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Chemistry of Boranes. XI.[1] Diamine Derivatives of the Hypothetical $B_4H_{10}^{-2}$ and $B_5H_{11}^{-2}$ Ions

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N,N,N′,N′-Tetramethylethylenediamine (TMED) and pentaborane(9) react at 25° to give $B_5H_9 \cdot$TMED. Methanol at 0° converts $B_5H_9 \cdot$TMED to $B_4H_8 \cdot$TMED. These two diamine adducts may be considered derivatives of the hypothetical anions $B_5H_{11}^{-2}$ and $B_4H_{10}^{-2}$. Both adducts are subject to degradation by hydroxylic reagents and the type of product is a function of the pH of the medium. The cation $H_2B(TMED)^+$ is formed nearly quantitatively in acidic hydrolyses whereas the triborohydride ion, $B_3H_8^-$, is the sole B–H product surviving in basic hydrolyses. In essentially neutral hydrolyses, the principal BH products are $H_2B(TMED)^+$, $B_3H_8^-$, and $(TMED)(BH_3)_2$.

$B_5H_{11}^{-2}$ Derivative.—Pentaborane (9) reacts smoothly and exothermally with N,N,N′,N′-tetramethylethylenediamine (TMED) to form a colorless crystalline solid; no hydrogen is evolved in this reaction. The product, $B_5H_9 \cdot$TMED, is a polar species with the low solubility typical of TMED adducts; it can be purified by recrystallization from chlorinated hydrocarbons.

No detectable reaction occurs between $B_5H_9 \cdot$TMED and the oxygen of air at 25°. This oxidation resistance contrasts with the air sensitivity and instability of $B_5H_9[N(CH_3)_3]_2$.[2] Thermal stability is relatively low. Decomposition commences at 140° with considerable vigor to give hydrogen and an intractable material of unestablished structure. Small amounts of $(TMED)(BH_3)_2$[3] and $[H_2B(TMED)]_2B_{12}H_{12}$[3] are also formed in the pyrolysis. The solvolytic behavior of $B_5H_9 \cdot$TMED is discussed below.

$B_4H_{10}^{-2}$ Derivative.—A slurry of $B_5H_9 \cdot$TMED in methanol at 0° evolves hydrogen for a short period and then reaction essentially ceases. The remaining solid phase is $B_4H_8 \cdot$TMED and the observed hydrogen evolution agrees with that expected for reaction 1.

$$B_5H_9 \cdot \mathrm{TMED} + 3CH_3OH \longrightarrow B_4H_8 \cdot \mathrm{TMED} + B(OCH_3)_3 + 2H_2 \quad (1)$$

Definitive characterization of $B_4H_8 \cdot$TMED was achieved through analysis, hydrolytic hydrogen determination, and molecular weight studies. Crystallization of $B_4H_8 \cdot$TMED from an acetonitrile–ether mixture gave needles that were found to be triclinic by Mr. Keith Babcock of this laboratory.

$B_4H_8 \cdot$TMED resembles $B_5H_9 \cdot$TMED in its relatively low solubility in most organic solvents and in thermal behavior. At ~150°, $B_4H_8 \cdot$TMED decomposes with volatilization of $(TMED)(BH_3)_2$. The nonvolatile residue is a mixture of $B_3H_8^-$, $B_{12}H_{12}^{-2}$, and $H_2B(TMED)^+$ salts. Generation of the $B_{12}H_{12}^{-2}$ anion is a rather general thermal characteristic of borane anions and base–borane complexes.[4,5]

Structural Considerations.—The B_5 and B_4 tetramethylethylenediamine adducts may be considered as derivatives of the hypothetical $B_5H_{11}^{-2}$ and $B_4H_{10}^{-2}$ anions. The diamine ligand could span two boron atoms, chelate one boron atom, or serve as a mono- or dibridging element. Most of these possibilities for $B_4H_8 \cdot$TMED are represented in Fig. 1.

In the infrared spectrum of $B_4H_8 \cdot$TMED, the relatively strong absorption in the region characteristic of a bridge BH stretching vibration rules out structure **6** from further consideration.

A minimum of two boron atom environments for $B_4H_8 \cdot$TMED was established from the B^{11} n.m.r. spectrum, which consists of two broad peaks of relative intensities 1 and 3. Structure **4** is eliminated because it has two different boron atom environments which have identical numbers of boron atoms.

