$H_{17}OH$ 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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$B_{11}H_{14}^-$ anion, and, in fact, this anion is obtained exclusively when dioxane is the solvent and the reaction temperature is 90–120°. Since one synthesis[12] of $B_{11}H_{14}^-$ comprises addition of diborane or borane to $B_{10}H_{13}^-$, the latter anion may be inferred as another building block in the possibly sequential formation of polyhedral boranes. Excess boron hydride will always convert $B_{11}H_{14}^-$ to $B_{12}H_{12}^{2-}$ at temperatures above ~100°.

Formation of $B_{12}H_{12}^{2-}$ from diborane and sodium borohydride (or NaB_3H_8) begins at ~100°.[13] The rate of conversion is markedly dependent upon solvent. With one of the best solvents, triethylamine, $B_{12}H_{12}^{2-}$ formation is fast and nearly quantitative at 175°.

The polyhedral borane synthesis represented in a general form in eq. 6 may be considered primarily as a sequential buildup of a boron lattice by reaction of a

$$aH^- + bB_xH_y \rightarrow [B_{bx}H_{by+a-z}]^{a-} + (z/2)H_2 \qquad (6)$$

boron hydride or borane complex with hydride or borohydride ion. Such a generalized description is reasonable on the basis of the nature of the reactants and the experimental findings. The hydride or borohydride ions are nucleophiles and should be susceptible to attack by the strongly electrophilic boron hydrides. Any borohydride ion, *e.g.*, $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{10}H_{10}^{2-}$, can be used in place of H^- or BH_4^-, and any boron hydride, from B_2H_6 to $B_{18}H_{22}$, can be used as the electrophile.

In principle, it should be possible to start with H^- and borane and generate successively more complex borane anions. The steps from BH_4^- to $B_2H_7^-$ to $B_3H_8^-$ are established. In the formally analogous base plus boron hydride reaction, a derivative of $B_9H_{14}^-$, $B_9H_{13}S(CH_3)_2$, was isolated from the reaction of dimethyl sulfide and diborane (*vide infra*). Thus, it might be inferred that $B_9H_{14}^-$ is involved in a sequential buildup. Isolation of $B_{11}H_{14}^-$ from sodium borohydride and diborane in dioxane establishes another step in reaction 6. Ease of isolation of $B_{11}H_{14}^-$ reflects the experimental facts that $B_{11}H_{14}^-$ is stable to at least 180° and that reaction with excess boron hydride or a base–borane complex does not occur at a significant rate below ~100°. The only requirements for sole formation of $B_{12}H_{12}^{2-}$ rather than $B_3H_8^-$ or $B_{11}H_{14}^-$ in reaction 1 are excess hydride and high temperatures (130–180°).

The $B_{10}H_{10}^{-2}$ anion could be involved in the reaction sequence 6 as shown by the formation of $B_{10}H_{10}^{2-}$ as a minor product in the pyrolysis of $B_3H_8^-$ reported by Ellis, Gaines, and Schaeffer.[8b] It has not been found as a product of sequence 6. This is consistent with our finding that under typical synthesis conditions, $B_{10}H_{10}^{2-}$ is converted to $B_{12}H_{12}^{2-}$, the apparent terminal species in sequence 6. It is our opinion that $B_{10}H_{10}^{2-}$ is not an important intermediate in $B_{12}H_{12}^{2-}$ synthesis since the rate of conversion of B_{10} to B_{12} appears to be lower than the rate of B_{12} formation from diborane.

Reaction of Base and Boron Hydride.—The formation of polyhedral boranes in the reaction of a boron hydride and an organic Lewis base or base–borane complex must be closely related, in a mechanistic sense, to the synthesis based on hydride or borohydride ion. The first step is formation of a base–borane complex, *e.g.*

$$\text{base} + {}^1/_2B_2H_6 \rightleftharpoons H_3B\text{–base}$$

From this point, the base may follow either of two paths: (1) it may remain bonded to the boron atom and sequential buildup may take place on the adduct to give a derivative of a polyhedral borane anion or (2) the base may be displaced and then captured by a proton to give an onium ion and sequential buildup may then ensue with a borohydride ion. The first role is best illustrated in the methyl sulfide–diborane reaction in which the major product at 150° is $B_{12}H_{10}[S(CH_3)_2]_2$. There is, however, some base displacement and significant amounts of $B_{12}H_{11}S(CH_3)_2^-$ and $B_{12}H_{12}^{2-}$ are formed. At lower synthesis temperatures, $B_9H_{13}S(CH_3)_2$,[14] as well as $B_{11}H_{14}{,}^-$ is formed. A similar mixing of the two types of base roles was observed with trimethylamine, -phosphine, and -arsine. In the case of triethylamine, displacement prevails at 180° and the triethylammonium salt of $B_{12}H_{12}^{2-}$ is the sole product.

In addition to the polyhedral boranes, borane cations of the type $H_2B(\text{base})_2^+$ are formed. Characterization of these cations is the subject of another paper.[15]

The type of products from the base–borane reactions appears to be a function of the strength of the base with reference to the hydrogen ion and to the steric hindrance about the donor atom. Strong bases, such as the amines, give primarily ammonium salts of $B_{12}H_{12}^{2-}$, although if the amine is less sterically hindered than triethylamine (*vide infra*) the cation $H_2B(NR_3)_2^+$ and the substituted anion $B_{12}H_{11}NR_3^-$ are also formed in small amounts. Weaker bases such as phosphines and arsines give primarily the $H_2B(\text{base})_2^+$ salt of $B_{12}H_{11}(\text{base})^-$ with small amounts of $B_{12}H_{10}(\text{base})_2$. With the very weak and relatively unhindered base, methyl sulfide, the disubstituted B_{12} derivative, $B_{12}H_{10}[S(CH_3)_2]_2$, and the $H_2B[S(CH_3)_2]_2^+$ salt of $B_{12}H_{11}S(CH_3)_2^-$ are the major products.

A detailed study was made of the effect of steric factors of the tertiary amine reactants on product distribution. Cationic derivatives $H_2B(NR_3)_2^+$ formed only when there was at least one methyl group present in the amine. Yields of the cation fell significantly with increase in the size of the amine. The anionic derivative $B_{12}H_{11}NR_3^-$ was invariably formed; yields were inversely related to the size of the amine. The data are summarized in Table I.

The novel base derivatives of $B_{12}H_{12}^{2-}$, *i.e.*, $B_{12}H_{11}$(base)$^-$ and $B_{12}H_{10}(\text{base})_2$, display the general cage

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(13) Pyrolysis of $NaB_3H_8 \cdot 3O(CH_2CH_2)_2O$ occurs at 150–200° in the absence of solvent to give $Na_2B_{12}H_{12}$: $5NaB_3H_8 \cdot 3O(CH_2CH_2)_2O \rightarrow Na_2B_{12}H_{12} + NaBH_4 + 15O(CH_2CH_2)_2O$. Ellis, Gaines, and Schaeffer[8b] have shown that pyrolysis of $B_3H_8^-$ to $B_{12}H_{12}^{2-}$ occurs at ~100–130° in diethylene glycol dimethyl ether solvent.

(14) A referee pointed out that $B_9H_{13}S(CH_3)_2$ could have been formed in the work-up procedure from a species such as $B_{10}H_{12} \cdot 2S(CH_3)_2$.

(15) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

Table I

Relative Yields of Borane Species from Amines and Diborane at 175°

Amine	Yields[a] of borane products		
	$H_2B(NR_3)_2^+$	$B_{12}H_{11}NR_3^-$	$B_{12}H_{12}^{2-}$
$N(CH_3)_3$	6	27	64
$N(CH_3)_2C_2H_5$	2	11	80
$NCH_3(C_2H_5)_2$	0.6	8	80
$N(C_2H_5)_3$	0	0–5	80–100
$N(CH_2)_5CH_3$[b]	1.5	13	55

[a] Based on total boron charged. [b] N-Methylpiperidine.

stability and the susceptibility to substitution reactions characteristic of the parent ion. Substitution reactions of these derivatives will be described in another paper.[16]

Experimental

Reagents and Procedures.—The diborane and pentaborane used were commercial grade. Decaborane(14) was generally recrystallized from *n*-heptane to remove small amounts of boric acid usually present. All solvents were dried by standard procedures. Triethylamine borane was prepared *in situ* from triethylamine and diborane or was preformed by introducing gaseous diborane onto triethylamine contained in a pressure vessel, and then purified by distillation at 87° (12 mm.).

