaks at  $\tau$  7.22 (relative intensity 1.6), 7.60 (relative intensity 0.5), and 7.64 (relative intensity 0.5).

1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  was recrystallized from acetone-ethanol to give needles with m.p. 203–204° (cor.). The infrared spectrum of the product is identical with that of authentic 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ .

1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  was recrystallized from acetonitrile-ethanol to give plates with m.p. 267.5–268° (bubbling). *Anal.* Calcd. for  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$ : C, 25.3; H, 9.8; B, 45.6; N, 5.9; S, 13.5. Found: C, 25.1; H, 10.0; B, 46.0; N, 5.9; S, 13.4. The infrared spectrum and X-ray powder pattern of the product are identical with those of the 1,2- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{N}(\text{CH}_3)_3$  prepared above. The  $\text{H}^1$  n.m.r. spectrum of the product in acetonitrile- $d_3$  (external TMSi) shows two peaks at  $\tau$  7.19 (relative intensity 1) and 7.54 (relative intensity 1.5) corresponding to apical  $\text{S}(\text{CH}_3)_2$  and equatorial  $\text{N}(\text{CH}_3)_3$ , respectively.

**1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}=\text{CH}-p-\text{C}_6\text{H}_4\text{Cl}$ .**—To a solution of 185 mg. (0.95 mmoles) of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}_3$  and 140 mg. (1 mmole) of *p*-chlorobenzaldehyde in 15 ml. of ethanol was added 12 drops of 10% aqueous sodium hydroxide. A deep yellow color formed. Several drops of acetic acid was added, and the crystals which gradually separated were collected by filtration to give 135 mg. of yellow crystals. Recrystallization from ethanol-acetonitrile gave 70 mg. of yellow plates, m.p. 282–284° dec. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}=\text{CHC}_6\text{H}_4\text{Cl}$ : C, 34.0; H, 6.3; B, 34.1; N, 4.4; Cl, 11.2. Found: C, 33.9; H, 6.5; B, 34.8; N, 4.6; Cl, 11.0, 11.6.

The ultraviolet spectrum of the product in acetonitrile showed absorption maxima ( $m\mu$ ) at 370 (sh,  $\epsilon$  8280), 297 ( $\epsilon$  12,580), and 272 ( $\epsilon$  12,480).

The infrared spectrum of the product showed absorption at 3200 ( $\text{N}-\text{H}$  str.), 1620, and 1565  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$ ,  $\text{N}-\text{H}$  def., and/or aromatic).

**1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}=\text{CH}-p-\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ .**—To a warm solution of 185 mg. (0.95 mmole) of 1,6- $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}_3$  and 150 mg. (1 mmole) of *p*-dimethylaminobenzaldehyde in 15 ml. of ethanol was added 5 drops of 5% ethanolic sodium hydroxide. A deep yellow color formed. Two drops of acetic acid was added. The resulting precipitate was collected by filtration to give 285 mg. of a yellow solid. Recrystallization from acetonitrile gave yellow crystals. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{NH}=\text{CHC}_6\text{H}_4\text{N}(\text{CH}_3)_2$ : C, 40.5; H, 8.0; B, 33.2; N, 8.6. Found: C, 40.8; H, 8.2; B, 33.1; N, 8.6.

The infrared spectrum of the product shows absorption at 3220 ( $\text{N}-\text{H}$  str.), 1612, 1570, and 1515  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$ , aromatic, and/or  $\text{N}-\text{H}$  def.).

**Acknowledgment.**—We wish to thank Mr. Eugene Pier of Varian Associates for the 100 Mc./sec.  $\text{H}^1$  n.m.r. spectrum and for the 32 Mc./sec.  $\text{B}^{11}$  n.m.r. spectrum of 2,7(8)- $\text{B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2$ .