Line-width studies of the B^{11} n.m.r. spectra provide additional data that may bear on the structure of $B_4H_8 \cdot$TMED. The low-field resonance (~0 p.p.m. from trimethyl borate) of intensity 1 is very broad with a half-height width of about 300 c.p.s. Since the B^{11} resonances for boron atoms attached to nitrogen atoms are often significantly broadened,[6,7] the low-field resonance may represent a boron atom attached to one or two nitrogen atoms. The high-field (+44 p.p.m.) resonance has a half-height line width of ~200 c.p.s., which may result from the overlap of two different boron atom resonances or may be a slightly broadened multiplet representing environmentally different boron atoms of spectroscopic equivalence equally coupled to all eight hydrogen atoms. Behavior of the latter type has been observed for $B_3H_8^-$.[8]

Since B^{11} n.m.r. spectroscopic equivalence of three boron atoms in $B_4H_8 \cdot$TMED would appear rather un-

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[1] Paper X: N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964)

[2] A. B. Burg, *ibid.*, **79**, 2129 (1957).

[3] Characterization of $(TMED)(BH_3)_2$, $H_2B(TMED)^+$, and the salt $[H_2B(TMED)]_2B_{12}H_{12}$ is described by N. E. Miller and E. L. Muetterties, ref. 1.

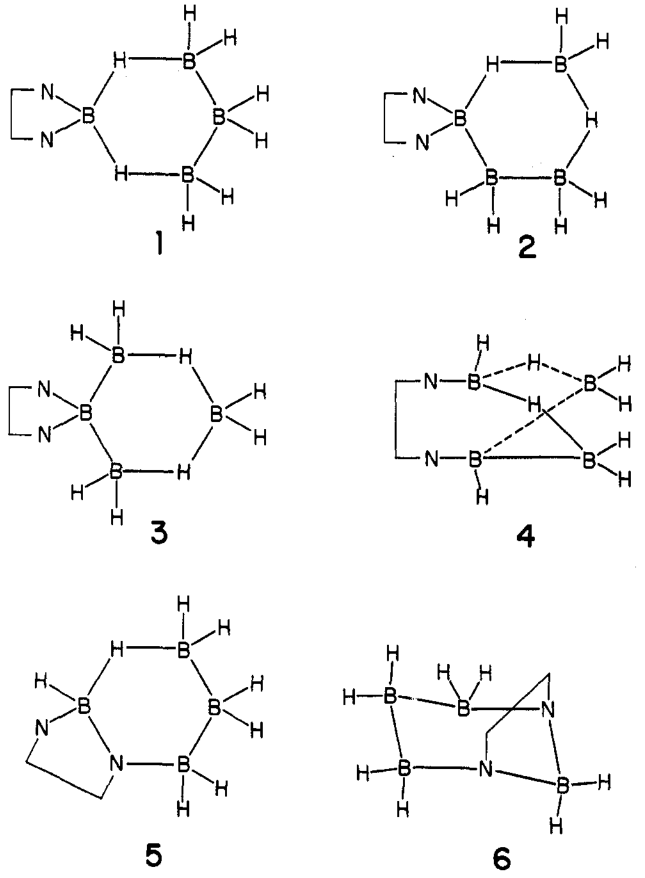
[4] I. A. Ellis, D. F. Gaines, and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3885 (1963)

[5] H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963), and manuscript in preparation.

[6] This was most clearly shown for $[H_3BCNBH_3]^-$: V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

[7] Since both the B^{11} and N^{14} nuclei possess quadrupole moments, the line width may be presumed to result from an intermediate rate of quadrupolar relaxation.

[8] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959); H. C. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 265 (1962); W. N. Lipscomb, *ibid.*, **1**, 132 (1959).



