

[CONTRIBUTION NO. 1187 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

Studies of Boron-Nitrogen Compounds. VII.¹ Synthesis and Properties of 1,3-Methyl-Substituted Diborazanes²

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RECEIVED SEPTEMBER 3, 1963

A new compound, 1,1,3,3-tetramethyldiborazane, has been isolated in small yields as a by-product in the preparation of dimethylaminoborane by reaction of dimethylammonium chloride with sodium borohydride in diethylene glycol dimethyl ether. ¹¹B n.m.r. of the compound shows it to be an analog of tetramethylbutane. The reactions of trimethylamine and ammonia with μ -dimethylaminoborane, first studied by Burg and Randolph,³ have been repeated and their tentative structural assignment confirmed by n.m.r. studies. Related reactions with mono- and dimethylamines confirm the generality of the reaction and open a general synthetic route to butane analogs.

Introduction

During the past thirty years numerous inorganic analogs of organic compounds have been prepared in which a C-C bond has been replaced by the isoelectronic unit B-N. The largest single class of compounds thus far studied is that containing the borazine group isoelectronic with benzene. More recently the analogs of cyclohexane have received some attention as have rings of other sizes and rings containing both carbon and boron-nitrogen pairs. (It is to be observed that a molecule must contain equal numbers of borons and nitrogens to be analogous to alkanes and thus the many compounds of the type $\text{HB}[\text{N}(\text{CH}_3)_2]_2$ are not strictly analogous to propane.)

In the course of an unrelated research problem it was necessary to prepare large amounts of dimethylaminoborane; the modified method of Schaeffer and Anderson⁴ was adopted in which reaction of sodium borohydride with dimethylammonium chloride was carried out in diethylene glycol dimethyl ether ("diglyme") solution. In some cases, particularly those preparations where the products were not separated shortly after the evolution of hydrogen had stopped, a small quantity of a slightly volatile by-product was also formed. This substance has been shown to be identical with the compound formed from dimethylamine and μ -dimethylaminodiborane.

The literature records two instances where products analogous to butane were thought to have been formed by reaction of amines with μ -aminodiboranes.^{3,5} The structures assigned to these compounds have been confirmed in the present work by the use of n.m.r. Additional examples of the general type have been prepared and a number of properties measured.

Experimental

A. Preparation and Isolation of 1,1,3,3-Tetramethyldiborazane from Sodium Borohydride and Dimethylammonium Chloride.—In a typical reaction 1 mole of sodium borohydride was mixed with 1 mole of dimethylammonium chloride in a 2-l. flask, and 150 ml. of ethylene glycol dimethyl ether (dried by refluxing over lithium aluminum hydride and then distilled from the solution) was added dropwise over a period of about 1 hr. The resulting very exothermic reaction was moderated by cooling the reaction vessel

(1) See D. F. Gaines and R. Schaeffer [*J. Am. Chem. Soc.*, **85**, 3592 (1963)] for part VI of this series.

(2) The nomenclature of compounds of the present type has not been considered by the Advisory Committee on the Nomenclature of Boron Compounds. The names used here appear to be consistent with the Committee's intention and are capable of extension as our knowledge of compounds of this type increases.

(3) A. B. Burg and C. L. Randolph, *J. Am. Chem. Soc.*, **71**, 3451 (1949).

(4) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

(5) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 2297 (1938).

with an ice bath. In the normal course of the preparation the mixture was allowed to warm slowly to room temperature after addition of solvent was complete and was then refluxed for 1 or 2 hr. In the experiments where the new product was first observed the reaction was stirred at room temperature for 48 hr. Distillation of the product was subsequently carried out without a period of reflux. The flask containing the crude product was attached to a standard vacuum apparatus and dimethylaminoborane removed for further purification. Small quantities of a material of much lower volatility remained in the flask and could be purified by vacuum sublimation at room temperature to a cold finger cooled to 0°. A second sublimation produced a relatively pure material with a melting range of 58–59°, thus eliminating the possibility that the substance might be dimethylamine borane (a not unexpected intermediate of melting point 35.5°).

B. Identification and Properties of 1,1,3,3-Tetramethyldiborazane (I).—A small portion of the material was dissolved in carbon tetrachloride and introduced into an n.m.r. tube together with a capillary containing boron trichloride as a reference. The ¹¹B spectrum (Table I) was observed at 19.3 Mc./sec. and was found to consist of a quartet and a triplet, indicating the presence of BH₂ and BH₃ groups in the molecule in equal numbers.

TABLE I
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE ¹¹B
NUCLEAR MAGNETIC RESONANCE SPECTRA OF DIBORAZANES^a

| Sample | BH ₂ | | BH ₃ | |
|---------------------------------|-----------------|-------------------|-----------------|-------------------|
| | J, c.p.s. | δ , p.p.m. | J, c.p.s. | δ , p.p.m. |
| 3,3-Dimethyldiborazane | 104 | +2.9 | 94.5 | +10.2 |
| 1,3,3-Trimethyldiborazane | 106 | +3.18 | 95 | +12.1 |
| 1,1,3,3-Tetramethyldiborazane | 110 | -3.0 | 95 | +12.4 |
| 1,1,1,3,3-Pentamethyldiborazane | 108 | -3.45 | 95 | +11.65 |

^a All chemical shifts reported with respect to the diethyl etherate of boron trifluoride as 0.0 p.p.m.

