

## Nuclear Magnetic Resonance Studies of Diborane and Sodium Diborohydride

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The  $^{11}\text{B}$  n.m.r. spectrum of diborane, in the glycol ethers at room temperature and in diethyl ether at elevated temperatures, consists of a seven-lined multiplet with  $J = 60 \pm 2$  c.p.s. and  $\delta = -17.5 \pm 0.3$  p.p.m. ( $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 = 0.0$ ). This multiplet is interpreted as arising from ether induced intramolecular proton exchange. The activation energy for this exchange is approximately 4.8 kcal. in diethyl ether solution. The  $^{11}\text{B}$  n.m.r. spectrum of sodium diborohydride in diethylene glycol dimethyl ether consists of a 1:3:3:1 quartet with  $J = 102 \pm 2$  c.p.s. and  $\delta = +25.3 \pm 0.3$  p.p.m. At elevated temperatures sodium diborohydride exchanges with sodium borohydride in diethylene glycol dimethyl ether solution. The activation energy for this exchange is approximately 8.6 kcal.

## Introduction

The  $^{11}\text{B}$  n.m.r. spectrum of liquid or gaseous diborane under conditions of slow exchange<sup>1-3</sup> consists of a triplet of triplets (Fig. 2-A). The large coupling arises from terminal protons, the small coupling from bridge protons. At sufficiently high temperatures the spectrum of diborane dissolved in aliphatic ethers is collapsed to a seven-lined multiplet.<sup>4</sup> This collapse probably is due to intramolecular proton exchange brought about by ether displacement of bridge protons.

The empirical formula of sodium diborohydride,  $\text{NaB}_2\text{H}_7$ , in diethylene glycol dimethyl ether has been well established by vapor pressure and electrolytic studies.<sup>5-7</sup> All investigators have agreed that the ion probably consists of two borane groups connected through a single bridge proton—the only structure predicted by the topological theory of Dickerson and Lipscomb.<sup>8</sup>

The  $^{11}\text{B}$  n.m.r. spectrum of the diborohydride ion consists of a quartet with relative intensities of 1:3:3:1 (Fig. 4-A, low field group). Williams reported, however, that preliminary  $^{11}\text{B}$  n.m.r. studies indicated that the diborohydride ion underwent rapid tautomerism giving rise to what was thought to be the visible components of an eight-lined multiplet with  $J = 33$  c.p.s. and  $\delta = +25$  p.p.m. ( $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 = 0.0$ ).<sup>9</sup> Recent studies in this Laboratory have shown that diethylene glycol dimethyl ether solutions of sodium diborohydride decompose slowly at room temperature to sodium triborohydride.<sup>10</sup> The  $^{11}\text{B}$  n.m.r. spectrum of the tri-

borohydride ion consists of a nine-lined multiplet with  $J = 33$  c.p.s. and  $\delta = 30.0$  p.p.m. (lit.<sup>3a</sup>:  $J = 32$  c.p.s.,  $\delta = 28.3$  p.p.m.); and the overlapping spectrum of the diborohydride ion with that of the triborohydride ion probably is responsible for what previously was interpreted as  $\text{BH}_2^+$  ion overlapping with tautomerizing diborohydride ion.

## Experimental

**Diborane-Ether Solutions.**—The solvents (ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and diethyl ether) were commercial materials refluxed with and distilled from lithium aluminum hydride and were, with the exception of triethylene glycol dimethyl ether, redistilled on the vacuum line from lithium aluminum hydride directly into the n.m.r. tubes. Diborane was prepared from sodium borohydride (Metal Hydrides) and excess polyphosphoric acid,<sup>11</sup> and was mass spectrometrically pure except for 0.03% carbon dioxide and traces of silane. In a typical experiment, 0.28 ml. of ethylene glycol dimethyl ether and 0.89 mmole of diborane were condensed into a thick-walled n.m.r. tube (o.d. = 5 mm., i.d. = 3 mm.) on the vacuum line. The tube then was sealed and stored at  $-196^\circ$ . The tubes were made long enough so that pressures were not likely to exceed about 30 atm. with the quantity of diborane used.