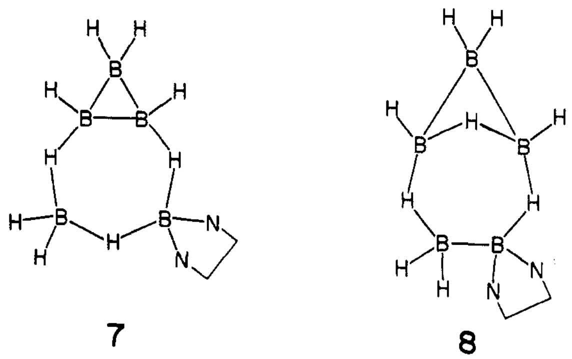
1 2 3 4 5 6

Fig. 1.—Possible structures of $B_4H_8 \cdot$TMED.

likely for structure **5**, and since there are no examples of a tertiary amine bridging group in boron hydride chemisty, the spectroscopic data would appear to reduce the possibilities to **1**, **2**, and **3**.

Proton n.m.r. spectra of D_3CCN and $(D_3C)_2SO$ solutions of $B_4H_8 \cdot$TMED consist of a single CH_2 resonance of intensity 4, two CH_3 resonances each of intensity 6,[9] and a broad multiplet whose relative intensity was established as 8 by a double resonance experiment (irradiation of the B^{11} nuclei). Since the four boron atoms are not necessarily coplanar, there should be at least a long-range environmental nonequivalence for the two methyl groups attached to each nitrogen atom. However, if the barrier to B_4 ring inversions should be low, there would be equivalence of N-CH_3 protons on the n.m.r. time scale in structures **1** and **3**. It may be argued that these proton n.m.r. data favor **2**, but this is not a rigorous conclusion.

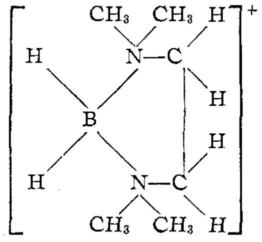
The infrared spectrum of $B_5H_9 \cdot$TMED shows both BH and BHB stretching absorptions. A minimum of four boron atom environments was established by B^{11} n.m.r. studies. The B^{11} n.m.r. spectrum consists of three broad peaks of relative intensities 1, 3, 1. The low-field peak of relative intensity 1 is in the same region as the unique boron atom in $B_4H_8 \cdot$TMED and is assigned to the boron atom bearing a nitrogen atom or atoms. The high-field peak is shifted to slightly higher field than is the apical boron atom in B_5H_9. Irradiation of the hydrogen atoms does not affect the low and high field B^{11} resonances but the large central peak separates into two peaks of relative intensities 1 and 2. These data are consistent with either structure **7** or **8** in Fig. 2. A referee suggested that $B_5H_9 \cdot$TMED may be a salt of the type $H_2B(TMED)^+B_4H_7^-$. This possibility is ruled out by the basic hydrolysis studies described below which show no $H_2B(TMED)^+$ is produced; this cation is stable toward base and would survive such treatment. Furthermore, the B^{11} n.m.r. spectrum of $B_5H_9 \cdot$TMED showed no resonance in the region where the $H_2B(TMED)^+$ triplet is found.[1]



7 8

Fig. 2.—Possible structures of $B_5H_9 \cdot$TMED.

Solvolysis of $B_4H_8 \cdot$TMED and $B_5H_9 \cdot$TMED.—Hydrolysis of the tetramethylethylenediamine adducts of B_4 and B_5 under strongly acidic conditions gives hydrogen, boric acid, and nearly quantitative yields of the cation **9**. Formation of this cation in such high yields is probably the strongest evidence for structures of the type **1**, **2**, and **3** for $B_4H_8 \cdot$TMED and **7** and **8** for $B_5H_9 \cdot$TMED. This hydrolysis behavior might also be presumed to weigh the evidence in favor of structures **1** and **7** for the B_4 and B_5 adducts, respectively, since, for these structures, generation of the cation would not even require hydrogen atom rearrangements.



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Hydrolysis under essentially neutral conditions follows a similar course for both the B_4 and B_5 adducts. The cation **9** is still the major product but significant amounts of $B_3H_8^-$ are also formed. Relative ratios of cation to anion produced are similar for both adducts, approximately 2:1 for $B_4H_8 \cdot$TMED and 3:1 for $B_5H_9 \cdot$TMED. The bisborane complex of tetramethylethylenediamine, $(TMED)(BH_3)_2$, is also formed in the

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[9] The separation between the two methyl resonances is 0.1 p.p.m. and it is field dependent. The proton n.m.r. spectrum of $H_2B(TMED)^+$ shows only one kind of methyl resonance. Thus the origin of the N-CH_3 nonequivalence in $B_4H_8 \cdot$TMED would not appear to be the chelate ring itself.

neutral hydrolysis. The ratio of cation to (TMED)-$(BH_3)_2$ is about 8:1 and 4:1 for the B_4 and B_5 adducts, respectively.

