and cooling the solution to precipitate the crystalline product or by evaporating the solution to dryness and distilling the residue under reduced pressure. In a typical experiment bis(methoxydimethylsilyl)neocarborane was recovered by the crystallization method in 93.5% yield.

C,C′-Bis(dihydroxymethylsilyl)neocarborane (VIII).—This compound is readily prepared by adding excess water to an acetone solution of bis(methyldichlorosilyl)neocarborane (IV) at room temperature. On evaporation in air, the product separates as crystals and can be recrystallized from xylene to give a practically quantitative yield.

C,C′-Bis(hydroxydiphenylsilyl)neocarborane (IX).—The preparation is identical with that for VIII using bis(chlorodiphenylsilyl)neocarborane. The crude product is crystallized from hexane, and bis(hydroxydiphenylsilyl)neocarborane is obtained in practically quantitative yield.

C,C′-Bis(methoxydiphenylsilyl)neocarborane (X).—This compound was prepared from 28.1 g. (0.0484 mole) of bis(chlorodiphenylsilyl)neocarborane (III) and 250 ml. of absolute methanol. Ethyl ether (150 ml.) was added to obtain a homogeneous solution and this solution was heated at reflux for 45 min. The product was evaporated to dryness and the residue recrystallized from ethanol. Bis(methoxydiphenylsilyl)neocarborane was recovered in 76% yield.

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Chemistry of Boranes. XVIII.[1] Oxidation of $B_{10}H_{10}^{-2}$ and Its Derivatives

BY B. L. CHAMBERLAND AND E. L. MUETTERTIES

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The chemical oxidation of $B_{10}H_{10}^{-2}$ and some of its substituted derivatives has produced a series of coupled ions and several neutral compounds. The reaction of these coupled ions and the neutral derivatives with hydroxide ion yields a variety of ionic species. The preparation and properties of several substituted derivatives of $B_{20}H_{18}^{-2}$ and $B_{20}H_{19}^{-3}$ are presented.

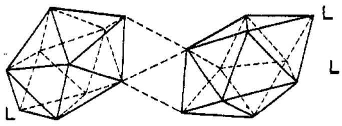
Results and Discussion

(A) $B_{20}H_{16}L_2$ Compounds.—Oxidative coupling of $B_{10}H_9L^-$ derivatives yielded several new $B_{20}H_{16}L_2$ compounds which may be considered as derivatives of the known $B_{20}H_{18}^{-2}$ ion.[2]

$$2B_{10}H_9L^- \longrightarrow B_{20}H_{16}L_2 + 2H^+ + 4e \qquad (1)$$

The $B_{10}H_9L^-$ ions[3] which have yielded coupled structures are $B_{10}H_9S(CH_3)_2^-$, $B_{10}H_9IC_6H_5^-$, $B_{10}H_9O{=}\underline{C(CH_2)_3N}CH_3^-$, and $B_{10}H_9O_2S(CH_2)_4^-$. The ceric ion has proved most generally effective as the oxidant in these preparations. During the oxidation reaction, the neutral product appears as a water-insoluble solid which can be easily isolated and recrystallized from organic solvents.

Molecular weight and analytical data indicate a composition $B_{20}H_{16}L_2$. There are no bridge B–H–B stretching absorptions in the infared spectra of these compounds. The B_{10} polyhedra are believed to be structurally analogous to the $B_{20}H_{18}^{-2}$ ion.[4] The exact location of the ligands, L, has not been established, but it is reasonable to assume that they occupy the same position as in the parent ion and that no displacement or rearrangement occurs during the coupling reaction.[5] The location of the ligands on the B_{10} cage for the reagents used in this study had been previously determined.[3] The $S(CH_3)_2$ and IC_6H_5 groups occupy an apical position, while the $(CH_2)_4SO_2$ and $CH_3\underline{N(CH_2)_3C}{=}O$ ligands occupy an equatorial site. Structure **1** is proposed for the apically-substituted derivatives $B_{20}H_{16}[S(CH_3)_2]_2$ and $B_{20}H_{16}[IC_6H_5]_2$, and there is only one stereoisomer in this case. There are several possible stereoisomers for the equatorially-substituted compounds, $B_{20}H_{16}[O_2S(CH_2)_4]_2$ and $B_{20}H_{16}[\underline{OC(CH_2)_4N}CH_3]_2$, one of which is represented by structure 2.



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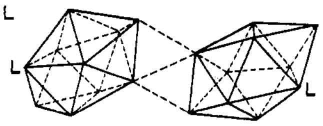

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(B) $B_{20}H_{16}(OH)L_2^-$ and $B_{20}H_{15}(OH)L_2^{-2}$ Derivatives.—Hydroxyl ion reacts with $B_{20}H_{16}L_2$ compounds to form ionic derivatives. This cleavage probably proceeds by the insertion of a hydroxyl group at an equatorial boron site and finally the formation of a direct two-center B–B bond.

$$B_{20}H_{16}L_2 + OH^- \longrightarrow B_{20}H_{16}(OH)L_2^- \qquad (2)$$

$$B_{20}H_{16}(OH)L_2^- + OH^- \longrightarrow B_{20}H_{15}(OH)L_2^{-2} + H_2O \qquad (3)$$

An acid–base equilibrium exists between these two substituted anions.

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[1] Paper XVII: N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1064 (1964).

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

[3] To be published.

[4] W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **47**, 1791 (1961), proposed a centrosymmetric structure like **1** with B–H–B bonds between interapex–equatorial polyhedral boron atoms. However, R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.*, **86**, 3568 (1964), from a B^{11} n.m.r. study at 60 Mc. suggest two three-center B–B–B bonds for the linkage of the two polyhedra.

[5] Isomerizations of the type described by Kaczmarczyk, Dobrott, and Lipscomb (ref. 2) and by Lipscomb, *Inorg. Chem.*, **2**, 231 (1963), are considered to be quite unlikely in the oxidation of substituted polyhedral derivatives at room temperature. Polyhedral isomerizations in $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ derivatives are high-energy processes. Detailed studies of this type have been made in these laboratories and will be published.

TABLE I

SALTS OF THE $B_{20}H_{18}^{-2}$ ION

Compound	% C		% H		% B		% X	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(C_2H_5)_3NH]_2B_{20}H_{18}$	32.8	32.6	11.5	11.4	49.3	49.4	6.38 (N)	6.24
$[(C_6H_5)_3PCH_3]_2B_{20}H_{18}$	57.8	57.7	6.90	7.30	27.4	27.3	7.85 (P)	7.92
$[(CH_3)_3S]_2B_{20}H_{18}$	18.5	18.8	9.33	9.74	55.6	55.2	16.5 (S)	16.5
$[(C_6H_5)_2I]_2B_{20}H_{18}$	36.2	37.4	4.81	4.88	27.2	25.8	31.9 (I)	29.1
$(NH_4)_2B_{20}H_{18}\cdot 0.5H_2O$	0	0.25	9.73	9.87	77.4	77.4	10.0 (N)	10.1
$Cs_2B_{20}H_{18}\cdot 0.5H_2O$	0	0.32	3.76	3.90	42.5	42.4	52.2 (Cs)	52.1
$Na_2B_{20}H_{18}\cdot 2H_2O$			7.01	7.25	68.3	68.2	14.5 (Na)	13.4

