Chemistry of Boranes. XIV. Amination of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with Hydroxylamine-O-sulfonic Acid

By W. R. Hertler and M. S. Raasch

$B_{10}H_{10}^{-2}$ reacts with aqueous hydroxylamine-O-sulfonic acid to give 2-$B_{10}H_9NH_3^-$ (I) and 2,4-, 2,3-, and 2,7(8)-$B_{10}H_8(NH_3)_2$ (II). Under similar conditions $B_{12}H_{12}^{-2}$ gives $B_{12}H_{11}NH_3^-$ (III) and 1,2-, 1,7-, and 1,12-$B_{12}H_{10}(NH_3)_2$ (IV). The high basicity of amino derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ is reflected in their ready formation of conjugate acid, even under alkaline conditions. Amination of 1-$B_{10}H_9S(CH_3)_2^-$ and $B_{12}H_{11}N$-$(CH_3)_3^-$ gives, respectively, 1,6-$(CH_3)_2SB_{10}H_8NH_3$ and $(CH_3)_3NB_{12}H_{10}NH_3$ (predominantly 1,7- isomer). Methylation of I with dimethyl sulfate in alkaline solution can be controlled to give either 2-$B_{10}H_9NH(CH_3)_2^-$ or 2-$B_{10}H_9N(CH_3)_3^-$. Methylation of II gives 2,4-, 2,3-, and 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$. Predominant equatorial amination of $B_{10}H_{10}^{-2}$ is demonstrated with the aid of B^{11} magnetic resonance spectroscopy.

Introduction

The stable, polyhedral boron hydride anions $B_{10}H_{10}^{-2}$ [1,2] and $B_{12}H_{12}^{-2}$ [2,3] undergo a variety of substitution reactions, some of which are reminiscent of electrophilic aromatic substitutions. Examples are the halogenation of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ and the benzoylation of $B_{10}H_{10}^{-2}$.[2] The reactivity of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ toward electrophilic reagents generally exceeds that of all but the most reactive of aromatic compounds. Thus, chlorination or bromination of these anions normally produces polyhalogenated derivatives with ease.[2] The subject of the present paper is a study of the reaction of hydroxylamine-O-sulfonic acid with $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$.

Hydroxylamine-O-sulfonic acid long has been known as a reagent for direct introduction of amino groups into aromatic compounds,[4,5] but an acid catalyst, usually aluminum chloride, is normally required. Kovacic and Bennett[5,6] proposed that the mechanism for the amination of toluene involves electrophilic attack by a polarized hydroxylamine-O-sulfonate-aluminum chloride complex on the aromatic substrate,
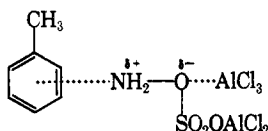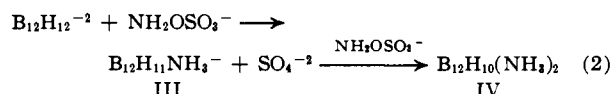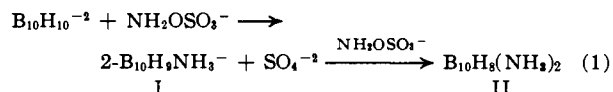

and evidence was presented against NH_2^+ as the attacking species. In the amination of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, by contrast, no acid catalyst is required, and the reaction can be carried out in aqueous solution at pH 7. This is consistent with the high order of reactivity of these borane anions toward electrophilic reagents (as compared with toluene, for example). Hydroxylamine-O-sulfonic acid has also been used as a reagent for preparing substituted hydrazines from amines, apparently via electrophilic attack on the amine.[7] Hydroxylamine-O-sulfonic acid has been

shown to behave as an electrophilic reagent toward iodide ion.[8]

Results

Hydroxylamine-O-sulfonic acid reacts smoothly with $B_{10}H_{10}^{-2}$ or $B_{12}H_{12}^{-2}$ in aqueous solution to give the corresponding mono or diamino derivatives which, because of their high basicity (vide infra), are readily isolated in the N-protonated forms (eq. 1 and 2).

$$B_{10}H_{10}^{-2} + NH_2OSO_3^- \longrightarrow$$
$$2\text{-}B_{10}H_9NH_3^- + SO_4^{-2} \xrightarrow{\ NH_2OSO_3^-\ } B_{10}H_8(NH_3)_2 \quad (1)$$
$$\text{I} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{II}$$

$$B_{12}H_{12}^{-2} + NH_2OSO_3^- \longrightarrow$$
$$B_{12}H_{11}NH_3^- + SO_4^{-2} \xrightarrow{\ NH_2OSO_3^-\ } B_{12}H_{10}(NH_3)_2 \quad (2)$$
$$\text{III} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{IV}$$

The $B_{10}H_8(NH_3)_2$ (II) which precipitates from the reaction solution is a mixture of two isomers the less soluble of which is 2,4-II, and the more soluble of which is 2,3-II. 1,10-$B_{10}H_8(NH_3)_2$, which was recently prepared by Knoth, Sauer, Miller, and Muetterties[9] from the reaction of ammonia with 1,10-$B_{10}H_8$-$(N_2)_2$ and from the reaction of hydroxylamine-O-sulfonic acid with 1,10-$B_{10}H_8(CO)_2$, differs from 2,4-II and 2,3-II in the positions of substitution, but chemically the compounds appear to be similar. The $B_{12}H_{10}$-$(NH_3)_2$ (IV) which is isolated from the reaction solution (eq. 2) is a mixture of two isomers, the less soluble of which is 1,12-IV (para) and the more soluble of which is 1,7-IV (meta) (see Fig. 1).

The presence of electronegative substituents on the B_{10} or B_{12} cage would be expected to render the anion less reactive than the corresponding unsubstituted cage[2,10] toward electrophilic attack by hydroxylamine-O-sulfonic acid. Nevertheless, it is possible to aminate 1-$B_{10}H_9S(CH_3)_2^{-2}$ and $B_{12}H_{11}N(CH_3)_3^-$ [11] with hydroxylamine-O-sulfonic acid to give, respectively, 1,6-$(CH_3)_2SB_{10}H_8NH_3$ (V) and $(CH_3)_3NB_{12}H_{10}NH_3$ (VI) according to eq. 3 and 4.

$$1\text{-}B_{10}H_9S(CH_3)_2^- + NH_2OSO_3^- \longrightarrow$$
$$1,6\text{-}(CH_3)_2SB_{10}H_8NH_3 + SO_4^{-2} \quad (3)$$
$$\text{V}$$
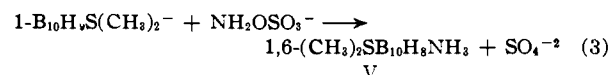
(1) M. F. Hawthorne and A. R. Pitochelli, J. Am. Chem. Soc., 81, 5519 (1959).

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

(3) M. F. Hawthorne and A. R. Pitochelli, ibid., 82, 3228 (1960).

(4) R. N. Keller and P. A. S. Smith, ibid., 66, 1122 (1944); 68, 899 (1946).

(5) P. Kovacic and R. P. Bennett, ibid., 83, 221 (1961).

(6) P. Kovacic, R. P. Bennett, and J. L. Foote, ibid., 84, 759 (1962).

(7) P. Gosl and A. Meuwsen, Chem. Ber., 92, 2521 (1959), and references cited therein.

(8) P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, J. Am. Chem. Soc., 86, 1139 (1964).

(9) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, ibid., 86, 115 (1964).

(10) For example, iodination of $B_{12}H_{12}^{-2}$ proceeds 2.07 × 10² times faster than iodination of $B_{12}H_{11}N(CH_3)_3^-$ (unpublished results).