In basic hydrolysis, the triborohydride ion, $B_3H_8^-$, is the only BH species produced.[10] Base attack must be occurring at the boron atom bound to the nitrogen atoms, which is consistent with the fact that this boron atom must bear the highest positive charge in the ground state structure. Generation of $B_3H_8^-$ after nucleophilic attack at the $\mathrm{B}{<}_{\mathrm{N}}^{\mathrm{N}}$ boron atom requires relatively minor rearrangements (hydrogen migrations) for structures **1**, **2**, **3**, **7**, and **8**. Base attack requires more forcing conditions than acid hydrolysis. This is consistent with the fact that the bis adducts are relatively electron rich.

Formation of both cation **9** and $B_3H_8^-$ in neutral hydrolysis is readily rationalized on the basis of competing electrophilic and nucleophilic attack of the B_4 and B_5 adducts. Any explanation for the formation of $(TMED)(BH_3)_2$ in neutral hydrolysis must at the very least involve boron atom migration. This, however, does not present a serious conflict to the above arguments because the amount of $(TMED)(BH_3)_2$ formed is quite small. The hydrolytic formation of the bisborane adduct and the nonequivalence of N-CH_3 protons are the only inhibiting factors in proposing structure **1** for $B_4H_8 \cdot$TMED.

Experimental

Reagents and Procedure.—Pentaborane(9) was purchased from Olin Mathieson and used without further purification; the vapor pressure at 0° was 66 mm. All the other solvents and reagents were reagent grade and were used without purification.

The B^{11} and H^1 n.m.r. spectra were obtained with a Varian high resolution spectrometer at frequencies of 19.2 and 60 Mc., respectively. Double irradiation was effected with an NMR Specialties Model SD 60 spin decoupler. B^{11} spectra were calibrated relative to trimethyl borate and the H^1 spectra to tetramethylsilane by the side-band technique.

Identification of $(TMED)(BH_3)_2$ and of salts of $B_3H_8^-$, $B_{12}H_{12}^{-2}$, and $H_2B(TMED)^+$ was based on comparison of infrared spectra with those of authentic samples.

Yields of $(TMED)(BH_3)_2$ and $H_2B(TMED)^+$ in solvolyses were calculated on the basis of the TMED content of the starting material. Yields of $B_3H_8^-$ were calculated on the assumption that only one $B_3H_8^-$ anion could be generated from a molecule of $B_5H_9 \cdot$TMED or $B_4H_8 \cdot$TMED.

Synthesis of $B_5H_9 \cdot$TMED.—A flask containing TMED (19 g., 0.16 mole) was attached to a vacuum line cooled to −78° and evacuated. Pentaborane was condensed into the reaction flask in 1-ml. portions. After each addition of pentaborane, the mixture was warmed to permit reaction. When a total of 5.2 ml. (~0.05 mole) of B_5H_9 had been added, the mixture was heated to 40–50° for several minutes. The excess TMED was then removed by distillation to leave 9.0 g. (100% of theory) of white solid which was recrystallized from hot ethylene chloride. In a sealed capillary, the adduct softens at 177° but does not melt up to 300°.

Anal. Calcd. for $B_5H_9 \cdot$TMED: C, 40.2; H, 14.0; B, 30.1; N, 15.6. Found: C, 41.0; H, 14.4; B, 29.7; N, 15.7.

Large quantities were prepared in 90% yield by slow addition of a 50% solution of B_5H_9 in petroleum ether to a stirred 30–50% solution of TMED in petroleum ether at 25°. After addition, the solid was removed by filtration and vacuum dried.

The infrared spectrum of TMED$\cdot B_5H_9$ (Nujol mull) is characterized by bridge hydrogen stretching at 1780/1830 cm.$^{-1}$ (m) and strong B–H stretching as a multiplet centered at 2400 cm.$^{-1}$ and a sharp singlet at 2300 cm.$^{-1}$. The long wave length region is complex with strong bands at 820, 960, 1080, 1130, and 1155 cm.$^{-1}$.