Anal. Calcd. for $(C_2H_5)_3NBH_3$: B, 9.4; N, 12.2. Found: B, 9.3; N, 12.0.

Experiments at pressures above atmospheric were conducted behind heavy metal barricades in stainless steel pressure vessels equipped with a thermocouple well, a high pressure inlet valve, and a rupture disk designed to release at 2400 p.s.i.g. (100-ml. reactor) or 1200 atm. (400-ml. reactor). The reactors were flushed with nitrogen, charged with solids and liquids, and then closed, cooled to $-78°$, and evacuated with a mechanical pump. Diborane was then pressured into the chilled reactor from a storage cylinder. The amount of diborane introduced was determined by weighing either the reactor or the supply cylinder before and after the addition. In exploratory experiments, or when known hazardous reactions could conceivably take place, the diborane was introduced remotely and measured by the pressure drop of a calibrated volume. The reactor was heated with shaking for the required time and then cooled to room temperature. The volatile gases were vented into a nitrogen stream directed to an efficient hood system. In order to ensure that all the diborane and other noxious gases were removed, the reactor was pressured to 200 p.s.i.g. with dry nitrogen and then vented. This was repeated, usually twice, and then the reactor was opened and the solid product removed. Occasionally the volatile contents were introduced into a vacuum line for characterization. In this case, all the gases were removed by thorough evacuation and nitrogen was introduced to bring pressure to 1 atm. and the reactor opened.

In some work-up procedures a high speed Osterizer blender was employed to grind solids with a solvent. The motor housing was tapped and a nitrogen inlet attached to keep an inert atmosphere around the motor in order to prevent explosions which are possible when solvent vapors enter the spark area of the motor. In the detailed experiments this apparatus is referred to as a blender.

Characterization of the products by melting point was generally unsatisfactory. These salts usually decomposed at high temperatures, frequently without melting. Infrared absorption was, however, generally useful. Spectra were recorded on Perkin-Elmer Model 21 or Infracord spectrophotometers. Only the strong bands characteristic of each species, exclusive of C–H frequencies, are reported.

Synthesis of NaB_3H_8 from Sodium Borohydride and Diborane. (A) **Above Atmospheric Pressure.**—A 100-ml. stainless steel pressure vessel was charged with 1.9 g. (0.05 mole) of sodium borohydride, 10 ml. of dimethoxyethane, and 2.0 g. (0.07 mole) of diborane. The tube was heated with agitation for 10 hr. at 60° under autogenous pressure. Diborane (0.01 mole) and 0.8 mole of hydrogen were recovered. The clear, amber, liquid product was held under reduced pressure (less than 1 μ) at room temperature until all volatile material was removed to leave 9.2 g. of oily product, probably the dimethoxyethane complex of NaB_3H_8. The oil was dissolved in 50 ml. of water. A water solution of 5 g. of tetramethylammonium chloride was added, and the white solid that separated was redissolved by heating the mixture to reflux. The hot solution was diluted with an equal volume of methanol and then chilled in an ice bath. The tetramethylammonium salt of $B_3H_8^-$ separated as white crystals (4.97 g., 87%). The identity of the compound as $(CH_3)_4NB_3H_8$ was confirmed by comparison of its infrared spectrum with that of an authentic sample.

Alternatively the NaB_3H_8 was isolated as its dioxanate. In a typical experiment, 1.9 g. (0.05 mole) sodium borohydride and 3.36 g. (0.122 mole) of diborane in 10 ml. of dimethoxyethane in a 100-ml. pressure vessel were held at room temperature for 10 hr. Unused diborane (0.06 mole), hydrogen (0.05 mole), and a clear ether solution were obtained. Dilution of the solution with dioxane gave a colorless precipitate. The solid was collected, washed with dioxane, and dried at <1 μ and room temperature to give 14.8 g. (89%) of solid which showed the infrared bands characteristic of $B_3H_8^-$ salts.

Anal. Calcd. for $NaB_3H_8 \cdot 3C_4H_8O_2$: C, 43.9; H, 9.8; B, 9.9; Na, 7.0. Found: C, 43.8; H, 10.0; B, 9.9; Na, 7.1.

(B) **Atmospheric Pressure Synthesis.**—A solution of 2.0 g. (0.053 mole) of sodium borohydride in 25 ml. of tetraethylene glycol dimethyl ether was stirred in an inert atmosphere, and diborane was bubbled through slowly (about 2 g./hr.) while raising the temperature. At about 105°, hydrogen evolution began, continued about 40 min., and then stopped. To a small sample of the solution was added dioxane to precipitate $NaB_3H_8 \cdot 3C_4H_8O_2$ (identified by its infrared spectrum). Addition of aqueous cesium chloride to a solution of the dioxanate in water gave a white solid which had the infrared spectrum of authentic CsB_3H_8.

$B_{11}H_{14}^-$ Synthesis.—A 400-ml. stainless steel shaker tube was charged with 2.54 g. (0.067 mole) of sodium borohydride, 4.6 g. (0.166 mole) of diborane, and 25 ml. of dioxane. This B_2H_6/$NaBH_4$ ratio is only one-half that required by the equation

$$NaBH_4 + 5B_2H_6 \longrightarrow NaB_{11}H_{14} + 10H_2$$

but at the stoichiometric ratio violent uncontrolled reactions occurred which caused serious equipment damage. The reactor was heated to 80° for 10 hr. with shaking and then was unloaded as described above. The contents were added to ~250 ml. of dimethoxyethane and the mixture was filtered. Addition of several volumes of dioxane to the filtrate gave a colorless precipitate of $NaB_{11}H_{14} \cdot 2.5O(CH_2)O$ which was collected after the mixture was chilled to 5°; yields ranged from 5 to 10 g. (35–70%). This product was identical spectroscopically with the $NaB_{11}H_{14} \cdot 2.5C_4H_8O_2$ obtained from sodium borohydride and decaborane(14).[12]

$B_{12}H_{12}^{2-}$ Synthesis. (A) From Sodium Borohydride and Diborane.—A 400-ml. stainless steel pressure vessel was charged with 15 g. (0.4 mole) of sodium borohydride, 60 ml. (0.43 mole) of triethylamine, and 34 g. (1.23 moles) of diborane, then heated to 180° over 1.5 hr. and held at that temperature with agitation for 8 hr. The solid product was scraped out, and the reactor was then washed with 100 ml. of tetrahydrofuran. The solid and wash liquid were combined in a blender with an additional 100 ml. of tetrahydrofuran. Most of the solid dissolved in 5–10 min. as the blender was run at medium speed to leave some finely divided amorphous material in suspension. The solution was clarified by vacuum filtration through a mat of Celite filter aid. The clear filtrate was diluted with 250 ml. of dimethoxyethane, and a white solid (crystalline) separated. It was collected after the mixture was held at 0 to 5°

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for 2 hr. and washed with 40 ml. of dimethoxyethane. The solid was returned to the blender with 160 ml. of dimethoxyethane to remove as completely as possible the triethylamine borane by-product. The solid was again collected and washed with 40 ml. of fresh dimethoxyethane. The product at this point was $Na_2B_{12}H_{12}$ solvated with dimethoxyethane and may also contain water (acquired during work-up). A sample dried to $<1\ \mu$ pressure at 100° contained 1 mole of the ether.

Anal. Calcd. for $Na_2B_{12}H_{12}\cdot C_4H_{10}O_2$: C, 17.3; H, 7.9; B, 46.7; Na, 16.5. Found: C, 17.4; H, 8.0; B, 46.2; Na, 16.1.

Another sample gave a monohydrate when dried at 150° and 1 μ.

Anal. Calcd. for $Na_2B_{12}H_{12}\cdot H_2O$: C, 0.0; H, 6.8; B, 63.0; Na, 22.3. Found: C, 1.6; H, 7.1; B, 63.5; Na, 21.6.

The unsolvated salt was conveniently prepared by steam distillation of the solvate in the following manner. The solid was combined with 40 ml. of water and heated on a steam bath while steam was bubbled through until the issuing vapors were free of the odor of the ether. The remaining solution was cooled to room temperature, clarified by filtration, and evaporated to dryness. The resulting solid, dried *in vacuo* over P_2O_5, contained from 0.1 to 3 moles of water per mole of $B_{12}H_{12}^{2-}$ and weighed from 25 to 35 g. depending upon the extent of drying; yields ranged from 75 to 85%.

