

by some nonspecific poisoning effect of its gross structure.

In summary, we believe that these data indicate that the irreversible inhibition of adenosine deaminase by XII is not a random bimolecular process but proceeds through an initial reversible E-I complex which is dependent on the gross structure of the inhibitor. The enzyme is then irreversibly inhibited by alkylation within the E-I complex by the bromoacetamido moiety of XII with the resultant formation of a relatively

stable covalent bond between the enzyme and inhibitor. The inhibitor which is covalently bound to the enzyme may then exert its inhibitory effect on the enzymic reaction by any one of a number of processes, *e.g.*, the enzyme-bound inhibitor may prevent, for steric reasons, the approach of the substrate to the enzyme, or the enzyme-bound inhibitor may cause a conformational change in the enzyme with the result that there no longer exists an attraction of the substrate to the enzyme.

## Boron Hydride Anions. I. Nitrogen Mustards<sup>1,2</sup>

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Received November 5, 1965

Reactions of carbonyl-containing boron hydrides, 1,12-B<sub>12</sub>H<sub>10</sub>(CO)<sub>2</sub> and 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>CO, with amines, in work directed toward the synthesis of boron cage compounds containing a nitrogen mustard moiety, have shown the high polarizability of the carbonyl group. This is demonstrated by infrared spectra, the nucleophilicity of the carbonyl oxygen, and the facile hydrolysis of amides and esters. Synthesis of a nitrogen mustard containing boron hydride was accomplished by acylation of the decahydrodecaborate anion.

Use of boron-10 neutron-capture therapy in the treatment of brain tumors has been unsuccessful to date.<sup>3</sup> Failure to a great extent has resulted from an inability to incorporate a boron compound into the tumor without concomitantly high levels in the surrounding tissues, such as normal brain, muscle, and more especially blood. To overcome these difficulties, the concept of developing compounds which have two moieties: one, a "handle" for incorporation into tumors, and two, a neutron absorber, was tried,<sup>4</sup> but was without success.<sup>5</sup> This approach has become more pertinent with the recently described synthesis of stable boron hydride anions, B<sub>12</sub>H<sub>12</sub><sup>2-</sup> and B<sub>10</sub>H<sub>10</sub><sup>2-</sup>,<sup>6</sup> and the carboranes.<sup>7</sup> These structures possess high boron percentages and, in view of their chemical stability, it is highly possible that they will not be extensively destroyed by the normal biological processes.<sup>8</sup>

Nitrogen mustards, RN(CH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub>, have a profound effect on tumors and there is evidence of incorporation of certain mustards into brain tumors.<sup>9</sup> On

this basis the synthesis of a nitrogen mustard containing boron hydride anion was undertaken with the idea that such a compound might concentrate preferentially in brain tumor relative to other adjacent tissues. The reaction<sup>10</sup> of the carbonyl derivatives of these boron hydride cage compounds with primary and secondary amines and with ammonia itself occurs with the formation of ammonium salts of the corresponding carboxamide derivatives of the cage anions, *e.g.*, (NH<sub>4</sub>)<sub>2</sub>B<sub>12</sub>H<sub>10</sub>(CONH<sub>2</sub>)<sub>2</sub>. We have sought to apply this reaction to bis(2-chloroethyl)amine with the thought of incorporating the mustard moiety into a boron hydride cage compound.

### Results and Discussion

**B<sub>12</sub>-Cage Compounds.**—As a model for this reaction, 1,12-B<sub>12</sub>H<sub>10</sub>(CO)<sub>2</sub><sup>10</sup> was treated with diethylamine in an acetonitrile solution. The expected amide derivative, [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>B<sub>12</sub>H<sub>10</sub>[CON(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> (I), was obtained. Such structures appeared to have a low order of stability as shown by the cleavage of the amide linkage by both cold aqueous sodium hydroxide and refluxing ethanol. In the former case the sodium salt of the carboxylic acid derivative of the cage anion was obtained, and this was characterized as the triethylammonium, tetramethylammonium, and methyltriethylphosphonium salts of the B<sub>12</sub>H<sub>10</sub>(COOH)<sub>2</sub><sup>2-</sup> anion (IIa-c). In the latter case the carbethoxy derivative of the cage anion was obtained, B<sub>12</sub>H<sub>10</sub>(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>2-</sup>, characterized as the diethylammonium, triethylammonium, and tetramethylammonium salts (IIIa-c).