The proton n.m.r. consisted of two overlapping quartets arising from protons bonded to the boron atoms with three sharp lines arising from methyl groups in the molecule. Two of the sharp lines arise from one methyl resonance split by spin coupling to the proton attached to the same nitrogen; the second methyl resonance was a singlet. Proton chemical shifts and coupling constants are given in Table II.

TABLE II
PROTON NUCLEAR MAGNETIC RESONANCE OF
1,1,3,3-TETRAMETHYLDIBORAZANE^a

| Group | J, c.p.s. | δ , p.p.m. |
|-----------------------------------|-----------|-------------------|
| N(CH ₃) ₂ | | -2.28 |
| NH(CH ₃) ₂ | 7.2 | -2.58 |
| BH ₂ | 110 | -2.00 |
| BH ₃ | 95 | -0.73 |

^a Chemical shifts reported with respect to tetramethylsilane as 0.0 p.p.m.

The results of the nuclear magnetic resonance studies clearly point to the diborazane structure. Equal intensities of the boron triplet and doublet would be difficult to approximate with a compound having more than two borazane units. Added confirmation

from the proton n.m.r. that a terminal $\text{NH}(\text{CH}_3)_2$ group is present makes an alternate interpretation still less likely.

The infrared spectrum of the material provided little further information but was consistent with the proposed structure. The major infrared frequencies are listed in Table III.

TABLE III
INFRARED SPECTRA OF THE DIBORAZANES^a

| 3,3-Dimethyl- diborazane | | 1,3,3-Trimethyl- diborazane | | 1,1,3,3-Tetra- methyl- borazane | | 1,1,1,3,3-Penta- methyl- borazane | |
|-----------------------------|----------------|--------------------------------|----------------|---------------------------------------|----------------|---|----------------|
| Cm. ⁻¹ | In- tensity | Cm. ⁻¹ | In- tensity | Cm. ⁻¹ | In- tensity | Cm. ⁻¹ | In- tensity |
| 3300 | S | 3250 | S | 3190 | M | 2970 | S |
| 2960 | S | 3150 | M | 2950 | S | 2820 | S |
| 2945 | M | 2995 | S | 2385 | S | 2780 | S |
| 2845 | W | 2945 | M | 2275 | S | 2550 | S |
| 2440 | S | 2820 | W | 1465 | S | 2485 | M |
| 2385 | S | 2630 | W | 1440 | S | 2380 | M |
| 2300 | S | 2420 | S | 1415 | M | 1640 | S |
| 2260 | S | 2380 | S | 1395 | M | 1480 | M |
| 1830 | W | 2300 | S | 1380 | W | 1460 | M |
| 1660 | W | 2255 | S | 1305 | M | 1443 | M |
| 1600 | S | 2105 | W | 1225 | M | 1398 | M |
| 1470 | S | 1585 | S | 1205 | S | 1275 | M |
| 1390 | S | 1480 | S | 1180 | S | 1195 | M |
| 1240 | S | 1435 | M | 1150 | S | 1180 | S |
| 1205 | S | 1400 | M | 1045 | W | 1120 | W |
| 1190 | S | 1320 | S | 1023 | M | 1065 | S |
| 1175 | S | 1235 | S | 973 | M | 947 | S |
| 1155 | S | 1198 | S | 915 | M | 850 | W |
| 1115 | M | 1158 | S | 899 | M | 830 | M |
| 1085 | M | 1115 | M | 878 | W | | |
| 1040 | S | 1035 | M | 820 | M | | |
| 1020 | S | 1025 | S | | | | |
| 953 | S | 1010 | S | | | | |
| 925 | S | 975 | S | | | | |
| 910 | M | 928 | S | | | | |
| 905 | M | 900 | M | | | | |
| 819 | M | 833 | S | | | | |
| 777 | W | 815 | S | | | | |
| | | 720 | W | | | | |
| | | 694 | W | | | | |

^a S = strong absorption, M = medium absorption, W = weak absorption.

The molecular weight of the compound was determined in chloroform solution using a Mechrolab Model 302A osmometer. The range of molecular weight was from 102.3 to 129.5 and an average of 34 measurements gave a value of 112.6, in fair agreement with 115.6 calculated for the diborazane.

A microanalysis of the compound led to an empirical formula of $\text{B}_{2.03}\text{N}_{1.95}\text{C}_{4.06}\text{H}_{18.00}$,⁶ in fair agreement with that expected for the diborazane. All individual per cents were below those calculated for the pure material by an average of 5.5% and it seems most likely that a small amount of sample was lost by sublimation during analysis or that some contamination remained despite three sublimations of the analytical sample. (A 6% difference between the total sample weight analyzed and the total weight of elements recovered was reported by the analyst.)

