

figuration of two B_9 fragments necessary to result in condensation to form $n-B_{18}H_{22}$. It is important to observe that examination of a model of $n-B_{18}H_{22}$ reveals the fact that cleavage of this molecule into two B_9 fragments produces either two threefold symmetrical B_9 structures similar to $i-B_9H_{15}$, or two less symmetrical fragments having the boron arrangement of $n-B_9H_{15}$. Similarly, separation of a model of $i-B_{18}H_{22}$ into two B_9 components in all cases leads to one fragment having the threefold symmetry of $i-B_9H_{15}$ and the other fragment having the boron structure of $n-B_9H_{15}$. These facts could account for the absence of $i-B_{18}H_{22}$ in the products of the decomposition of $i-B_9H_{15}$ although it is to be noted that there are no reported physical properties for $i-B_{18}H_{22}$ and small yields might escape detection in our workshop.

It is also interesting to note that Wang, Simpson, and Lipscomb discussed formation of $B_9H_{13}L$ compounds in terms of a hypothetical B_9H_{15} molecule of C_{3v} symmetry and argued against the existence of the latter on the basis of violations of topological theory.¹⁸ We cannot now be certain that $i-B_9H_{15}$ has the structure

suggested by them (and indeed the instability of the substance may effectively prevent more detailed structural studies than those based on nmr). If the structure is assumed to be correct, this provides an interesting measure of the strength of one assumption of topological theory: the steric effects of attaching two bridge hydrogens to a boron attached to four other nearest neighbor borons are not as severe as first considerations might suggest. If true, numerous new structures can be considered as intermediates in synthesis of boranes or in rearrangement reactions. Sufficiently delicate studies may succeed in isolating one or more additional compounds and shed additional light on an important aspect of borane chemistry.

Acknowledgments.—This work was supported at various stages by the National Science Foundation under Grant GP-4944X and the Office of Naval Research. We also thank the National Aeronautics and Space Administration for a traineeship held by P. C. K.

(18) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961).

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Studies of Boranes. XXIV. Some Chemistry of Octaborane-12 and Preparation of Octaborane-14¹

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Octaborane-12 has been found to be a strong monobasic Lewis acid; several compounds of the type $B_8H_{12} \cdot L$ were prepared. Octaborane-12 was nearly quantitatively converted to hexaborane-10 by limited hydrolysis and in about 45% yield to n -nonaborane-15 by diborane. A new octaborane, octaborane-14, was prepared from octaborane-12 in a two-step conversion.

Introduction

The earlier literature contained several reports of the probable existence of an octaborane-12 but it was not until 1964 that such a compound was isolated from the products of a discharge reaction involving diborane, pentaborane-9, and hydrogen.^{2,3} This method of preparation is not satisfactory for producing workable quantities because of low yield and simultaneous production of many other boranes requiring difficult and tedious separations. Only one other compound which could be considered to be an octaborane-12 derivative has been reported, $C_2H_6NHB_8H_{11}NH_2C_2H_5$.⁴⁻⁶

(1) For paper XXIII of this series see J. Dobson, P. C. Keller, and R. Schaeffer, *Inorg. Chem.*, **7**, 399 (1968).

(2) R. E. Enrione, P. F. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964).

(3) R. E. Enrione, P. F. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

(4) R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 478 (1963).

(5) R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1532 (1963).

(6) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962). This reference describes the preparation of a material thought to be $C_2H_6NH_3^+B_8H_{12}NH_2C_2H_5^-$ but which was identified as the octaborane derivative by X-ray studies.

In the course of recent work in this laboratory a method was developed by which one can prepare gram quantities of octaborane-12 as part of a readily separated reaction mixture. It thus seemed opportune to undertake the investigation of some of the chemistry of this little known borane.