In contrast with the extreme lability of the amide linkage, the product obtained by the reaction of B<sub>12</sub>H<sub>10</sub>(CO)<sub>2</sub> with excess bis(2-chloroethyl)amine was surprisingly stable. Instead of the expected 4 moles of

(1) This work was supported by the U. S. Atomic Energy Commission (AT(30-1)-3267), U. S. Public Health Service (CA-07368 from the National Cancer Institute), and the John A. Hartford Foundation, Inc.

(2) The authors are greatly indebted to Drs. E. L. Muetterties and W. H. Knoth of the E. I. DuPont de Nemours and Co. for kindly supplying the 1,12-B<sub>12</sub>H<sub>10</sub>(CO)<sub>2</sub> and 1,6-(CH<sub>3</sub>)<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>CO which were used for the preparation of the described compounds.

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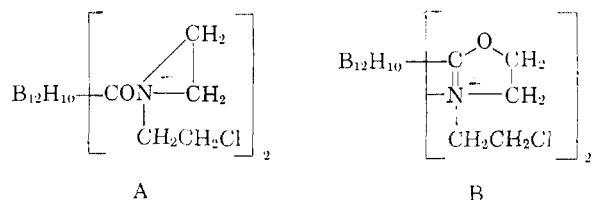
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amine to 1 mole of  $B_{12}H_{10}(CO)_2$  only 2 moles were incorporated with a simultaneous elimination of 2 moles of HCl, the product having the empirical formula,  $B_{12}H_{10}(CO)_2 \cdot 2N(C_2H_4)_2 \cdot 2Cl$  (IV). This compound was unaltered by treatment with water, refluxing alcohol, or amines. In view of the base:cage ratio of 2 and its highly unreactive nature, it appears likely that the compound is an internal salt of either of the following structures.



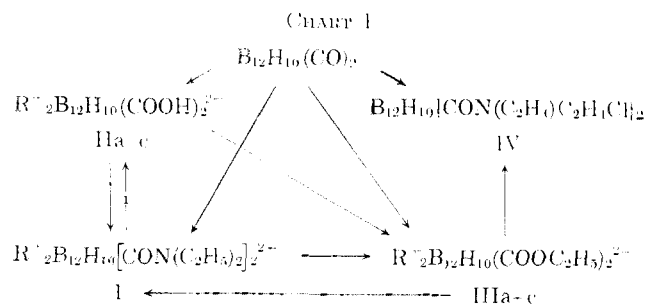
A definitive attempt at structure proof was inconclusive. However, attempts to prepare compounds of structure type  $-N^+R_3$  (A) resulted in unstable products. Reaction of  $B_{12}H_{10}(CO)_2$  with triethylamine under anhydrous conditions gave a mixture of materials from which no single stable product could be isolated. This is in marked contrast with the compound derived from bis(2-chloroethyl)amine. Also, reactions of ethylenimine with  $B_{12}H_{10}(CO)_2$  resulted in polymeric products and again indicated the instability of type A compounds. On this basis it would appear more likely that the structure of the compound is B.

There is corroborative evidence of others,<sup>11</sup> that the carbonyl function can assist in the nucleophilic displacement of leaving groups such as halogens even with the formation of an oxazoline structure,<sup>11c</sup> as is proposed for IV. The high electron concentration about the carbonyl group attached to both  $B_{12}$ - and  $B_{10}$ -cage hydrides would make such moieties extremely potent nucleophiles and account for the ready elimination of a halogen atom by an anchimeric effect of the carbonyl oxygen. Mustard amides, however, in which electron-withdrawing groups are attached to the carbonyl function do not readily eliminate halogen.<sup>12</sup>

Additional evidence for the strong electron releasing effect of the boron cage has appeared in the infrared spectra.<sup>13</sup> The compounds, reported here as well, show a reduced carbonyl frequency, compared with the normal absorption.<sup>14</sup> These values are as follows (in  $cm^{-1}$ ): I, 1600; IIa, 1670; IIb, 1625; IIc, 1640; IIIa, 1640; IIIb, 1630; and IIIc, 1645.