Solvolysis of $B_5H_9 \cdot$TMED.—A sample of $B_5H_9 \cdot$TMED (2.5 g., 13.7 mmoles) was slurried with a solution of 2.8 g. of sodium methoxide in 28 ml. of methanol at 25°. Gas was evolved vigorously on warming to 50° as the $B_5H_9 \cdot$TMED dissolved. The solution was held at incipient reflux until gas evolution subsided. To half of the solution was added aqueous tetramethylammonium chloride to give a precipitate of 0.59 g. (5.15 mmoles, 76% yield) of the tetramethylammonium salt of $B_3H_8^-$. To the other half was added aqueous NH_4PF_6 to give a precipitate of $H_2B(TMED)$-PF_6 (0.7 mmole, 10% yield).

A sample of $B_5H_9 \cdot$TMED (4.0 g., 22.2 mmoles) was slowly added to a well stirred mixture of ethanol (10 ml.) and water (10 ml.) at 0°. There was a small amount of hydrogen evolution during the addition. The mixture was allowed to warm to room temperature and then heated carefully to reflux. A vigorous reaction occurred near reflux with gas evolution. The solution was held at incipient reflux until gas evolution subsided. Upon chilling the weakly basic solution, crystals of $(TMED)(BH_3)_2$ separated (0.48 g., 15% yield). The filtrate was boiled to remove the alcohol. Water was added to maintain an approximately constant volume. Upon chilling, $H_2B(TMED)B_3H_8$ separated (0.78 g., 21% yield). The filtrate was made strongly basic with aqueous NaOH and divided into two portions. One was treated with an excess of aqueous $(CH_3)_4NCl$. Upon chilling, the tetramethylammonium salt of boric acid separated (1.25 g.). Thus all of the $B_3H_8^-$ which had formed during hydrolysis was obtained as the $H_2B(TMED)^+$ salt in the earlier fraction. The other half of the filtrate was treated with an excess of aqueous NH_4PF_6 and chilled to give $H_2B(TMED)PF_6$ (1.35 g., 45% yield).

To a stirred mixture of 5 ml. of 5 *N* hydrochloric acid, 5 ml. of water, and 10 ml. of ethanol, cooled in an ice bath, was added, in small portions, 4.0 g. (22.2 mmoles) of $B_5H_9 \cdot$TMED. The solid reacted vigorously with evolution of gas. The mixture was heated cautiously to reflux and held at this temperature until gas evolution subsided. Upon chilling, boric acid separated and was collected (3.38 g., 54.5 mmoles, 62% yield for a mole of adduct to give 4 moles of boric acid). The filtrate was made basic, treated with an excess of aqueous NH_4PF_6, and cooled, whereupon H_2B-$(TMED)PF_6$ (4.94 g., 85% yield) separated.

Pyrolysis of $B_5H_9 \cdot$TMED.—A sample of $B_5H_9 \cdot$TMED (3.0 g., 17 mmoles) was heated to 140° under vacuum in a sublimation vessel. A vigorous decomposition occurred at 140° and crystals of $(TMED)(BH_3)_2$ (0.23 g., 1.6 mmoles, 9% yield) collected on the cold finger. The nonvolatile residue (2.5 g.) was largely intractable. The residue was treated with hot acetonitrile and the slurry was filtered. Upon chilling the filtrate, a few crystals of $[H_2B(TMED)]_2B_{12}H_{12}$ (trace to 1% yield) separated.

Synthesis of $B_4H_8 \cdot$TMED.—A sample of $B_5H_9 \cdot$TMED (10.0 g., 0.056 mole) was stirred with a mixture of 80 ml. of methanol and 5 ml. of acetonitrile at 0°. The appearance of the slurry changed slightly, and about 0.1 mole of hydrogen (85% of theory) evolved in 20 min. No further change occurred. After 1 hr., the solid was collected, washed with a few ml. of acetonitrile, and dried under reduced pressure at room temperature to give 7.4 g. of $B_4H_8 \cdot$TMED (78% of theory). The adduct was recrystallized from acetonitrile in 70–80% recovery. Although the adduct softened at 180°, there was no detectable fusion to 300°.