**Sodium Diborohydride.**—In a typical experiment, 1.0 ml. of a diethylene glycol dimethyl ether solution of sodium borohydride (1.31 *M*) was placed in a thin-walled n.m.r. tube (o.d. = 5 mm., i.d. = 4 mm.). The tube was attached to the vacuum line and carefully evacuated, and the desired amount of diborane condensed onto the frozen solution at  $-196^\circ$ . The tube then was sealed from the line, cautiously warmed to room temperature to allow formation of the diborohydride ion, and then refrozen and stored at  $-196^\circ$  to prevent decomposition. The solutions were allowed to warm to room temperature only when spectra were being obtained. The ratio of borohydride to borane in the solutions varied from 0.40 to 1.50.

**Spectra.**—The  $^{11}\text{B}$  n.m.r. spectra were obtained using a Varian high resolution spectrometer, Model 4300B, at a frequency of 19.3 Mc.p.s. Spectra at other than room temperature were obtained using standard Varian accessories. Temperature uncertainty was about  $\pm 1^\circ$ . Line positions were determined using the side-band technique.

## Results and Discussion

**Diborane-Ether Solutions.**—The  $^{11}\text{B}$  n.m.r. spectrum of diborane in glycol ether solutions, at room temperature, consists of a seven-lined multiplet (Fig. 1)

- (1) R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954).
- (2) J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).
- (3) (a) W. D. Phillips, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959); (b) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).
- (4) Results obtained in this Laboratory indicate the  $^{11}\text{B}$  spectrum of diborane gas does not vary over a range of temperatures and pressures: R. Schaeffer and F. Tebbe, to be published.
- (5) H. C. Brown and P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).
- (6) E. B. Baker, R. B. Ellis, and W. S. Wilcox, *J. Inorg. Nucl. Chem.*, **23**, 41 (1961).
- (7) R. M. Adams, "Preparation of Diborane," in "Borax to Boranes," R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, p. 60 ff.
- (8) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).
- (9) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961); R. E. Williams, 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1960.
- (10) D. F. Gaines, R. Schaeffer, and F. N. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

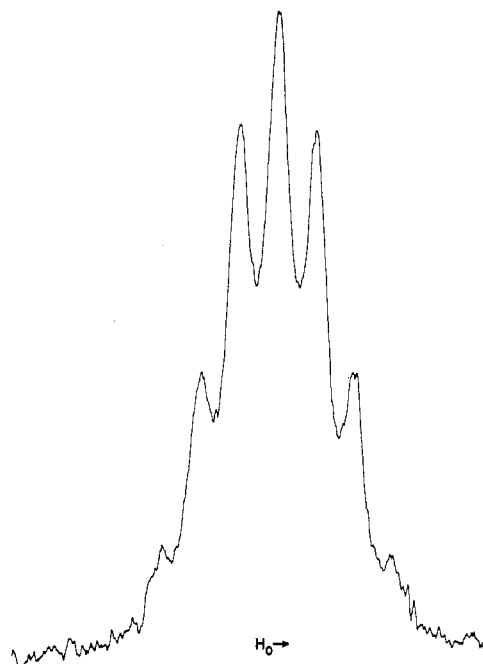


Fig. 1.—The  $^{11}\text{B}$  n.m.r. spectrum of diborane $^{\text{a}}$  in glycol ether solutions at room temperature.

with a coupling constant,  $J$ , of  $60 \pm 2$  c.p.s. and a chemical shift,  $\delta$ , of  $-17.5 \pm 0.3$  p.p.m. ( $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 = 0.0$ ;  $\text{B}_2\text{H}_6$  (neat) $^{\text{3a}} = -17.7$  p.p.m.). This multiplet structure results from the coupling of each boron with six equivalent protons. The theoretical line intensities of a seven-lined multiplet are 1:6:15:20:15:6:1, and though the observed peak heights do not exhibit these intensity ratios (presumably because of peak broadening and overlap), rough attempts at total integration, assuming idealized signal shapes, give ratios in reasonable agreement with the theoretical values.