Additional small amounts of crude $Na_2B_{12}H_{12}$ were obtained by concentration of the first tetrahydrofuran–dimethoxyethane filtrates. Generally these second crops were about 10% the size of the first.

(B) **From Triethylamine and Diborane.**—A 400-ml. stainless steel pressure vessel was charged with 80 ml. (58 g., 0.575 mole) of triethylamine and 34 g. (1.23 moles) of diborane, heated for 2 hr. at 180° with agitation, and then unloaded. The 69 g. of off-white solid product was ground in a blender with about 400 ml. of ether. The insoluble solid was washed with ether and dried to give 66 g. (93% based on boron charged) of crude $[(C_2H_5)_3NH]_2B_{12}H_{12}$. Recrystallization from 120 ml. of boiling water containing 25 ml. of 4 *N* hydrochloric acid gave 56 g. (after vacuum drying at 110°) of colorless needles. A second crop of 3.0 g. obtained on concentrating the filtrate raised the yield to 59 g. (83%) of pure $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

Anal. Calcd. for $[(C_2H_5)_3NH]_2B_{12}H_{12}$: C, 41.6; H, 12.8; B, 37.5; N, 8.1. Found: C, 41.2; H, 12.6; B, 37.3; N, 8.0.

The gaseous reaction products were examined in experiments carried out in 100-ml. reactors. In one run at 180°, 0.39 mole of triethylamine and 0.074 mole of diborane gave 0.142 mole of hydrogen, 1.25 g. (0.011 mole) triethylamine borane, and 4.2 g. (91% yield) of $[(C_2H_5)_3NH]_2B_{12}H_{12}$. In experiments at 100° in which very low conversions to $[(C_2H_5)_3NH]_2B_{12}H_{12}$ were observed, small amounts of pentaborane(9) were found in the volatile products.

(C) **From Triethylamine Borane and Pentaborane(9).**—In a 100-ml. stainless steel bomb, 0.044 mole of pentaborane(9) and 0.043 mole of triethylamine borane were heated at 125° for 10 hr. to give 0.129 mole of hydrogen (100%) and 6.8 g. (90%) of $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

(D) **From Triethylamine Borane and Decaborane(14).**—A solution of 30 g. (0.246 mole) of decaborane(14) in 52.5 g. (0.54 mole) of triethylamine borane was prepared under nitrogen. The solution was added over a 20-min. period with stirring to 240 ml. of Ultrasene (a high-boiling kerosene, especially purified and free of unsaturation, available from the Atlantic Refining Company) maintained at 190° by means of an oil bath. The air in the flask had previously been displaced with nitrogen. A reflux condenser on the flask was connected to a wet test meter to follow roughly the rate and amount of gas evolution. As the solution was added, gas evolved rapidly (17.9 l., 98%) and a white solid separated. Gas evolution ceased almost as soon as the last of the solution had been added. The resulting slurry was cooled to room temperature and the solid collected. The solid was washed with ether and dried to give 72 g. (92% of theory) of nearly pure $[(C_2H_5)_3NH]_2B_{12}H_{12}$. Upon recrystallization from 1.5 l. of boiling water, about 3 g. of amorphous material was not soluble and was removed by filtration of the hot solution. Upon chilling, the filtrate deposited 67.2 g. (80%) of colorless needles.

The ether used to wash the crude product yielded 1 g. of colorless solid upon dilution with petroleum ether. This solid was recrystallized from ethanol and found to be the triethylammonium salt of the anion, $B_{12}H_{11}N(C_2H_5)_3^-$.

Anal. Calcd. for $(C_2H_5)_3NHB_{12}H_{11}N(C_2H_5)_3$: C, 41.9; H, 12.3; B, 37.7; N, 8.1. Found: C, 41.5; H, 12.2; B, 37.1; N, 8.2.

An ethanol solution of this product was passed through a strong acid ion-exchange resin. When the acid effluent was neutralized with cesium hydroxide, a white solid separated and was recrystallized from water.

Anal. Calcd. for $CsB_{12}H_{11}N(C_2H_5)_3$: C, 19.2; H, 7.0; B, 34.6; Cs, 35.4; N, 3.7. Found: C, 19.8; H, 8.2; B, 34.0; Cs, 35.5; N, 3.8.

The $B_{12}H_{11}N(C_2H_5)_3^-$ anion had strong characteristic infrared absorptions at 2500, 1050, 980, 825, and 740 cm.$^{-1}$.

The Synthesis of $H_2B(base)_2^+$, $B_{12}H_{11}(base)^-$, and $B_{12}H_{10}(base)_2$. (A) The Reaction of Trimethylamine Borane with Diborane.—In a 400-ml. stainless steel shaker tube, 21.0 g. (0.287 mole) of trimethylamine borane and 12 g. (0.435 mole) of diborane were heated under autogenous pressure to 175° for 10 hr. with shaking. The solid product was freed of volatile material by evacuation to leave 31 g. of white solid. On treatment of the solid with 50 ml. of boiling water, some gas evolution occurred. After the gas evolution subsided, the material insoluble in boiling water was collected to give 8.5 g. (0.026 mole) of $H_2B[N(CH_3)_3]_2B_{12}H_{11}N(CH_3)_3$. When the hot filtrate was chilled, 15.6 g. (0.056 mole) of $[H_2B[N(CH_3)_3]_2]_2B_{12}H_{12}$ separated. The former salt was recrystallized from methanol, and the latter from water.

Anal. Calcd. for $H_2B[N(CH_3)_3]_2B_{12}H_{11}N(CH_3)_3$: C, 32.6; H, 12.2; B, 42.5; N, 12.7. Found: C, 32.6; H, 12.3; B, 42.5; N, 12.6.

Anal. Calcd. for $[H_2B[N(CH_3)_3]_2]_2B_{12}H_{12}$: C, 35.7; H, 13.0; B, 37.5; N, 13.9. Found: C, 35.7; H, 13.0; B, 37.0; N, 13.8.

An aqueous alcohol solution of $H_2B[N(CH_3)_3]_2B_{12}H_{11}N(CH_3)_3$ (2.0 g., 0.006 mole) was passed through a strong acid ion-exchange resin (Amberlite IR 120-H). The acidic effluent was neutralized with aqueous cesium hydroxide. When the solution was concentrated and chilled, $CsB_{12}H_{11}N(CH_3)_3$ separated. It weighed 0.55 g. (0.0165 mole, 27% yield) after one recrystallization from water.

Anal. Calcd. for $CsB_{12}H_{11}N(CH_3)_3$: C, 10.8; H, 6.0; B, 39.0; Cs, 39.9; N, 4.2. Found: C, 9.6; H, 5.9; B, 38.6; Cs, 41.0; N, 4.2.

The $(CH_3)_3SB_{12}H_{11}N(CH_3)_3$ salt was made in a similar fashion.

Anal. Calcd. for $(CH_3)_3SB_{12}H_{11}N(CH_3)_3$: C, 26.0; H, 10.5; B, 46.8; N, 5.0; S, 11.6. Found: C, 26.0; H, 10.3; B, 45.2; N, 5.0; S, 11.6.

The characterizing features of the infrared spectrum of the $B_{12}H_{11}N(CH_3)_3^-$ anion were at 2500, 1055, 955, and 898 cm.$^{-1}$.

When this experiment was repeated at 125° in a 100-ml. vessel with 1.6 g. of trimethylamine borane (0.022 mole) and 1.8 g. of diborane (0.065 mole), the volatile material contained 0.12 mole of hydrogen, 0.005 mole of diborane, and 0.004 mole of pentaborane(9). The nonvolatile residue was a white crystalline solid (2.6 g.) in which $B_{12}H_{11}N(CH_3)_3^-$ and $B_{12}H_{12}^{2-}$ were identified by infrared analysis.

(B) **The Reaction of Ethyldimethylamine with Diborane.**—In a 400-ml. stainless steel pressure vessel, ethyldimethylamine (20.4 g., 0.28 mole) and diborane (16 g., 0.58 mole) were heated for 10 hr. at 175°. The 27 g. of gummy solid product was taken up in hot aqueous alcohol, clarified by filtration, and chilled to give 3.9 g. (0.0195 mole) of $H_2B[N(CH_3)_2C_2H_5]_2B_{12}H_{11}N(CH_3)_2C_2H_5$.