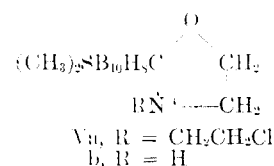
The over-all sequence is shown in Chart I below and the individual reactions are discussed in the Experimental Section.

**$B_{10}$ -Cage Compounds.**—To determine whether this type of transformation was peculiar to  $B_{12}$  type of compounds or applied to cage compounds generally, 1,6- $(CH_3)_2SB_{10}H_5CO$ <sup>15</sup> was treated with bis(2-chloro-



R =  $(C_2H_5)_2NH_2$  (I, IIa);  $(C_2H_5)_2NH$  (IIa, IIb);  $iCH_3$  (IIb, IIc);  $CH_3(C_6H_5)_2P$  (IIc)

ethyl)amine and 2-bromoethylamine to give after elimination of HCl and HBr, respectively, compounds entirely similar to IV in their properties. It is presumed that they have the following structures (Va and b).



This is supported by analytical evidence and the fact that as with  $B_{12}H_{10}(CO)_2$ ,  $(CH_3)_2SB_{10}H_5CO$  under anhydrous conditions gave only highly sensitive materials with tertiary amines such as pyridine and polymeric products upon reaction with ethylenimine. However, on exposure to air, the pyridine salt of the corresponding acid,  $C_6H_5NH(CH_3)_2SB_{10}H_5COOH$  (VI), was obtained. Reaction of the carbonyl compound with excess aniline did give the hydrolytically stable product  $C_6H_5NH_2(CH_3)_2SB_{10}H_5CONHC_6H_5$  (VII). This compound, however, was rapidly cleaved by aqueous cesium chloride solution to give the corresponding acid salt,  $Cs(CH_3)_2SB_{10}H_5COOH$  (VIII).

The shift of the  $C=O$  absorption in the infrared spectra, described in the  $B_{12}$  series, was obtained for the  $B_{10}$  compounds as well. The amide VII ( $1540\text{ cm}^{-1}$ ) absorbs well below the regular secondary amides<sup>14</sup> and the absorption of the acids VI ( $1640\text{ cm}^{-1}$ ) and VIII ( $1645\text{ cm}^{-1}$ ) occur at lower values than is observed for the usual organic carboxyl groups.<sup>14</sup> This substantiates once again the strong electron-releasing effect of the boron cage.

Apparent failure to produce a mustardlike boron hydride from the foregoing reactions prompted a different approach in the synthetic scheme. The acylation of the boron hydride anions by acid chlorides has been carried out recently.<sup>15,16</sup> Consequently, the acylation of  $B_{10}H_{10}^{2-}$  with a mustard-containing acid chloride, such as *p*-bis(2-chloroethyl)aminobenzoyl chloride, was undertaken. The expected product was obtained and characterized as its tetramethylammonium derivative,  $[(CH_3)_4N]_2B_{10}H_9COC_6H_4N(CH_2CH_2Cl)_2$  (IX). The ultraviolet spectra of this compound showed an absorption at  $319\text{ m}\mu$  in alkaline solution and  $424\text{ m}\mu$  in dilute acid. This unusual shift to longer wavelengths in acid may be explained by the following structure for the anion.

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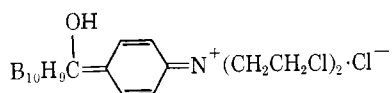
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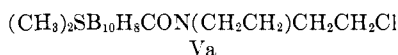
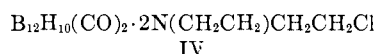
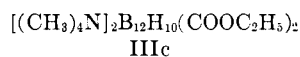
(14) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963.

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Under such conditions there could conceivably be resonance interaction between the aromatic nucleus and the boron cage and an absorption at longer wavelengths would be expected. It is of interest, if this hypothesis is true, that in a competition between the polarized carbonyl group and the tertiary aromatic amine for the proton in an acid, the former appears to be more nucleophilic. Further work is needed to elucidate the precise nature of the changes which occur under acidic and alkaline conditions, since the compound itself may be readily regenerated from such treatment.