The  $^{11}\text{B}$  n.m.r. spectrum of diborane in diethyl ether solution at and below  $-26^\circ$  (Fig. 2-A) is the same as that of neat diborane;  $J_{\text{BH}_2} = 135 \pm 2$  c.p.s. (lit. $^{\text{3a}} = 137$  c.p.s.), and  $J_{\text{BHB}} = 46 \pm 2$  c.p.s. (lit. $^{\text{3a}} = 48$  c.p.s.). As the temperature is raised, the spectrum collapses, reversibly, first to a broad singlet at  $30^\circ$  (Fig. 2-C); at  $84^\circ$  it is resolved into the seven-lined spectrum (Fig. 2-D) that is observed in the glycol ethers at room temperature. Cooling an ethylene glycol dimethyl ether solution of diborane to  $-56^\circ$  produces a spectrum similar to that shown in Fig. 2-B. The freezing points of the glycol ether solutions prohibited experiments at lower temperatures, but the trend is clearly the same as that observed in diethyl ether solutions of diborane. An estimate of the activation energy,  $\Delta E$ , for the exchange process in diethyl ether solution was obtained by comparing the line shapes of the spectra at various temperatures with theoretical line shapes shown by Pople, *et al.*, $^{12}$  for various values of the mean lifetime,  $\tau$  (Table I), and then constructing an Arrhenius plot of  $\log 1/\tau$  vs.  $1/T$  (Fig. 3-A). The slope of this line gave  $\Delta E = 4.8$  kcal. The error involved in the determination of  $\tau$

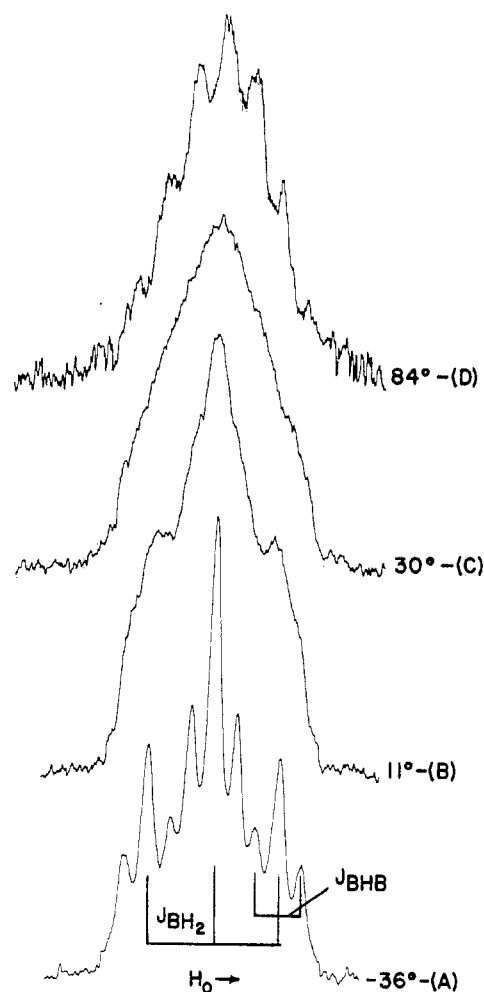


Fig. 2.—The temperature dependence of the  $^{11}\text{B}$  n.m.r. spectra of diborane in diethyl ether solution.

by this $^{\text{a}}$  method is fairly large, because the rate of exchange of the protons is estimated by observing the effect of this exchange rate on the borons of diborane. The total width of the spectra thus remains constant and the change observed is in the shape and/or complexity of the spectra. The only method currently available for estimating  $\tau$  under these conditions is that of comparing those regions of spectral collapse that clearly match the line shapes shown by Pople, *et al.* $^{12}$  The maximum error anticipated in the activation energy in this study is about  $\pm 1.5$  kcal.

