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A Novel Synthesis of the Triborohydride Anion, $^{-}B_3H_8$

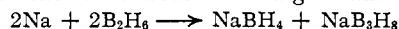
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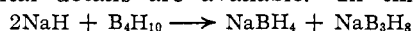
The synthesis of tetramethylammonium triborohydride, $(CH_3)_4NB_3H_8$, has been achieved from decaborane. The preparative scheme, characterization and properties of the product are given. A discussion of the B^{11} resonance spectrum along with structural implications is presented. The tetramethylammonium salt was converted to trimethylamine triborane by reaction with trimethylammonium chloride.

Introduction

The synthesis of sodium triborohydride, NaB_3H_8 , was recently reported by Hough and co-workers¹ from the reaction of sodium amalgam and diborane



in ether. Although the yields in this reaction are quite good, the use of gaseous diborane and the requisite high vacuum equipment make this synthesis inconvenient for preparing large quantities of the triborohydride anion. Another synthesis was reported involving tetraborane,² but no experimental details are available. In this paper



we wish to report the preparation of tetramethylammonium triborohydride, $(CH_3)_4NB_3H_8$, utilizing decaborane as the boron hydride source.

Experimental

Standard laboratory glassware was used throughout the procedure.

Materials.—Decaborane was sublimed before use. Benzene was purified by distillation from lithium aluminum hydride. Tetrahydrofuran (Eastman White label) was dried and distilled from lithium aluminum hydride. All other materials were reagent grade chemicals.

B^{11} Nuclear Magnetic Resonance.—The B^{11} resonance spectrum was obtained in dimethylformamide solution with a Varian Model V4300 B high resolution n.m.r. spectrometer at a frequency of 12.8 mc.

I—Bis-diethylsulfide Decaborane (12).—In a 500 cc. round-bottom flask, equipped with condenser, was placed 45 g. of sublimed decaborane (0.34 moles), 100 ml. of dry benzene and 120 ml. of ethyl sulfide. The mixture was refluxed under dry nitrogen for about 3 hr. or until no more gas was evolved. The yellow solution was cooled to room temperature and the product crystallized out by adding ether and pentane. After cooling, the fluffy crystals were filtered and washed with ether, m.p. 90–91°. The total yield was 85 g. (83%).

Anal. Calcd. for $B_{10}C_8H_{32}S_2$: B, 36.07; C, 31.98; H, 10.66. Found: B, 34.97; C, 32.43; H, 11.02.

II—Diethylsulfide Nonaborane (13).—Bis-diethylsulfide decaborane (12) (25 g., 0.083 mole) in 100 ml. of methanol evolved hydrogen during 1 hr. of refluxing. The solvent was removed *in vacuo* at ambient temperatures. The crystalline residue was recrystallized from ether–pentane and yielded 12 g. of product (72%), m.p. 50–51°.

Anal. Calcd. for $B_9C_8H_{28}S$: B, 48.58; C, 23.95; H, 11.47; S, 15.99. Found: B, 48.94; C, 23.86; H, 11.91; S, 14.52.

It is not necessary, however, to crystallize the crude diethylsulfide nonaborane (13) before converting it to tetramethylammonium nonaborohydride.

III—Tetramethylammonium Nonaborohydride (12).—A 17.0 g. sample of crude diethylsulfide nonaborane (13) was dissolved in 200 ml. of ethanol with gentle warming. Tetramethylammonium hydroxide, as a 10% aqueous solution, was slowly added until the mixture was distinctly basic ($pH > 9$). The white solid tetramethylammonium nonaborohydride (12) precipitated from solution. The mixture was cooled to 0° and filtered. The solid was washed once with cold ethanol and then with ether. A yield of 11.5 g. or 74% of product was obtained.

(1) W. V. Hough, L. J. Edwards and A. D. McElroy, *J. Am. Chem. Soc.*, **78**, 689 (1956); *ibid.*, **80**, 1328 (1958).

(2) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3554 (1959).

Anal. Calcd. for $B_9C_4H_{24}N$: B, 53.24; C, 26.20; H, 13.10; N, 7.64. Found: B, 52.24; C, 26.50; H, 13.52; N, 7.16.

