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**PREPARATION AND STUDY OF A SERIES
OF BORANE AND OCTAHYDROTRIBORATE
DERIVATIVES OF METHYLATED POLYAMINES**

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Contribution from the Lawrence Radiation Laboratory
University of California, Livermore, California

Preparation and Study of a Series of Borane and
Octahydrotriborate Derivatives of Methylated Polyamines

By F. E. WALKER and R. K. PEARSON

A series of borane and octahydrotriborate derivatives of methylated polyamines have been prepared to determine the variance in certain chemical and physical properties with increasing chain length of the basic amines and with an increase in the number of carbon atoms between adjacent nitrogen atoms.

Introduction

The preparation of tetramethylammonium octahydrotriborate¹ and the

(1) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, J. Am. Chem. Soc., 83, 2669 (1961).

diborane adduct of tetramethyl ethylenediamine² indicated that a series of

(2) Correspondence from Callery Chemical Co.

borane and octahydrotriborate derivatives of methylated polyamines could be prepared. The facile methylation of some specific amines through the use of sodium formate and formaldehyde was reported,^{3,4} and a study^{4,5} of the

(3) H. T. Clark, H. B. Gillespie, and S. Z. Weiss Haus, J. Am. Chem. Soc., 55, 4571 (1933).

(4) A. Marxer and K. Miescher, Helv. Chim. Acta, 34, 924 (1951).

(5) R. Rometsch, A. Marxer, and K. Miescher, *ibid.*, 34, 1611 (1951).

quaternization of polyamines showed that the precursors of interest were or could be made available.

The carbon-nitrogen chains of the polyamines considered are: (a) NCCN, (b) NCCNCCN, (c) NCCNCCNCCN, and (d) NCCCNCCCN.

Representative formulae for the preparation of the amine boranes and the octahydrotriborate derivatives, respectively, follow:

Experimental

The polyamine boranes were synthesized in a vacuum line system with carefully dried reagents and solvents, and they were handled in an evacuated dry box until their qualitative air and moisture stabilities were evaluated. Adequate safety precautions were observed because of the well-known hazardous properties of diborane.

Materials. — Except in the case of ethylenediamine, where the tetramethyl diammonium diiodide was readily available,⁶ the methylated

(6) This material was prepared by E. R. Bissell of Lawrence Radiation Laboratory, Livermore.

polyamines and the ammonium iodides were prepared and characterized as reported.^{4,7} Gas chromatographic separation and purity, infrared, n. m. r.,

(7) Lawrence Radiation Laboratory, Livermore, Report UCRL-7973.

and elemental analyses were made in addition to the b. p. determinations of the methylated polyamines considered. X-ray diffraction, infrared, and elemental analyses were made of each of the ammonium iodides to complement the m. p. data.

Preparation of Polyamine Boranes. — The following synthesis of pentamethyl diethylenetriamine tris-borane is typical for the production of polyamine boranes. A vacuum line reaction tube filled with dry argon was charged with 0.5260 g. (3.035 mmoles) of pentamethyl diethylenetriamine. The argon was then removed; 4 ml. of dry ether was distilled into the tube, and 0.522 g. (5.499 mmoles) of diborane was added, all while the tube was cooled in liquid nitrogen. The mixture was allowed to warm to room temperature. It was then sealed, shielded in a hood overnight, and opened on the vacuum line. A white solid extended about 1 inch up in the bottom of the tube. The ether, excess diborane, and hydrogen were removed and measured. There was 0.572 mmoles of diborane and 0.690 mmoles of hydrogen. The mole ratio of reacted diborane to amine was 1.585:1. The product was cautiously removed from the tube in a dry box. The yield of pure product was 0.644 g. (99%). After slurrying in hot water, collecting by filtration, washing with water, and drying in vacuo at 25°, the m. p. was 185-186°.

Anal. Calcd. for $C_9H_{32}N_3B_3$: C, 50.32; H, 15.02; N, 19.56. Found: C, 50.17; H, 14.50; N, 19.23.

Two diborane adducts were formed with hexamethyl triethylenetetramine. When the reaction was carried out with no solvent, the material recovered in 92% yield was the bis-borane, m. p. 118.5-119.5° after recrystallization from water. The mole ratio of reactants was 1.018:1 (diborane to amine).

Anal. Calcd. for $C_{12}H_{36}N_4B_2$: C, 55.85; H, 14.06; N, 21.71. Found: C, 55.11; H, 13.58; N, 21.42.