Experimental Section

Methods.—Standard high-vacuum techniques were employed wherever possible throughout this investigation and have been treated elsewhere.⁷ Direct weighing of octaborane-12 was inadvisable because of its poor thermal stability. When crude measurements of quantity were sufficient, it was convenient to measure octaborane-12 by noting the volume of frozen sample at -45° in a calibrated tube. The density reported from X-ray studies was used to calculate weight.³ When care was taken to avoid bubbles in the sample, the accuracy of this method was found to be within about 5%. When quantitative measurements were necessary, they were obtained by difference using a tared reaction tube and accurate weights of other more easily handled reagents.

Materials.—The octaborane-12 used in this work was prepared

(7) R. T. Sanderson, "High-Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

by decomposition of isononaborane-15 as described elsewhere.^{8,9} All other solvents and reagents were highest purity commercial grades and were carefully dried before use to avoid reaction with the moisture-sensitive materials.

Nuclear Magnetic Resonance.—The nmr data cited in this work were obtained using a Varian Model 4300B spectrometer operating at 19.3 MHz. Chemical shifts are reported relative to 0.0 ppm for $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and were obtained using an external standard with calibration by the side-band technique.

Some Precautions for Handling Octaborane-12.—In order to handle this material successfully without undue decomposition, it is essential that all transfers be made through a minimum distance and that the highest possible vacuum be maintained in the system by continuous evacuation. Condensation directly into a closed tube is recommended for only small samples, less than about 1 mmole. Larger samples are best handled by affixing the receiving vessel to the bottom of a U trap in order that the transfer may be carried out with continuous pumping. After transfer to the U trap the sample is allowed to melt and run into the receiver with little or no apparent decomposition. When the presence of diethyl ether is not objectionable, it is convenient to use it as a solvent since octaborane-12 is greatly stabilized in ethereal solution.

¹¹B Nmr Spectrum of Octaborane-12.—The nmr spectrum of octaborane-12 was determined in pentane solution at about -30° . The spectrum consisted of two simple doublets of equal intensity at (ppm, cps): $-6.8, 168$; $20.5, 153$.

Reactions of Octaborane-12

Diethyl Ether.—Octaborane-12 (0.51 mmole) and diethyl ether (15.49 mmoles) were condensed into a tube and sealed from the vacuum system. A white precipitate formed during warming but redissolved as the mixture neared room temperature. Cooling reprecipitated the solid at temperatures above the melting point of octaborane-12. No appreciable amount of hydrogen was found upon opening the reaction tube to the vacuum system. Excess ether was recovered by pumping on the reaction mixture for 2 hr at -45° and a white solid was deposited in the reaction tube. The recovery of 14.96 mmoles of ether, a loss of 0.53 mmole, established the composition of the residue as $\text{B}_8\text{H}_{12}[\text{O}(\text{C}_2\text{H}_5)_2]_{1.04}$. The residue remained solid at room temperature and if opened to a liquid nitrogen cooled trap appeared to sublime slowly. Two distinct condensation bands could be observed, one above the nitrogen level and one below. The ¹¹B nmr spectrum of octaborane-12 in diethyl ether was very similar to that of the pure hydride. The spectrum consisted of two doublets of equal intensity at (ppm, cps): $-3.4, 169$; $20.0, 141$.

Trimethylamine.—An nmr tube was charged with 2.80 mmoles of octaborane-12, about 4 ml of diethyl ether, and 6.90 mmoles of trimethylamine and sealed under vacuum; the reaction mixture was allowed to warm to room temperature. A white precipitate formed during warming as in the experiment when only ether was present but did not redissolve when thoroughly warm. The ¹¹B nmr spectrum was found to be very different from that of octaborane-12 in ether. After about 30 min at room temperature the tube was opened to the vacuum system; no hydrogen was found. All volatiles were removed to a tared tube containing about