IV—Tetramethylammonium Triborohydride.—Tetramethylammonium nonaborohydride (12), 11.0 g., was suspended in 150 ml. of methanol in a round-bottom flask. The flask was fitted with a reflux condenser and the mixture was stirred for 12 hr. at ambient temperature. It was necessary to place a 25° water-bath around the flask to moderate the reaction. The white crystalline product separated from solution. It was filtered off and washed with cold methanol. The yield was 5.4 g. or 79% based on the conversion from tetramethylammonium nonaborohydride (12). The product was recrystallized from hot methanol and did not melt up to 275°.

Anal. Calcd. for $B_3C_4H_{20}N$: B, 28.36; C, 41.94; H, 17.47; N, 12.23. Found: B, 28.45; C, 39.89; H, 17.27; N, 11.92.

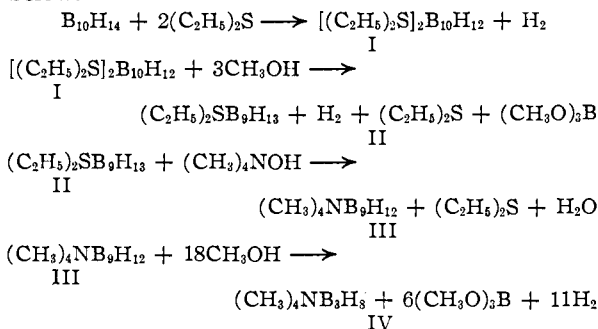
The over-all yield of tetramethylammonium triborohydride from decaborane was 35%.

Trimethylamine Triborane.—Tetramethylammonium triborohydride, 3.5 g., was allowed to react with 2.7 g. of trimethylammonium chloride in 100 ml. of tetrahydrofuran. The mixture was refluxed for 2 to 2.5 hr. Gas evolution had ceased. After cooling, the mixture was filtered. The THF was removed from the filtrate *in vacuo*. The white solid residue was loaded into a cold-finger (10°) sublimator and sublimed at 70–75° under high vacuum. A 1.9 g. sample of the product was obtained from the cold-finger, m.p. 119–120°. This is a yield of 64%.

Anal. Calcd. for $B_3C_3H_{19}N$: B, 32.95; N, 14.22. Found: B, 32.71; N, 13.81.

Results and Discussion

Preparation.—Tetramethylammonium triborohydride was prepared by a stepwise degradation of decaborane. The preparative scheme is given below.



Compound I was synthesized in 80–90% yield from decaborane and diethylsulfide in benzene at the reflux temperature. Methanolysis of I under controlled conditions afforded II in fair yield. Compound II is a stable intermediate in the total methanolysis of I since both I and II may be degraded completely to methyl borate under prolonged reaction with methanol. The conversion of II into III was easily accomplished with a slight excess of tetramethylammonium hydroxide in ethanol. In the last step, the methanolysis of III at ambient temperatures produced the product IV. Tetramethylammonium triborohydride crystal-

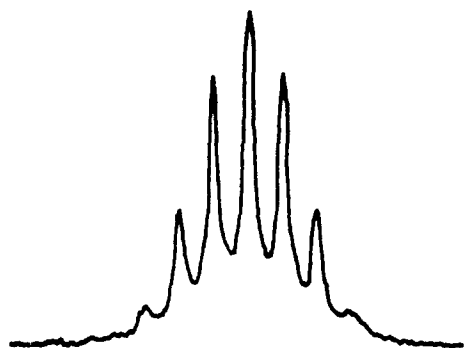


Fig. 1.— B^{11} n.m.r. spectrum of $(CH_3)_4N^+B_3H_8^-$.

lized from the solution as it was formed. The insolubility of the product in methanol permitted its easy isolation and probably prevented further degradation to methyl borate. Therefore, the use of the tetramethylammonium cation is felt to be essential in order to obtain good results. Other large organic cations may also work as well.

Unfortunately it was found necessary to isolate each of the intermediate compounds I, II and III. All attempts to make this a "one-pot" synthesis were unsuccessful. The intermediate compounds were recently reported elsewhere³ and a more detailed discussion of their characterization and properties will soon appear.