Anal. Calcd. for $B_4H_8 \cdot$TMED: C, 43.0; H, 14.4; N, 16.7; B, 25.9; mol. wt., 168. Found: C, 43.5; H, 14.7; N, 16.7; B, 25.7; (cryoscopic, $(CH_3)_2SO$) mol. wt., 172.

The infrared spectrum of TMED$\cdot B_4H_8$ (Nujol mull) is charac-

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[10] The cation **9** resists degradation by both acid and base. The bis adduct $(TMED)(BH_3)_2$ is slowly degraded in acid and in hot alcoholic sodium methoxide. Thus, the bis adduct could be an intermediate in the basic solvolysis.

terized by bridge BH stretching at 2040 (m, with a 2080 cm.$^{-1}$ shoulder) and a multiplet B–H stretching centered at 2380 cm.$^{-1}$. The complex long wave length region has strong bands at 820, 945, 960, 1030, and 1275 cm.$^{-1}$.

Quantitative Hydrolysis of $B_4H_8\cdot$TMED.—Platinum black (0.1 g.) contained in a 200-ml. heavy-walled ampoule was saturated with hydrogen at near atmospheric pressure. The solution was made basic with 3 ml. of 10% sodium hydroxide and frozen to −78°. With the tube in a nearly horizontal position, a weighed sample (0.1062 g.) of $B_4H_8\cdot$TMED in a platinum boat was inserted into the stem of the ampoule. The ampoule was evacuated, and the contents were melted and refrozen to remove residual gas. The ampoule was thoroughly evacuated, sealed off, and then inverted to mix the sample with the hydrolysis solution. The mixture was heated 20 hr. in a steam bath with intermittent shaking. After cooling to −196°, the tube was opened to the vacuum line, and the noncondensable gas was removed with a Toepler pump through a −196° cold trap into a known volume and measured. The observed value of 58.3 ± 0.3 mmoles of hydrogen/g. agreed almost within experimental error with the theoretical value of 59.0 mmoles/g. calculated according to the stoichiometry of the equation

$$B_4H_8\cdot\text{TMED} + 12H_2O \longrightarrow 4B(OH)_3 + \text{TMED} + 10H_2$$

Two additional samples were hydrolyzed in much the same way except that the hydrolyses were conducted in a side-arm vessel equipped with a reflux condenser. The sample was pushed from the side arm with a magnet into the degassed hydrolysis mixture. Hydrogen evolution proceeded smoothly at room temperature and was completed finally at reflux temperature (40–60°) in 2 hr. The hydrolysis residue was acidified and treated with $AuCl_4^-$ solution. Since no reduction occurred and the precipitated $AuCl_4^-$ salt showed no evidence of $H_2B(\text{TMED})^+$ in the infrared spectrum, hydrolysis was considered complete. The values of 59.4 and 59.2 mmoles/g. observed were in agreement with the calculated value for $B_4H_8\cdot$TMED.

Solvolysis of $B_4H_8\cdot$TMED.—At high pH, $B_4H_8\cdot$TMED proved relatively inert to water and alcohols and was recrystallized from a hot methanolic sodium hydroxide solution with only small loss. However, it dissolved slowly with hydrogen evolution when refluxed with methanolic sodium methoxide. A 0.82-g. sample (4.8 mmoles) added to 28 ml. of methanol containing 2.8 g. of sodium methoxide dissolved after 40 min. at incipient reflux temperature. To half of the clear solution was added aqueous tetramethylammonium chloride to give 0.21 g. (1.84 mmoles, 76% yield) of $(CH_3)_4NB_3H_8$. No hexafluorophosphate salt of $H_2B(\text{TMED})^+$ was obtained upon treating the other half of the reaction mixture with aqueous ammonium hexafluorophosphate.

A slurry of $B_4H_8\cdot$TMED (1.0 g., 6.0 mmoles) in 20 ml. of 1:1 H_2O–ethanol gassed vigorously, and the solid completely dissolved on warming the slurry to reflux. The solution was held at reflux until gas evolution subsided and the clear solution was then chilled. Colorless crystals of $(\text{TMED})(BH_3)_2$ (0.65 g., 0.45 mmole, 7.5%) separated and were collected by filtration. The filtrate, which was weakly basic, was made strongly basic with aqueous sodium hydroxide, and 2 ml. of saturated aqueous NH_4PF_6 was added. On cooling, crystals of $H_2B(\text{TMED})PF_6$ (0.48 g., 3.7 mmoles, 61%) formed. In a second experiment the first filtrate obtained upon isolation of $(\text{TMED})(BH_3)_2$ was treated with an excess of aqueous tetramethylammonium chloride and chilled to give $(CH_3)_4NB_3H_8$ (0.22 g., 1.9 mmoles, 32%).