TABLE II

SALTS OF THE $B_{20}H_{19}^{-3}$, $B_{20}H_{18}^{-4}$, $B_{20}H_{18}OH^{-3}$, AND $B_{20}H_{17}OH^{-4}$ IONS

Compound	% C		% H		% B		% X	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(C_2H_5)_3NH]_3B_{20}H_{19}$[a]	39.9	40.2	12.5	13.0	39.9	39.9	7.75 (N)	7.63
$[(CH_3)_3S]_4B_{20}H_{18}$	26.5	26.3	10.0	10.3	39.8	39.7	23.6 (S)	23.7
$(NH_4)_3B_{20}H_{19}\cdot 2.5H_2O$[b]	0	0.75	10.8	10.7	64.5	64.4	15.2 (NH_3)	14.6
$Cs_4B_{20}H_{17}OH\cdot H_2O$	0	0.30	2.52	2.70	27.0	27.4	66.4 (Cs)	66.1
$K_4B_{20}H_{17}OH\cdot 0.5H_2O$	0	0.34	4.60	4.58	52.0	51.9	37.6 (K) 5.77 (O)	39.5 5.40
$(NH_4)_4B_{20}H_{17}OH\cdot H_2O$	0	0.29	10.65	10.65	63.5	68.2	20.0 (NH_3)	19.8
$(N_2H_5)_4B_{20}H_{17}OH$	0	0.90	10.0	10.0	56.5	56.8	29.3 (N)	28.8
$[(CH_3)_4N]_{2.5}(H_3O)_{0.5}$-$B_{20}H_{18}OH$	26.9	26.5	11.4	11.3	48.45	48.85	7.84 (N)	7.86
$Cs_{2.5}(H_3O)_{0.5}B_{20}H_{18}$-$OH\cdot 2.5H_2O$	0	0.26	4.02	3.90	33.9	33.9	52.0 (Cs)	50.0

[a] Hydrolytic hydrogen determination: calcd. 1694 cc./g.; found 1685, 1658 cc./g. [b] Salt found to be a 3:1 electrolyte in conductance determination.

$$H_2O + B_{20}H_{16}(OH)L_2^- \rightleftharpoons B_{20}H_{15}(OH)L_2^{-2} + H_3O^+ \quad (4)$$

In the preparation of salts, the pH of the precipitating medium largely determines which ion is formed. Acid precipitation yields salts of the $B_{20}H_{16}(OH)L_2^-$ ion, while salts of the $B_{20}H_{15}(OH)L_2^{-2}$ ion are formed in alkaline media.

Under strongly basic conditions further reaction can occur if the ligand bonded to the boron atom in the polyhedron can be removed by the hydroxide ion. This displacement reaction leads to the formation of highly water-soluble species.

$$B_{20}H_{15}(OH)L_2^{-2} + 2HO^- \longrightarrow B_{20}H_{15}(OH)_3^{-4} + 2L \quad (5)$$

In some instances the ligands were only partially replaced by the hydroxyl group to yield a mixture of products. Hydroxide ion cleaved the ligands completely in $B_{20}H_{16}[OC_5H_9N]_2$, partially in $B_{20}H_{16}[O_2S(CH_2)_4]_2$, and not at all in $B_{20}H_{16}[S(CH_3)_2]_2$.

(C) **$B_{20}H_{18}^{-2}$ Ion.**—It has already been shown[2] that the $B_{10}H_{10}^{-2}$ ion can be coupled in the presence of ferric ion at 95–100°. The coupled anion, $B_{20}H_{18}^{-2}$, can also be prepared by the chemical oxidation of $B_{10}H_{10}^{-2}$ with a number of metal-containing oxidizing agents having a half-cell oxidation potential between 1.33 and 1.51 volts, *e.g.*, Ce^{+4}, PbO_2, MnO_4^-, and $Cr_2O_7^{-2}$. Ceric ion has given the best results, yielding 90–95% of a pure product.

A number of new $B_{20}H_{18}^{-2}$ salts have been prepared and are listed in Table I. These compounds are all yellow and their solutions show the characteristic[2] ultraviolet spectra. Conductance studies on water-soluble salts show that the metal salts are indeed 2:1 electrolytes.

A complete three-dimensional, single-crystal, X-ray determination of $[(CH_3)_3S]_2B_{20}H_{18}$ was carried out in these laboratories by Mr. K. R. Babcock[6] and the location of the boron atoms but not the hydrogen atoms was established. The structure is consistent with that shown in **1** with the apex–equatorial and equatorial–equatorial separations (dotted lines between the two polyhedra in **1**) being within bonding distance.

The general substitution chemistry of the $B_{20}H_{18}^{-2}$ ion has been investigated. N-Chloro- and N-bromosuccinimide react with $B_{20}H_{18}^{-2}$ to yield partially-substituted derivatives. Halogenation under more drastic conditions results in the cleavage of the $B_{20}H_{18}^{-2}$ ion to yield $B_{10}X_{10}^{-2}$ [7] derivatives and boric acid.

(D) **$B_{20}H_{19}^{-3}$ and $B_{20}H_{18}^{-4}$ Ions.**—Acid solutions of the $B_{20}H_{18}^{-2}$ ion can be reduced by active metals, such as Mg, Al, and Zn, to yield the $B_{20}H_{19}^{-3}$ ion[4] which has recently been prepared[8] by the 0° oxidation of $B_{10}H_{10}^{-2}$. The $B_{20}H_{19}^{-3}$ ion can be reoxidized at room temperature by the ceric, ferric, or argentous ion to yield the $B_{20}H_{18}^{-2}$ ion.

The $B_{20}H_{19}^{-3}$ ion is present and stable only in acid medium. Solutions of the pure acid are stable indefinitely in air, but the crystalline acid slowly decomposes to boric acid and $B_{18}H_{22}$. This decomposition is similar to that reported[9] for $(H_3O)_2B_{20}H_{18}$. At high pH a proton is lost from the B–H–B bridge in $B_{20}H_{19}^{-3}$, to form the $B_{20}H_{18}^{-4}$ ion.[8] The $B_{20}H_{19}^{-3}$ ion is re-

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(6) K. R. Babcock, to be published.

(7) A general description of the preparation and properties of $B_{10}X_{10}^{-2}$ compounds is given in W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962), and W. H. Knoth, J. C. Sauer, H. C. Miller, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

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

(9) A. R. Pitochelli and M. F. Hawthorne, *ibid.*, **84**, 3218 (1962).

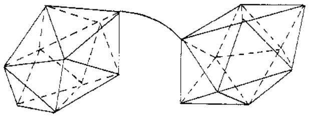
generated when the $B_{20}H_{18}^{-4}$ ion is treated with acid.

$$B_{20}H_{19}^{-3} + H_2O \rightleftharpoons B_{20}H_{18}^{-4} + H_3O^+ \qquad (6)$$

The titration curve for $(H_3O)_3B_{20}H_{19}$ shows two distinct inflection points. The first point appears at pH 5 and the second, upon addition of a fourth equivalent of base, occurs at pH 9. The pK_a for $B_{20}H_{19}^{-3}$ is 7.3, which differs considerably from that reported earlier.[8]

The salts of the $B_{20}H_{19}^{-3}$ and $B_{20}H_{18}^{-4}$ ions prepared in this study are listed in Table II. Conductance studies on water-soluble salts show that the basic solutions are 4:1 electrolytes while the acid solutions are 3:1 electrolytes.