**Biological Results.**—Only those compounds which were hydrolytically stable were considered for biological evaluation. Of those, the following representative compounds were screened for possible incorporation into brain tumors in a manner which has been previously described.<sup>17</sup> Compounds IIIc and IX were



extremely toxic. Doses of 9  $\mu\text{g}$  of boron/g of mouse, administered intraperitoneally, produced severe convulsions and frequently caused death. Implicated at least in part is the tetramethylammonium ion. Attempts at isolating and crystallizing the sodium salts were singularly unsuccessful. There were indications that compound IX was incorporated to some extent in the tumor, but the levels which could be administered on a daily basis were so low as to preclude its usefulness. Both compounds IV and Va were well tolerated in doses as high as 140  $\mu\text{g}$  of boron/g. However, there was no selective incorporation of either in the ependymoblastoma used.

### Experimental Section

Melting points were taken on Kofler microheating stage and are reported as they were observed. Infrared spectra were determined on a Perkin-Elmer Model 137 spectrometer. Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

**Bis(diethylammonium) 1,12-Bis(N,N-diethylcarboxamido)decahydrododecaborate**,  $[(\text{C}_2\text{H}_5)_2\text{NH}]_2\text{B}_{12}\text{H}_{10}[\text{CON}(\text{C}_2\text{H}_5)_2]_2$  (I).—To a stirred solution of 1 g (5.1 mmoles) of 1,12- $\text{B}_{12}\text{H}_{10}(\text{CO})_2$  in 45 ml of anhydrous acetonitrile was added dropwise at room temperature 25 ml (243 mmoles) of diethylamine. A white precipitate formed during the addition. The mixture was filtered to give 2.1 g (84%) of I, which after recrystallization from acetonitrile–Diglyme melted at 225–226°.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{34}\text{B}_{12}\text{N}_4\text{O}_2$ : C, 44.26; H, 11.14; B, 26.58; N, 11.47. Found: C, 44.03; H, 11.02; B, 26.33; N, 11.09.

This same product was obtained by the reaction of 0.20 g (0.5 mmole) of IIa in refluxing acetonitrile with an excess of diethylamine. After 15 min 0.15 g (67%) of I was obtained as shown by melting point and infrared spectra.

Likewise, IIIa was converted to I by a similar procedure.

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**Bis(triethylammonium) 1,12-Dicarboxydecahydrododecaborate**,  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{12}\text{H}_{10}(\text{COOH})_2$  (IIa).—To a stirred solution of 0.5 g (2.6 mmoles) of  $\text{B}_{12}\text{H}_{10}(\text{CO})_2$  in 50 ml of a 1:1 benzene–acetonitrile mixture (exposed to the atmosphere) was added dropwise at room temperature, 3.6 ml (26 mmoles) of triethylamine in 10 ml of benzene. The mixture was stirred for 1 hr, filtered, washed, and dried. The yield of the white precipitate was 1 g (86.5%) which upon recrystallization from acetonitrile–ethyl ether gave IIa with mp 173–176°.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{44}\text{B}_{12}\text{N}_2\text{O}_4$ : C, 38.72; H, 10.21; B, 29.89; N, 6.45. Found: C, 38.61; H, 10.72; B, 29.40; N, 6.46.

**Bis(methyltriphenylphosphonium) 1,12-Dicarboxydecahydrododecaborate**,  $[\text{CH}_3(\text{C}_6\text{H}_5)_3\text{P}]_2\text{B}_{12}\text{H}_{10}(\text{COOH})_2$  (IIc).—A solution of 2 g (5.6 mmoles) of methyltriphenylphosphonium bromide in 3 ml of water was added dropwise with stirring to an aqueous (2 ml) solution of 0.1 g (0.5 mmole) of  $\text{B}_{12}\text{H}_{10}(\text{CO})_2$ . A white precipitate promptly formed, which was filtered, washed, and dried. Upon recrystallization from water, the product melted over the range of 235–240°.