(11) H. C. Miller, N. E. Miller, and E. L. Muetterties, J. Am. Chem. Soc., 85, 3885 (1963).
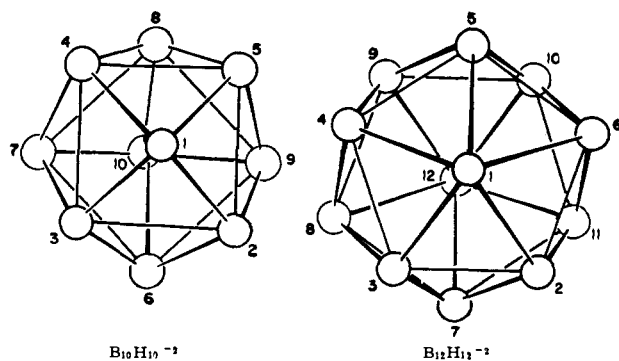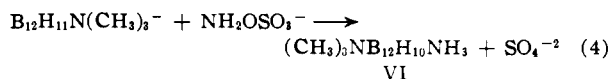
$B_{10}H_{10}^{-2}$ $B_{12}H_{12}^{-2}$

Figure 1.

$$B_{12}H_{11}N(CH_3)_3^- + NH_2OSO_3^- \longrightarrow$$
$$(CH_3)_3NB_{12}H_{10}NH_3 + SO_4^{-2} \quad (4)$$
$$VI$$

The reaction of $2\text{-}B_{10}H_9NH_3^-$ with dimethyl sulfoxide and hydrochloric acid[2] gives $(CH_3)_2SB_{10}H_8NH_3$, which is identical in all respects with V.

Properties.—The most striking property of the aminated boron hydride anions I–VI is the high basicity of the conjugate bases. This characteristic has already been noted for the conjugate base of $B_{10}H_9NH\text{-}(CH_3)_2^-$.[2] The N-protonated forms of these amino compounds can be isolated directly from alkaline solution. The weakly acidic proton, however, can be removed rapidly and efficiently by sodium hydride in an inert solvent. The basicity of these amino derivatives may be attributed to the powerful electron-donating ability of the B_{10} and B_{12} cages. The high order of basicity observed for amino derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ contrasts sharply with the non-basicity of $B_{20}H_{18}NH_2^{-3}$ reported by Wiesboeck.[12] The oxidative instability reported for $B_{20}H_2Cl_{16}NH_2^{-3}$ also contrasts with the stability (to air) of amino derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$. The reasons for such gross differences in properties is not immediately obvious.

Isolation of $2\text{-}B_{10}H_9NH_3^-$ and $B_{12}H_{11}NH_3^-$ is normally accomplished by precipitation from aqueous solution as a sparingly soluble, high melting tetramethylammonium or cesium salt. The neutral derivatives (in the acid form) such as $1,6\text{-}(CH_3)_2SB_{10}H_8NH_3$ (V) and $2,4\text{-}B_{10}H_8(NH_3)_2$ (II) are sparingly soluble in water and are generally high melting (above $300°$) with the exception of V which melts at $285°$. The various isomers of II and IV differ markedly in their water solubility.

Alkylation.—Methylation of the amino–boron hydride anions can be accomplished readily with dimethyl sulfate in alkaline solution. Thus, treatment of $2\text{-}B_{10}H_9NH_3^-$ with dimethyl sulfate in refluxing aqueous sodium hydroxide gives $2\text{-}B_{10}H_9NH(CH_3)_2^-$ (VII) which was prepared earlier by another method.[2] Under more forcing conditions a third methyl group is introduced giving $2\text{-}B_{10}H_9N(CH_3)_3^-$ (VIII).

Methylation of neutral species such as II, IV, V, and VI is facile, and the permethylated products are invariably highly insoluble in water, thus permitting near-quantitative isolation. This feature is quite valuable in permitting isolation of methylated derivatives of highly soluble isomers of II and IV.

Identification of Products. Derivatives of $B_{12}H_{12}^{-2}$. —The reaction of $B_{12}H_{12}^{-2}$ with hydroxylamine-O-

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

sulfonic acid gives two isolable isomers of $B_{12}H_{10}\text{-}(NH_3)_2$ (IV) which we may temporarily designate IVA (water insoluble) and IVB (water soluble). Each of these isomers reacts with dimethyl sulfate and sodium hydroxide in aqueous tetrahydrofuran (eq. 5) to give an isomeric $B_{12}H_{10}[N(CH_3)_3]_2$ (IX) which we can

$$B_{12}H_{10}(NH_3)_2 + (CH_3)_2SO_4 \xrightarrow{NaOH} B_{12}H_{10}[N(CH_3)_3]_2 \quad (5)$$
$$IV \qquad\qquad\qquad\qquad\qquad\qquad IX$$
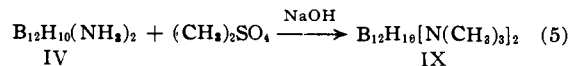
designate IXA (m.p. $>450°$) and IXB (m.p. $378°$), respectively. If, instead of isolating IVA and IVB from the reaction of $B_{12}H_{12}^{-2}$ with hydroxylamine-O-sulfonic acid, the entire reaction mixture is methylated with dimethyl sulfate, the IX thus obtained can be shown by thin layer chromatography (t.l.c.) on silica gel (methylene chloride solvent) to contain IXA (R_f 0.83), IXB (R_f 0.72), and a third isomer IXC which has an R_f of 0.16. Because of its relative insolubility in acetonitrile, it is possible to isolate IXC (m.p. $374°$ dec.) in pure form.

In seeking to make configurational assignments for the three isomers of $B_{12}H_{10}[N(CH_3)_3]_2$ it was found that B^{11} magnetic resonance was of little value since δ for the various kinds of unsubstituted boron atoms seems to be fairly constant (see Fig. 4). Fortunately, however, chemical correlation of one of the isomers (IXA) with a compound of known configuration was possible. The synthesis of $B_{12}H_{10}(CO)_2$ has recently been described.[9] The structure of the 1,12-isomer of $B_{12}H_{10}\text{-}(CO)_2$ has been elucidated by Babcock,[13] who performed an X-ray study of the corresponding acid salt, $Cs_2B_{12}H_{10}(COOH)_2 \cdot H_2O$. $1,12\text{-}B_{12}H_{10}(CO)_2$[9] reacts with hydroxylamine-O-sulfonic acid to give $1,12\text{-}B_{12}H_{10}\text{-}(NH_3)_2$, which is identical in all respects with IVA. Thus, IVA and IXA must have a 1,12-configuration. The assignments for IXB and IXC are based for the present on chemical intuition pending the completion of X-ray studies now in progress. The amination of $B_{12}H_{11}N(CH_3)_3^-$ with hydroxylamine-O-sulfonic acid would not be expected to produce $1,2\text{-}(CH_3)_3NB_{12}H_{10}\text{-}NH_3$ as the *predominant* isomer because of the bulk and powerful electron withdrawing ability of the $(CH_3)_3N^+$ substituent. Indeed, when $B_{12}H_{11}N(CH_3)_3^-$ is allowed to react with hydroxylamine-O-sulfonic acid and the reaction mixture then treated directly with dimethyl sulfate, the water-insoluble product can be shown by t.l.c. to contain predominantly IXB with very little IXA or IXC. The only product isolated in pure form (in good yield) from this reaction is IXB. On this basis, we assign a 1,7-configuration to IXB (and IVB) and a 1,2-configuration to IXC. These assignments are consistent with the observed mobilities in t.l.c. where the least polar isomer, $1,12\text{-}B_{12}H_{10}[N(CH_3)_3]_2$, has the highest R_f value and the most polar isomer, $1,2\text{-}B_{12}H_{10}[N(CH_3)_3]_2$, has the lowest R_f value.

