

olefins to form the anticipated derivatives,¹⁶ roughly characterized by infrared spectra, the presence or absence of halogen and elemental analysis of the crude product. [Because of the trifunctionality of these chelates and less than quantitative yields in these reactions, most of the crude products could not be purified.] As an example, the reaction of the chelate sulfonyl chlorides with triethyl phosphite produced a material presumed to be the thiophosphate A ($X = -SPO(\dot{O}C_2H_5)_2$). The parent β -diketone previously had been prepared by a different route, but its chelates were not reported.¹⁷ In addition to these typical reactions and analytical data, the structures of these chelate sulfonyl chlorides were confirmed by infrared spectra which showed only single peaks in the 6.25–6.75 μ region and no peak at 8.2 μ . This is characteristic of 3-substituted metal 2,4-pentanedionates in which the substituent does not conjugate strongly with the ring.^{6,7,18} Also, the sulfonyl chlorides of the normally colorless beryllium and aluminum chelates were yellow in color due to the $-SCl$ chromophore. This color disappeared upon reaction with reagents such as cyclohexene, again a characteristic of sulfonyl chlorides. Chromium tris-(3-bromo-2,4-pentanedionate) was unreactive toward sulfur dichloride, emphasizing the importance of an unsubstituted 3-position and supporting the direct substitution of the 3-position rather than an initial radical attack on a side chain methyl group followed by an allylic migration to the ring.

The structure was confirmed further by the reaction of the sulfonyl chloride A ($M = Cr, n = 3, X = -SCl, R_1 = R_2 = CH_3$) with cyanide ion to form the thiocyanate A ($M = Cr, n = 3, X = -SCN, R_1 = R_2 = CH_3$). This was independently synthesized by the action of thiocyanogen on chromium tris-(2,4-pentanedionate) A ($M = Cr, n = 3, X = H, R_1 = R_2 = CH_3$). As a pseudohalogen, thiocyanogen reacted in a manner similar to bro-

mine which substitutes the 3-position. This substitution reaction of thiocyanogen was found to be relatively general for this class of chelates with the cobalt (III) and aluminum (III) thiocyanates being analogously prepared. The labile copper (II) bis-(2,4-pentanedionate) was cleaved in the presence of thiocyanogen to give an organic material believed to be 3-thiocyanato-2,4-pentanedione. This ring cleavage could be eliminated by adding to the reaction mixture an excess of solid sodium bicarbonate to scavenge the liberated acid. In this manner copper (II) bis-(3-thiocyanato-2,4-pentanedionate) A ($M = Cu, n = 2, X = -SCN, R_1 = R_2 = CH_3$) was obtained. Under these conditions, thiocyanolation appears to be a general reaction of these chelates.

The nature of the reagents used in ring substitution of these chelates does not allow the mechanism of these reactions to be unambiguously assigned. Thus, reagents such as N-bromosuccinimide or bromine can produce the halide by either a radical or ionic mechanism. In support of electrophilic substitution, chromium tris-(2,4-pentanedionate) has been acetylated in the 3-position under mild Friedel-Crafts conditions.⁷ However, oxidative degradation of these chelates, presumably a radical process, also has been found to be favored by an unsubstituted 3-position.¹⁹ In the course of attempts to prepare other derivatives of the 2,4-pentanedione chelates, it was observed that cyanogen bromide brominates chromium tris-(2,4-pentanedionate) slowly in the 3-position in the absence of any added catalyst. This reaction finds analogy in the ring bromination of other resonance stabilized systems such as phenols and the α bromination of ketones.¹² Attempts to change the course of this reaction with chelates by use of Friedel-Crafts catalysts only markedly accelerated the rate of ring bromination. In the absence of an exact mechanistic study, firm conclusions cannot be made, but, superficially, it appears that this reaction is an additional example of electrophilic substitution of the chelate ring.

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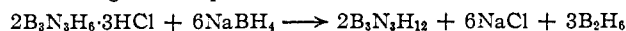
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Studies of Boron-Nitrogen Compounds. III.¹ Preparation and Properties of Hexahydroborazole, $B_3N_3H_{12}$

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The compound $B_3N_3H_{12}$ has been prepared by addition of hydrogen chloride to borazole followed by reduction with sodium borohydride in diglyme according to the equation



Studies of its physical and chemical properties confirm that it is a six membered ring system composed of alternate BH_2 and NH_2 groups. The substance is a slightly volatile solid forming well defined crystals on sublimation in high vacuum and shows generally the physical properties of a moderately polar compound.