We observed the same B^{11} n.m.r. spectrum of $B_{20}H_{19}^{-3}$ as did Hawthorne, Pilling, Stokely, and Garrett,[8] and we also favor the structure, **3**, which had been proposed by these earlier workers and by Lipscomb.[4] The structure of the anion is based on one B–H–B bridge bond (curved line in structure **3**) which joins an apical boron atom of one polyhedron to an equatorial boron atom of the other polyhedron.



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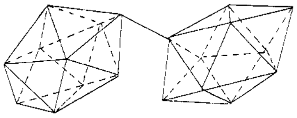

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One of the three possible structures for the $B_{20}H_{18}^{-4}$ ion is represented by **4**, wherein the straight line between the two polyhedra represents a B–B linkage. The terminal hydrogens and charges are omitted in structures **3** and **4** for clarity.

It is apparent from the acid–base titration curve for $B_{20}H_{18}^{-4}$ that in an aqueous solution of a $B_{20}H_{18}^{-4}$ salt there should exist an equilibrium between $B_{20}H_{18}^{-4}$ and $B_{20}H_{19}^{-3}$. We find that the B^{11} n.m.r. spectrum of $B_{20}H_{18}^{-4}$ is affected by the pH of the solution but the changes are not striking. Possibly the rate constants for the equilibrium are sufficiently large that even in strongly basic solution the B^{11} n.m.r. spectrum reflects an averaged environment. We find the B^{11} n.m.r. of $B_{20}H_{18}^{-4}$ in a strongly basic solution (pH >12) consists of a low-field peak, an apparent doublet, and an apparent high-field doublet (Fig. 3) which is in agreement with the observations of Hawthorne, Pilling, Stokely, and Garrett.[8] However, our integration data do not agree with the 2:2:16 ratios found by the earlier workers[8]; our data indicate 1:2–2.5:9–12 ratios. The discrepancy may be due to the fact that our samples of $B_{20}H_{18}^{-4}$ contain both isomers which are described by Hawthorne, Pilling, Stokely, and Garrett.[8]

(E) **$B_{20}H_{18}OH^{-3}$ and $B_{20}H_{17}OH^{-4}$ Ions.**—The reaction of $B_{20}H_{18}^{-2}$ with hydroxide ion was previously reported[2] to yield $B_{10}H_9OH^{-2}$. The product of this reaction, however, has recently been shown[8] to be a different B_{20} ion and not a B_{10} species. We have independently obtained conclusive evidence for the formation of the $B_{20}H_{17}OH^{-4}$ ion in this reaction.

$$B_{20}H_{18}^{-2} + 2OH^- \longrightarrow B_{20}H_{17}OH^{-4} + H_2O \qquad (7)$$

The $B_{20}H_{17}OH^{-4}$ ion can be considered as a substituted derivative of the $B_{20}H_{18}^{-4}$ ion. Table II lists the salts that we have prepared. These salts are all colorless and most of them retain water of crystallization even on prolonged drying at 100° *in vacuo*.

An acid–base equilibrium also exists between the ions $B_{20}H_{18}OH^{-3}$ and $B_{20}H_{17}OH^{-4}$, similar to that observed for $B_{20}H_{19}^{-3}$ and $B_{20}H_{18}^{-4}$ (eq. 6). The titration curve of the acid $(H_3O)_3B_{20}H_{18}OH$ also exhibits two inflection points. The plot of the titration data for this acid is similar to that for $B_{20}H_{19}^{-3}$. The pK_a for $B_{20}H_{18}OH^{-3}$ is 6.8.

In agreement with previous studies,[8] we have also carried out the cleavage of $B_{20}H_{18}^{-2}$ with methoxide ion to yield an anhydrous $B_{20}H_{17}OCH_3^{-4}$ salt. A sample recrystallized from water retained its methyl and methoxy absorptions in the infrared spectrum. Attempts to cleave the methyl group with aqueous HBr and HCl failed, but on boiling with HI the $B_{20}H_{17}OH^{-4}$ ion was formed. This hydroxy product was found to be identical with that obtained by the direct reaction of the hydroxide ion with $B_{20}H_{18}^{-2}$. Alkyl cleavage has previously been observed[10] in other alkoxy-substituted B_{10} and B_{12} derivatives.

The ferric oxidation of $B_{20}H_{17}OH^{-4}$ has been shown[8] to yield $B_{20}H_{17}OH^{-2}$. Our experiments are in agreement with this observation, and we have obtained further evidence for the formulation of this oxidation product. Conductance studies on solutions of the $B_{20}H_{17}OH^{-2}$ ion indicate a 2:1 electrolyte, and its reaction with formic acid has yielded a formate derivative, $B_{20}H_{17}OCOH^{-2}$. We have also observed that ceric oxidation of $B_{20}H_{18}OH^{-3}$ generates $B_{20}H_{16}(OH)_2^{-2}$ in low yields.

Partial chlorination of $B_{20}H_{17}OH^{-4}$ ion has been achieved. Halogenation with excess halogen resulted in cleavage of the $B_{20}H_{18}OH^{-3}$ ion to form $B_{10}X_{10}^{-2}$ and boric acid.

Experimental

Reagents.—Analyzed or reagent grade chemicals were used in all reactions. Reagent grade ceric ammonium sulfate was obtained from G. Frederick Smith Chemical Co. The cation-exchange resin was either Rexyn RG(H) or Amberlite IR-120(H).

Instrumentation.—Infrared data were obtained on Perkin-Elmer Model 21 and Model 137 infrared recording spectrophotometers. Ultraviolet spectra were recorded on Spectracord and Beckman Model DK-1 spectrophotometers. The n.m.r. data were obtained on a Varian Model V4300 spectrometer. Boron spectra were examined at 14.2 and 19.2 Mc., and proton spectra were obtained at 60 Mc. An N.M.R. Specialties spin decoupler, Model SD60, was used to observe B^{11} resonance at 19.2 Mc. with saturation of the hydrogen nuclei. Trimethyl borate was used as reference in all the reported n.m.r. spectra.

Conductometric Studies.[11]—The conductance of aqueous solutions of water-soluble boron hydride salts or the acid was measured at 25° at various concentrations. The plot of the equivalence conductance *vs.* square root of concentration (normality) of an anion under study was compared with the corresponding plots of known 2:1, 3:1, and 4:1 electrolytes to establish the charge of the unknown anion.

$B_{20}H_{16}[S(CH_3)_2]_2$.—An acid solution of $B_{10}H_9S(CH_3)_2^-$, prepared from 5 g. of $(CH_3)_4NB_{10}H_9S(CH_3)_2$ and a cation-exchange

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[10] W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

[11] Y. T. Chia, to be published.

resin, was treated with 25.3 g. of $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$ in 200 ml. of water to form an insoluble crude product. Recrystallization from methanol–acetonitrile yielded the pure product, $B_{20}H_{16}[S(CH_3)_2]_2$, m.p. 228–230°.

Anal. Calcd. for $C_4H_{28}B_{20}S_2$: C, 13.5; H, 7.91; B, 60.6; S, 18.0; mol. wt., 357. Found: C, 13.3; H, 7.98; B, 60.1; S, 18.1; mol. wt., 365 (ebullioscopic in dichloroethane).