The mechanism of exchange probably involves ether displacement of a bridge proton from one of the boron

TABLE I  
 $\tau$  VALUES AT VARIOUS TEMPERATURES FOR THE DIBORANE-DIETHYL ETHER SYSTEM

|                    | $-26^\circ$ | $+30^\circ$ | $+84^\circ$ |
|--------------------|-------------|-------------|-------------|
| $\tau \times 10^4$ | 119.8       | 16.77       | 5.99        |
| $X^{\text{a}}$     | 10          | 1.4         | 0.5         |

$^{\text{a}}$  The term  $X$  is a function of the line shape of the spectrum at a given state of collapse and is related to  $\tau$  by the equation $^{12}$

$$\tau = \frac{X}{\sqrt{2}\pi(\nu_a - \nu_b)}$$

where  $(\nu_a - \nu_b) = 135$  c.p.s.

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York N. Y., 1959, p. 223.

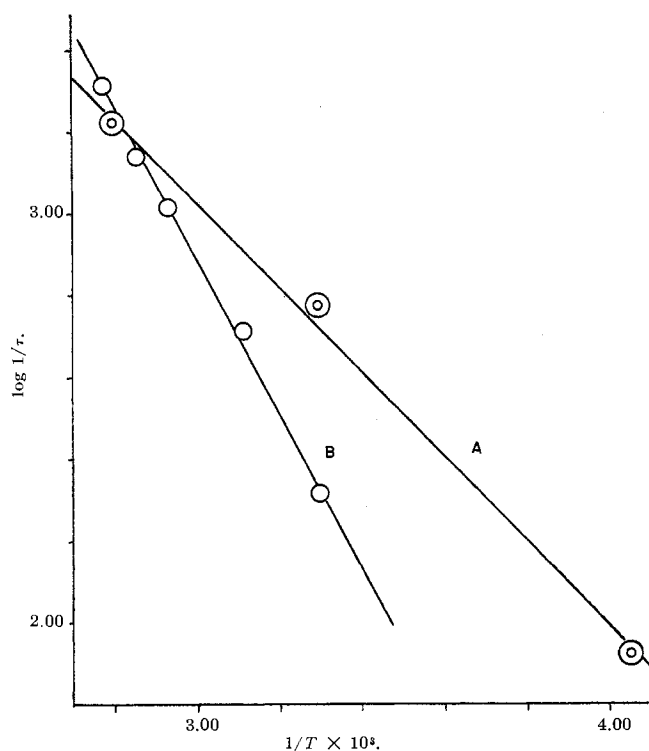
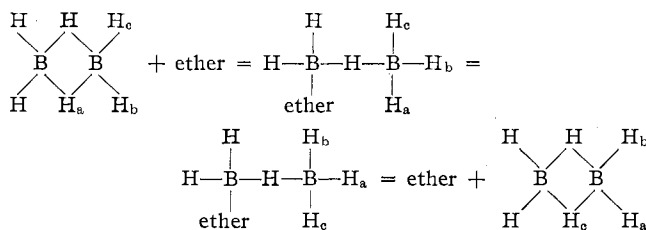


Fig. 3.—The temperature dependence of  $1/\tau$  for (A) intramolecular proton exchange of diborane in diethyl ether and (B) 1:1 sodium borohydride:sodium diborohydride exchange in ethylene glycol dimethyl ether.

atoms followed by rotation about the remaining bridge proton.



This mechanism is similar in form to that proposed by Phillips, *et al.*,<sup>3a</sup> for the intramolecular proton exchange of  $\mu$ -dimethylamino diborane. The nature of the ether-diborane interaction is at best only partially understood at this time. However, the rate of the intramolecular proton exchange appears to be proportional to the basic strength of the ether solvent employed.

**Sodium Diborohydride.**—The  $^{11}\text{B}$  n.m.r. spectrum of the diborohydride ion in the presence of excess borohydride ion (Fig. 4-A) in diethylene glycol dimethyl ether solution consists of a 1:3:3:1 quartet with  $J = 102 \pm 2$  c.p.s. and  $\delta = +25.3 \pm 0.3$  p.p.m. partially overlapping with the borohydride quintet. The broadening of the peaks is thought to be due to weak, unresolvable coupling of the bridge proton with the borane groups. This absence of resolved bridge coupling is not unexpected, as it has been clearly observed in only a few boron compounds: diborane,<sup>1-3</sup> tetraborane,<sup>13</sup>  $\mu$ -dimethylamino diborane,<sup>3</sup> and alkyl diboranes.<sup>14</sup>