Anal. Calcd.: B, 18.71; C, 41.55; H, 15.69; N, 24.15. Found: B, 17.68; C, 39.47; H, 14.59; N, 22.04.

The X-ray diffraction pattern of the solid was obtained using CuK radiation and a camera of 57.3-mm. radius over a period of 4 hr. Characteristic interplanar spacings are given in Table IV.

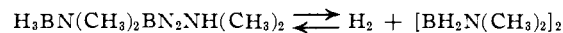
A sample of the material (0.424 g., 0.366 mole) was heated in a sealed tube for 1 hr. at 280°. On opening, the tube was found to contain 0.361 mole of hydrogen corresponding to a 98.5%

(6) Microanalysis was carried out by Alfred Bernhardt, Microanalytical Laboratory, Mulheim, Germany.

TABLE IV
INTERPLANAR SPACING OF $\text{BH}_3\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2$

| <i>d</i> | In- tensity | <i>d</i> | In- tensity | <i>d</i> | In- tensity | <i>d</i> | In- tensity |
|----------|----------------|----------|----------------|----------|----------------|----------|----------------|
| 8.23 | 6 | 5.81 | 5 | 4.70 | 10 | 2.98 | 3 |
| 6.92 | 7 | 5.57 | 5 | 4.10 | 8 | 2.81 | 1 |
| 6.28 | 4 | 5.25 | 9 | 3.65 | 2 | 2.40 | 3 |
| | | | | 3.23 | 3 | 1.99 | 4 |

yield based on the equation



The solid material remaining in the decomposition tube was purified and shown to be a 98% yield of the dimer of dimethylaminoborane by weight, vapor pressure measurement, and comparison of the infrared spectrum with that of an authentic sample.

C. Preparation of I from Dimethylaminodiborane and Dimethylamine.—The structure of the isolated diborazane suggested that it might be more conveniently prepared by nucleophilic attack of dimethylamine on dimethylaminodiborane in a manner similar to that used by Burg and Randolph.³ Equal quantities of the two reactants were mixed and allowed to warm slowly from liquid nitrogen temperature to room temperature. In a typical preparation 1.46 mmoles of each reactant was condensed separately into a tube and allowed to warm slowly to room temperature. The sublimed product weighed 122.3 mg., corresponding to a 72.6% yield.

D. Preparation of Other Diborazanes.—The compounds 3,3-dimethyldiborazane (II, m.p. 96.5–97.5°), 1,3,3-trimethyldiborazane (III, m.p. 89–90°), and 1,1,1,3,3-pentamethyldiborazane (IV, m.p. 36.8–38°) were prepared in good yield in the manner described in C by reactions of ammonia, monomethylamine, or trimethylamine, respectively, with μ -dimethylaminodiborane (compounds II and IV are identical with those of Burg and Randolph).³ N.m.r. studies confirmed the structural assignments and various physical properties were studied. Vapor pressures (Table V), n.m.r. (Table II and III), and infrared spectra (Table IV) were obtained. The di- and trimethyldiborazanes were easily purified by one sublimation onto a 0° cold finger whereas tetramethyldiborazane required three sublimations to obtain high purity. Pentamethyldiborazane was purified by fractional condensation in which it passed through a trap at –55° and stopped in one maintained at –63°. All melting points were obtained by rapid heating and were sharp; however, during measurement of vapor pressures it was noticed that all of the compounds began to decompose slightly above 50°. Burg and Randolph had observed eventual breakup of the pentamethyl compound to dimethylaminoborane and trimethylamine borane. To avoid this complication samples were heated as briefly as possible in making measurements and the measurements were discontinued when the 0° vapor tension could not be reproduced after measurements at higher temperatures.

TABLE V
VAPOR PRESSURES OF METHYL-SUBSTITUTED DIBORAZANES

| Temp., °C. | 3,3-Dimethyl- diborazane | 1,3,3-Tri- methyl- borazane | 1,1,3,3-Tetra- methyl- borazane | 1,1,1,3,3-Penta- methyl- borazane |
|------------|---------------------------------|-----------------------------------|---------------------------------------|---|
| | <i>P</i> _{obsd.} , mm. | <i>P</i> _{obsd.} , mm. | <i>P</i> _{obsd.} , mm. | <i>P</i> _{obsd.} , mm. |
| 40 | 1.1 | 1.2 | 0.6 | 14.4 |
| 50 | 2.0 | 1.2 | 1.4 | 17.3 |
| 60 | 2.8 | 1.6 | 1.6 | 24.7 |
| 70 | 5.1 | 2.3 | 2.6 | 34.3 |
| 80 | 7.6 | 2.9 | 4.1 | 49.3 |
| 102 | 19.8 | 7.7 | 13.3 | 64.5 |

Acknowledgment.—This work was carried out under subcontract with the U. S. Borax Research Corporation under Air Force Contract AF 33(616)-7303.