The ultraviolet spectrum of the compound in acetonitrile contained absorptions at 2870 Å. (ϵ 11,600) and 2330 Å. (ϵ 30,000). The infrared spectrum showed bands attributable to the $(CH_3)_2S$ ligand, a strong B–H absorption at 2520 cm.$^{-1}$, and several absorptions between 1000 and 700 cm.$^{-1}$.

$B_{20}H_{16}(IC_6H_5)_2$.—A 2.16-g. sample of $CsB_{10}H_9IC_6H_5$ was passed through a cation-exchange resin and the effluent was treated with 6.03 g. of $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$ in 50 ml. of water and 10 ml. of concentrated sulfuric acid, whereupon an insoluble solid formed. The crude product was purified by recrystallization from methanol–acetonitrile and then benzene. The pure product, $B_{20}H_{16}(IC_6H_5)_2$, decomposes at 160°.

Anal. Calcd. for $C_{12}H_{26}B_{20}I_2$: C, 22.5; H, 4.09; B, 33.8; I, 39.6; mol. wt., 641. Found: C, 22.8; H, 4.42; B, 32.6; I, 38.8; mol. wt., 679. (ebullioscopic in acetone).

$B_{20}H_{16}[O\underline{C(CH_2)_3N}CH_3]_2$.—The acid solution formed from 3.0 g. of $(C_3H_7)_4NB_{10}H_9(OC_5H_9N)$ and a cation-exchange resin was treated with 9.22 g. of ceric ammonium sulfate in 100 ml. of water and 10 ml. of concentrated sulfuric acid. A white, insoluble solid formed on stirring the mixture. The crude solid was collected and recrystallized from acetonitrile to yield the pure product, $B_{20}H_{16}(OC_5H_9N)_2$. The off-white product decomposes on heating to 260°.

Anal. Calcd. for $C_{10}H_{34}B_{20}N_2O_2$: C, 27.9; H, 7.96; N, 6.50; B, 50.2. Found: C, 27.0; H, 8.02; N, 6.83; B, 49.2.

$B_{20}H_{16}[O_2S(CH_2)_4]_2$.—A 4.38-g. sample of $(CH_3)_4NB_{10}H_9O_2S(CH_2)_4$ was passed through a column charged with cation-exchange resin. The effluent was concentrated and treated with 18.8 g. of ceric ammonium sulfate in 100 ml. of water and 10 ml. of concentrated sulfuric acid. A white flocculent solid appeared on stirring the mixture. The crude product was separated by filtration and then recrystallized from a warm methanol–acetonitrile mixture. The product, $B_{20}H_{16}[O_2S(CH_2)_4]_2$, decomposes at 245°.

Anal. Calcd. for $C_8H_{32}S_2B_{20}O_4$: C, 20.3; H, 6.82; S, 13.6; B, 45.8. Found: C, 20.6; H, 6.96; S, 13.6; B, 43.2.

Reaction of $B_{20}H_{16}[S(CH_3)_2]_2$ with Base.—An acetonitrile–methanol solution of $B_{20}H_{16}[S(CH_3)_2]_2$ was made basic with ammonium hydroxide and heated to boiling until colorless. The basic solution was evaporated to dryness to yield a hydrated ammonium salt, $(NH_4)_2B_{20}H_{15}OH[S(CH_3)_2]_2 \cdot H_2O$, which showed water bands in the infrared spectrum.

Anal. Calcd. for $C_4H_{38}N_2S_2B_{20}O_2$: NH_3, 7.94; S, 15.0; B, 50.5. Found: NH_3, 7.94; S, 14.9; B, 49.1.

In another experiment, an alcohol solution containing $B_{20}H_{16}[S(CH_3)_2]_2$ was boiled with ammonium hydroxide for 90 min. The solution was then acidified and treated with $(CH_3)_4NCl$ to yield a white precipitate. The infrared spectrum of this product contained a B–H–B absorption at 1800 cm.$^{-1}$ and water bands. The product, $[(CH_3)_4N]_{1.75}(H_3O)_{0.25}B_{20}H_{15}OH[S(CH_3)_2]_2 \cdot H_2O$, decomposes on heating to 175–180°.

Anal. Calcd. for $C_{11}H_{51.75}N_{1.75}S_2B_{20}O_{2.25}$: H, 9.55; N, 4.65; B, 41.0. Found: H, 9.21; N, 4.61; B, 41.2.

Reaction of $B_{20}H_{16}(OC_5H_9N)_2$ with Base.—A 1.0-g. sample of $B_{20}H_{16}(OC_5H_9N)_2$ and excess potassium hydroxide were heated to boiling in a methanol–water medium for 90 min. On cooling an organic phase separated on the surface of the glass vessel. The solution, separated by decantation, was concentrated to 50 ml. Treatment with cesium hydroxide and cooling yielded a white solid. The hygroscopic solid was removed by filtration and was found to contain a strong OH absorption at 3500 cm.$^{-1}$, a BH stretch, water bands, and a strong B–O absorption at 1120 cm.$^{-1}$. The absorptions associated with N-methylpyrrolidone were absent. An absorption at 1000 with shoulder at 975 cm.$^{-1}$ indicated the hydroxy B_{20}^{-4} moiety.

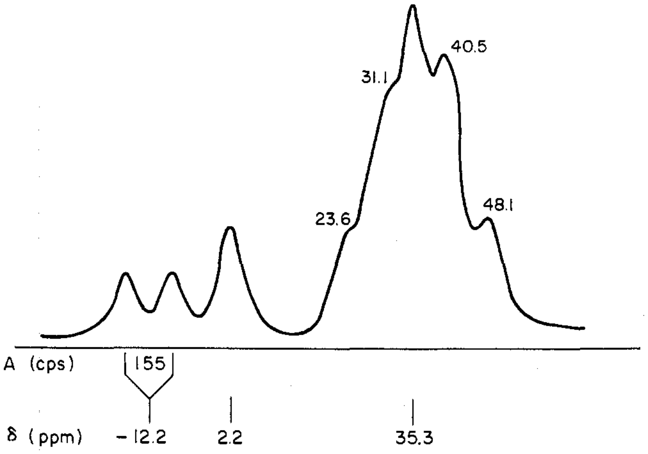

Fig. 1.—B^{11} n.m.r. spectrum of $(H_3O)_2B_{20}H_{18}$ in H_2O at 19.25 Mc.

$[(CH_3)_4N]_2B_{20}H_{18}$.—A solution containing 126.4 g. (0.20 mole) of ceric ammonium sulfate in 1000 ml. of water and 50 ml. of concentrated sulfuric acid was slowly added to a stirred solution of 15.4 g. (0.10 mole) of $(NH_4)_2B_{10}H_{10}$ in 250 ml. of water. The insoluble white precipitate of hydrated cerous sulfate was removed by filtration. An excess of $(CH_3)_4NOH$ was added to the filtrate to produce a white precipitate. The crude white product was collected and recrystallized from an acetonitrile–water mixture to form a yellow crystalline solid, 17.7 g. (92.7% theoretical yield). The air-dried product, $[(CH_3)_4N]_2B_{20}H_{18} \cdot H_2O$, contained water of crystallization which was removed by drying under vacuum.