*Anal.* Calcd for  $\text{C}_{40}\text{H}_{48}\text{B}_{12}\text{O}_4\text{P}_2$ : C, 61.23; H, 6.16; B, 16.55; P, 7.90. Found: C, 61.05; H, 6.15; B, 16.30; P, 7.91.

The same product was formed by the reaction of bis(tetramethylammonium) 1,12-dicarboxydecahydrododecaborate (IIb) with methyltriphenylphosphonium bromide. IIb was characterized in this manner, having been produced by the reaction of I in an aqueous alkaline solution with tetramethylammonium chloride.

**Bis(diethylammonium) 1,12-Dicarbethoxydecahydrododecaborate**,  $[(\text{C}_2\text{H}_5)_2\text{NH}]_2\text{B}_{12}\text{H}_{10}(\text{COOC}_2\text{H}_5)_2$  (IIIa).—Recrystallization of I from ethanol gave white crystals, mp 226–228°, depressed upon admixture with I (160–163°).

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{44}\text{B}_{12}\text{N}_2\text{O}_4$ : C, 38.72; H, 10.21; B, 29.89; N, 6.45. Found: C, 38.76; H, 10.26; B, 29.53; N, 6.17.

**Bis(triethylammonium) 1,12-Dicarbethoxydecahydrododecaborate**,  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{12}\text{H}_{10}(\text{COOC}_2\text{H}_5)_2$  (IIIb).—To a solution of 0.15 g (0.8 mmole) of  $\text{B}_{12}\text{H}_{10}(\text{CO})_2$  in 10 ml of ethanol was added with stirring 3 ml (2.3 mmoles) of triethylamine. White needles formed after 1 hr. The product (0.25 g, 66%) was filtered off and recrystallized from an ethanol–acetonitrile mixture, mp 185–188°.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{52}\text{B}_{12}\text{N}_2\text{O}_4$ : C, 44.08; H, 10.69; B, 26.47; N, 5.69. Found: C, 44.27; H, 10.88; B, 26.02; N, 5.89.

The same product, as shown by infrared spectra and melting point, was obtained by recrystallizing IIa from an ethanol–triethylamine mixture.

**Bis(tetramethylammonium) 1,12-Dicarbethoxydecahydrododecaborate**,  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_{10}(\text{COOC}_2\text{H}_5)_2$  (IIIc).—To a solution of 0.2 g (0.5 mmole) of IIIa in 4 ml of water was added at room temperature an aqueous solution (2 ml) of 0.5 g (4.6 mmoles) of tetramethylammonium chloride. After 5 min 0.1 g (50%) of a white crystalline product separated from solution, mp > 350°. An analytical sample was prepared by recrystallizing the compound from ethanol–water.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{44}\text{B}_{12}\text{N}_2\text{O}_4$ : C, 38.72; H, 10.21; B, 29.89; N, 6.45. Found: C, 38.15; H, 10.21; B, 29.38; N, 6.44.

The same compound was obtained by dissolving IIb in cold ethanol or by treating either  $\text{B}_{12}\text{H}_{10}(\text{CO})_2$  or IIIb in ethanol with tetramethylammonium chloride.

**1,12-Bis(3- $\beta$ -chloroethyloxazolin-2-yl)dodecaborane (10)**,  $\text{B}_{12}\text{H}_{10}[\text{CON}(\text{C}_2\text{H}_4)\text{C}_2\text{H}_4\text{Cl}]_2$  (IV).—A freshly prepared benzene solution (100 ml) containing 42 mmoles of bis(2-chloroethyl)amine<sup>18</sup> was added dropwise at room temperature, under anhydrous conditions, to a stirred solution of 2 g (10.2 mmoles) of  $\text{B}_{12}\text{H}_{10}(\text{CO})_2$  in 100 ml of acetonitrile. A white precipitate (6.8 g) formed at the end of the addition and proved to be a 1:2 mixture of IV and bis(2-chloroethyl)amine hydrochloride. This product was triturated with water to remove bis(2-chloroethyl)amine hydrochloride and the residue upon recrystallization from a mixture of acetonitrile–Monoglyme gave white plates of IV, mp 287–288°.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{26}\text{B}_{12}\text{Cl}_2\text{N}_2\text{O}_2$ : C, 29.50; H, 6.44; B, 31.89; Cl, 17.42; N, 6.88. Found: C, 29.64; H, 6.58; B, 31.60; Cl, 17.26; N, 6.61.