10 mmoles of hydrogen chloride and the mixture was allowed to react. The trimethylammonium chloride formed was 4.11 mmoles, a loss of 2.79 mmoles, in good agreement with the formation of a 1:1 adduct. Recrystallization of the product *in vacuo* from acetonitrile gave material which, redissolved in acetonitrile, exhibited a ¹¹B nmr spectrum identical with that obtained from the reaction mixture. The spectrum consisted of an unresolved lower field structure with a peak at 1.0 ppm, a sharp, intense peak at 7.8 ppm, and a moderately intense peak at 15.7 ppm; an intermediate field triplet was observed at 29.2 ppm, $J = 126$ cps, which was somewhat overlapped with the low-field group, and at highest field a cleanly resolved doublet was observed at 54.3 ppm, $J = 155$ cps. The integrated intensities of doublet:triplet:low-field group were in the ratios 1.50:1.05:5.90.

Acetonitrile.—A reaction tube was charged with 1.76 mmoles of octaborane-12 and 10.96 mmoles of acetonitrile, sealed under vacuum, and allowed to warm to room temperature. After about 30 min the tube was reopened and only traces of hydrogen were found. Excess acetonitrile was removed and found to be 9.19 mmoles, a loss of 1.77 mmoles, in good agreement with the formation of $\text{B}_8\text{H}_{12} \cdot \text{NCCH}_3$. Recrystallization of the slightly yellow residue from acetonitrile afforded white crystalline material. The ¹¹B nmr spectrum of the product in acetonitrile bore an obvious family similarity to that of the trimethylamine adduct. It consisted of an unresolved low-field group with peaks at $-2.1, 4.4, \text{ and } 11.5$ ppm, an intermediate field structure which appeared to be an overlapping triplet and doublet with peaks at 20.5, 26.7, and 33.2 ppm, and a well-resolved high-field doublet at 54.7 ppm, $J = 152$ cps. The integrated intensities of these structures were in the ratios 5.0:1.9:1.0, respectively.

When a solution of $\text{B}_8\text{H}_{12} \cdot \text{NCCH}_3$ in acetonitrile was treated with an equimolar amount of trimethylamine, the ¹¹B nmr spectrum indicated an immediate and, within the limits of nmr detection (*ca.* 5%), quantitative conversion to $\text{B}_8\text{H}_{12} \cdot \text{N}(\text{CH}_3)_3$.

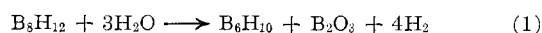
Diborane.—A reaction tube of about 30-ml capacity was charged with 2.25 mmoles of octaborane-12 and about 40 mmoles of diborane, sealed from the vacuum system, and placed in a bromobenzene slush bath; the mixture was allowed to react at -30° . A considerable amount of liquid diborane was present at the reaction temperature. During the reaction the solution yellowed slightly and rather large crystals deposited. After 4 hr the reaction was quenched with liquid nitrogen, the tube was opened, and hydrogen (1.98 mmoles) was collected by a Toepler pump. The excess diborane was stripped off at -112° , and the remaining volatiles were allowed to distil from the reaction tube at room temperature. The residue, a somewhat sticky solid, was transferred to a sublimator, and only decaborane-14 was recovered. The residue which did not sublime was apparently polymeric material and was not further investigated. Fractionation of the volatile products, using a low-temperature fractionating column,

(8) J. Dobson, P. C. Keller, and R. Schaeffer, *J. Am. Chem. Soc.*, **87**, 3522 (1965).

(9) J. Dobson, P. C. Keller, and R. Schaeffer, *Inorg. Chem.*, **7**, 399 (1968).

yielded octaborane-12 (0.28 mmole), *n*-nonaborane-15 (0.89 mmole), and decaborane-14. The combined decaborane-14 yield was 0.80 mmole.