Anal. Calcd. for $C_8H_{42}N_2B_{20}$: C, 25.1; H, 11.1; N, 7.32; B, 56.5. Found: C, 25.2; H, 12.0; N, 7.30; B, 56.3.

A combined hydrolytic B–H and B–B determination[12] on the anhydrous salt was performed by platinum-black hydrolysis.

Anal. Calcd. for $[(CH_3)_4N]_2B_{20}H_{18}$: 2340 cc. of H_2/g. Found: 2335, 2345 cc./g.

The X-ray single crystal data on several salts were obtained by K. R. Babcock. $[(CH_3)_4N]_2B_{20}H_{18}$ has the monoclinic structure with the following lattice constants: $a \sin \beta = 12.06$, $b = 15.85$, and $c = 13.50$. $[(C_6H_5)_3PCH_3]_2B_{20}H_{18}$ has the monoclinic structure with the following lattice constants: $a = 11.96$, $b = 15.42$, $\beta = 94°$, and $c = 12.37$. The density is 1.167 g./ml. The cell weight constant corresponds to two molecules per unit cell and a molecular weight of 795; theory 789. $[(CH_3)_3S]_2B_{20}H_{18}$ has the orthorhombic structure with cell dimensions: $a = 11.20$, $b = 10.3$, and $c = 21.25$. The density is 1.06 g./ml. and the cell weight constant corresponds to four formula weights per unit cell. The molecular weight found was 384; theory 389.

The electrical conductivity data obtained on $[(CH_3)_4N]_2B_{20}H_{18}$ indicated a 2:1 electrolyte.

The ultraviolet spectra of the $B_{20}H_{18}^{-2}$ salts in water and acetonitrile were similar in that they contained a strong absorption at 2300–2340 Å. and a weak absorption at 2900–2930 Å. The infrared spectra of the $B_{20}H_{18}^{-2}$ salts contained a strong B–H absorption at 2510 cm.$^{-1}$ and several absorptions between 1000 and 650 cm.$^{-1}$. The B^{11} n.m.r. spectrum of the $B_{20}H_{18}^{-2}$ ion is shown in Fig. 1.

$(H_3O)_2B_{20}H_{18}$ Hydrate.—An acetonitrile water solution of $[(CH_3)_4N]_2B_{20}H_{18}$ was passed through a column charged with a cation-exchange resin. The effluent was heated to expel the acetonitrile, and the aqueous concentrate was evaporated to near dryness *in vacuo* to yield large, intensely colored yellow crystals.

Anal. Calcd. for $(H_3O)_2B_{20}H_{18} \cdot 3.5H_2O$: H, 9.31; B, 64.5; O, 26.2; neut. equiv., 191.4. Found: H, 9.55; B, 64.3; O, 25.75; neut. equiv., 192.

The crystalline acid is not stable but slowly decomposes at room

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[12] The general method for the quantitative hydrolysis of B–H and B–B linkages is outlined in N. E. Miller, H. C. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 866 (1964).

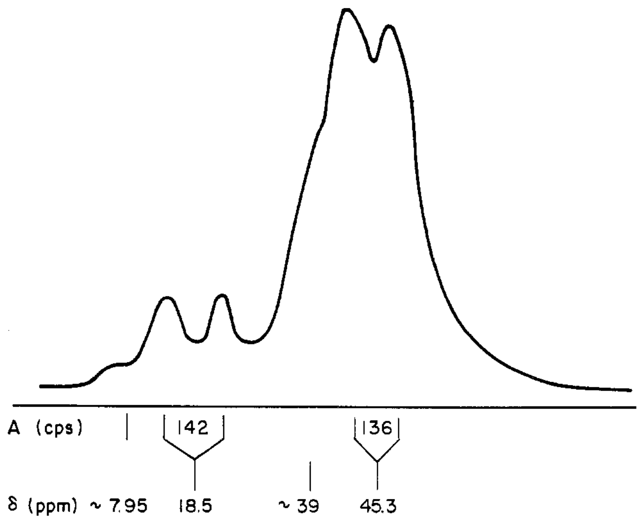

Fig. 2.—B^{11} n.m.r. spectrum of $(NH_4)_3B_{20}H_{19}$ in H_2O at 19.25 Mc.

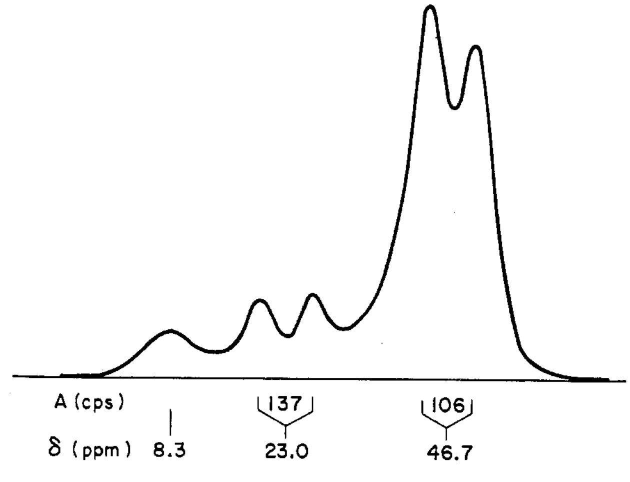

Fig. 3.—B^{11} n.m.r. spectrum of $K_4B_{20}H_{18}$ in H_2O at 19.25 Mc.

temperature to form boric acid and $B_{18}H_{22}$ with the evolution of gas. Aqueous solutions of the acid, however, are stable on prolonged storage without any appreciable decomposition.

Chlorination of $B_{20}H_{18}^{-2}$.—To 5.73 g. of $[(CH_3)_4N]_2B_{20}H_{18}$ in 100 ml. of acetonitrile was added 20.03 g. of N-chlorosuccinimide dissolved in 50 ml. of acetonitrile and 100 ml. of water. The mixture was stirred at room temperature for 3 hr. Acetonitrile was slowly removed by distillation until a solid appeared. On cooling, the mixture yielded large yellow crystals. Recrystallization from acetonitrile–water yielded the pure product, $[(CH_3)_4N]_2B_{20}H_{12}Cl_6$, m.p. 285° dec.

Anal. Calcd. for $C_8H_{36}N_2B_{20}Cl_6$: C, 16.3; H, 6.16; N, 4.75; B, 36.7; Cl, 36.1. Found: C, 16.7; H, 6.25; N, 4.64; B, 36.2; Cl, 36.8.

The ultraviolet spectrum of this salt in acetonitrile contained absorptions at 3140 Å. (ϵ 9300) and 2420 Å. (ϵ 13,300).

Bromination of $B_{20}H_{18}^{-2}$.—To 3.82 g. of $[(CH_3)_4N]_2B_{20}H_{18}$ in 50 ml. of acetonitrile and 20 ml. of methanol was added 8.90 g. of N-bromosuccinimide in 50 ml. of acetonitrile and 20 ml. of methanol. The resulting solution was stirred at room temperature for 3 hr., then concentrated to 50 ml. On cooling to room temperature, a yellow precipitate formed. Recrystallization from acetonitrile–water yielded the pure product, $[(CH_3)_4N]_2B_{20}H_{13}Br_5$, m.p. 260° dec.