Anal. Calcd. for $H_2B[N(CH_3)_2C_2H_5]_2B_{12}H_{11}N(CH_3)_2C_2H_5$: C, 38.6; H, 12.4; B, 37.7; N, 11.2. Found: C, 39.1; H, 12.3; B, 37.6; N, 11.2.

By concentration of the filtrate two additional crops totalling 4.2 g. (0.009 mole) of $[H_2B[N(CH_3)_2C_2H_5]_2]_2B_{12}H_{12}$ were obtained.

It was recrystallized from 10% aqueous sodium hydroxide and then from water.

Anal. Calcd. for $[H_2B[N(CH_3)_2C_2H_5]_2]_2B_{12}H_{12}$: C, 41.8; H, 13.1; B, 32.9; N, 12.2. Found: C, 41.5; H, 12.9; B, 32.8; N, 12.3.

An aqueous solution of 1.9 g. of $H_2B[N(CH_3)_2C_2H_5]_2B_{12}H_{11}N(CH_3)_2C_2H_5$ was passed through a strong acid ion-exchange resin column. The effluent was divided into two portions which were neutralized with aqueous cesium hydroxide and trimethylsulfonium hydroxide, respectively. The crystalline salts were recrystallized from water.

Anal. Calcd. for $CsB_{12}H_{11}N(CH_3)_2C_2H_5$: C, 13.8; H, 6.4; B, 37.4; N, 4.1. Found: C, 13.7; H, 6.4; B, 36.8; N, 4.2.

Anal. Calcd. for $(CH_3)_3SB_{12}H_{11}N(CH_3)_2C_2H_5$: C, 28.9; H, 10.7; B, 44.6; S, 11.0. Found: C, 28.9; H, 10.8; B, 44.0; S, 11.0.

The strong infrared bands characteristic of the $B_{12}H_{11}N(CH_3)_2C_2H_5^-$ anion occurred at 2500, 1050, 980, 870, and 725 cm.$^{-1}$.

(C) The Reaction of Diethylmethylamine with Diborane.—The above experiment was repeated with diethylmethylamine (25 g., 0.287 mole) and diborane (16 g., 0.58 mole). After removal of volatile material, 34.4 g. of white semisolid remained. The solid was washed with ether to remove amine borane, then boiled with dilute aqueous sodium hydroxide to remove free amine. Upon cooling, 3.1 g. (0.0075 mole) of white solid $H_2B[N(C_2H_5)_2CH_3]_2B_{12}H_{11}N(C_2H_5)_2CH_3$ separated. It was recrystallized from water.

Anal. Calcd. for $H_2B[N(C_2H_5)_2CH_3]_2B_{12}H_{11}N(C_2H_5)_2CH_3$: C, 43.4; H, 12.6; B, 33.9; N, 10.1. Found: C, 44.1; H, 13.0; B, 33.8; N, 10.1.

The strong infrared absorptions shown by the $B_{12}H_{11}N(C_2H_5)_2CH_3^-$ anion occurred at 2500, 1050, 975, 870, and 725 cm.$^{-1}$. From the mother liquor, $B_{12}H_{12}^{2-}$ salts free of the $B_{12}H_{11}N(C_2H_5)_2CH_3^-$ anion were obtained upon adding Cs^+ or $(CH_3)_3S^+$. In a second experiment held at 175° for 25 hr. a nearly identical yield was obtained.

(D) The Reaction of N-Methylpiperidine with Diborane.—As above, N-methylpiperidine (27 g., 0.273 mole) and diborane (17 g., 0.615 mole) were held at 175° for 10 hr. The nonvolatile solid residue weighed 26.4 g. It was washed with ether and boiled with water acidified with hydrochloric acid. A portion (6.7 g.) of the solid was insoluble in the hot acid, 2.7 g. separated on cooling the filtrate, and another 1 g. was obtained from the mother liquor after it was made basic and boiled to expel free amine. Addition of aqueous trimethylsulfonium iodide to this filtrate gave 4.3 g. (0.014 mole) of $[(CH_3)_3S]_2B_{12}H_{12}$. The 2.7-g. and 1.0-g. crops were mixtures of the $CH_3NH(CH_2)_5^+$ and $H_2B[N(CH_2)_5CH_3]_2^+$ salts of $B_{12}H_{12}^{2-}$ and $B_{12}H_{11}N(CH_2)_5CH_3^-$ by infrared analysis. The 6.7-g. crop was $H_2B[N(CH_2)_5CH_3]_2B_{12}H_{11}N(CH_2)_5CH_3$ (0.015 mole). It was recrystallized from water.

Anal. Calcd. for $H_2B[N(CH_2)_5CH_3]_2B_{12}H_{11}N(CH_2)_5CH_3$: C, 47.0; H, 11.6; B, 31.2; N, 9.3. Found: C, 47.7; H, 11.6; B, 31.0; N, 8.8.

This salt showed strong infrared bands at 2500, 1235, 1205, 1050, and 870 cm.$^{-1}$.

(E) The Reaction of Cyclohexyldimethylamine with Diborane.—As above, cyclohexyldimethylamine (37 g., 0.29 mole) and diborane (16 g., 0.58 mole) were held at 175° for 10 hr. to give 47 g. of gray semisolid nonvolatile material. The solid was boiled with acidified water in which it all dissolved except for a small amount (<1.0 g.) of oil which was decanted and retained. Cooling the hot solution gave 3.0 g. (0.0716 mole) of crystals identical in infrared spectrum with authentic $[C_6H_{11}NH(CH_3)_2]_2B_{12}H_{12}$. The insoluble oil was boiled with aqueous sodium hydroxide and the cooled mixture extracted with ether to remove free amine. Addition of aqueous trimethylsulfonium iodide gave 1.8 g. of solid which by elemental analysis appeared to be a 1:3 mixture of $[(CH_3)_2S]_2B_{12}H_{12}$ and $(CH_3)_3SB_{12}H_{11}N(CH_3)_2C_6H_{11}$. Thus, 0.0039 mole of $B_{12}H_{11}N(CH_3)_2C_6H_{11}^-$ was isolated.

Anal. Calcd. for the mixture: C, 35.2; H, 10.6; B, 39.0; N, 3.2; S, 12.0. Found: C, 35.4; H, 11.1; B, 37.9; N, 2.9; S, 11.9.

(F) The Reaction of Tri-*n*-butylamine with Diborane.—In a 100-ml. pressure vessel, tri-*n*-butylamine (4.9 g., 0.026 mole) and diborane (2.11 g., 0.076 mole) were heated for 5 hr. at 125°. The volatile material contained 0.128 mole of hydrogen. The nonvolatile, nearly dry, yellow solid was washed with ether to leave 4.6 g. of yellow solid. Evaporation of the ether left 1.1 g. of oil, probably tri-*n*-butylamine borane (0.0055 mole). Recrystallization of the solid from water gave 4.0 g. (0.0078 mole) of white crystals identical in infrared spectrum with authentic $[(n\text{-}C_4H_9)_3NH]_2B_{12}H_{12}$.

(G) The Reaction of N-Methylmorpholine with Diborane.—In a 100-ml. pressure vessel, N-methylmorpholine (2.4 g., 0.024 mole) and diborane (2.02 g., 0.073 mole) were heated to 125° for 5 hr. to give 0.105 mole of hydrogen and 2.1 g. of yellow, sticky solid. The solid dissolved when boiled in acidified water. An excess of triethylammonium chloride was added to the hot solution which on cooling gave 0.9 g. of $[(C_2H_5)_3NH]_2B_{12}H_{12}$ (0.0026 mole).