Derivatives of $B_{10}H_{10}^{-2}$.—Magnetic resonance of B^{11} has been useful in making configurational assignments for substituted derivatives of $B_{10}H_{10}^{-2}$, and these assignments are described below. The amination of $B_{10}H_{10}^{-2}$ with hydroxylamine-O-sulfonic acid gives $2\text{-}B_{10}H_9NH_3^-$ (*vide infra*) and, in low yield, $B_{10}H_8(NH_3)_2$ (II). Recrystallization of the crude II from water

(13) K. Babcock, unpublished results. The authors are indebted to Mr. Babcock for permission to use these results prior to publication and to Dr. J. H. Balthis for a generous sample of isomerically pure $1,12\text{-}B_{12}H_{10}(CO)_2$.

gives pure $2,4-B_{10}H_8(NH_3)_2$ which reacts with dimethyl sulfate to give $2,4-B_{10}H_8[N(CH_3)_3]_2$ (2,4-X, eq. 6). A second isomer of II can be isolated from the

$$B_{10}H_8(NH_3)_2 + (CH_3)_2SO_4 \xrightarrow{\text{NaOH}} B_{10}H_8[N(CH_3)_3]_2 \quad (6)$$
$$\text{II} \qquad\qquad\qquad\qquad\qquad \text{X}$$
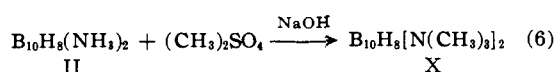
recrystallization liquors of 2,4-II. This isomer is assigned 2,3-stereochemistry (vide infra) since methylation gives an isomer of $B_{10}H_8[N(CH_3)_3]_2$ identified by B^{11} magnetic resonance as the 2,3- isomer. If, instead of isolating 2,4-II and 2,3-II, the entire reaction mixture is methylated with dimethyl sulfate, the X thus obtained is shown by t.l.c. on silica gel (methylene chloride solvent) to contain 2,4-X, 2,3-X, a third compound whose R_f value corresponds precisely to that of $2,7(8)-B_{10}H_8[N(CH_3)_3]_2$ which was recently prepared by another method,[14] and at least one unidentified component. A pure sample of 2,7(8)-X was isolated by chromatography on alumina. Unfortunately it is not possible at this time to estimate the relative amounts of 2,3-, 2,4-, and $2,7(8)-B_{10}H_8(NH_3)_2$ formed in the amination reaction.

N.m.r. Studies.[15] $2-B_{10}H_9NH_3^-$ and $2-B_{10}H_9N(CH_3)_3^-$. —The B^{11} n.m.r. spectrum of $B_{10}H_9N(CH_3)_3^-$ (VIII) clearly suggests that the compound is equatorially substituted with a minimum isomeric purity of 95%. The same assignment must apply to $B_{10}H_9NH_3^-$ (I) from which VIII was obtained in good yield. The B^{11} spectrum of VIII (see Fig. 2) shows a multiplet with maxima at $+14.8$ and $+22.8$ p.p.m. (with a high-field shoulder) and a larger multiplet at higher field with maxima at $+40$, $+45.8$, and $+51.4$ p.p.m. The low-field multiplet may be assigned to two unsubstituted apical boron atoms (two doublets) and a substituted equatorial boron atom (singlet). The high-field multiplet then represents the remaining unsubstituted equatorial boron atoms. The observed intensity ratio for the two multiplets of $2.7:7.3$ compares with a theoretical value of $3:7$. When the B^{11} spectrum is observed while irradiating at 60 Mc., the low-field multiplet collapses to a somewhat broad peak with a low-field shoulder. The components of the high-field multiplet decouple separately. The observed shift to low field by the substituted boron atom is consistent with similar shifts to low field observed for the substituted boron atoms in the B^{11} spectra of $B_{12}H_{11}N(CH_3)_3^-$ (Fig. 3) and $1,7-B_{12}H_{10}-[N(CH_3)_3]_2$ (Fig. 4) in which the substituted boron atoms are shifted -17.8 and -17.9 p.p.m., respectively, relative to the unsubstituted boron atoms. In agreement with this interpretation, the B^{11} spectrum of $1,10-B_{10}H_8[N(CH_3)_3]_2$[16] shows a somewhat broad singlet at $+0.68$ p.p.m. corresponding to the substituted apical boron atoms and a doublet at $+47.1$ p.p.m. ($J = 132$ c.p.s.) representing the eight unsubstituted equatorial boron atoms. Thus, the absence of any resonance in the vicinity of 0.68 p.p.m. in the B^{11} spectrum of VIII precludes any apical substitution (within the limits of sensitivity of the instrument) in the material isolated. It is, of course, possible that a small amount of 1-

(14) W. R. Hertler, *Inorg. Chem.*, **3**, 1195 (1964).

(15) The B^{11} n.m.r. spectra were determined at 19.25 Mc., and the chemical shifts are referred to external methyl borate. Decoupling experiments were performed with an NMR Specialties Model SD60 spin decoupler.

(16) This compound was prepared by methylation of $1,10-B_{10}H_8(NH_3)_2$, the preparation of which is given in ref. 9 (see Experimental section for details.)
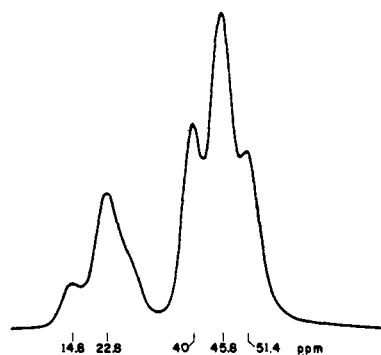
Fig. 2.—B^{11} n.m.r. spectrum of $(CH_3)_4N[2-B_{10}H_9N(CH_3)_3]$ in acetonitrile–dimethylformamide.
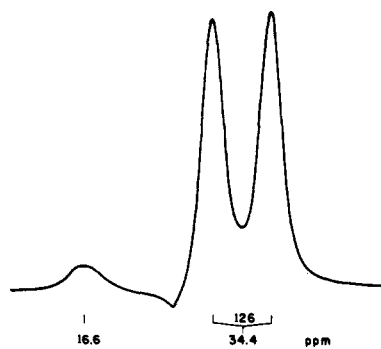

Fig. 3.—B^{11} n.m.r. spectrum of $(CH_3)_4NB_{12}H_{11}N(CH_3)_3$ in aqueous acetonitrile (J in c.p.s.).

$B_{10}H_9N(CH_3)_3^-$ or $1-B_{10}H_9NH_3^-$ was formed but was selectively lost during isolation or purification. Nevertheless, the conclusion seems inescapable that equatorial substitution of $B_{10}H_{10}^{-2}$ has occurred to a large extent.

The B^{11} spectrum of $B_{10}H_9NH_3^-$ is likewise in accord with an equatorial NH_3 group (see Fig. 5). The chemical shift to low field for the NH_3-substituted boron atom is considerably less than the shift observed for a $N-(CH_3)_3$-substituted boron atom. Thus, the two unsubstituted apical boron atoms appear as a doublet at $+20.6$ p.p.m. ($J = 146$ c.p.s.) which can be spin-decoupled to a singlet on irradiating at 60 Mc. The $+33.4$ p.p.m. peak can be assigned to the substituted equatorial boron atom since this peak cannot be decoupled. The high-field multiplet with a maximum at $+46.4$ p.p.m. can be assigned to the seven unsubstituted equatorial boron atoms. This multiplet can be decoupled to a single peak on irradiation at 60 Mc. The observed intensity ratio of the $+20.6$ p.p.m. peak to the sum of the $+33.4$ and the $+46.4$ p.p.m. peaks of $2:8$ is in agreement with theory. The B^{11} spectrum of $B_{12}H_{11}NH_3^-$ (Fig. 6) shows a shift of about -9.6 p.p.m. for the NH_3-substituted boron atom relative to the unsubstituted boron atoms (doublet at $+33.3$ p.p.m., $J = 135$ c.p.s.).

$1,6-(CH_3)_2SB_{10}H_8NH_3$ (V).—The amination of $1-B_{10}H_9S(CH_3)_2^-$ with hydroxylamine-O-sulfonic acid also gives predominantly equatorial amination. This is demonstrated chemically by the reaction of $2-B_{10}H_9-NH_3^-$ with dimethyl sulfoxide and hydrochloric acid which gives the same $(CH_3)_2SB_{10}H_8NH_3$. The orientation in V could be either 1,2 or 1,6, but the latter assignment seems preferable for steric and electronic reasons. X-Ray studies are in progress to determine

Fig. 4.—B^{11} n.m.r. spectrum of $1,7\text{-}B_{12}H_{10}[N(CH_3)_3]_2$ in aceto-nitrile–dimethylformamide (J in c.p.s.).
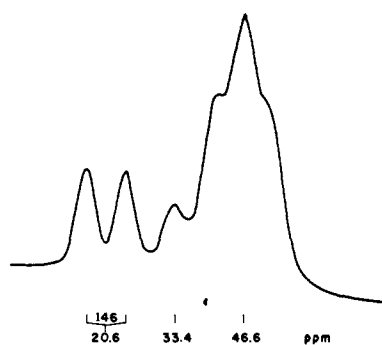

Fig. 5.—B^{11} n.m.r. spectrum of $NaB_{10}H_9NH_3$ in water (J in c.p.s.).