The second adduct, hexamethyl triethylenetetramine tetrakis-borane, was prepared in dry ether in 99% yield. The reacting mole ratio was 2.016:1 (diborane to amine), and the m. p., after slurrying in hot water, collecting by filtration, washing, and drying in vacuo, was 208-210°.

Anal. Calcd. for $C_{12}H_{42}N_4B_4$: C, 50.44; H, 14.82; N, 19.61. Found: C, 50.62; H, 14.77; N, 19.62.

Pentamethyl di-n-propylene tris-borane was produced readily in ether. The mole ratio of diborane to amine, 1.491:1, supported the gravimetric yield data (99%). After washing with water and drying as before, the m. p. was 185-186.5°.

Anal. Calcd. for $C_{11}H_{36}N_3B_3$: C, 54.40; H, 14.94; N, 17.30. Found: C, 54.15; H, 15.01; N, 17.13.

Preparation of Polyamine Octahydrotriborates. — The procedures which follow for the preparation of hexamethyl ethylenediammonium bis-octahydrotriborate and heptamethyl diethylenediammonium bis-octahydrotriborate are representative of two general methods used to synthesize the polyamine octahydrotriborates herein reported. To a 1.200-g. (3.00 mmoles) sample of hexamethyl ethylenediammonium diiodide in 50.0 ml. of isopropanol was added 0.48 g. (6.0 mmoles) of potassium octahydrotriborate. The mixture was refluxed for 30 min., the isopropanol was evaporated in vacuo to approximately one-third the original volume, and a few ml. of water was added. Long, colorless needles formed on cooling to 0°. They were separated by filtration, washed with water, and dried in vacuo; yield, 0.517 g. (76%). After recrystallization from water, this material exhibited what was found to be a characteristic melting profile for the octahydrotriborate derivatives. There was a slight amber discoloration and some softening near 250° and some evidence of slight decomposition, but much of the sample was still solid

at 350°. This same product was obtained in a reaction with water used as a solvent as described in the following method.

Anal. Calcd. for $C_8H_{38}N_2B_6$: C, 42.28; H, 16.85; N, 12.33. Found: C, 42.21; H, 16.75; N, 12.33.

At room temperature, 2.0065 g. (4.389 mmoles) of heptamethyl diethyleneaminediammonium diiodide was dissolved in 3.0 ml. of water, and 1.0209 g. (12.83 mmoles) of potassium octahydrotriborate was dissolved in 2.0 ml. of water. The octahydrotriborate solution was poured into the diiodide solution, and immediately a white slurry formed. This was quickly collected by filtration, washed with water, and dried in vacuo. The product had a weight of 1.1852 g. (95% yield). Recrystallization from water gave fine, colorless needles which appeared to melt at 117-119° with an apparent change in structure and some decomposition to give a solid material that fused at 340°C.

Anal. Calcd. for $C_{11}H_{45}N_3B_6$: C, 46.46; H, 15.95; N, 14.78. Found: C, 46.65; H, 15.69; N, 14.88.

Octamethyl diethylenetriammonium tris-octahydrotriborate was prepared from water solutions in 81% yield as long, narrow platelets which started fusing at 305°.

Anal. Calcd. for $C_{12}H_{56}N_3B_9$: C, 42.40; H, 16.61; N, 12.36. Found: C, 42.33; H, 16.23; N, 12.76.

Octamethyl triethylenediaminediammonium bis-octahydrotriborate was produced in isopropanol as white prisms in 34% yield, which, after recrystallization from water, fused near 350°.

Anal. Calcd. for $C_{14}H_{52}N_4B_6$: C, 49.25; H, 15.35; N, 16.41. Found: C, 49.67; H, 14.87; N, 16.10.

Decamethyl triethylenetetraammonium tetrakis-octahydrotriborate was formed from water solutions in 77% yield. Recrystallization from water gave small white prisms which started fusing at 310°.

Anal. Calcd. for $C_{16}H_{74}N_4B_{12}$: N, 12.38. Found: N, 12.36.

Octamethyl di-n-propylenetriammonium tris-octahydrotriborate was also prepared from water solutions, and the yield of pure material, after recrystallization from water, was 72%. The small white prisms started fusing at 320°.

Anal. Calcd. for $C_{14}H_{60}N_3B_9$: N, 11.42. Found: N, 11.33.

The infrared spectra of the polyamine boranes and the octahydrotriborate salts were taken from the solids in potassium bromide wafers on a Perkin-Elmer Infracord Spectrophotometer.