Slow addition of $B_4H_8\cdot$TMED (3.0 g., 17.9 mmoles) to a stirred mixture of 6 ml. of 4 *N* hydrochloric acid, 4 ml. of water, and 10 ml. of ethanol cooled to 0° was accompanied by vigorous reaction with gas evolution and dissolution of the B_4H_8 complex. When the reaction had subsided, the clear solution was boiled and the alcohol displaced with water. Upon chilling the hot, acidic solution 1.48 g. of boric acid separated. The filtrate was made strongly basic with aqueous sodium hydroxide. Addition of an excess of aqueous NH_4PF_6 gave a colorless precipitate. The mixture was heated to boiling to give a clear solution which on chilling gave crystals of $H_2B(\text{TMED})PF_6$ (4.49 g., 16.4 mmoles, 91.5% yield).

Pyrolysis of $B_4H_8\cdot$TMED.—The $B_4H_8\cdot$TMED derivative (0.39 g., 2.34 mmoles) decomposed slowly under vacuum at 150–155°. After 5 hr., 0.13 g. (0.9 mmole) of $\text{TMED}\cdot(BH_3)_2$ had collected on a water-cooled condenser to leave a residue of 0.17 g. which gave infrared absorption bands characteristic of $H_2B(\text{TMED})^+$, $B_{12}H_{12}^{-2}$, and $B_3H_8^-$.

Nuclear Magnetic Resonance Spectra.—The B^{11} magnetic resonance of $B_5H_9\cdot$TMED in 1,2-dichloroethane consisted of three broad peaks of estimated relative intensities of 1:3:1, respectively, at +73.5 p.p.m. (~200 c.p.s. wide at half-height), +27.3 p.p.m. (~400 c.p.s. wide), and 0 p.p.m. (~200 c.p.s. wide). Upon simultaneous irradiation at 56.4 Mc., the peaks of intensity 1 were not changed but the large peak resolved into two sharper resonances at +30.1 p.p.m. (estimated relative intensity of 2) and 22.3 p.p.m. (relative intensity of 1). The width at half-height of these peaks was about 120–160 c.p.s. The proton resonance of the methyl and methylene groups dominated the hydrogen spectrum. In deuterioacetonitrile, the methyl hydrogens were observed as a sharp resonance at −2.5 p.p.m. and the methylene hydrogens at −3.02 p.p.m. The relative intensities were 6.4:2. The hydrogens bonded to boron gave a broad plateau-like signal extending upfield from the methyl hydrogen resonance to about 0 p.p.m. beyond which were two weak broad shoulders at about +1 and +1.5 p.p.m. The hydrogen spectrum was not completely resolved upon simultaneous 19.2 Mc. irradiation. The high-field shoulders did collapse to a weak peak at +0.44 p.p.m. At another setting of the oscillator, the broad plateau began to sharpen to a −0.5 p.p.m. resonance.

The B^{11} resonance of $B_4H_8\cdot$TMED in acetonitrile was comprised of two broad peaks at +44 p.p.m. (about 200 c.p.s. wide at half-height) and 0 p.p.m. (about 300 c.p.s. wide) of relative intensities of 3:1. These broad resonances were not sharpened upon simultaneous irradiation at 56.4 Mc. The proton spectrum of $B_4H_8\cdot$TMED in deuterioacetonitrile showed sharp singlets at −2.42, −2.53, and −2.95 p.p.m. of relative intensity 2:3.3:3.5. The hydrogens bonded to boron gave a very broad resonance extending from the methyl hydrogen resonance to about +2 p.p.m. Irradiation at 19.2 Mc. collapsed this broad signal to a sharp peak at +0.3 p.p.m. but left the three sharp low-field peaks unchanged. The 0.3 p.p.m. resonance had a relative intensity of 1:2.15 to the rest of the spectrum.