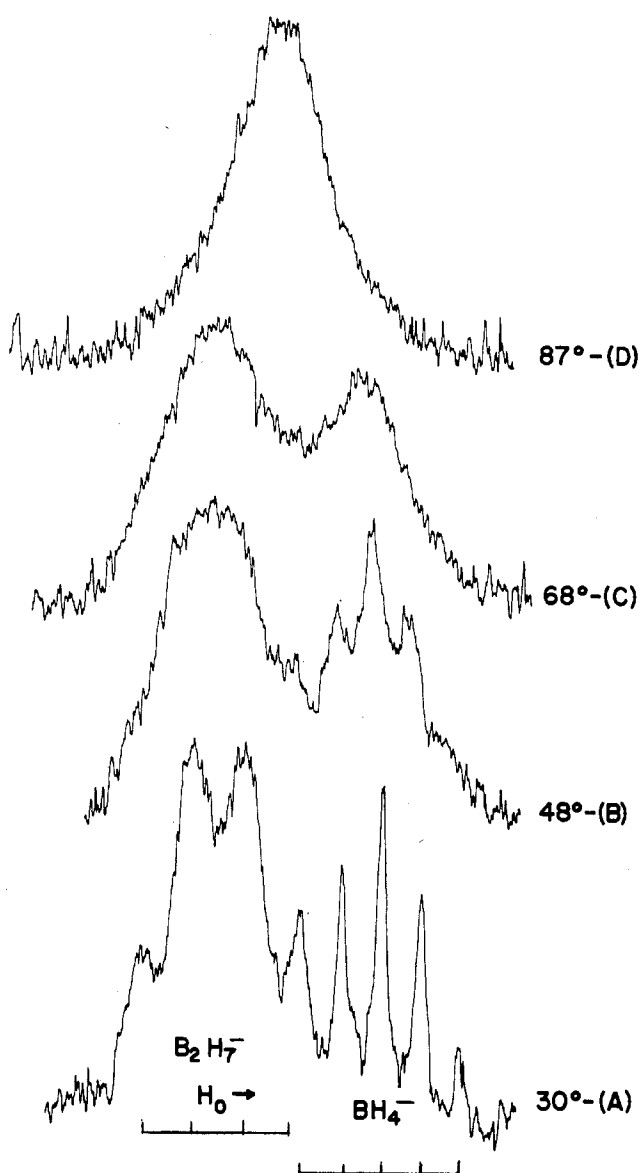


Fig. 4.—The temperature dependence of the  $^{11}\text{B}$  n.m.r. spectra of 1:1 sodium borohydride:sodium diborohydride in ethylene glycol dimethyl ether.

The diborohydride ion exchanges very rapidly with diborane, and a single sharp peak is observed with a downfield shift proportional to the ratio of diborane to diborohydride ion. The exchange of borohydride ion with diborohydride ion at room temperature is slow. The temperature dependence of the spectra of a 1:1 solution of borohydride ion and diborohydride ion (Fig. 4) was correlated with values of  $\tau$  (Table II) by comparing the collapse of the chemical shift of the two ions, at various temperatures, with the theoretical line shapes

TABLE II

$\tau$  VALUES AT VARIOUS TEMPERATURES FOR THE EXCHANGE OF 1:1 BOROHYDRIDE:DIBOROHYDRIDE

|                    | 30°  | 48°  | 68°  | 77°  | 87°  |
|--------------------|------|------|------|------|------|
| $\tau \times 10^4$ | 48.3 | 19.3 | 9.65 | 7.24 | 4.83 |
| $X^a$              | 10   | 4    | 2    | 1.5  | 1.0  |

<sup>a</sup> The term  $X$  is as in Table I;  $(\nu_a - \nu_b) = 330$  c.p.s.

(13) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 8164 (1959); J. S. Rigden, R. C. Hopkins, and J. D. Baldeschwieler, *J. Chem. Phys.*, **35**, 1532 (1961).