Anal. Calcd. for $C_8H_{37}N_2B_{20}Br_5$: C, 12.4; H, 4.80; B, 27.8; Br, 51.4. Found: C, 12.9; H, 5.15; B, 28.0; Br, 49.5.

$Cs_4B_{20}H_{18}$ Hydrate.—To 50 ml. of 0.2 *M* $(H_3O)_2B_{20}H_{18}$ was slowly added 3.0 g. of magnesium turnings. A vigorous exothermic reaction occurred with the evolution of gas. The reaction was moderated by dilution with water and kept at room temperature for 25 hr. The mixture was filtered to remove unreacted metal, and the filtrate was treated with cesium hydroxide to yield a white precipitate. This solid was recrystallized from hot water to yield a hydrated product. This solid was dried at 100° *in vacuo* to form $Cs_4B_{20}H_{18}\cdot H_2O$.

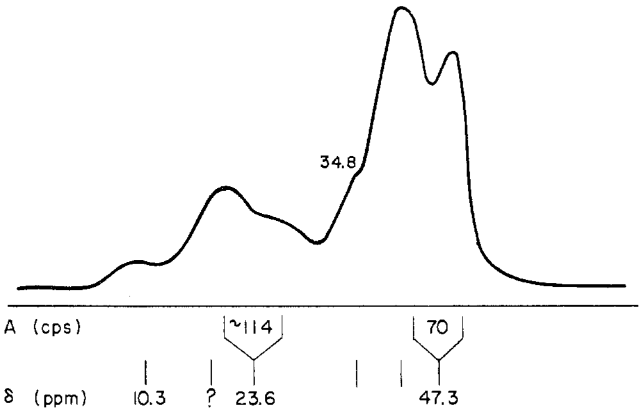

Fig. 4.—B^{11} n.m.r. spectrum of $(NH_4)_4B_{20}H_{17}OH$ in H_2O at 19.25 Mc.

Anal. Calcd. for $Cs_4B_{20}H_{20}O$: H, 2.57; B, 27.6; Cs, 67.8. Found: H, 3.23; B, 27.5; Cs, 66.5.

The infrared spectrum of the product showed weak water bands, a strong B–H absorption at 2480 cm.$^{-1}$, and absorption at 1010 cm.$^{-1}$.

A platinum-black hydrolysis performed on $Cs_4B_{20}H_{18}\cdot 3.254H_2O$ yielded 1078 and 1087 cc. of H_2/g. of B_{20} salt used. The theoretical value is 1114 cc. Then B^{11} n.m.r. spectrum of the $B_{20}H_{19}^{-3}$ is shown in Fig. 2.

$[(CH_3)_4N]_3B_{20}H_{19}$.—A solution containing 12.6 g. of ceric ammonium sulfate in 100 ml. of water and 10 ml. of concentrated sulfuric acid was cooled to 0° and slowly added to an ice–water-cooled solution containing 3.0 g. of $(NH_4)_2B_{10}H_{10}$ in 100 ml. of ice-water. The solution was then warmed to room temperature and treated with a saturated $(CH_3)_4NCl$ solution. The precipitate was collected by filtration. Repeated washings with acetonitrile removed all the $[(CH_3)_4N]_2B_{20}H_{18}$ and yielded an insoluble white solid. Recrystallization of this solid from hot water yielded the pure hydrated product, $[(CH_3)_4N]_3B_{20}H_{19}\cdot 0.5H_2O$. This product decomposes without fusion at 300°.

Anal. Calcd. for $C_{12}H_{56}N_3B_{20}O_{0.5}$: C, 30.9; H, 12.1; N, 9.00; B, 46.3. Found: C, 30.0; H, 12.0; N, 9.07; B, 46.7.

A hydrolytic determination gave 1967 and 1963 cc. of H_2/g., the theoretical value for $[(CH_3)_4N]_3B_{20}H_{19}\cdot 0.5H_2O$ is 1967 cc. of H_2/g.

The infrared spectrum of $[(CH_3)_4N]_3B_{20}H_{19}\cdot H_2O$ contained a weak OH absorption at 3500 cm.$^{-1}$, a strong B–H absorption at 2480 cm.$^{-1}$, a B–H–B absorption at 1850 cm.$^{-1}$, a weak water band at 1600 cm.$^{-1}$, anion absorption at 1000 cm.$^{-1}$, and a strong cation band at 952 cm.$^{-1}$.

$K_4B_{20}H_{18}$ Hydrate.—In an evacuated system connected to a vacuum assembly, 0.82 g. of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ in 10 ml. of water and 30 ml. of 0.10 *N* potassium hydroxide were mixed and heated to boiling. No evolution of hydrogen was observed during the reaction. The solution was evaporated to dryness to yield a white solid. Recrystallization from water yielded a crystalline hydrated product which was dried *in vacuo* to give $K_4B_{20}H_{18}\cdot 1.16H_2O$.

Anal. Calcd. for $K_4B_{20}H_{20.32}O_{1.16}$: H, 4.97; B, 52.85; K, 38.0. Found: H, 4.83; B, 52.7; K, 36.8.

A conductance study on this salt indicated that it was a 4:1 electrolyte. The infrared spectrum shows a strong B–H absorption at 2450 cm.$^{-1}$, weak absorption at 3500 cm.$^{-1}$, water bands at 1600 cm.$^{-1}$, and anion absorptions at 1020, (sh 1000), 795, 750, and 725 cm.$^{-1}$. The B^{11} n.m.r. spectrum is shown in Fig. 3.

Oxidation of $B_{20}H_{19}^{-3}$.—A 0.410-g. sample of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ was passed through a column packed with cation-exchange resin, and the effluent was treated with 1.52 ml. of 1 *M* ferric chloride solution at 0°. The stirred solution did not evolve any gas and yielded 0.232 g. (80%) of $[(CH_3)_4N]_2B_{20}H_{18}$ on treatment with $(CH_3)_4NCl$. The product was identified by infrared and ultraviolet spectroscopy as pure $[(CH_3)_4N]_2B_{20}H_{18}$, identical with that previously prepared.

$[(CH_3)_4N]_4B_{20}H_{17}OH$ Hydrate.—Approximately 5 g. of $[(CH_3)_4N]_2B_{20}H_{18}$ and 5 g. of $(CH_3)_4NOH$ hydrate were dissolved in an acetonitrile–water mixture and heated to boiling until the solution was colorless. On concentrating and cooling the solution a white solid appeared. The product was separated by filtration and air dried. The hydrated sample, $[(CH_3)_4N]_4B_{20}H_{17}OH \cdot 7H_2O$, was analyzed and also found to be a 4:1 electrolyte.

Anal. Calcd. for $C_{16}H_{80}N_4B_{20}O_8$: C, 28.55; H, 12.0; B, 32.1. Found: C, 28.8; H, 11.3; B, 29.6.

$(NH_4)_4B_{20}H_{17}OH$ Hydrate.—An aqueous solution containing 5 g. of $(NH_4)_2B_{20}H_{18}$ was treated with excess ammonium hydroxide and heated to boiling until it became colorless. The solution was then concentrated and cooled to yield a white crystalline product. This solid was recrystallized from water and dried *in vacuo* at 100° to yield a pure hydrated product, $(NH_4)_4B_{20}H_{17}OH \cdot 0.5H_2O$.