Water.—Octaborane-12 (0.57 mmole), water (1.87 mmoles), and approximately 3 ml of diethyl ether were condensed into an nmr tube, and the mixture was allowed to warm to room temperature with shaking. After about 2 hr at room temperature the ^{11}B nmr spectrum was recorded and found to be completely assignable to hexaborane-10. The tube was opened and 2.35 mmoles of hydrogen was collected by a Toepler pump. Fractionation of the volatile products yielded only hexaborane-10, vapor pressure 7.5 mm at 0° (lit.¹⁰ 7.47 mm). The yield, 0.56 mmole, was 98% based upon



In one experiment water was added in small increments to an ethereal solution of octaborane-12 (0.43 mmole) and the course of the reaction was monitored by observing the ^{11}B nmr spectrum and measuring evolved hydrogen. It was found that as little water as 1 mole/mole of octaborane-12 effected nearly complete decomposition of the latter. The spectrum also showed resonances not attributable to hexaborane-10; these were doublets at approximately 20 and 40 ppm. When the addition of water was continued these extraneous resonances persisted even after the water:octaborane-12 ratio had well exceeded 3. Their relative intensities seemed to be affected little, if at all, by the addition of water and represented a substantial part of the total intensity. Addition of water was terminated when the mole ratio was 3.6. Fractionation of the volatile products yielded only hexaborane-10 (0.36 mmole). No other volatile boron-containing material was found, and the involatile residue, redissolved in ether, exhibited a ^{11}B nmr spectrum which appeared to be a simple singlet at -19 ppm. A plot of evolved hydrogen *vs.* added water was a very straight line with a slope of 1.20 until the water:octaborane-12 ratio approached 2, after which the line broke to an apparent slope of about $1/3$.

Alkynes.—Octaborane-12 and acetylene were allowed to react in ether solution at room temperature for about 1 hr. Only traces of hydrogen appeared in the reaction products. Fractionation of the volatile materials yielded a small amount of white crystalline solid which was of comparable volatility to decaborane-14. Further fractionation of the solid material was monitored by mass spectrometry and showed at least two components to be present. The more volatile fraction had a parent mass envelope in the *m/e* range from 114 to 124 with a maximum intensity at 118; the parent mass envelope of decaborane-14 was quite dissimilar to that observed in this case. The less volatile material had parent mass peaks from 101 to 111 with the maximum at 107.

An nmr tube was charged with about 0.35 mmole of

octaborane-12, 2.8 mmoles of ethylacetylene, and about 0.5 ml of toluene, sealed, and allowed to warm to room temperature. The ^{11}B nmr spectrum of the reaction mixture was found to be quite complex. Upon opening the tube, 0.017 mmole of hydrogen was removed and all volatiles were transferred to the vacuum system by prolonged pumping. Fractionation yielded 1.7 mmoles of ethylacetylene and a small amount of very low volatility liquid which exhibited a ^{11}B nmr spectrum nearly identical with that recorded from the reaction mixture. A sample of volatile product was injected into a silicone gum rubber gas chromatograph column operating at about 140° . After about 30 min the first component emerged followed by at least six others. Separation was poor, all components overlapped well into succeeding components, and the peaks were very broad. A similar experiment using an Apiezon L column failed to show any emerging components after 4 hr.

Sodium Hydride.—In a typical reaction a 200-ml flask was charged with approximately 15 mmoles of octaborane-12, 50 ml of diethyl ether, about 100 mmoles of sodium hydride, and a magnetic stirring bar. After sealing from the vacuum system, the reaction mixture was stirred at 0° for 8 hr; during the course of the reaction the solution became slightly yellow. The flask was then reopened and an appreciable amount of hydrogen was removed which ranged in various experiments between 0.58 and 0.66 mole/mole of octaborane-12 used. The ethereal solution was filtered from excess sodium hydride and concentrated by evaporation to a thick oil. The oil was taken up in a small amount of water made slightly basic with potassium hydroxide and then added to a concentrated, aqueous solution of tetramethylammonium chloride. The resulting curdy yellow precipitate was filtered, washed with water, and dried under vacuum overnight. Extraction of the product with acetonitrile was effective in removing insoluble impurities. No suitable solvent for recrystallization was found, and a product of suitable purity for final identification could not be obtained. Analysis of several samples judged quite pure by the "cleanness" of their ^{11}B nmr spectra quite definitely showed a $\text{B}:\text{N}:(\text{CH}_3)_4^+$ ratio of 8, but the hydrogen content as assayed by the hydrolytic hydrogen to boric acid ratio showed a range from $\text{B}_8\text{H}_{11.5}^-$ to $\text{B}_8\text{H}_{12.0}^-$ in three samples with a fourth sample at $\text{B}_8\text{H}_{13.0}^-$.