Reaction of IIIa with bis(2-chloroethyl)amine in a refluxing benzene–acetonitrile mixture also yielded IV.

**1-Dimethylsulfonium-6-(3- $\beta$ -chloroethyloxazolin-2-yl)dodecaborane (8)**,  $(\text{CH}_3)_2\text{SB}_{12}\text{H}_8\text{CON}(\text{C}_2\text{H}_4)\text{C}_2\text{H}_4\text{Cl}$  (Va).—A benzene

solution of 6 mmoles of bis(2-chloroethyl)amine was added at room temperature under anhydrous conditions to a stirred mixture of 0.6 g (2.9 mmoles) of  $1,6-(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{CO}$  in 4 ml of acetonitrile. The precipitate was a 1:1 mixture of Va and bis-(2-chloroethyl)amine hydrochloride. After recrystallization from acetonitrile, Va was obtained as a pure product, mp 176–177°.

*Anal.* Calcd for  $\text{C}_7\text{H}_{22}\text{B}_{10}\text{Cl}_2\text{NOS}$ : C, 26.94; H, 7.11; B, 34.67; Cl, 11.36; N, 4.49; S, 10.28. Found: C, 26.76; H, 7.04; B, 34.73; Cl, 11.24; N, 4.56; S, 10.04.

**1-Dimethylsulfonium-6-(oxazolin-2-yl)decaborane (8),  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{CON}(\text{C}_2\text{H}_4)\text{H}(\text{Vb})$ .**—A solution containing 4.0 mmoles of 2-bromoethylamine in ethyl ether was prepared by adding dropwise an ice-cold 50% NaOH solution to a suspension of 2-bromoethylamine hydrobromide in ethyl ether at 0°. The aqueous layer was extracted several times with small portions of ether; the ether layers were combined and dried ( $\text{Na}_2\text{SO}_4$ ). This freshly prepared solution was added with stirring to a solution of 0.4 g (1.9 mmoles) of  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{CO}$  in 10 ml of benzene at room temperature under anhydrous conditions. An oily solid began to separate shortly after the start of amine addition. After the total addition of the amine and further stirring, to allow the reaction to go to completion, the solid was separated by filtration. This product was readily soluble in acetonitrile and a white crystalline material separated out of solution upon the addition of a benzene-petroleum ether (bp 30–60°) mixture (0.55 g). The solid was a 1:1 mixture of 2-bromoethylamine hydrobromide and Vb, containing 1 mole of acetonitrile of solvation. This latter compound was separated from the mixture by successive recrystallizations from acetonitrile, mp 224–225°, and had no halogen present.

*Anal.* Calcd for  $\text{C}_9\text{H}_{19}\text{B}_{10}\text{NOS}\cdot\text{CH}_3\text{CN}$ : C, 28.95; H, 7.64; B, 37.25; N, 9.65; S, 11.04. Found: C, 29.01; H, 7.80; B, 37.82; N, 9.32; S, 10.82.

**Pyridinium 1-Dimethylsulfonium-6-carboxydecaborate,  $\text{C}_5\text{H}_5\text{NH}(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{COOH}$  (VI).**—To a stirred solution of 0.5 g (2.5 mmoles) of  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{CO}$  in 10 ml of benzene, exposed to the atmosphere, was added dropwise at room temperature 2 ml (25 mmoles) of pyridine in 5 ml of benzene. An oily yellow precipitate separated, which gradually solidified. The product (0.7 g, 95%) was filtered off and readily recrystallized from acetonitrile, yielding white crystals, mp 142–144°.

*Anal.* Calcd for  $\text{C}_8\text{H}_{14}\text{B}_{10}\text{NO}_2\text{S}$ : C, 31.66; H, 6.98; B, 35.66; N, 4.62; S, 10.56. Found: C, 31.04; H, 7.02; B, 35.53; N, 4.62; S, 10.20.