Anal. Calcd. for $N_4H_{36}B_{20}O_{1.5}$: H, 10.6; B, 65.2; NH_3, 20.5. Found: H, 10.6; B, 65.0; NH_3, 20.7.

The infrared spectrum of this salt shows an OH stretch at 3500 cm.$^{-1}$, NH stretch at 3200 cm.$^{-1}$, strong B–H absorption at 2420 cm.$^{-1}$, water bands at 1600 cm.$^{-1}$, and absorptions at 1100 and 1000 cm.$^{-1}$. The B^{11} n.m.r. spectrum is shown in Fig. 4.

$[(CH_3)_4N]_3B_{20}H_{18}OH$ Hydrate.—A mixture of 135 g. of $[(CH_3)_4N]_2B_{20}H_{18}$ and 61 g. of $(CH_3)_4NOH \cdot 5H_2O$ in 1000 ml. of water was heated to boiling for 3 hr. The solution was filtered hot, and the filtrate was cooled to room temperature. The first crop, 151 g., was hydrated $[(CH_3)_4N]_4B_{20}H_{17}OH$. The filtrate was acidified and 4 g. of $[(CH_3)_4N]_3B_{20}H_{18}OH$ was isolated. This solid was recrystallized from hot water and dried under vacuum to yield pure $[(CH_3)_4N]_3B_{20}H_{18}OH \cdot H_2O$.

Anal. Calcd. for $C_{12}H_{57}N_3B_{20}O_2$: C, 30.4; H, 11.4; N, 8.96; B, 44.4. Found: C, 30.5; H, 11.2; N, 9.15; B, 41.5.

The infrared spectrum contained several absorptions attributable to the cation and water in addition to a B–H absorption at 2450 cm.$^{-1}$, a B–H–B absorption at 1810 cm.$^{-1}$, and absorptions at 1140 and 1000 cm.$^{-1}$. The B^{11} n.m.r. spectrum of the anion is shown in Fig. 5.

$Cs_4B_{20}H_{17}OCH_3$.—A methanol solution containing 10 g. of $Cs_2B_{20}H_{18}$ was treated with excess sodium methoxide and heated to boiling for 2 hr. The colorless solution was then cooled to room temperature and treated with a saturated aqueous solution of cesium chloride to precipitate a fine white solid. Several recrystallizations from water and drying *in vacuo* at 100° yielded the pure product $Cs_4B_{20}H_{17}OCH_3$.

Anal. Calcd. for $Cs_4B_{20}H_{20}CO$: C, 1.51; H, 2.53; B, 27.2. Found: C, 1.56; H, 3.09; B, 27.2.

The infrared spectrum of the product contained a strong B–H absorption at 2425 cm.$^{-1}$, two bands at 1190 and 1130 cm.$^{-1}$, and an anion absorption at 1020 with a shoulder at 980 cm.$^{-1}$.

The salt was treated with aqueous HI (56%) and heated to boiling for 3 hr. to cleave the methyl group. Repeated recrystallization of the product from base then water yielded pure hydrated $Cs_4B_{20}H_{17}OH$, identified by its infrared spectrum.

Oxidation of $B_{20}H_{18}OH^{-3}$.—An aqueous solution of ferric ammonium sulfate, 23.0 g. in 200 ml., was added dropwise at room temperature to a stirred solution containing 14.8 g. of $(H_3O)_3B_{20}H_{18}OH$. A gas evolved during the addition and the resulting yellow solution was divided into three parts. Precipitation of one aliquot with an aqueous solution of tetramethylammonium chloride yielded a crude product which was separated by filtration and recrystallized from water–alcohol to yield the product, $[(CH_3)_4N]_2B_{20}H_{17}OH$, m.p. 263° dec.

Anal. Calcd. for $C_8H_{42}N_2B_{20}O$: C, 24.1; H, 10.6; N, 7.03; B, 54.2. Found: C, 23.9; H, 10.6; N, 7.03; B, 54.1.

Conductance studies on this salt indicated that its solutions are 2:1 electrolytes.

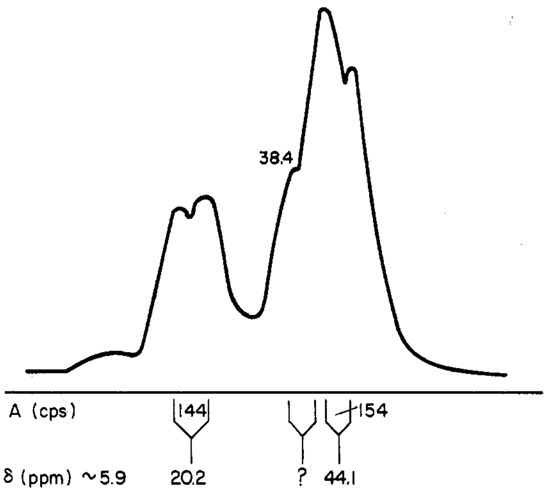

Fig. 5.—B^{11} n.m.r. spectrum of $(H_8O)_3B_{20}H_{18}OH$ in H_2O at 19.25 Mc.

The second aliquot was treated with CsCl to yield crude $Cs_2B_{20}H_{17}OH$, which was recrystallized from water and dried *in vacuo* to form the hydrate $Cs_2B_{20}H_{17}OH \cdot 0.5H_2O$.

Anal. Calcd. for $Cs_2B_{20}H_{19}O_{1.5}$: Cs, 50.6; H, 4.65; B, 41.2; O, 4.57. Found: Cs, 48.8; H, 3.78; B, 40.4; O, 4.04.

The last portion of the filtrate was treated with $(CH_3)_3SI$ to yield a product which was recrystallized from water–alcohol. The yellow crystalline product, $[(CH_3)_3S]_2B_{20}H_{17}OH$, decomposes at 250°.

Anal. Calcd. for $C_6H_{36}S_2B_{20}O$: C, 17.8; H, 8.96; S, 15.8; B, 53.4. Found: C, 16.7; H, 8.72; S, 15.9; B, 53.6.

$[(CH_3)_4N]_2B_{20}H_{17}OCOH$.—Formic acid, 25 ml., and $[(CH_3)_4N]_2B_{20}H_{17}OH$, 3 g., were heated on a steam bath for 1 hr., then allowed to stand at room temperature for several days. Large yellow crystals of crude product formed. Purification was accomplished by recrystallization from water to yield the product, $[(CH_3)_4N]_2B_{20}H_{17}OCOH$, m.p. 205° dec.

Anal. Calcd. for $C_9H_{42}N_2B_{20}O_2$: C, 25.3; H, 9.92; N, 6.56; B, 50.7. Found: C, 24.1; H, 10.0; N, 6.53; B, 50.8.

The infrared spectrum contained a strong B–H stretching frequency at 2510 cm.$^{-1}$, a strong CO absorption at 1690 cm.$^{-1}$, strong absorptions at 1200 and 1120 cm.$^{-1}$, and anion absorptions in the 1000–700 cm.$^{-1}$ region.