Fig. 6.—B^{11} n.m.r. spectrum of $NaB_{12}H_{11}NH_3$ in water (J in (c.p.s.).

Fig. 7.—B^{11} n.m.r. spectrum of $1,6\text{-}(CH_3)_2SB_{10}H_8NH_3$ in aceto-nitrile (J in c.p.s.).

the stereochemistry of V and related compounds. The B^{11} n.m.r. spectrum of V (Fig. 7) shows an unsymmetrical doublet at $+14.7$ p.p.m. ($J = 128$ c.p.s.) which represents an unsubstituted apical boron atom (doublet) and a $(CH_3)_2S$-substituted apical boron atom (singlet). This multiplet can be decoupled to a single peak on irradiating at 60 Mc. The lack of a significant chemical shift (relative to the unsubstituted apex), for the $(CH_3)_2S$-substituted boron atom is consistent with the B^{11} n.m.r. spectrum of $1\text{-}B_{10}H_9S(CH_3)_2^-$ in which the chemical shift for both apical boron atoms is nearly the same.[17] The $+35.2$ p.p.m. shoulder represents the NH_3-substituted equatorial boron atom and cannot be decoupled. The $+41.1$ and $+46.9$ p.p.m. peaks represent the remaining seven equatorial boron atoms and can be decoupled by irradiating at 60 Mc. The observed intensity ratio of the $+14.7$ p.p.m. peak to the sum of the 35.2, 41.1, and 46.9 p.p.m. peaks is 2:8 in agreement with theory.

2,3-$B_{10}H_8[N(CH_3)_3]_2$.—The methylated derivative of the more soluble isomer of $B_{10}H_8(NH_3)_2$ (II) is assigned 2,3-geometry on the basis of the B^{11} n.m.r. spectrum (Fig. 8 and 9) which is consistent with a structure in which both $N(CH_3)_3$ groups are equatorial since the observed intensity ratio of the low-field trio (16.7, 20.6, and 26.1 p.p.m. peaks) to the high-field quartet (34.8, 40.8, 47, and 53.9 p.p.m. peaks) is 3.4:6.6 (theory requires 3.5:6.5). Thus, the low-field group represents two substituted equatorial boron atoms, one unsubstituted apical boron atom, and one-half of another unsubstituted apical boron atom. This is clearly shown by a decoupling experiment (Fig. 9) in which the 26.1 and 34.8 p.p.m. peaks collapse to a single peak at 30.4 p.p.m. In this partially decoupled spectrum the intensity ratios of the 20.6 p.p.m. peak : 30.4 p.p.m. peak : 43.6 multiplet are 3:1.1:5.9 (theory requires 3:1:6) where the 20.6 p.p.m. peak represents a decoupled unsubstituted apical boron atom and two substituted equatorial boron atoms, the 30.4 p.p.m. peak represents a decoupled unsubstituted apical boron
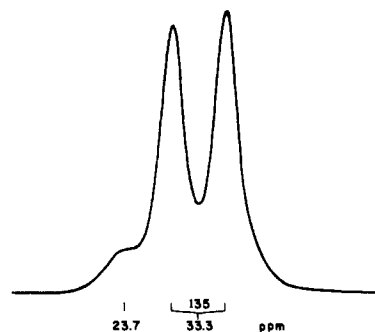
(17) Unpublished results.
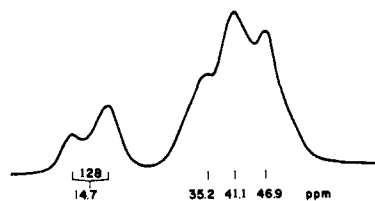
atom which is shifted to high field, and the 43.6 p.p.m. multiplet represents the remaining six unsubstituted equatorial boron atoms. The gross nonequivalence of the two apical doublets requires that the two substituents be on the *same equatorial belt*, *i.e.*, 2,3-, or $2,4\text{-}B_{10}H_8[N(CH_3)_3]_2$. The 2,3- isomer has only one equatorial boron atom which is adjacent to both of the substituted boron atoms (*i.e.*, B_6) and in view of the substantial high-field shift observed for the apical boron atom which is adjacent to both substituted boron atoms (*ca.* 13 p.p.m.), this unique equatorial boron atom might be expected to undergo a similar shift to high field. The 53.9 p.p.m. peak (Fig. 8) can be assigned to one-half of a doublet representing an unsubstituted equatorial boron atom shifted about 7 p.p.m. to high field. The intensity of the 53.9 p.p.m. peak seems more consistent with one-half of a boron atom than one boron atom (as would be required in a 2,4- isomer). Thus, the B^{11} n.m.r. spectrum is better interpreted in terms of a 2,3- isomer than a 2,4- isomer. Perhaps the smaller high-field shift for B_6 compared to the shift for B_1 is related to the shorter B–B bond distance which would be expected to exist between B_1 and the substituted boron atoms (B_2 and B_3) relative to the B–B bond distance between B_6 and the substituted boron atoms.[18] Similar chemical-shift behavior has been reported[19] in alkyldecaboranes in which 2,4-substitution produces a low-field shift of the 2,4-boron atoms and a high-field shift for the adjacent unsubstituted 6,9-boron atoms. Consistent with the 2,3-formulation, this isomer has by far the smallest chromatographic R_f value of all of the isomers of X now in hand (1,10-X has the highest R_f).

2,4-$B_{10}H_8[N(CH_3)_3]_2$.—The B^{11} n.m.r. spectrum of the methylated derivative of the least soluble isomer of II is more useful than the spectrum of II itself for making structural assignments because of the larger

(18) For a summary of bond distances in $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ based on X-ray studies, see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, pp. 16–18.

(19) R. L. Williams, I. Dunstan, and N. J. Blay, *J. Chem. Soc.*, 5006 (1960).
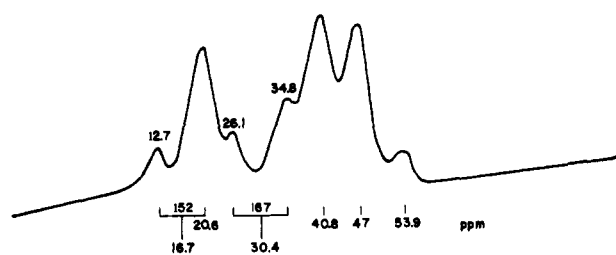
Fig. 8.—B^{11} n.m.r. spectrum of 2,3-$B_{10}H_8[N(CH_3)_3]_2$ in acetonitrile–tetrahydrofuran (J in c.p.s.).

Fig. 10.—B^{11} n.m.r. spectrum of 2,4-$B_{10}H_8[N(CH_3)_3]_2$ in acetonitrile–dimethylformamide (10:1) (J in c.p.s.).

Fig. 9.—B^{11} n.m.r. spectrum of 2,3-$B_{10}H_8[N(CH_3)_3]_2$—partially decoupled.
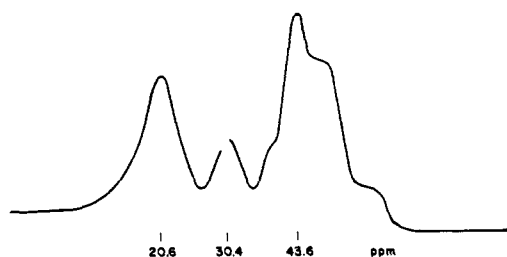

Fig. 11.—B^{11} n.m.r. spectrum of 2,4-$B_{10}H_8[N(CH_3)_3]_2$—partially decoupled.

chemical shifts observed in the former, and the stereochemistry of the two compounds should be identical. The B^{11} n.m.r. spectrum (Fig. 10 and 11) of $B_{10}H_8[N(CH_3)_3]_2$ is consistent with a structure in which both $N(CH_3)_3$ groups are equatorial since the observed intensity ratio of the low-field quartet (partially decoupled, Fig. 11) to the high-field multiplet is 4.2:5.8 (theory 4:6). Thus, the low-field quartet represents two substituted equatorial boron atoms and two unsubstituted apical boron atoms. Moreover, the two apical doublets display different chemical shifts, 16.9 (J = 139 c.p.s.) and ~29.2 p.p.m. ($J \sim$ 170 c.p.s.). This is clearly shown by a decoupling experiment (at 60 Mc.) in which the peaks at 24.8 and 33.6 p.p.m. collapse, and at a slightly different irradiating frequency the 13.3 and 20.5 p.p.m. peaks collapse. Presumably a broad singlet representing the two substituted equatorial boron atoms is buried near the center of the low-field quartet, accounting for the rise in the center of the quartet. The peaks at 40.2 and 46 p.p.m. can be decoupled to a single peak. The dissimilarity of the two apical doublets requires a structural assignment in which the two substituents are *on the same equatorial belt*, i.e., 2,3- or 2,4-$B_{10}H_8[N(CH_3)_3]_2$. Since the 2,3-assignment has already been used (*vide supra*) for another compound, we must tentatively assign this compound 2,4-stereochemistry pending completion of X-ray studies.