**Anilinium 1-Dimethylsulfonium-6-carboxanilidoctahydrodecaborate,  $(\text{C}_6\text{H}_5\text{NH}_2)(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{CONHC}_6\text{H}_5$  (VII).**—A solution of 4 ml of aniline in 5 ml of benzene was added dropwise with stirring to a solution of 0.5 g (2.4 mmoles) of  $(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{CO}$  in 10 ml of anhydrous benzene at room temperature. After total addition and upon completion of the reaction, the solvent was removed under reduced pressure. The remaining yellow oil was soluble in an ether-petroleum ether mixture and gradually crystallized. Recrystallization from benzene gave 0.4 g (42%) of white crystals of VII, mp 154–159°. This product was stable to hydrolytic conditions.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{22}\text{B}_{10}\text{N}_2\text{OS}$ : C, 45.88; H, 7.18; B, 27.55; N, 7.13; S, 8.16. Found: C, 45.82; H, 7.34; B, 27.52; N, 7.11; S, 8.51.

**Cesium 1-Dimethylsulfonium-6-carboxydecaborate,  $\text{Cs}(\text{CH}_3)_2\text{SB}_{10}\text{H}_3\text{COOH}$  (VIII).**—To a saturated solution of 0.1 g (0.3 mmole) of VII in water was added 1 ml of a cesium chloride solution (0.6 g). White needles began to separate after 2 min and these were recrystallized from water, mp 251–253°.

*Anal.* Calcd for  $\text{C}_9\text{H}_{15}\text{B}_{10}\text{CsO}_2\text{S}$ : C, 10.11; H, 4.24; B, 30.37; Cs, 37.30; S, 9.00. Found: C, 10.47; H, 4.46; B, 29.93; Cs, 36.70; S, 8.82.

The same product was formed by the reaction of VI with cesium chloride.

**Bis(tetramethylammonium) *p*-Bis(2-chloroethyl)aminobenzoylnonahydrodecaborate,  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_9\text{COC}_6\text{H}_4\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2$  (IX).**—A solution of 4.35 g (15.5 mmoles) of *p*-bis(2-chloroethyl)aminobenzoyl chloride<sup>18</sup> in 15 ml of Monoglyme was added dropwise to a stirred solution of 22 mmoles of  $(\text{H}_3\text{C})_2\text{B}_{10}\text{H}_{10}$ <sup>19</sup> in 15 ml of Monoglyme maintained at 0° in an ice bath. The solution became deep red during addition, and after completion, the mixture was allowed to warm gradually to room temperature overnight. This solution was then added to a stirred methanolic (45 ml) solution containing 10 g of tetramethylammonium chloride. Unreacted  $\text{B}_{10}\text{H}_{10}^{2-}$  separated out as its tetramethylammonium salt (4.2 g) and was removed. The orange filtrate was neutralized with 45 ml of a 10% tetramethylammonium hydroxide solution (the color turned yellow) and concentrated under reduced pressure at room temperature to yield 3.1 g (39%) of an orange solid. Recrystallization from methanol afforded yellow-orange plates of IX, mp 175–180° dec.

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{45}\text{B}_{10}\text{Cl}_2\text{N}_3\text{O}$ : C, 44.68; H, 8.88; B, 21.18; Cl, 13.88; N, 8.23. Found: C, 44.75; H, 8.87; B, 20.66; Cl, 13.04; N, 8.09.

A dimethyl sulfoxide adduct of IX was obtained by recrystallizing the compound from dimethyl sulfoxide-benzene mixtures, mp 165–170° dec.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{51}\text{B}_{10}\text{Cl}_2\text{N}_3\text{O}_2\text{S}$ : C, 42.83; H, 8.73; B, 18.37; Cl, 12.04; N, 7.13; S, 5.44. Found: C, 42.45; H, 8.85; B, 18.20; Cl, 11.51; N, 6.68; S, 5.41.

**Acknowledgments.**—The authors wish to thank Dr. William H. Sweet, Chief of the Neurosurgical Service of the Massachusetts General Hospital and Professor of Surgery at the Harvard Medical School, for his great interest in this project. The important technical assistance of Mr. J. E. Lyons, Miss Mary Hagny, Miss Beverly Whitman, and Mrs. Janette Messer is gratefully acknowledged.

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