(H) The Reaction of N,N,N′,N′-Tetramethylethylenediamine with Diborane.—In a 400-ml. pressure vessel, N,N,N′,N′-tetramethylethylenediamine (TMED) (19 g., 0.164 mole) and diborane (16 g., 0.58 mole) were heated to 175° for 10 hr. The nonvolatile product (35 g.) was a brownish powder. A satisfactory separation procedure was not developed, but the presence of $(TMED)(BH_3)_2$, $H_2B(TMED)^+$, and $B_{12}H_{12}^{2-}$ in the crude product was demonstrated. Upon heating *in vacuo*, a portion of the crude product gave a white sublimate of $(TMED)(BH_3)_2$ which was identified by comparison of its infrared spectrum with that of an authentic sample. The crude product was partly soluble in boiling water. The hot filtrate gave a colorless solid on cooling. Extraction of this solid with 20% aqueous sodium hydroxide at room temperature gave an extract which deposited $[(CH_3)_3S]_2B_{12}H_{12}$ on addition of aqueous trimethylsulfonium hydroxide. The portion insoluble in cold base was freed of $(TMED)(BH_3)_2$ by extraction with benzene, boiled with a suspension of strong base ion-exchange resin, and filtered. The filtrate was mixed with aqueous ammonium hexafluorophosphate, concentrated, and chilled to give crystals of $H_2B(TMED)PF_6$.[15]

(I) The Reaction of Diborane with Trimethylphosphine.—In a 400-ml. stainless steel bomb, 6.7 g. (0.088 mole) of trimethylphosphine and 4.5 g. (0.163 mole) of diborane were heated at 175° under autogenous pressure with shaking for 10 hr. There was obtained 11.1 g. of yellow solid which was extracted with boiling water to leave a yellow residue. When chilled, the extract deposited 5.5 g. (0.0014 mole) of very sparingly water-soluble colorless crystals of $H_2B[P(CH_3)_3]_2B_{12}H_{11}P(CH_3)_3$, m.p. 240–247° dec. The residue was recrystallized from methylene chloride containing a small amount of ether to give 1.8 g. (0.0062 mole) of slightly off-white crystals of $B_{12}H_{10}[P(CH_3)_3]_2$, m.p. 337–350° dec. The tetramethylammonium salt of $B_{12}H_{11}P(CH_3)_3$, m.p. 337–338° dec., was obtained by ion exchange from $H_2B[P(CH_3)_3]_2B_{12}H_{11}P(CH_3)_3$.

Anal. Calcd. for $B_{12}H_{10}[P(CH_3)_3]_2$: C, 24.7; H, 9.7; B, 44.5; P, 21.2; mol. wt., 292. Found: C, 24.8; H, 10.2; B, 43.2; P, 21.8; mol. wt., 286 (ebullioscopic, 1,2-$C_2H_4Cl_2$).

Anal. Calcd. for $H_2B[P(CH_3)_3]_2B_{12}H_{11}P(CH_3)_3$: C, 28.3; H, 10.6; B, 36.8; P, 24.3. Found: C, 28.2; H, 10.8; B, 36.3; P, 23.6.

Anal. Calcd. for $(CH_3)_4NB_{12}H_{11}P(CH_3)_3$; C, 28.8; H, 11.1; N, 4.8; P, 10.6. Found: C, 27.6; H, 11.5; N, 4.8; P, 10.7.

The strong infrared absorptions characteristic of $B_{12}H_{10}[P(CH_3)_3]_2$ were at 2500, 1290, 1000, 950, and 765 cm.$^{-1}$, and those of $B_{12}H_{11}P(CH_3)_3^-$ at 2500, 1290, 1045, and 960 cm.$^{-1}$.

In a similar experiment at 150°, the only water-soluble material obtained was 150 mg. of $[H_2B[P(CH_3)_3]_2]_2B_{12}H_{12}$.

Anal. Calcd. for $[H_2B[P(CH_3)_3]_2]_2B_{12}H_{12}$: C, 30.5; H, 11.1; B, 32.1; P, 26.2. Found: C, 30.1; H, 11.0; B, 31.3; P, 26.1.

(J) The Reaction of Trimethylarsine with Diborane.—In a 400-ml. pressure vessel, trimethylarsine (10.4 g., 0.087 mole) and diborane (5.0 g., 0.18 mole) were heated to 175° for 10 hr. to give 8.1 g. of white, crystalline, nonvolatile product, of which 5.3 g. was insoluble in dimethoxyethane at room temperature.

When added to 1 l. of hot water, this solid dissolved, gas was evolved, and the resulting solution was acidic. On cooling, 1.7 g. (0.0033) mole of $H_2B[As(CH_3)_3]_2B_{12}H_{11}As(CH_3)_3$ separated. It was recrystallized from water and melted at 171–173°.

Anal. Calcd. for $H_2B[As(CH_3)_3]_2B_{12}H_{11}As(CH_3)_3$: C, 21.1; H, 7.8; B, 27.4; As, 43.7. Found: C, 21.0; H, 8.2; B, 27.5; As, 39.8.

Upon recrystallization from boiling water, the recovery of $H_2B[As(CH_3)_3]_2B_{12}H_{11}As(CH_3)_3$ is poor, and the solution becomes highly acidic as $H_3OB_{12}H_{11}As(CH_3)_3$ forms with hydrolysis of the cation. For example, the above recrystallization of 5.3 g. (0.0103 mole) of the salt gave only 1.7 g. (0.0033 mole, 32% yield) of recovered product. Neutralization of three-fourths of the acidic mother liquor with aqueous tetramethylammonium hydroxide gave 0.5 g. (0.0015 mole corresponding to 0.002 mole or 19.4% of the starting material) of $(CH_3)_4NB_{12}H_{11}As(CH_3)_3$ after recrystallization from water.

Anal. Calcd. for $(CH_3)_4NB_{12}H_{11}As(CH_3)_3$: C, 25.1; H, 9.6; B, 38.7; N, 4.2; As, 22.4. Found: C, 25.4; H, 9.7; B, 38.4; N, 4.1; As, 20.6.

Neutralization of the remaining one-fourth with aqueous trimethylsulfonium hydroxide gave 0.17 g. (0.0005 mole corresponding to 0.002 mole or 19.4% of the starting material) after recrystallization from water.

Anal. Calcd. for $(CH_3)_3SB_{12}H_{11}As(CH_3)_3$: C, 21.3; H, 8.6; B, 38.4; S, 9.5. Found: C, 20.7; H, 8.7; B, 37.8; S, 9.7.

The strong infrared bands characteristic of $B_{12}H_{11}As(CH_3)_3^-$ were at 2500, 1070, 1040, 920, 855, 840, and 715 cm.$^{-1}$.

The portion of the reaction product soluble in dimethoxyethane was recrystallized from aqueous ethanol after evaporation of the dimethoxyethane to give 1.4 g. (0.0037 mole) of colorless, crystalline $B_{12}H_{10}[As(CH_3)_3]_2$.

Anal. Calcd. for $B_{12}H_{10}[As(CH_3)_3]_2$: C, 19.0; H, 7.4; B, 34.2. Found: C, 19.5; H, 7.9; B, 35.0.

The strong infrared absorptions characteristic of $B_{12}H_{10}[As(CH_3)_3]_2$ were at 2500, 920, 860, and 720 cm.$^{-1}$.

(K) The Reaction of Methyl Sulfide and Diborane.—In a 400-ml. pressure vessel, methyl sulfide (30 ml., 25.5 g., 0.41 mole) and diborane (20 g., 0.72 mole) were heated 12 hr. at 70°. A clear yellow liquid, reactive with atmospheric moisture, was left after the hydrogen formed during the reaction had been vented. Evaporation of the methyl sulfide borane or dilution with a variety of nonreactive solvents failed to give tractable material. A portion treated with aqueous ethanol evolved gas and gave an insoluble white solid and an acidic solution. Recrystallization of the solid from dichloromethane gave 0.7 g. of $B_9H_{13}S(CH_3)_2$, m.p. 110–112°.

Anal. Calcd. for $B_9H_{13}S(CH_3)_2$: C, 13.9; H, 11.1; B, 56.4; S, 18.6. Found: C, 14.1; H, 11.0; B, 55.1; S, 16.6.

Addition of triethylammonium chloride to the acidic solution gave 1.3 g. of $(C_2H_5)_3NHB_{11}H_{14}$ with an infrared spectrum identical with that of an authentic sample.[12] The strong infrared bands of $B_9H_{13}S(CH_3)_2$ were at 2570, 1040, 1005, and 950 cm.$^{-1}$.

In a 400-ml. stainless steel pressure vessel, 30 ml. (25.5 g., 0.41 mole) of methyl sulfide and 20 g. (0.725 mole) of diborane were heated with shaking to 150° for 10 hr. under autogenous pressure. The tan semisolid product (18 g.) was treated with boiling water. Gas evolved to leave a strongly acidic solution and 10.1 g. of an insoluble tan solid. The insoluble material was $B_{12}H_{10}[S(CH_3)_2]_2$ (0.038 mole) containing a trace of $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$. The crude solid was dried and dissolved in dichloromethane and filtered to remove the trace of salt. After evaporation of the solvent, the residue was recrystallized from ethanol. The pure $B_{12}H_{10}[S(CH_3)_2]_2$ melted with decomposition at 220–250°.