Since the discovery of borazole in 1926 many investigators have studied this molecule and numerous derivatives have been prepared.² The

fact that borazole is isoelectronic with benzene has attracted much attention and it is perhaps not unfair to say that the analogy between the two

(1) For paper II of this series see G. L. Brennan, G. H. Dahl and R. Schaeffer, *J. Am. Chem. Soc.*, **82**, 6248 (1960).

(2) For a general review of borazole chemistry see J. C. Sheldon and B. C. Smith, *Quart. Rev.*, **14**, 200 (1960).

compounds has been somewhat overworked and from a chemical point of view differences between the two are at least as important as similarities. Thus, one of the most characteristic reactions of the borazole ring system is the facile addition reaction of compounds of general formula HX whereas the corresponding reactions of the benzene ring could not be considered to be of nearly so much importance. It has been generally assumed that the adducts of formula $B_3N_3H_6 \cdot 3HX$ thus formed are structurally similar to cyclohexanes although proof of this assumption has not been clearly presented and at the present time only two well characterized substances of this type have been reported (neither formed from a borazole). In 1955 Bissot and Parry³ reported that the compound $(CH_3NHBH_2)_3$ could be isolated in good yield by decomposition of $CH_3NH_2BH_3$ at 100°. The compound proved to be rather unexpectedly stable but lost hydrogen to form N-trimethylborazole in 74% yield when heated for 4 hr. at 200°. Two years later Burg⁴ isolated the N-hexamethyl derivative from the products of reaction of dimethylamine with pentaborane-9. Conclusive determination of the structure of the compound was subsequently carried out by Campbell and Johnson⁵ and by Trefonas and Lipscomb.⁶ The only reported attempt to prepare the parent compound of the series, $B_3N_3H_{12}$, was that of Wiberg and Bolz⁷ who reported that the interaction of hydrogen with borazole in the presence of a catalyst did not yield the desired product. Reported below are experiments which not only have produced the desired cyclohexane analog, $B_3N_3H_{12}$, but which moreover point the way to a relatively general synthetic method for preparing many derivatives.

Experimental

A. Preparation of $B_3N_3H_{12}$.—Thirty cc. of dry diethyl ether was condensed into a dry 50 cc. flask at -196° and 2.5 g. (31 mmoles) of pure borazole (prepared and purified by the procedure of Dahl and Schaeffer⁸) condensed on top of the ether. The mixture was warmed to -80° and with continuous stirring allowed to absorb an excess (about 120 mmoles) of hydrogen chloride. Within minutes a white precipitate of $B_3N_3H_6 \cdot 3HCl$ was observed. After apparent completion of the reaction the mixture was allowed to slowly warm to room temperature. Ether and excess hydrogen chloride were pumped off and the solid residue was heated to 60° with pumping with a mercury diffusion pump to remove all possible volatile reactants. About 35 cc. of dry diglyme was condensed onto the solid and on warming to room temperature all of the solid dissolved. The flask then was chilled with liquid nitrogen and 4.5 g. of sodium borohydride dropped onto the frozen solution under cover of a dry helium stream. The flask then was evacuated again and warmed to room temperature with continuous stirring. Diborane evolution and deposition of a white solid began at once; after several hours a 75% yield of diborane was found to have been produced based on the equation

$$2B_3H_5Cl_3N_3H_6 + 6NaBH_4 \longrightarrow 2B_3N_3H_{12} + 3B_2H_6 + 6NaCl$$

Volatile ether cleavage products were present as by-products and were discarded without further study. Decantation of the supernatant liquid from the white solid

followed by removal of the diglyme by vacuum distillation left a white solid (undoubtedly containing some excess sodium borohydride). On slow warming with continuous pumping a white solid began to sublime between 90 and 100° at pressures below one micron. This substance was re-sublimed and used for the studies reported below.

B. Analysis.—Samples of the solid substance were treated with 6 M aqueous hydrogen chloride for 12 hr. at 100°. Substantially lower acid concentrations or shorter times resulted in incomplete hydrolysis. Hydrogen produced by hydrolysis was measured in the vacuum system, nitrogen was determined by a Kjeldahl procedure and boron was determined by the usual titration in the presence of mannitol following removal of the ammonia. Calcd. for $B_3N_3H_{12}$: B, 37.5%; N, 48.6%; H by hydrolysis, 6.93%. Found: B, 38.4%, 36.9%; N, 47.6%, 47.5%; H, 6.92%, 6.93%.