The lack of a well-resolved high-field peak representing one-half of a doublet corresponding to two equatorial boron atoms (B_3 and B_5) shifted to high field by two adjacent $N(CH_3)_3$-substituted boron atoms deserves comment. Although a shoulder on the high-field side of the 46 p.p.m. peak (Fig. 10) is apparent, the lack of resolution would indicate that the shift to high field is appreciably less than the ~7 p.p.m. observed for B_6 in 2,3-X and much less than the ~13 p.p.m. observed for B_1 in both 2,3-X and 2,4-X. This may be related to the fact that the B–B bond distances within an equatorial belt are probably greater than the distances between belts or between apex and belt.[18]
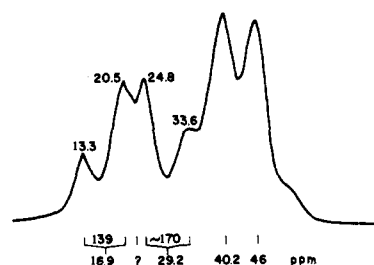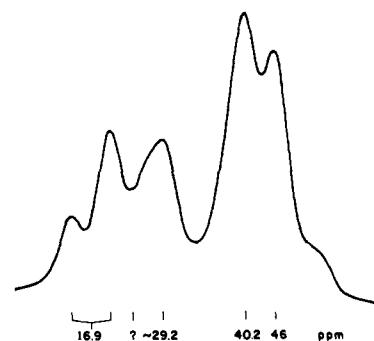
Discussion

Amination of $B_{10}H_{10}^{-2}$.—The stereochemistry of the products of amination of $B_{10}H_{10}^{-2}$ is of special importance since the reaction presumably can be classed as an electrophilic substitution, and both experimental[2] and theoretical[20] attention has been given to the stereochemistry of electrophilic substitution on $B_{10}H_{10}^{-2}$. It has been found, for instance, that acid-catalyzed deuterium exchange occurs somewhat more rapidly at the apical positions of $B_{10}H_{10}^{-2}$ than at the equatorial positions.[2,21,22] This exchange may be regarded as proceeding by electrophilic attack by D_3O^+. Reaction of $B_{10}H_{10}^{-2}$ with dimethyl sulfoxide in acid has given[2] 1-$B_{10}H_9S(CH_3)_2^-$, and this reaction may be regarded as an electrophilic attack by $(CH_3)_2SOH^+$. The reaction of $B_{10}H_{10}^{-2}$ with nitrous acid has likewise given predominantly apical substitution, presumably by an electrophilic substitution mechanism.[9] Hoffmann and Lipscomb[20] have made predictions of the order of sequential electrophilic substitution on $B_{10}H_{10}^{-2}$ based on simple LCAO–MO calculations of the ground state. From these calculations Hoffmann and Lipscomb predicted preferential electrophilic substitution at an apex of $B_{10}H_{10}^{-2}$. Preferential apical substitution (at position 10) was also predicted for 1-$B_{10}H_9X^{-2}$ regardless of the nature of X. The 'agreement of this simple treatment with the orientation observed in the above-cited examples of electrophilic substitutions of $B_{10}H_{10}^{-2}$ contrasts with the failure of this treatment to predict correctly the orientation observed in the reaction of hydroxylamine-O-sulfonic acid with $B_{10}H_{10}^{-2}$ and with 1-$B_{10}H_9S(CH_3)_2^-$ in which predominant equatorial attack seems to be the rule.

(20) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 520 (1962).
(21) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).
(22) A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

For purposes of discussion it must be assumed that polyhedral isomerizations of the type discussed by Kaczmarzcyk, Dobrott, and Lipscomb[22] do not occur *under normal reaction conditions* and that the stereochemistry of the products isolated represents the stereochemistry of the initially formed products. In support of this assumption, the various isomers of $B_{10}H_8[N-(CH_3)_3]_2$ have been shown to retain their identities under the reaction conditions to which they have been subjected in this report. The reported observation of the isomerization of a $B_{10}H_9OH^{-2}$ [22] has been shown to be erroneous.[23] At high temperatures (*ca.* $300°$), however, the various isomers of $B_{10}H_8[N(CH_3)_3]_2$ do undergo polyhedral isomerization and this is the subject of a forthcoming contribution. In the absencé of quantitative knowledge of the stereochemistry of amination of $B_{10}H_{10}^{-2}$, it is not possible to determine whether statistical substitution occurs to give 80% $2\text{-}B_{10}H_9NH_3^-$ and 20% $1\text{-}B_{10}H_9NH_3^-$ or whether the equatorial positions of $B_{10}H_{10}^{-2}$ have a higher reactivity than the apical positions which would result in >80% of $2\text{-}B_{10}H_9NH_3^-$ and <20% $1\text{-}B_{10}H_9NH_3^-$. However, the predominant equatorial substitution observed with hydroxylamine-O-sulfonic acid does not appear to be unique. Preliminary results with other electrophilic reagents indicate some generality for predominant equatorial electrophilic substitution of $B_{10}H_{10}^{-2}$. Details of these studies will be forthcoming soon.

Amination of $B_{12}H_{12}^{-2}$.—The predictions of Hoffmann and Lipscomb[20] for electrophilic substitution on a singly substituted derivative of $B_{12}H_{12}^{-2}$, $B_{12}H_{11}X^{-2}$, based on LCAO–MO calculations for the ground state can be summarized as follows. Where X is an inductive electron-withdrawing substituent, electrophilic substitution will occur at the 7 (*meta*) and 12 (*para*) positions (in a ratio of 5:1). Where X is a resonance electron-supplying substituent, electrophilic substitution will occur at position 2. These predictions are in accord with the reported predominant formation of $1,7\text{-}B_{12}H_{10}I_2^{-2}$ along with a small amount of $1,12\text{-}B_{12}H_{10}I_2^{-2}$ in the iodination of $B_{12}H_{12}^{-2}$, if in $B_{12}H_{11}I^{-2}$ the substituent is considered to exert an inductive electron-withdrawing effect.[24] Application of this treatment to the amination of $B_{12}H_{12}^{-2}$ with hydroxylamine-O-sulfonic acid requires that, since all three isomers of $B_{12}H_{10}(NH_3)_2$ (IV) are formed, both $B_{12}H_{11}NH_3^-$ and $B_{12}H_{11}NH_2^{-2}$ must be involved as intermediates, the former accounting for formation of 1,7- and 1,12-IV, and the latter accounting for formation of 1,2-IV. However, the observation that all three isomeric products are produced in the reaction of hydroxylamine-O-sulfonic acid with $B_{12}H_{11}N(CH_3)_3^-$, a compound in which the electrical effect of the substituent is unambiguous, suggests an alternative explanation; namely, that hydroxylamine-O-sulfonic acid, or some reactive species derived from it, is simply not very discriminating. Furthermore, in the transition state for the product-determining step steric effects do not seem to be of overwhelming importance.

In the absence of quantitative data regarding the relative amounts of isomers of II formed in the amination of $B_{12}H_{12}^{-2}$ it is not possible to ascertain whether an

$-NH_2$ group is really intervening as an "*ortho*-directing" substituent.

Experimental[25]

Materials.—Baker and Adamson hydroxylamine-O-sulfonic acid and Eastman Kodak practical grade dimethyl sulfate were used without further purification. Silica gel thin layer chromatography plates (5 × 20 cm.) were purchased from Custom Service Chemicals, Inc., of Wilmington, Del. The chromatograms were treated with palladium chloride in aqueous acetonitrile to detect the spots.