Chilling the strongly acidic aqueous solution from above gave a small amount of $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$ which was removed by filtration. The cold filtrate was neutralized with triethylamine to precipitate $(C_2H_5)_3NHB_{12}H_{11}S(CH_3)_2$ which was recrystallized from ethanol–water to give 5.4 g. (0.018 mole) of purified material. Other salts derived from $B_{12}H_{11}S(CH_3)_2^-$ were obtained by ion-exchange techniques.

Anal. Calcd. for $B_{12}H_{10}[S(CH_3)_2]_2$: C, 18.2; H, 8.4; B, 49.1; S, 24.3. Found: C, 18.5; H, 8.5; B, 48.5; S, 24.9.

Anal. Calcd. for $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$: C, 21.4; H, 9.3; B, 46.2; S, 22.8. Found: C, 21.3; H, 9.2; B, 46.6; S, 23.1.

Anal. Calcd. for $(C_2H_5)_3NHB_{12}H_{11}S(CH_3)_2$: C, 31.5; H, 10.8; B, 42.5; N, 4.6; S, 10.5. Found: C, 31.6; H, 10.8; B, 43.0; N, 4.6; S, 9.5.

Anal. Calcd. for $CsB_{12}H_{11}S(CH_3)_2$: C, 7.2; H, 5.1; B, 38.7; S, 9.5; Cs, 39.6. Found: C, 7.3; H, 5.4; B, 38.8; S, 9.6; Cs, 37.0.

The strong infrared absorptions characteristic of $B_{12}H_{10}[S(CH_3)_2]_2$ were observed at 2500, 1040, 1000, 965, 810, and 725 cm.$^{-1}$ and those of the $B_{12}H_{11}S(CH_3)_2^-$ anion at 2500, 1015, 960, 825, and 715 cm.$^{-1}$.

(L) The Reaction of *n*-Propyl Sulfide with Diborane.—In a 400-ml. stainless steel vessel, *n*-propyl sulfide (24 g., 0.22 mole) and diborane (10 g., 0.36 mole) were heated to 150° for 10 hr. The 20 g. of viscous, colorless liquid resulting evolved gas when treated with water to give an oil and an acidic solution. When the oil was dissolved in acetone and reprecipitated with water, it became a soft solid.

Anal. Calcd. for $B_{12}H_{10}[S(C_3H_7)_2]_2$: C, 38.3; H, 10.2; B, 34.4; S, 17.0. Found: C, 37.6; H, 10.3; B, 35.4; S, 17.3.

The acidic solution was neutralized with aqueous cesium hydroxide to give 1.12 g. (0.0029 mole) of $CsB_{12}H_{11}S(n\text{-}C_3H_7)_2$ after two recrystallizations from water. The anion was characterized by strong infrared absorptions at 2500, 1070, 1050, 975, 825, and 720 cm.$^{-1}$.

Anal. Calcd. for $CsB_{12}H_{11}S(C_3H_7)_2$: C, 18.4; H, 6.4; B, 33.1; S, 8.8. Found: C, 17.7; H, 6.5; B, 32.8; S, 8.6.

(M) The Reaction of Triethylamine Borane with $B_9H_{13}PH(C_6H_5)_2$.[17]—A solution of 3.0 g. (0.01 mole) $B_9H_{13}PH(C_6H_5)_2$ in 25 ml. of triethylamine borane under nitrogen was held at reflux (~185°) for 3 hr. About 0.055 mole of hydrogen evolved, and a solid separated. After cooling to room temperature, the mixture was diluted with dichloromethane and the solid (1.6 g., 0.0046 mole) collected. Infrared analysis showed it to be $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

(N) The Reaction of Triethylamine Borane with $B_{10}H_8(N_2)_2$.—A solution of 0.4 g. (0.023 mole) of $B_{10}H_8(N_2)_2$[5] in 10 ml. of triethylamine borane was heated under nitrogen at 122° for 1.5 hr. Upon cooling, 0.25 g. (0.0007 mole, 3% yield) of $[(C_2H_5)_3NH]_2B_{12}H_{12}$ separated and was identified by its infrared spectrum.

(O) The Reaction of Triethylamine Borane with $B_{18}H_{22}$.—Addition of 1.0 g. (0.0026 mole) of $B_{18}H_{22}$[18] to 6 ml. of triethylamine borane gave a yellow slurry which evolved gas slowly. At 120°, gas evolution increased, and a clear solution resulted. At 185°, gas was evolved rapidly, and a solid separated. A total of 26.1 mmoles of hydrogen was formed. The slurry was cooled to room temperature and treated with ether. The insoluble material was $[(C_2H_5)_3NH]_2B_{12}H_{12}$ (1.1 g., 0.0031 mole).

(P) The Reaction of Dimethylaminoborane with Decaborane(14).—Solid $[(CH_3)_2NBH_2]_2$ (8.5 g., 0.076 mole) was mixed with solid decaborane(14) (6.1 g., 0.05 mole), evacuated, brought to 700 mm. with nitrogen, and heated over 2 hr. to 124°. Gas pressure in excess of 700 mm. was allowed to escape through a liquid N_2 trap to a known volume. The mass began to foam at 100°, and heating was discontinued at 124° as the mass began to foam out of the reaction flask. The evolved gas contained 0.06 mole of noncondensables (hydrogen?), 0.9 g. of $(CH_3)_2NB_2H_5$, and 0.9 g. of unreacted dimethylaminoborane. There remained 11.0 g. of solid residue. A satisfactory work-up procedure was not uncovered. A sample in methanol dissolved with gassing. Addition of aqueous tetramethylammonium chloride precipitated $[(CH_3)_4N]_2B_{12}H_{12}$ and $(CH_3)_4NB_9H_{14}$ in successive crops (infrared analyses). The product was partly soluble in dichloromethane. The soluble material, isolated by evaporation of the solvent, gave a yellow pasty mass from which $(CH_3)_4NB_9H_{14}$ was obtained by

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[17] E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962).

[18] A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3218 (1962).

treatment with methanol and aqueous tetramethylammonium chloride. The dichloromethane-insoluble white solid was extracted with boiling 1,2-dichloroethane. About half of it dissolved. Upon chilling the extract, colorless crystals of $H_2B[NH(CH_3)_2]_2B_{12}H_{11}NH(CH_3)_2$ separated.

Anal. Calcd. for $H_2B[NH(CH_3)_2]_2B_{12}H_{11}NH(CH_3)_2$: C, 24.9; H, 11.9; B, 48.6; N, 14.6. Found: C, 24.9; H, 11.6; B, 48.4; N, 14.0.

The material insoluble in hot 1,2-dichloroethane was a $B_{12}H_{12}^{2-}$ salt, probably of $H_2B[NH(CH_3)_2]_2^+$ since, when it was boiled in aqueous base, hydrogen and an amine were evolved and then $[(C_2H_5)_3NH]_2B_{12}H_{12}$ was obtained upon addition of aqueous triethylammonium chloride to the acidified hydrolysate. Similarly, $H_2B[NH(CH_3)_2]_2B_{12}H_{11}NH(CH_3)_2$, when boiled in aqueous base, evolved hydrogen and the issuing vapors had an amine odor and were basic. When the hydrolysate was treated with aqueous trimethylsulfonium iodide, $(CH_3)_3SB_{12}H_{11}NH(CH_3)_2$ resulted.

Anal. Calcd. for $(CH_3)_3SB_{12}H_{11}NH(CH_3)_2$: C, 22.8; H, 10.4; B, 49.4; N, 5.3; S, 12.2. Found: C, 23.0; H, 10.4; B, 49.2; N, 5.0; S, 12.0.

This anion had strong infrared bands at 3200, 2500, 1140, 995, 910, 855, and 720 cm.$^{-1}$.