Sodium Amalgam.—Ethereal solutions of octaborane-12 were allowed to react with three- to fourfold molar excesses of sodium amalgam for several hours at room temperature. Upon opening to the vacuum system, no appreciable amount of hydrogen was found. When the reaction products were separated from the amalgam and worked up as described for the sodium hydride product, a tetramethylammonium salt was obtained which appeared identical in ^{11}B nmr spectra and solubility properties with the product obtained in the sodium hydride reaction. In addition, two analyses gave calculated compositions of $\text{B}_8\text{H}_{11.5}^-$ and $\text{B}_8\text{H}_{12.1}^-$ in good agreement with the data obtained from the sodium hydride product.

(10) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

Octaborane-14, B_8H_{14}

Preparation.—Octaborane-14 was prepared and isolated in the apparatus shown in Figure 1. This apparatus was designed after initial experiments conducted in sealed tubes indicated that severe decomposition (estimated by nmr as about 30%) occurred when octaborane-14 was distilled only a few inches through the conventional vacuum system.

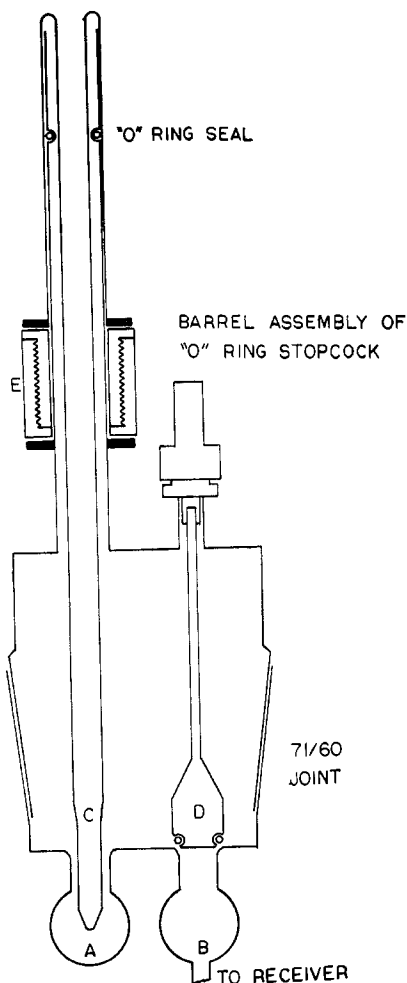


Figure 1.—Apparatus for isolation of octaborane-14.

Bulb A was charged with 0.1–0.15 g of either tetramethylammonium salt described above and enough hydrogen chloride was added to ensure complete wetting of the solid by liquid hydrogen chloride at the Dry Ice slush bath reaction temperature. After the reaction had proceeded about 0.5 hr, the excess hydrogen chloride was carefully distilled away, and complete removal was ensured by several hours continuous pumping on the material held at Dry Ice slush bath temperature. Condensing finger C was lowered into A by turning screw E, the finger was filled with liquid nitrogen, and bulb A was warmed to -45° by replacing the Dry Ice bath with a chlorobenzene slush bath. The apparatus was continuously evacuated and after 4 hr the collection of product was terminated. C was raised and the female taper was rotated 180° which positioned bulb A below D. D was then screwed down

to set its O-ring tip firmly in the neck of bulb A to prevent contamination of the sample by any volatile impurities which might distil from A upon warming. C was lowered into B which was chilled with liquid nitrogen, and the liquid nitrogen in C was allowed to evaporate to transfer the product into B. When transfer was completed the nitrogen level on B was slowly lowered until the product had moved into the receiving tube affixed to the bottom of B. The receiving tube, usually an nmr tube for a preliminary monitor of purity, was then sealed from the apparatus.