Oxidation of $B_{20}H_{17}OH^{-4}$.—A solution of ceric ammonium sulfate was slowly added to a stirred solution containing the $B_{20}H_{18}OH^{-4}$ ion until the solution became quite dark. During the last stages of addition, a gas was evolved. The solution was then treated with $(CH_3)_4NCl$ to form an insoluble gray precipitate. This solid was collected and recrystallized from water–acetonitrile to yield long yellow needles. The product, $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$, was dried *in vacuo* and showed an OH absorption at 3580 cm.$^{-1}$ but no HOH rocking absorption at 1600 cm.$^{-1}$ in the infrared spectrum.

Anal. Calcd. for $C_8H_{42}N_2B_{20}O_2$: C, 23.2; H, 10.2; N, 6.75; B, 52.2. Found: C, 22.4; H, 10.2; N, 6.67; B, 52.3.

Chlorination of $B_{20}H_{17}OH^{-4}$.—Chlorine was passed through an aqueous solution of $Cs_4B_{20}H_{17}OH$ at room temperature. Several color changes were observed during the course of the reaction. After several hours the solution became colorless and was treated with CsCl with the formation of a white precipitate. This solid was recrystallized from hot water to yield a pure white crystalline product, which, when dried *in vacuo*, had an infrared spectrum identical with that of $Cs_2B_{10}Cl_{10}$ obtained by the direct chlorination of $B_{10}H_{10}^{-2}$. The X-ray and ultraviolet data on the product were in good agreement with those of pure $Cs_2B_{10}Cl_{10}$.

Anal. Calcd. for $Cs_2B_{10}Cl_{10}$: B, 14.85; Cl, 48.7; Cs, 36.5. Found: B, 14.7; Cl, 48.9; Cs, 35.6.

Bromination of $B_{20}H_{17}OH^{-4}$.—An aqueous solution of Na_4B_{20}-

$H_{17}OH$ was treated with N-bromosuccinimide in a water–methanol medium. The mixture was stirred for several hours and then heated on a steam bath. The solution was treated with CsCl to yield a precipitate which was washed several times with alcohol to remove traces of succinimide. The product was then recrystallized from water to yield a hydrated salt, $Cs_4B_{20}Br_{13}H_4OH \cdot 4H_2O$, which showed a weak B–H stretch at 2500 cm.$^{-1}$ and water bands in the infrared spectrum.

Anal. Calcd. for $Cs_4B_{20}Br_{13}H_{13}O_5$: B, 11.5; Br, 55.3; Cs, 28.3. Found: B, 11.5; Br, 56.15; Cs, 27.4.

Acknowledgment.—We are indebted to Dr. V. A. Engelhardt for his suggestions and helpful advice and to Professor M. F. Hawthorne for advising us of his results on $B_{20}H_{18}^{-2}$ and on the isomerization of B_{20}^{-4} species.

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Chemistry of Boranes. XX.[1] Syntheses of Polyhedral Boranes

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High-yield syntheses of polyhedral borane structures such as $B_{12}H_{12}^{2-}$ and $B_{11}H_{14}^{-}$ have been achieved in two basic reactions: (1) a hydride ion source and a boron hydride, *e.g.*, $NaBH_4 + B_2H_6$; and (2) an organic Lewis base and a boron hydride. The triborohydride ion $B_3H_8^-$ appears to be an important intermediate in all these syntheses; thermal disproportionation of crystalline NaB_3H_8 occurs with formation of $Na_2B_{12}H_{12}$ and $NaBH_4$. In reactions 1 and 2, solvent can play a critical role in determining the nature of the product. Derivatives of $B_{12}H_{12}^{2-}$, $B_{12}H_{11}(\text{base})^-$ and $B_{12}H_{10}(\text{base})_2$, and borane cations, $H_2B(\text{base})_2^+$, are formed in reaction 2 with certain sulfides, amines, phosphines, and arsines.

Introduction

The polyhedral borane anions, particularly $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, have assumed considerable stature because of their very high kinetic stability[2] and the great scope of their derivative chemistry.[1-6] It is therefore of considerable importance to establish simple, high-yield syntheses of these anions from readily available boron compounds. Earlier we described a direct synthesis of diborane from boron oxides.[7] In this article, high-yield syntheses of $B_{12}H_{12}^{2-}$ from diborane are detailed,[8] thus linking this complex anion and its chemistry in two steps to borax, the principal boron ore.

The new syntheses of polyhedral boranes are based on two class reactions (eq. 1 and 2). Other boron

$$2NaBH_4 + 5B_2H_6 \longrightarrow Na_2B_{12}H_{12} + 13H_2 \qquad (1)$$

$$2(C_2H_5)_3N + 6B_2H_6 \longrightarrow [(C_2H_5)_3NH]_2B_{12}H_{12} + 11H_2 \qquad (2)$$

hydrides may be used instead of diborane. In reaction 1, a basic solvent is necessary for high conversions; however, certain solvents alter the course of the reaction. Other Lewis bases can be substituted for triethylamine in reaction 2, but some displace hydride ion and derivatives of $B_{12}H_{12}^{2-}$ and of H_2B^+ are formed in significant amounts.

Reaction of Hydride Ion and Boron Hydrides.—Reaction of diborane or borane complexes with hydride ion to give the borohydride ion is well-character-

$$B_2H_6 + 2MH \longrightarrow 2MBH_4 \qquad (3)$$

ized.[9] The equilibrium between BH_4^-, B_2H_6, and $B_2H_7^-$ has also been established.[10] Consistent with the report

$$2BH_4^- + B_2H_6 \rightleftharpoons 2B_2H_7^- \qquad (4)$$

of Gaines, Schaeffer, and Tebbe,[11] we find that sodium borohydride and diborane react in ether solvents irreversibly at elevated temperatures to form the triborohydride ion.

$$NaBH_4 + B_2H_6 \longrightarrow NaB_3H_8 + H_2 \qquad (5)$$

Reaction 5 is quantitative at 25–60° if the diborane pressure exceeds 1–2 atm. At atmospheric pressure, measurable rates of $B_3H_8^-$ formation are achieved only at temperatures of $\sim 100°$ with a high-boiling, ether solvent. If pentaborane is substituted for diborane in reaction 5, some progression beyond the $B_3H_8^-$ stage occurs at 60°, and the $B_{11}H_{14}^-$ anion is formed in significant amounts.

The $B_{11}H_{14}^-$ anion[12] is formed under a variety of conditions in the reaction of sodium borohydride and diborane. Certain ether solvents favor formation of the

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[1] Paper XIX: W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 3973 (1964).

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

[3] W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

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

[5] W. H. Knoth, 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] G. H. Kalb, T. A. Ford, A. L. McClelland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1032 (1964).

[8] (a) A preliminary note on this synthesis has been published: H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3885 (1963). Related syntheses are reported by (b) I. A. Ellis, D. F. Gaines, and R. Schaeffer, *ibid.*, **85**, 3885 (1963); (c) N. N. Greenwood and J. H. Morris, *Proc. Chem. Soc.*, 338 (1963); (d) R. M. Adams, A. R. Siedle, and J. Grant, *Inorg. Chem.*, **3**, 461 (1964).

[9] H. C. Brown and P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

[10] H. C. Brown, P. F. Stehle, and P. A. Tierney, *ibid.*, **79**, 2020 (1957); E. B. Baker, R. B. Ellis, and W. S. Wilcox, *J. Inorg. Nucl. Chem.*, **23**, 41 (1961).

[11] D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

[12] V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *ibid.*, **1**, 734 (1962).