(Q) **The Reaction of Methyl Sulfide Borane and Decaborane(14).**—Methyl sulfide borane was prepared from 12 ml. (10.1 g. 0.163 mole) of methyl sulfide and 2.0 g. (0.075 mole) of diborane. The diborane was rapidly and completely absorbed at −78°. The product was warmed to room temperature and evacuated to a pressure of about 30 mm. to remove the slight excess of methyl sulfide which had been used. The flask was then brought to atmospheric pressure with dry argon, 4.2 g. (0.034 mole) of decaborane(14) was added, and the mixture was heated to reflux (100–110°) for 1.5 hr., at which time 3.3 l. of gas had been evolved and gas evolution had become very slow. The mixture was cooled to 40–50° and held under high vacuum to remove all volatile material. There remained 10.3 g. of yellow solid. When the solid was boiled in water, there was vigorous gas evolution. The water-insoluble $B_{12}H_{10}[S(CH_3)_2]_2$ was separated by filtration (3.5 g., 0.021 mole). The hot filtrate deposited a small amount (1.3 g., 0.0046 mole) of $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$ upon chilling. The cold, highly acidic filtrate was neutralized with aqueous cesium hydroxide, and 3.7 g. (0.019 mole) of $CsB_{12}H_{11}S(CH_3)_2$ precipitated. Based on decaborane(14), the reaction yielded 32% of $B_{12}H_{11}S(CH_3)_2^-$, 39% of $B_{12}H_{10}[S(CH_3)_2]_2$, and 1% of $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$. The anion was present in the crude yellow product as the salt of the hydrolytically unstable $H_2B[S(CH_3)_2]_2^+$ cation.

The methyl sulfide can be displaced from $H_2B[S(CH_3)_2]_2^+$ as follows: A dichloromethane solution containing about 28 g. of crude product prepared as above was treated with 10 ml. of N,N,N′,N′-tetramethylethylenediamine (TMED). An exothermic reaction occurred with evolution of some methyl sulfide. After standing for 1 hr., the temperature had returned to room temperature and the dichloromethane was evaporated. Water was added, and a gummy solid separated. Repeated extraction of the solid with boiling water yielded the sparingly soluble $H_2B(TMED)B_{12}H_{11}S(CH_3)_2$, which separated upon cooling the hot extract. A total of 10 g. was obtained. The $H_2B(TMED)^+$ cation was converted to its water-soluble chloride salt by ion exchange. Addition of aqueous ammonium hexafluorophosphate or chloroauric acid to a solution of the chloride salt gave the corresponding PF_6^- or $AuCl_4^-$ salt of $H_2B(TMED)^+$. Other dihydroboron bis-base (1+) cations prepared by this technique were $H_2B[CH_3N(CH_2CH_2)_2NCH_3]^+$, $H_2B[(CH_3)_2PCH_2CH_2P(CH_3)_2]^+$, $H_2B[\alpha,\alpha'\text{-dipyridyl}]^+$, and $H_2B[(CH_3)_2NCH_2CH_2CH(CH_3)N(CH_3)_2]^+$. Attempts to use more hindered bases failed to yield the borane cations. These dihydroboron bis-base (1+) cations are the subject of a separate paper.[15]

Variables in Reaction 1.—Preferred procedures are described above for the synthesis of $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ from a hydride ion source and a borohydride. As these experiments show, the final product is a function primarily of temperature, pressure, and donor solvent. Other experiments bearing on these variables are summarized below.

(A) **The Reaction of Sodium Borohydride and Diborane in Triethylamine Borane.**—A 100-ml. stainless steel pressure vessel was charged with sodium borohydride (4.0 g., 0.106 mole), triethylamine (15 ml., 0.31 mole), and diborane (8.0 g., 0.29 mole) and heated for 8 hr. at 60°. The volatile material consisted of 0.2 mole of hydrogen and 0.138 mole of diborane. The residue, a white solid suspended in a yellow liquid, was treated with tetrahydrofuran. The insoluble white solid was sodium borohydride (2.6 g., 65%). The tetrahydrofuran solution was free of $Na_2B_{12}H_{12}$ since no solid separated on addition of dimethoxyethane. Solid $NaB_{11}H_{14}$ dioxanate was obtained on dilution with dioxane. A similar experiment at 100° (1.9 g., 0.05 mole, of sodium borohydride, 2.8 g., 0.1 mole, of diborane in 10 ml. of triethylamine) gave 0.13 mole of hydrogen, no unchanged diborane, 1.25 g. (65%) of unchanged sodium borohydride, no $B_{11}H_{14}^-$, and 0.0061 mole (24% conversion, 71% yield based on sodium borohydride) of $B_{12}H_{12}^{2-}$ isolated as its tetramethylammonium salt. This salt was isolated from an aqueous solution of the $Na_2B_{12}H_{12}$ etherate (precipitated by dilution of the tetrahydrofuran filtrate with dimethoxyethane) by addition of aqueous tetramethylammonium chloride.

At atmospheric pressure, about 1 g./hr. of diborane was bubbled through a well-stirred suspension of 2.0 g. of sodium borohydride (0.053 mole) in 25 ml. of triethylamine borane at 80°. After 4 hr. the mixture was cooled to room temperature and filtered to recover 1.8 g. of sodium borohydride (90%). The filtrate showed no infrared absorptions except those of triethylamine borane. In 3 hr. at 120°, about 2.24 l. (STP) of hydrogen evolved, 0.5 g. (0.18 mole) of diborane reacted (3.3 g. used, 2.8 g. recovered), 1.7 g. (85%) of the sodium borohydride was recovered, and 2.3 g. of an etherate of $Na_2B_{12}H_{12}$ containing about 0.005 mole (19% yield) of the anion was isolated.

(B) **The Reaction of Sodium Borohydride and Pentaborane(9) in Triethylamine.**—In a 100-ml. stainless steel pressure vessel sodium borohydride (1.9 g., 0.05 mole), pentaborane(9) (0.05 mole), and 15 ml. of triethylamine were heated 10 hr. at 70°. No pentaborane(9) was recovered. Hydrogen (0.013 mole) was found and $B_{12}H_{12}^{2-}$ and unchanged BH_4^- were identified in the nonvolatile material. After 10 hr. at 120°, 0.025 mole of hydrogen and a 14% yield of $B_{12}H_{12}^{2-}$ were obtained with no BH_4^- recovered.

(C) **The Reaction of $B_{11}H_{14}^-$ and Triethylamine Borane.**—A mixture of $(CH_3)_3NHB_{11}H_{14}$ (3 g., 0.016 mole) and an excess of triethylamine borane was heated in a flask equipped with a reflux condenser. A nitrogen atmosphere was maintained throughout the heating cycle. At about 130°, hydrogen evolution began, and the temperature was held at 150° for 0.5 hr. Water-methanol (50–50) was added to the cooled mixture and the excess amine and the methanol were removed by heating to reflux. The solution was then acidified and boiled to decompose the unchanged triethylamine borane. On cooling, a precipitate appeared and was collected (3.1 g.). Its infrared spectrum was that of $[(C_2H_5)_3NH]_2B_{12}H_{12}$ (yield, 58%).

A mixture of $(CH_3)_3NHB_{11}H_{14}$ (3 g., 0.16 mole) and triethylamine (23 ml.) was heated in a Carius tube to 180° for 1 hr. No hydrogen was produced, and the only boron product isolated was $(C_2H_5)_3NHB_{11}H_{14}$.

(D) **The Reaction of $B_{11}H_{14}^-$ with Sodium Borohydride.**—A mixture of $NaB_{11}H_{14}\cdot 2.5$ dioxane (7.52 g., 20 mmoles) and sodium borohydride (0.76 g., 20 mmoles) in 35 ml. of diethylene glycol dimethyl ether was heated to reflux for 2 hr. A gas (42 mmoles) not condensable at −196° was evolved and a solid separated from the hot solution. The mixture was cooled to room temperature. The solid was collected, then washed with fresh solvent. The solid was then extracted with about 75 ml. of tetrahydrofuran in several portions. The portion not soluble in tetrahydrofuran weighed 1.41 g. Its infrared spectrum was broad and diffuse. Upon dilution of the tetrahydrofuran with three volumes of dimethoxyethane, crystals separated. They were collected, washed with dimethoxyethane, and dried at 1 μ and 90°. This product weighed 1.97 g. and was an etherate of $Na_2B_{12}H_{12}$. When dissolved in water and treated with aqueous triethylammonium chloride, it gave 2.06 g. (6 mmoles, 30% yield) of $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

(E) **The Reaction of $B_{10}H_{10}^{-2}$ and Triethylamine Borane.**—A suspension of $(NH_4)_2B_{10}H_{10}$ (4.0 g., 0.026 mole) in 20 ml. (15.6 g., 0.136 mole) of triethylamine borane was stirred under nitrogen as the temperature was slowly raised to reflux (~190°). At about 158°, gas began to evolve. The large pieces of the $B_{10}H_{10}^{2-}$ salt disappeared as a finely divided solid began to separate. Gas evolution subsided in about 30 min. The mixture was cooled to room temperature after 110 min. to give a solid cake which was broken up in petroleum ether, collected, and washed with petroleum ether. The solid was taken up in hot water, acidified, treated with excess triethylammonium chloride, clarified by hot filtration, and chilled to give 2.43 g. (0.007 mole, 27% yield) of the triethylammonium salt of $B_{12}H_{12}^{2-}$.