The ^{11}B nmr spectrum was determined in pentane solution at -30 to -40° . The spectrum consisted of three nearly completely resolved doublets with δ and J values of (ppm, cps): $-24.1, 161$; $21.4, 153$; $38.9, 154$. The integrated intensities were 2.0:4.0:2.0, respectively. The thermal stability of octaborane-14 was qualitatively assessed in ^{11}B nmr experiments. A sample was warmed to room temperature for about 1–1.5 min and the ^{11}B nmr spectrum was observed; only resonances attributable to octaborane-12 were now found. A sample warmed to 0° for about 0.5 min was approximately 30% decomposed to octaborane-12. A sample held at -30° for 1 hr decomposed approximately 6% as estimated by the octaborane-12 intensity.

Analysis. A. Total Pyrolysis.—A sample of octaborane-14 was prepared as described and sealed in a 5-mm o.d. quartz tube equipped with a magnetic break-tip. The ^{11}B nmr spectrum revealed no appreciable amount of octaborane-12. The sample tube was then attached to a quartz pyrolysis tube having deep indentations to prevent a straight-line path to the vacuum system. After evacuation and heating the pyrolysis zone to a bright glow, the sample tube was opened and the sample was allowed to distil slowly into the hot zone with continuous Toepler pump operation to remove the hydrogen as it formed. Hydrogen was measured volumetrically and boron was dissolved in nitric acid for titration of boric acid as the mannitol complex using the identical pH method. The observed H:B ratio was 1.82 corresponding to $B_8H_{14.5}$.

B. Hydrolysis of Octaborane-14.—A sample was prepared and the ^{11}B nmr spectrum was found to have no extraneous resonances. Hydrolysis was carried to completion by heating the sample to 100° for 24 hr in the presence of about 2 ml of water. The hydrolytic hydrogen was measured volumetrically and the boric acid by titration of the mannitol complex. The observed hydrolytic hydrogen to boric acid ratio was 2.37 in good agreement with the theoretical value of 2.375 demanded by the hydrolysis of octaborane-14.

C. Decomposition to Octaborane-12 and Hydrogen.—The purity of a small sample was verified by nmr and the sample was then allowed to decompose quantitatively by warming to room temperature for 2 min. The ^{11}B nmr then showed only very pure octaborane-12. The tube was opened, hydrogen collected by a Toepler pump, and a weighed quantity of trimethylamine condensed into the tube. After allowing reaction with trimethylamine the excess amine was re-

covered and measured. The hydrogen collected was 0.127 mmole and the trimethylamine consumed was 0.129 mmole. The product was identified as $B_8H_{12} \cdot N(CH_3)_3$ by virtue of its ^{11}B nmr spectrum.

Discussion

One of the most striking features of octaborane-12 is the ready formation of simple Lewis base adducts. The reactions of other boranes with bases are characterized by either hydrogen elimination or skeletal degradation. In the former category, the borane-base adducts $B_2H_4L_2$, B_4H_8L , $B_6H_{10}L_2$, and $B_{10}H_{12}L_2$ are formally related to, although not actually accessible from all cases, known boranes by base addition accompanied by hydrogen loss. The second broad category includes the BH_3^- and BH_2^+ -cleavage reactions which occur with diborane, tetraborane-10, pentaborane-9 and -11, hexaborane-12, and *n*-nonaborane-15. Pentaborane-9 most nearly approaches the behavior of octaborane-12 by forming an adduct containing 2 moles of trimethylamine although this apparently undergoes slow degradation.¹¹