$(CH_3)_4N[2\text{-}B_{10}H_9NH_3]$ (I).—A cooled solution of 93 g. (0.6 mole) of $(NH_4)_2B_{10}H_{10}$ and 135 g. (1.2 mole) of hydroxylamine-O-sulfonic acid in 900 ml. of water was mixed with a solution ot 48 g. (1.2 moles) of sodium hydroxide in 300 ml. of water. The pH was adjusted to 6 by careful addition of more aqueous sodium hydroxide. The resulting solution was refluxed for 3.5 hr., cooled to room temperature, and treated with an excess of tetramethylammonium chloride. The resulting precipitate was recrystalized from water giving 46.5 g. (38%) of $(CH_3)_4NB_{10}H_9NH_3$ as colorless crystals. A sample was recrystallized one additional time from water for analysis giving crystals which do not melt to $405°$.

Anal. Calcd. for $B_{10}H_{24}C_4N_2$: B, 51.9; H, 11.6; C, 23.1; N, 13.4. Found: B, 51.9; H, 11.7; C, 22.4; N, 13.7.

The infrared spectrum of the product shows absorption at 3250 (NH str.), 1580 (NH def.), 1480, 950 (Me₄N⁺), and 1400 cm.⁻¹ (NH_3^+).

The ultraviolet spectrum of the product in water shows end absorption with no maximum.

2,4- and 2,3-$B_{10}H_8(NH_3)_2$ (II).—A solution of 15.4 g. (0.1 mole) of $(NH_4)_2B_{10}H_{10}$ and 22.6 g. (0.2 mole) of hydroxylamine-O-sulfonic acid in 150 ml. of water was neutralized by adding a solution of 8 g. (0.2 mole) of sodium hydroxide in 50 ml. of water. The solution was heated at $95°$ for 4 hr. and then was cooled to $4°$. $B_{10}H_8(NH_3)_2$ separated as a white crystalline solid which was collected by filtration. Two additional crops of the same product were obtained by concentrating the filtrate and cooling. The combined product (2.4 g., 16%) was recrystallized twice from water giving crystals of $2,4\text{-}B_{10}H_8(NH_3)_2$ which do not melt to $405°$.

Anal. Calcd. for $B_{10}H_{14}N_2$: B, 72.0; H, 9.4; N, 18.7. Found: B, 72.0; H, 8.5; N, 18.3.

The mother liquor from the final crop of product on treatment with a solution of 20 g. of tetramethylammonium chloride in 20 ml. of water gave 6.8 g. (32%) of $(CH_3)_4N[2\text{-}B_{10}H_9NH_3]$ which was purified by recrystallization from water and found to be identical with an authentic sample.

The mother liquor from the recrystallization of $2,4\text{-}B_{10}H_8(NH_3)_2$ was evaporated to dryness, and the residue was recrystallized twice from a small volume of water to give crystals of $2,3\text{-}B_{10}H_8(NH_3)_2 \cdot 0.5H_2O$, which do not melt to $360°$.

Anal. Calcd. for $B_{10}H_{14}N_2 \cdot 0.5H_2O$: B, 68.0; H, 9.5; N, 17.6. Found: B, 68.3; H, 9.6; N, 17.9.

The most prominent difference between the infrared spectra of 2,4-II and 2,3-II is the presence of a strong peak at 995 cm.⁻¹ and two moderate peaks at 3650 and 3550 cm.⁻¹ (water) in the latter spectrum.

$(CH_3)_4NB_{12}H_{11}NH_3$ (III).—A mixture of 8 g. (0.04 mole) of $Na_2B_{12}H_{12} \cdot 2H_2O$, 9 g. (0.079 mole)) of hydroxylamine-O-sulfonic acid, and 60 ml. of water was refluxed for 3 hr., cooled, and treated with tetramethylammonium chloride. The resulting precipitate was recrystallized from water to give 7.6 g. (82%) of $(CH_3)_4NB_{12}H_{11}NH_3$, which does not melt to $405°$. An additional crystallization from water followed by recrystallization from acetonitrile gave long needles of III.

Anal. Calcd. for $B_{12}H_{26}C_4N_2$: B, 55.9; H, 11.3; C, 20.8; N, 12.7. Found: B, 55.6; H, 11.3; C, 20.9; N, 12.2.

The infrared spectrum of the product shows absorption at 3240 (NH str.) and 1580 cm.⁻¹ (NH def.).

1,12- and 1,7-$B_{12}H_{10}(NH_3)_2$.—A solution of 67 g. (0.3 mole) of $Na_2B_{12}H_{12} \cdot 2H_2O$ and 102 g. (0.9 mole) of hydroxylamine-O-sulfonic acid in 250 ml. of water was neutralized by adding, below $25°$, a solution of 36 g. (0.9 mole) of sodium hydroxide in 100 ml. of water. The solution was heated cautiously until an exothermic reaction began (at about $70°$) and then cooled to moderate the reaction which continued for about 30 min. The solution was

(23) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *J. Am. Chem. Soc.*, **85**, 3704 (1963).

(24) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

cooled to 5° whereupon 9 g. (17%) of $B_{12}H_{10}(NH_3)_2$ precipitated as a white crystalline solid and was collected by filtration. An additional 7 g. (13%) of product precipitated when the filtrate was concentrated to one-half volume. Two recrystallizations of the first fraction from water gave 1,12-$B_{12}H_{10}(NH_3)_2$ as very sparingly soluble crystals.

Anal. Calcd. for $B_{12}H_{16}N_2$: B, 74.6; H, 9.27; N, 16.1. Found: B, 74.8; H, 9.20; N, 15.8.

Recrystallization of the second fraction from a relatively small volume of water gave crystalline 1,7-$B_{12}H_{10}(NH_3)_2$.

Anal. Found: B, 74.6; H, 8.50; N, 15.3.

1,12-$B_{12}H_{10}(NH_3)_2$ from 1,12-$B_{12}H_{10}(CO)_2$.—To an aqueous solution of 8.7 g. of 1,12-$B_{12}H_{10}(CO)_2$[9] was added portionwise 20 g. of hydroxylamine-O-sulfonic acid. When the evolution of gas ceased, the mixture was filtered, and the filter cake was recrystallized from 850 ml. of water to give 3.7 g. of 1,12-$B_{12}H_{10}(NH_3)_2$ as colorless crystals.

Anal. Calcd. for $B_{12}H_{16}N_2$: B, 74.6; H, 9.27; N, 16.1. Found: B, 73.8; H, 9.36; N, 15.7.

The X-ray powder pattern and infrared spectrum of the product are identical with those of the less soluble $B_{12}H_{10}(NH_3)_2$ described above.

1,6-$(CH_3)_2SB_{10}H_8NH_3$ (V). Method A.—A solution of 11.3 g. (0.1 mole) of hydroxylamine-O-sulfonic acid in 40 ml. of water was neutralized by adding a solution of 5.3 g. (0.05 mole) of anhydrous sodium carbonate in 20 ml. of water. This solution was added to a solution of 15 g. (0.069 mole) of $K[1-B_{10}H_9S(CH_3)_2]$ in 100 ml. of water. The mixture was heated at 95° for 2 hr. and then was cooled to about 4°. The semicrystalline mass that separated was isolated by filtration and recrystallized from ethanol-propanol to give 4 g. (41%) of 1,6-$(CH_3)_2SB_{10}H_8NH_3$ as colorless crystals, m.p. 282.5-283.5° (cor.).

Anal. Calcd. for $B_{10}H_{17}C_2NS$: B, 55.4; H, 8.77; C, 12.3; N, 7.17; S, 16.4. Found: B, 54.9; H, 8.55; C, 12.4; N, 7.35; S, 16.6.

The infrared spectrum of the product shows absorption at 3250 (NH str.) and 1590 cm.$^{-1}$ (NH def.).

Method B.—A solution of 2.09 g. of $(CH_3)_4N[2-B_{10}H_9NH_3]$ (0.01 mole) in 12 ml. of dimethyl sulfoxide and 4 ml. of concentrated hydrochloric acid was heated on a steam bath for 45 min. and then poured into ice-cold aqueous ammonium chloride. The oil which formed was removed by decantation, and the aqueous solution on standing for several hours deposited 380 mg. (20%) of crystals of $(CH_3)_2SB_{10}H_8NH_3$. After two recrystallizations from water the resulting needles had m.p. 283-285° (cor.). This product is identical with that obtained by method A above with respect to infrared spectrum, X-ray powder pattern, and mixture melting point.