C. Stability.—Hexahydroborazole appears to be reasonably stable in ordinary air and has been handled in our laboratory during summer months (relatively high humidity) with no apparent decomposition in reasonable periods. Microscopic examination of crystals in open air failed to reveal surface clouding or other signs of reaction for at least 1 hr.

Approximately 40 mg. of the substance was heated slowly in a sealed vessel with an attached manometer in an attempt to measure a vapor pressure curve. Although the material sublimed in vacuum readily at 100°, the substance did not melt and no measurable vapor pressure was exhibited up to 150°. At this temperature slow decomposition with evolution of hydrogen began.

A sample of 0.47 mmole was heated to 205° for 150 minutes. Almost exactly three moles of hydrogen (1.44) was produced per mole of sample taken, and 0.36 mmole of borazole (identified by its physical behavior and infrared spectrum) was also recovered. Essentially no residue remained, but during fractional condensation of the borazole some white solid deposited from the liquid phase. It is possible that slight amounts of ammonia were produced in the decomposition and reacted during fractionation to lower recovery of the borazole. No effort was made to increase the yield of borazole above the approximately 75% obtained in this experiment, but it would appear possible to do so with more attention to details.

D. Solubilities.—Hexahydroborazole is insoluble in and unreactive with cold water (possibly because it is not wetted by it). It is only slightly soluble in benzene and appears to be essentially insoluble in benzophenone, dimethylamine, diphenylamine and phenol but is readily soluble in diglyme, acetic acid, acetone, acetonitrile, formamide, liquid ammonia and warm dioxane. Measurement of molecular weight by vapor tension lowering in liquid ammonia was attempted, but the results were not entirely satisfactory. Measurement of pressure as a function of added ammonia at -63° and at -78° gave essentially constant pressures of 24.0 and 6.3 mm., respectively, until two moles of ammonia had been added per mole of $B_3N_3H_{12}$ used indicating formation of a diammoniate. A somewhat less satisfactory dissociation pressure of about 110 mm. was measured at -45° . A rough calculation based on these three values gives 7.8 kcal./mole for the dissociation energy per mole of diammoniate.

Attempts to measure a molecular weight by vapor pressure lowering in liquid ammonia cannot be considered to be particularly successful. The average of nine determinations at various concentrations gave a value of 83.5 in reasonable agreement with 86.5 calculated for $B_3N_3H_{12}$. However, individual values ranged from 65.2 to 118 and the average deviation was 14.0. Difficulties in measuring the molecular weight in ammonia may reside in unsolved experimental difficulties, but they might also reflect a more complex chemistry than presently suspected. Thus there is no apparent reason why only a diammoniate should be formed and further study of the system certainly is required. However, it is clear that the molecular weight demands that the substance contain relatively few BH_2NH_2 units. Only one measured molecular weight gave a value as high as would be required for a tetramer and none was as low as the dimeric weight. Taken in conjunction with other information, the molecular weight adds some support to the assumption that the molecule retains the six membered borazole ring.

E. Spectral Studies.—Infrared spectra of hexahydroborazole were obtained under a variety of conditions with a Perkin-Elmer Infracord Spectrometer equipped with sodium chloride optics. In potassium bromide pellet the N-H band

(3) T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 3481 (1955).

(4) A. B. Burg, *ibid.*, **79**, 2129 (1957).

(5) G. W. Campbell and L. Johnson, *ibid.*, **81**, 3800 (1959).

(6) L. M. Trefonas and W. N. Lipscomb, *ibid.*, **81**, 4435 (1959).

(7) E. Wiberg and A. Bolz, *Ber.*, **73B**, 209 (1940).

(8) G. Dahl and R. Schaeffer, *J. Inorg. Nuclear Chem.*, **12**, 380 (1960).

was cleanly resolved into components at 2.94 and 3.0 microns, but the B-H band at 4.2 to 4.3 microns was broad. In diglyme the N-H doublet at 2.96 microns was not resolved but the B-H band was cleanly split into components at 4.18 and 4.32 microns with an unresolved shoulder at 4.1 microns. Some structure may also be observed in the 6.4 micron band. Split N-H and B-H frequencies suggest the presence of NH_2 and BH_2 groups in the molecule.