Table I

Absorption Frequencies (cm.^{-1}) of Boron Hydride Series^a

Polyamine boranes	Octahydrotriborates
2860 (s)	2930 (m)
2310 (vs, b)	2380 (vs, b)
2040 (w)	2100 (m)
1460 (s)	1470 (s)
1160 (s)	1140 (s)
1010 (s)	1000 (s)
873 (m)	953 (m)

^as, strong; m, medium; w, weak; b, broad; v, very.

X-ray diffraction films were made for each compound reported, and the distinguishing data is summarized.⁷

Differential thermal analyses were completed for each compound reported herein, and the densities of pressed pellets of each were measured. These densities are compared with the specific gravities of the parent methylated polyamines in Table II.

Table II
DTA and Density Data

BH ₃ adducts	M. p.	DTA ^a	S. g. 20°/4 of amine	Density, g./cc.
C ₆ H ₂₂ N ₂ B ₂ ^b	80°C		0.775	0.91
C ₉ H ₃₂ N ₃ B ₃	186°	160°	0.839	0.953
C ₁₂ H ₄₂ N ₄ B ₄	210°	130°	0.861	0.902
C ₁₂ H ₃₆ N ₄ B ₂	119°	108°	0.861	0.943
C ₁₁ H ₃₆ N ₃ B ₃	186°	168°	0.835	0.895
B ₃ H ₈ salts				
C ₈ H ₃₈ N ₂ B ₆	> 300°	125°	0.775	0.839
C ₁₂ H ₅₆ N ₃ B ₉	222°	140°	0.839	0.853
C ₁₆ H ₇₄ N ₄ B ₁₂	> 300°	145°	0.861	0.878
C ₁₁ H ₄₅ N ₃ B ₆	110°	115°	0.839	0.863
C ₁₄ H ₅₂ N ₄ B ₆	> 300°	148°	0.861	0.862
C ₁₄ H ₆₀ N ₃ B ₉	> 300°	168°	0.835	0.859

^aThe temperature of the onset of the first major exotherm.

^bData on this compound obtained from Callery Chemical Co.

^cSublimation occurs.

a predominantly single-product reaction, even though an excess of diborane was available. It is considered, in analogy with the quaternization studies,^{4,5} that both steric and electrostatic factors favor the attachment of the BH_3 moiety to the terminal nitrogens. When dry ether was used as a solvent for III, 2 moles of diborane added quantitatively giving VI.

The octahydrotriborate salts (XV through XX) were synthesized metathetically in isopropanol and in water. The reaction in water was so facile a procedure, and it provided such good yields, that it was preferred. These octahydrotriborates could be recrystallized from water with negligible hydrolysis, when processed quickly, to give colorless to white crystalline materials.

One phase of this work was a study of the relation of chain length and chain spacing to the density and some thermal properties of the molecules synthesized. A summary of this data is given in Table II. The densities were calculated from measurements of pressed pellets, and they are, very probably, less than the theoretical values. A determination was made by helium densitometer on $\text{C}_8\text{H}_{38}\text{N}_2\text{B}_6$, XV, and the value obtained was 0.86 in contrast to the pellet value of 0.839. Some of the materials were compacted more readily than others, but, particularly with the B_3H_8 salts, density was greater with increasing chain length, and it changed little with the nitrogen spacing varying from two to three carbon atoms. The specific gravities of the methylated polyamines varied in this same pattern.

The temperature of the onset of the first major exotherm, as determined by differential thermal analysis, increased slightly as the chain length of the octahydrotriborate salts increased, and the compounds with three carbon atoms between nitrogens, VIII and XX, had the highest temperature, 168° . Except for these correlations, the pattern was irregular.

The infrared absorption of the boranes near 2310 and 2040 cm^{-1} and the strong peaks near 2380 and 2100 cm^{-1} in the spectra of the octahydrotriborate salts correspond with the B-H stretch frequencies in the BH_3 and B_3H_8 moieties, respectively. There is no prominent absorption in the 2000 to 2500 cm^{-1} range in any of the polyamine or ammonium iodide precursors. Potassium octahydrotriborate has additional strong peaks at 1160 and 1000 cm^{-1} , which are also found, with some minor shifting, in the B_3H_8 salts. The octahydrotriborate salts, XVII and XIX, prepared from the incompletely quaternized polyamines, exhibit the characteristic octahydrotriborate absorption. However, the peaks at 2930 and 953 cm^{-1} appear as doublets, and more fine structure is evident, as in the analogous ammonium iodides.

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