The ^{11}B nmr spectrum of octaborane-12 cannot be unambiguously assigned from the structure (Figure 2-I) determined by X-ray diffraction studies. The symmetry of the molecule, as it exists in the solid state, shows five types of borons.^{2,3} There are three pairs of equivalent borons—B-3,6, B-4,5, and B-7,8—and two unique borons—B-1 and B-2. A reasonable assignment of this structure to the observed nmr spectrum might be accidental overlap of B-4,5 and B-7,8 to give the low-field doublet and overlap of B-1, B-2, and B-3,6 to give the higher field doublet. Alternatively, it is possible that in the liquid state and in solution a rapid exchange of bridge hydrogens effectively increases the molecular symmetry to C_{2v} . This would lower the number of unequivalent types of borons to three. Assignment of this model requires only accidental overlap of the doublets arising from B-1,2 and B-3,6

Although the position of base addition to octaborane-12 is not known, both the ^{11}B nmr data and the reaction with water suggest some structural conclusions. These results are consistent with a structure, Figure 2-III, which has the substituent bonded to a B-4 boron. In fact, this is a predicted structure for this type of compound.¹²

The ^{11}B nmr spectra of both the acetonitrile and trimethylamine derivatives are seen to consist of at least five separate resonances, indicating a substantially lower symmetry than the parent hydride. The simpler spectrum of ethereal octaborane-12 solutions is probably due to such a rapid dissociation of the ether complex at room temperature that in the time of the nmr experiment an ether ligand has attacked all of the B-4,5,7,8 borons. Such an exchange would have no net effect upon the apparent molecular symmetry and the ^{11}B nmr experiment would detect an apparently uncomplexed octaborane-12, except perhaps for some

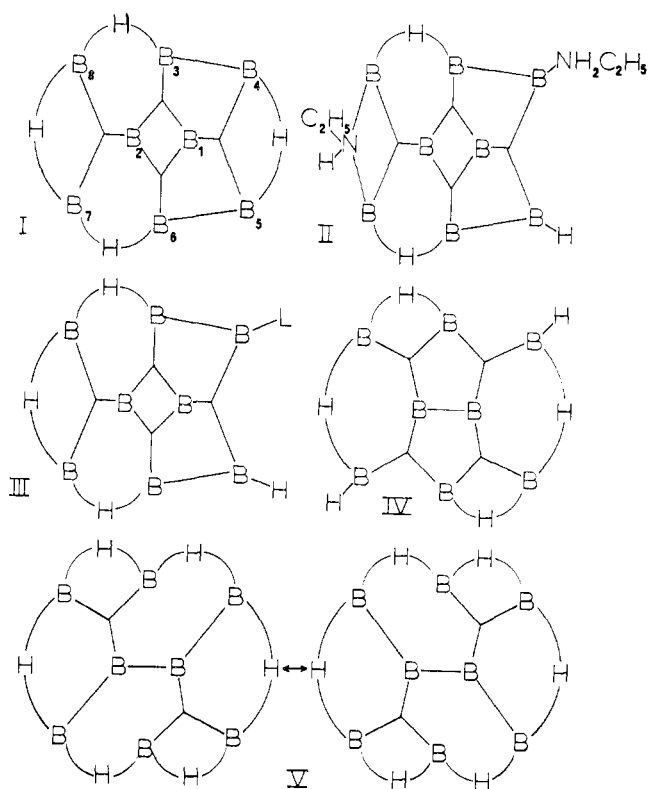


Figure 2.—I, structure of octaborane-12;^{2,3} II, structure of $C_2H_5NHB_8H_{11}NH_2C_2H_5$;^{4,5} III, predicted structure for $B_8H_{12} \cdot L$ adducts;¹² IV, a predicted 4412 structure for octaborane-14;^{20,21} V, a 6230 "hybrid" structure for octaborane-14.