The ^{11}B n.m.r. spectrum of the compound in diglyme solution was obtained at 19.3 Mc/s. with a Varian DP-60 Spectrometer and was found to consist of a single symmetrical 1:2:1 triplet. Thus, direct evidence is at hand showing that all boron atoms in the molecule are equivalent within the sensitivity of the method and are attached to two hydrogens (hydrolytic analysis only demonstrated that six hydrolyzable hydrogens are present for a total of three boron atoms). Possibility of a linear structure with B-H and BH_2 groups is thus eliminated. A satisfactory proton n.m.r. spectrum was not obtained owing to the low solubility of the compound in non-hydrogen containing solvents.

F. Powder Pattern.—In Table I are recorded characteristic interplanar spacings (d values) for hexahydroborazole. The powder pattern was obtained with a Phillips Geiger Counter Spectrometer with the powder in a flat, open aluminum holder and using copper $K\alpha$ radiation. No evidence for change of the pattern with time was observed, although no protection from the atmosphere was provided.

TABLE I

d	I	d	I
2.576	m.	3.07	m.
2.583	m.	3.10	m.
2.72	m.	3.95	m.
2.84	s.	4.50	s.
3.00	m.	5.79	v.s.
		6.28	v.s.

Discussion

Probably the most striking feature observed thus far in the study of hexahydroborazole is its highly polar character as indicated both by solubilities and by its lack of volatility. This follows, of course, from the positive and negative charges which alternate in the ring, but the intermolecular forces are much larger than had been anticipated by us. It is interesting to speculate on the possibility that strong transannular attractions may serve to enhance the stability of the boat form relative to the chair form—possibly to a degree sufficient to

allow positional isomerism. A more detailed structural investigation has been initiated with this in mind. It is probable that study of hexahydroborazole and its derivatives can add substantially to our knowledge of conformational characteristics of organic compounds by providing models with the most extreme polar character.

It should be noted that four different groups of investigators have reported preparation of a polymeric form of BH_2NH_2 .⁹⁻¹² The possibility of obtaining hexahydroborazole from the polymeric material deserves further attention.

Despite the somewhat unsatisfactory molecular weight measurements, the empirical formula, spectral information and decomposition studies can leave little doubt that the six membered ring structure has in fact been retained.

It is worth observing that if donation of an electron pair from nitrogen to boron were complete in borazole itself, the resulting charge distribution would be closely similar to that in hexahydroborazole and intermolecular attractions might be expected to be of comparable magnitude. In fact, borazoles are more volatile than the aromatic hydrocarbons. Thus, comparison of physical properties suggests that only relatively slight contribution of double bonded structures is present in borazole (and hence only relatively little resonance stabilization) in agreement with the more recent theoretical calculations.¹³

Acknowledgment.—Support of this research by NSF Grant 6224 and by a subcontract with the U. S. Borax Research Corporation under Air Force Contract AF 33(616)-7303 is gratefully acknowledged.

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(10) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 2297 (1938).

(11) G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955).

(12) H. C. Hornig, W. L. Jolly and G. W. Schaeffer, Abstracts of Papers Presented at the 131st American Chemical Society Meeting, Miami, Florida, April, 1957, page 4-R.

(13) For a discussion of recent work see H. Watanabe, K. Ito and M. Kubo, *ibid.*, **82**, 3294 (1960).

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Studies of Boron-Nitrogen Compounds. IV. Isotopic Exchange Reactions of Borazole

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The exchange of hydrogen between borazole and various compounds containing deuterium has been studied. Isotopic exchange was followed with a mass spectrometer and position of substitution characterized by infrared spectra. Deuteriated ammonia, deuterium chloride and deuterium cyanide exchange with the hydrogen attached to nitrogen atoms in the borazole ring at a rate comparable to that with which they add. The addition of hydrogen cyanide was found to be largely reversible. Molecular deuterium, diborane- d_6 and sodium borodeuteride undergo exchange with the hydrogens attached to boron atoms in the borazole ring. Borazole reacted rapidly with deuteriated ethanol and deuterium oxide but no isotopically substituted borazole was present in the recovered material. Neither exchange nor chemical reaction occurred with deuterium sulfide, deuteriated acetylene nor deuteriated phosphine. A partial mass spectrometric investigation of the borazole molecule and isotopic derivatives shows that the $\text{B}_2\text{N}_3\text{H}_5^+$ fragment (the most abundant ion in the mass spectrum) is primarily formed by loss of a hydrogen from a boron atom.

Borazole, $\text{B}_3\text{N}_3\text{H}_6$ possesses a six-membered ring structure of alternate boron and nitrogen atoms.

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The physical constants of this substance and its derivatives are remarkably similar to those of benzene and corresponding derivatives with which they are isosteric and isoelectronic. The older literature abounds in comparisons of borazole