(F) **The Reaction of Sodium Borohydride and Diborane in Tri-*n*-butylphosphine.**—A 100-ml. stainless steel pressure vessel was charged with 0.8 g. of sodium borohydride (0.021 mole), 3.1 g. of diborane (0.11 mole), and 15 ml. of tri-*n*-butylphosphine, closed, and heated for 10 hr. at 120°. There was no unchanged diborane or sodium borohydride but 0.188 mole of hydrogen was formed and about a 50% yield of $Na_2B_{12}H_{12}$, as its dimethoxyethane solvate, and a 5% yield of $NaB_{11}H_{14}$, as its dioxanate, were isolated. These products were obtained as follows: The nonvolatile product was taken up in tetrahydrofuran and the solution clarified by filtration. Dilution of the filtrate with one to two volumes of dimethoxyethane precipitated $Na_2B_{12}H_{12}$ etherate. The filtrate was concentrated to about one-third its volume and diluted with several volumes of dioxane to precipitate $NaB_{11}H_{14}$ dioxanate.

(G) **The Reaction of Sodium Borohydride and Diborane in Organic Sulfides.**—The above experiment was repeated using 15 ml. of methyl sulfide in place of the phosphine to give 0.12 mole of hydrogen, some free methyl sulfide, and about a 65% yield of $Na_2B_{12}H_{12}$ isolated as its dimethoxyethane solvate.

When diborane (about 2 g./hr.) was bubbled through a suspension of sodium borohydride (2.0 g., 0.053 mole) in *n*-butyl sulfide (25 ml.) at 195°, reaction occurred to give about 0.35 mole of hydrogen. About half of the sodium borohydride was recovered when the cooled reaction mixture was taken up in tetrahydrofuran (insoluble in tetrahydrofuran), and a 16% yield of $Na_2B_{12}H_{12}$ was precipitated as an etherate upon addition of dimethoxyethane to the filtrate.

(H) **The Reaction of Sodium Borohydride and Diborane in Ethers.**—A 100-ml. stainless steel pressure vessel was charged with sodium borohydride (1.9 g., 0.05 mole), diborane (2.7 g., 0.1 mole), and diethyl ether (10 ml.). After 10 hr. at 100°, there was no unchanged diborane, but 0.2 mole of hydrogen was obtained. In addition to a small amount of unchanged sodium borohydride, a 40% yield of $B_{12}H_{12}^{2-}$ was obtained as its tetramethylammonium salt upon treating, with tetramethylammonium chloride, an aqueous solution of the solids not soluble in ether. The same reaction at 120° gave no unchanged BH_4^-, while at 60° all of the diborane and sodium borohydride were recovered unchanged. Under similar conditions, the reaction in dimethoxyethane gave $B_3H_8^-$ at temperatures up to about 60° (*vide supra*), a 16% conversion to $Na_2B_{12}H_{12}$ and a 30% conversion to $NaB_{11}H_{14}$ at 100°, and a 44% conversion to $Na_2B_{12}H_{12}$ and a 28% conversion to $NaB_{11}H_{14}$ at 120°. At 180° the ether solvent was attacked to give hydrocarbons and an intractable residue. In these experiments, the nonvolatile portion of the reaction mixture was treated as described above to separate and isolate $Na_2B_{12}H_{12}$. When lithium borohydride (1.1 g., 0.05 mole) was substituted for sodium borohydride in the 100° experiment in dimethoxyethane, 0.13 mole of hydrogen was formed and $B_3H_8^-$ and $B_{12}H_{12}^{2-}$ were identified in the solid products.

As described above, sodium borohydride and diborane in tetraethylene glycol dimethyl ether at atmospheric pressure gave $B_3H_8^-$ at 105°. This experiment was repeated at 190°, at which temperature about 5 g. (0.18 mole) of diborane was passed through the reaction mixture of 2.0 g. of sodium borohydride (0.053 mole) in 25 ml. of the ether in 50 min. Hydrogen (about 0.24 mole) was evolved, 0.04 mole of diborane was recovered, and a heavy slurry of a white solid resulted. The solid was collected, washed with dimethoxyethane, and dried to leave 9.0 g. of white solid. Its infrared spectrum was that of an etherate of $Na_2B_{12}H_{12}$. The $B_{12}H_{12}^{-2}$ content was estimated as follows. An aliquot of the solid (0.5 g.) in water was passed through a strong acid ion-exchange column, and the column was washed with water until the initially strongly acid effluent was neutral. The acidic effluent required 14.2 ml. of 0.1 *N* base to neutralize to pH 7. Thus, the reaction gave 0.026 equivalent of $B_{12}H_{12}^{2-}$ (49% yield). Addition of trimethylsulfonium iodide to the neutral solution gave a white precipitate identified as $[(CH_3)_3S]_2B_{12}H_{12}$ by comparison of its infrared spectrum with that of an authentic sample.

(I) **The Reaction of Sodium Borohydride and Pentaborane(9) in Ethers.**—When sodium borohydride (1.9 g., 0.05 mole), pentaborane(9) (0.05 mole), and dimethoxyethane (10 ml.) were heated for 10 hr. at 60° in a 100-ml. pressure vessel, 0.1 mole of hydrogen formed, and 0.032 mole (64% conversion) of $NaB_{11}H_{14}$ was isolated as its dioxanate. At 40° the conversion to $B_{11}H_{14}^-$ was only 30% in 10 hr. and some sodium borohydride and NaB_3H_8 were detected in the crude product by infrared analysis. Infrared analysis of the crude product after 10 hr. at 100° showed the presence of $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ but no unchanged BH_4^-. Substitution of sodium borohydride in the 100° experiment with potassium borohydride gave a crude product which by infrared analysis showed only unchanged BH_4^- and $B_{11}H_{14}^-$.

(J) **The Reaction of Sodium Borohydride and $B_{10}H_{12}\cdot 2S(CH_3)_2$.**—A mixture of sodium borohydride (0.8 g., 0.021 mole), $B_{10}H_{12}\cdot 2S(CH_3)_2$[19] (2.3 g., 0.0094 mole), and 25 ml. of diethylene glycol dimethyl ether was refluxed under nitrogen for 6 hr. A fine yellow solid separated, which, after cooling the mixture to room temperature, was collected, washed with dimethoxyethane, and dried. The solid was taken up in tetrahydrofuran and filtered, and dimethoxyethane was added to the filtrate to precipitate 1.1 g. of $Na_2B_{12}H_{12}$ etherate (24% yield based on the $B_{10}H_{12}\cdot 2S(CH_3)_2$ charged).

(K) **The Thermolysis of NaB_3H_8.**—A 100-ml. pressure vessel was charged with $NaB_3H_8\cdot 3O(CH_2CH_2)_2O$ (5.0 g., 0.0152 mole) and heated to 100° for 8 hr. The material volatile at room temperature was pumped out and measured (1.5 mmoles). Heating was continued at 150° for 10 hr. to give an additional 8 mmoles of gas and finally at 200° for 10 hr. to give an additional 23.7 mmoles (33.2 mmoles total) of gas which, by mass spectral analysis, was hydrogen containing small amounts of ethane, methyl ether, ethyl ether, and dioxane. The infrared spectrum of the solid residue after the first two heating cycles was unchanged from that of the starting material but the spectrum of the 2.17 g. of final residue was unlike that of the starting material. The residue was readily soluble in water with slight gassing. Addition of aqueous cesium fluoride gave a white solid, recrystallizable from water. Its infrared spectrum was identical with that of the known[2] double salt, $Cs_2B_{12}H_{12}\cdot CsBH_4\cdot H_2O$. The total hydrogen evolution was 98% of the theoretical amount required by $5NaB_3H_8 \rightarrow Na_2B_{12}H_{12} + 3NaBH_4 + 8H_2$.

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[19] (a) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961); (b) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).