$(CH_3)_3NB_{12}H_{10}NH_3$ (VI).—A solution of 13 g. (0.058 mole) of $NaB_{12}H_{11}N(CH_3)_3$ and 11.3 g. (0.1 mole) of hydroxylamine-O-sulfonic acid in 75 ml. of water was treated with a solution of 4 g. (0.1 mole) of sodium hydroxide in 25 ml. of water, and the pH was adjusted to 6. After refluxing for 3 hr. the mixture was cooled and filtered to give 6.5 g. (52%) of white solid. Recrystallization from aqueous methanol gave 4 g. of crystals of $(CH_3)_3NB_{12}H_{10}$-NH_3. Further recrystallization from acetonitrile-benzene gave crystals which do not melt to 360°.

Anal. Calcd. for $B_{12}H_{22}C_2N_2$: B, 60.1; H, 10.3; N, 10.3; C, 16.7. Found: B, 59.3; H, 10.2; N, 13.0; C, 17.4.

The infrared spectrum of the product shows absorption at 3250 (NH str.), 1590 (NH def.), and 1490 cm.$^{-1}$ (Me_3N^+).

$(CH_3)_4N[2-B_{10}H_9NH(CH_3)_2]$.—A mixture of 1.04 g. (0.005 mole) of $(CH_3)_4N[2-B_{10}H_9NH_3]$ and 50 ml. of water was heated to reflux and treated 5 times at 15-min. intervals with 4 ml. of 10% aqueous sodium hydroxide and 0.5 ml. of dimethyl sulfate. Then 20 ml. of 10% aqueous sodium hydroxide was added, and refluxing was continued for 1 hr. Evaporation of the solvent under reduced pressure followed by treatment of the residue with aqueous tetramethylammonium chloride gave 400 mg. (34%) of white solid. Recrystallization from water gave 200 mg. of needles of $(CH_3)_4N[2-B_{10}H_9NH(CH_3)_2]$.

Anal. Calcd. for $B_{10}H_{28}C_5N_2$: B, 45.8; H, 11.9; C, 30.5; N, 11.9. Found: B, 46.1; H, 11.9; C, 30.4; N, 11.7.

The infrared spectrum of the product shows absorption at 3230 cm.$^{-1}$ (NH str.). The X-ray powder pattern of the product shows it to be identical with the $(CH_3)_4NB_{10}H_9NH(CH_3)_2$ prepared from the reaction of $B_{10}H_{10}^{-2}$ with dimethylformamide.[2]

$(CH_3)_4N[2-B_{10}H_9N(CH_3)_3]$.—An aqueous solution of 37 g. (0.178 mole) of $(CH_3)_4N[2-B_{10}H_9NH_3]$ was passed through a column filled with a strong acid ion-exchange resin (Rexyn RG 50-H),

and the acidic effluent was concentrated under reduced pressure to a volume of 350 ml. and made alkaline to litmus by addition of sodium hydroxide. The resulting solution was then heated at reflux and treated 25 times at 6-min. intervals with 50 ml. of 10% aqueous sodium hydroxide and 6 ml. of dimethyl sulfate. Then 10 g. of sodium hydroxide was added, and refluxing was continued for 10 min. The resulting solution was concentrated under reduced pressure to a volume of 500 ml., filtered, and treated with tetramethylammonium chloride. The resulting precipitate was collected and recrystallized from water to give 27.1 g. (61%) of $(CH_3)_4N[2-B_{10}H_9N(CH_3)_3]$ as colorless plates, m.p. >360°.

Anal. Calcd. for $B_{17}H_{37}C_0N_2$: B, 43.2; H, 12.1; C, 33.6; N, 11.2. Found: B, 43.2; H, 12.2; C, 34.0; N, 11.1.

1,12-$B_{12}H_{10}[N(CH_3)_3]_2$.—A refluxing solution of 500 mg. of 1,12-$B_{12}H_{10}(NH_3)_2$ in a mixture of 250 ml. of water and 10 ml. of 10% aqueous sodium hydroxide was treated five times at 10-min. intervals with 20 ml. of 10% aqueous sodium hydroxide solution and 2.4 ml. of dimethyl sulfate. Then 100 ml. of tetrahydrofuran was added, and while the resulting mixture was refluxing two more additions of 20 ml. of 10% sodium hydroxide solution and 2.4 ml. of dimethyl sulfate were made. The resulting mixture was concentrated to a small volume under reduced pressure, and the resulting slurry was filtered to give 660 mg. (89%) of 1,12-$B_{12}H_{10}[N(CH_3)_3]_2$. The product was purified by recrystallization from acetone-ethanol. The resulting crystals did not melt to 450°.

Anal. Calcd. for $B_{12}H_{28}C_6N_2$: B, 50.3; H, 10.9; C, 27.9; N, 10.9. Found: B, 50.7; H, 10.8; C, 28.2; N, 10.5.

1,7-$B_{12}H_{10}[N(CH_3)_3]_2$. A. From 1,7-$B_{12}H_{10}(NH_3)_2$.—A refluxing solution of 380 mg. of 1,7-$B_{12}H_{10}(NH_3)_2$ in 50 ml. of water and 10 ml. of 10% aqueous sodium hydroxide was treated twice with 20 ml. of 10% sodium hydroxide solution and 2.4 ml. of dimethyl sulfate. Then 50 ml. of tetrahydrofuran was added and refluxing was continued while three more additions of 20 ml. of 10% sodium hydroxide solution and 2.4 ml. of dimethyl sulfate were made at 5-min. intervals. The resulting mixture was concentrated under reduced pressure, and the resulting slurry was filtered to give 530 mg. (94%) of 1,7-$B_{12}H_{10}[N(CH_3)_3]_2$. The product was purified by recrystallization from acetone-ethanol which gave crystals of m.p. 376-378.5°.

Anal. Calcd. for $B_{12}H_{28}C_6N_2$: B, 50.3; H, 10.9; C, 27.9; N, 10.9. Found: B, 50.7; H, 11.0; C, 28.4; N, 10.9.

B. From $(CH_3)_3NB_{12}H_{10}NH_3$ (VI).—A refluxing solution of 1.4 g. (0.0065 mole) of $(CH_3)_3NB_{12}H_{10}NH_3$ in 50 ml. of water and 50 ml. of tetrahydrofuran was treated ten times at 10-min. intervals with 5 ml. of 10% aqueous sodium hydroxide and 0.6 ml. of dimethyl sulfate. Then 20 ml. of 10% sodium hydroxide solution was added, and refluxing was continued for 10 min.

The resulting mixture was concentrated under reduced pressure to one-half volume, and filtration of the resulting suspension gave 1.44 g. (86%) of crystals of 1,7-$B_{12}H_{10}[N(CH_3)_3]_2$. Recrystallization from ethanol-acetonitrile gave 880 mg. of crystals, m.p. 377-378°.

Anal. Calcd. for $B_{12}H_{28}C_6N_2$: B, 50.3; H, 10.9; C, 27.9; N, 10.9. Found: B, 50.3; H, 10.8; C, 28.1; N, 11.1.

The infrared spectrum and X-ray powder pattern of the product are identical with those of the product prepared by method A and different from those of 1,12- and 1,2-$B_{12}H_{10}[N(CH_3)_3]_2$.

1,2-$B_{12}H_{10}[N(CH_3)_3]_2$.—A solution of 11.2 g. of $Na_2B_{12}H_{12}$ and 17 g. of hydroxylamine-O-sulfonic acid in 50 ml. of water was neutralized with a solution of 6 g. of sodium hydroxide in 16 ml. of water, and the pH was adjusted to 6. The mixture was heated until an exothermic reaction began, and gentle refluxing was maintained for 30 min. by alternate cooling and warming. Then the solution was made alkaline with sodium hydroxide to destroy unreacted hydroxylamine-O-sulfonic acid. The mixture was boiled briefly to expel ammonia and was then diluted to 150 ml. with water and treated with 130 ml. of tetrahydrofuran. The resulting mixture was refluxed and treated four times with 16 ml. of 10% sodium hydroxide solution and 2 ml. of dimethyl sulfate at 5-min. intervals, and then eight times with 32 ml. of 10% sodium hydroxide solution and 4 ml. of dimethyl sulfate. The mixture was concentrated under reduced pressure, and the resulting slurry was filtered to give 7.43 g. of white solid. Thin layer chromatography of the product on silica gel using methylene chloride shows three substances, two of which correspond to 1,12- and 1,7-$B_{12}H_{10}[N(CH_3)_3]_2$ (R_f 0.83 and 0.72, respectively) and a third substance with R_f 0.16. In addition there is ionic or decomposition material which does not migrate from the origin.