The recent availability of decaborane and the ease with which these four reactions occur make this reaction scheme an attractive method for the preparation of large quantities of the triborohydride anion, even though the over-all yield of the product (IV) was only 30–35% based on decaborane.

Tetramethylammonium triborohydride is a stable white crystalline solid which does not melt up to 275° . It may be recrystallized easily from hot methanol. Elemental analysis agreed quite well with the formulation $(CH_3)_4NB_3H_8$. An authentic sample, prepared from sodium triborohydride and tetramethylammonium chloride, had an infrared spectrum identical with the product obtained by the degradative scheme from decaborane. The infrared spectrum showed B-H stretching bands at 4.1 and 4.7 microns and also strong absorption at 8.7, 9.9 and 10.55 microns.

B^{11} N.m.r. Spectrum.—The B^{11} n.m.r. spectrum of tetramethylammonium triborohydride was especially enlightening and aided in the characterization of the compound. The spectrum, shown in Fig. 1, is formally similar to that reported by Phillips⁴ for sodium triborohydride. The J value of 32 c.p.s. and the location of the center peak at +47.5 p.p.m. relative to methyl borate were essentially the same. The spectrum appears to be only a septet as reported by Phillips,⁴ but a careful measurement of peak heights revealed that it must be a nonet, with the two smallest peaks being lost in the background. The peak heights were in excellent agreement with the theoretical ratios for nine peaks but not for seven (see

(3) Presented at the 138th meeting of the American Chemical Society, New York, N. Y., September 11–16, 1960.

(4) W. D. Phillips, H. C. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

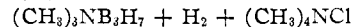
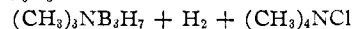
TABLE I
THE RELATIVE PEAK HEIGHTS OF THE B^{11} N.M.R. SPECTRUM OF THE TRIBOROHYDRIDE ANION

Obsd.	Calcd. for Nonet	Calcd. for Septet
..	0.1	..
1.1	1.0	1.0
3.5	3.5	6.0
6.8	7.0	15
8.5	8.7	20
6.8	7.0	15
3.3	3.5	6.0
0.9	1.0	1.0
..	0.1	..

Table I). Theory predicts that the two smallest peaks should be one-eighth the intensity of the smallest member of the septet and hence would be too weak to be observed.

The B^{11} n.m.r. spectrum, a nonet, implies that all three of the boron atoms are equivalent and that each one couples with all eight of the hydrogen atoms. This is in agreement with a statement by Lipscomb⁵ that the B^{11} resonance of the triborohydride ion is probably a nonet and lends support to Lipscomb's structural conclusions. Recently Peters and Nordman⁶ have shown by X-ray analysis that the structure of the triborohydride ion in the crystal state does not contain equivalent hydrogens but has two bridge hydrogens and three pairs of regular terminal hydrogens. The equivalency of the borons and hydrogen in solution, as indicated by the B^{11} resonance, must be achieved by an internal hydrogen exchange process suggested by Lipscomb.⁵ This is similar to the case found for aluminum borohydride in which all of the hydrogen atoms appear identical.⁷

Reactions.—The reaction of ammonium chloride with sodium triborohydride in ether has been reported⁸ to yield ammonia triborane in moderate yield. The analogous reaction with trimethylammonium chloride was not reported. Tetramethylammonium triborohydride was found to react with trimethylammonium chloride in tetrahydrofuran at the reflux temperature to produce trimethylamine triborane in good yield. Diethyl



ether could not be used as a solvent due to the insolubility of the triborohydride salt. Unfortunately the use of tetrahydrofuran at the reflux temperature as a reaction medium will probably prevent the preparation of ammonia triborane since this material is reported to decompose with evolution of hydrogen at its melting point.⁸

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(5) W. N. Lipscomb, "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959.

(6) C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, **82**, 5758 (1960)

(7) R. A. Ogg, Jr., and J. D. Ray, *Discussions Faraday Soc.*, **19**, 215 (1955).

(8) G. Kodama, R. W. Parry and J. C. Carter, *J. Am. Chem. Soc.*, **81**, 3534 (1959).