(14) R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960).

shown by Pople, *et al.*<sup>12</sup> The slope of the Arrhenius plot (Fig. 3-B) gave  $\Delta E = 8.6 \pm 1.5$  kcal. In this case, where the rate of exchange of borons between two environments is being observed, the observed and model<sup>12</sup> spectra are more easily correlated than in the case of diborane proton exchange, and the accuracy of the resulting activation energy is thus somewhat higher. The dissociation energy for gaseous diborane has been estimated to be 28.4 kcal.,<sup>15</sup> which corresponds to 14.2 kcal. for a single BHB bridge bond. The somewhat lower

(15) S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 5775 (1956).

value obtained for the diborohydride ion-borohydride ion exchange suggests that the mechanism of exchange probably involves dissociation of the diborohydride ion into borane and borohydride ion, rather than direct exchange between the two negative ions.

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## Convenient Preparations of Solutions Containing the Triborohydride Ion<sup>1,2</sup>

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The triborohydride ion has been conveniently prepared either by hydroboration of the alkali metal addition compounds of naphthalene or triphenylboron with diborane in ether solutions, or by reaction of metal borohydrides with diborane in ether solutions at 100°. The diborane necessary in the second case may be easily prepared *in situ* by using a deficiency of boron trifluoride etherate in the conventional diborane preparation from borohydrides. Triborohydride ion may be isolated in high yield by conversion to the tetramethylammonium salt.

Relatively few studies of the chemistry of the triborohydride ion have been reported, at least in part as a result of the fact that no convenient synthesis of the material was available. Nevertheless, the material promised to be of considerable synthetic use if a relatively simple preparation could be developed. Triborohydride salts previously have been prepared from sodium amalgam and diborane<sup>3</sup> or pentaborane-11<sup>4</sup> and tetraborane and sodium hydride,<sup>5</sup> sodium borohydride,<sup>6</sup> sodium amalgam,<sup>6</sup> or ammonia,<sup>7</sup> and by the stepwise degradation of decaborane.<sup>8</sup> The long period required for the diborane-sodium amalgam reaction, even in the presence of solvent, and the instability and/or expense of the higher boron hydrides have made the isolation of large quantities of such salts impractical.

Preliminary studies carried out in these Laboratories some years ago suggested that the rate of reaction of diborane with sodium might be greatly enhanced by the presence of a sodium carrier. Other studies, with little

success, concentrated on formal extraction of a proton from diborane *via* the postulated triborane-9 to produce the desired salts. Both types of reaction have now been demonstrated to be useful (although the mechanism of formation from diborane is unknown) and the second approach promises to make triborohydride ion in solution (and certain suitable derivatives) readily available laboratory reagents.

Tetrahydrofuran solutions of the alkali metal addition compounds of triphenylboron or naphthalene are deeply colored, but reaction to discharge the color occurs within a few seconds on addition of an equivalent amount of diborane, presumably according to the equation



The resulting pale yellow or brown solutions contain the liberated triphenylboron or naphthalene and suspended metal borohydride and reasonable yields of tetramethylammonium triborohydride could be recovered following addition of tetramethylammonium hydroxide. The rapidity of this reaction compared with the 2-day diborane-sodium amalgam reaction suggests that the rate of formation of the triborohydride is primarily dependent upon the efficiency with which the alkali metal can be supplied to the diborane or intermediate species. The triborohydride salts were converted to the tetramethylammonium derivative since other salts are difficult to recover free of yellow impurities formed during the reactions and strongly retained solvent.

(1) Interconversion of Boranes. VI. For part V see R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

(2) The commonly used borohydride ( $\text{BH}_4^-$ ), triborohydride ( $\text{B}_3\text{H}_8^-$ ) nomenclature is employed rather than the American "hydroborate," "octahydrotriborate" recommendation in the Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds.

(3) W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Am. Chem. Soc.*, **80**, 1828 (1958).

(4) M. D. Ford, W. V. Hough, and L. J. Edwards, U. S. At. Energy Comm., *Nucl. Sci. Abstr.*, **11**, Abstr. No. 6233 (1957).

(5) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(6) W. V. Hough and L. J. Edwards in "Borax to Boranes," Advances in Chemistry Series, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, pp. 189-190.

(7) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960).

(8) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *ibid.*, **83**, 2669 (1961).