To a solution of 1 g. of the product in ethylene chloride was added, dropwise, carbon tetrachloride to incipient precipitation.

Then acetonitrile was added, and the resulting solid was collected and washed with acetonitrile to give 125 mg. of white solid. Recrystallization from acetonitrile gave plates of 1,2-$B_{12}H_{10}$-[N(CH_3)$_3$]$_2$·CH_3CN, m.p. 373–374° dec.

Anal. Calcd. for $B_{12}H_{28}C_8N_3$·CH_3CN: B, 43.4; H, 10.4; C, 32.2; N, 14.0. Found: B, 43.7; H, 10.5; C, 32.4; N, 13.8.

2,4-$B_{10}H_8$[N(CH_3)$_3$]$_2$.—A refluxing solution of 1 g. (0.0067 mole) of 2,4-$B_{10}H_8$(NH_3)$_2$ in 50 ml. of water was treated seven times at 15-min. intervals with 4 ml. of 10% sodium hydroxide solution and 0.5 ml. of dimethyl sulfate. Then 20 ml. of 10% sodium hydroxide solution was added and refluxing continued for 15 min. The resulting mixture was cooled and filtered to give 1.19 g. (76%) of 2,4-$B_{10}H_8$[N(CH_3)$_3$]$_2$ as a white solid. Two recrystallizations from aqueous acetonitrile gave crystals with m.p. 307–308° (cor.).

Anal. Calcd. for $B_{10}H_{26}C_6N_2$: B, 46.1; H, 11.2; C, 30.7; N, 12.0; mol. wt., 234. Found: B, 46.6; H, 11.1; C, 30.9; N, 12.0; mol. wt., 231 (X-ray).

The infrared spectrum of the product shows absorption at 1490 cm.$^{-1}$ (Me_3N^+).

2,3-$B_{10}H_8$[N(CH_3)$_3$]$_2$.—A solution of 150 mg. of 2,3-$B_{10}H_8$-(NH_3)$_2$·$0.5H_2O$ in 15 ml. of water was heated at reflux and treated twice with 5 ml. of 10% aqueous sodium hydroxide and 0.6 ml. of dimethyl sulfate. After cooling, the precipitate was collected by filtration to give 210 mg. of colorless solid. Recrystallization from acetone–ethanol gave plates of 2,3-$B_{10}H_8$[N(CH_3)$_3$]$_2$, m.p. 238–239° (cor.).

Anal. Calcd. for $B_{10}H_{26}C_6N_2$: B, 46.1; H, 11.2; C, 30.7; N, 12.0; mol. wt., 234. Found: B, 46.3; H, 11.3; C, 30.4; N, 12.0; mol. wt., 231 (X-ray).

The infrared spectrum of the product differs from those of 2,4-II, 2,7(8)-II, and 1,10-II in the "fingerprint region."

2,7(8)-$B_{10}H_8$[N(CH_3)$_3$]$_2$.—A solution of 15.4 g. (0.1 mole) of (NH_4)$_2B_{10}H_{10}$ and 22.6 g. (0.2 mole) of hydroxylamine-O-sulfonic acid in 150 ml. of water was neutralized to pH 6 with a solution of 8 g. of sodium hydroxide in 50 ml. of water. The resulting solution was refluxed for 4 hr. and then treated with 16 g. of sodium hydroxide to destroy any unreacted hydroxylamine-O-sulfonic acid. The resulting solution was boiled until virtually all of the ammonia was expelled and then while refluxing treated with 3 ml. of dimethyl sulfate. Then, while refluxing, the mixture was treated four times at 5-min. intervals with 40 ml. of 10% aqueous sodium hydroxide and 4.8 ml. of dimethyl sulfate. Then 150 ml. of tetrahydrofuran was added and the resulting mixture was treated at reflux eight times at 5-min. intervals with 40 ml. of 10% sodium hydroxide and 4.8 ml. of dimethyl sulfate. The resulting mixture was concentrated under reduced pressure to *ca.* 300 ml., and the resulting precipitate was collected by filtration to give 13.7 g. of off-white solid (58.5% calculated as $B_{10}H_8$-

[N(CH_3)$_3$]$_2$). Thin layer chromatography of a sample of the product on silica gel using methylene chloride showed the presence of three substances (measured against known specimens) corresponding to 2,3-X, 2,4-X, and 2,7(8)-X. In addition, there was some presumably ionic or decomposition material which was not displaced from the origin and indication of substances with mobility slightly less than that of 2,4-X.

A 2-g. sample of the crude product was dissolved in ethylene chloride (350 mg. of insoluble material was removed) and chromatographed on 150 g. of acid-washed alumina (Woelm activity grade I) to give in the earliest fraction (six 50-ml. portions of ethylene chloride) 350 mg. of 2,7(8)-$B_{10}H_8$[N(CH_3)$_3$]$_2$ which after recrystallization from acetone–ethanol was identical with 2,7(8)-$B_{10}H_8$[N(CH_3)$_3$]$_2$ prepared from 2,7(8)-$B_{10}H_8$[N(CH_3)$_2CH_2Cl$]$_2$.[14] Later fractions contained other incompletely separated isomers of X.

1,10-$B_{10}H_8$[N(CH_3)$_3$]$_2$.—A refluxing solution of 690 mg. (0.0046 mole) of 1,10-$B_{10}H_8$(NH_3)$_2$[9] in 35 ml. of water was treated seven times at 10-min. intervals with 4 ml. of 10% aqueous sodium hydroxide and 0.5 ml. of dimethyl sulfate. The mixture was cooled and filtered giving 645 mg. (60%) of 1,10-$B_{10}H_8$[N(CH_3)$_3$]$_2$ as a pale tan solid. Recrystallization from aqueous acetone gave crystals of m.p. 286–288° (cor.).

Anal. Calcd. for $B_{10}H_{26}C_6N_2$: B, 46.1; H, 11.2; C, 30.7; N, 12.0. Found: B, 46.7; H, 11.2; C, 30.0; N, 12.4.

The infrared spectrum of the product shows absorption at 1480 cm.$^{-1}$ (Me_3N^+) and differs in the "fingerprint" region from the spectra of 2,3-X, 2,4-X, and 2,7(8)-X.

Stereochemistry of Amination of $B_{12}H_{11}N(CH_3)_3^-$.—A solution of 500 mg. of (CH_3)$_4NB_{12}H_{11}N(CH_3)_3$ in aqueous acetonitrile (5:1) was passed through a column of sodium cation-exchange resin. The effluent was evaporated to a volume of 15 ml. and treated with 1 g. of hydroxylamine-O-sulfonic acid. The pH was adjusted to 6 by addition of sodium hydroxide, and the resulting solution was refluxed for 3 hr. Then the solution was made alkaline with sodium hydroxide to destroy residual hydroxylamine-O-sulfonic acid and the mixture was boiled to expel ammonia. The volume was adjusted to 75 ml. by addition of water and the resulting solution was heated at reflux and treated three times with 0.8 ml. of 10% sodium hydroxide solution and 0.1 ml. of dimethyl sulfate. Then 30 ml. of tetrahydrofuran was added and the resulting mixture heated at reflux while treating three times with 5 ml. of 10% sodium hydroxide solution and 0.6 ml. of dimethyl sulfate. The resulting solution was concentrated under reduced pressure, and the resulting slurry was filtered to give 280 mg. of pale tan solid.

Thin layer chromatography of the product on silica gel (methylene chloride solvent) showed the presence of 1,2-, 1,7-, and 1,12-$B_{12}H_{10}$[N(CH_3)$_3$]$_2$ with the 1,7- isomer apparently predominating