change in the magnetic environment of the borons affected by the exchange process. This change in magnetic environment could explain the upfield shift of the low-field doublet of octaborane-12 in ether solution with respect to the corresponding resonance from pure octaborane-12. With the stronger bases a 1:2:1 triplet resonance and a characteristic high-field doublet resonance are observed, each of intensity corresponding to one boron. The former establishes the presence of a BH_2 group and the latter, if given the usual assignment of an apical boron, makes a B-3 substitution unlikely since this would lead to two equivalent (or nearly equivalent, depending upon hydrogen distribution) apical borons in which case a high-field doublet or doublets with a total intensity corresponding to two borons would be expected. Additional support for base attack at B-4 is the nearly quantitative degradation of octaborane-12 to hexaborane-10 since the hexaborane-10 framework could be obtained directly by removal of the B-4 and -5 borons. Thus, a structure paralleling that of $C_2H_5NHB_8H_{11}NH_2C_2H_5$,^{4,5} Figure 2-II, seems reasonable.

In view of the facility of neutral base addition to octaborane-12, it appeared reasonable to attempt formation of a $B_8H_{13}^-$ anion by reaction of octaborane-12 with a metal hydride. This system turned out to be considerably more complex and no concrete identification of products has yet been made. Both the stoichiometry of hydrogen evolution during the reaction and analyses of the product lend some support for an em-

(11) R. Schaeffer, unpublished results.

(12) W. N. Lipscomb, *J. Inorg. Nucl. Chem.*, **11**, 1 (1959).

pirical formulation $B_8H_{12}^-$. This formula was also supported by the formation of an apparently identical product from the reaction of octaborane-12 with sodium amalgam without loss of hydrogen. If the gross composition is indeed $B_8H_{12}^-$, then it appears necessary to consider the possibility of a mixture such as $B_8H_{11}^-$ and $B_8H_{13}^-$ or a dimer, $B_{16}H_{24}^{2-}$, since a $B_8H_{12}^-$ would be a free radical.¹³

The reaction of octaborane-12 with diborane helps to clarify the difficulty of isolating octaborane-12 from diborane-rich interconversion systems such as the pyrolysis and discharge reactions of diborane. In a period of only several hours at a temperature as low as -30° octaborane-12 is nearly completely converted to other products. It is interesting that the only discrete products formed in detectable amounts, *n*-nonaborane-15 and decaborane-14, are formed in approximately equal yield. This product distribution might be explained if diborane, acting as a base, attacks a B-4 boron of octaborane-12. Subsequent rearrangement of the incoming boron to a position between B-4 and -5 would yield *n*-nonaborane-15 while rearrangement of the new boron to a position between B-4 and -8 results in formation of isononaborane-15. Nearly equal facility of the two rearrangement paths would result in nearly equal *n*-nonaborane-15 and decaborane-14 yields since the latter is formed in good yield from isononaborane-15 under the conditions of the reaction.¹⁴

The nearly quantitative conversion of octaborane-12 to hexaborane-10 by limited hydrolysis would seem to extend a class of reaction, two of which have been reported. Pentaborane-11 and hexaborane-12 both yield tetraborane-10 when treated with water.^{15,16} In both of these cases as well as the octaborane-12 degradation, the net result is formation of a borane with one or two less BH units. The exact stoichiometry of the octaborane-12 degradation is not known although nearly quantitative yields of hexaborane-10 are obtained with water:octaborane-12 molar ratios of about 3, corresponding to formation of B_2O_3 as the oxygen-containing product.

An experiment to determine the minimum amount of water necessary for the degradation to hexaborane-10 was inconclusive because stepwise addition of water resulted in formation of products other than hexaborane-10. However, it was found that as little as 1 mole of water/mole of octaborane-12 was sufficient to effect nearly complete disappearance of octaborane-12 nmr resonances. The secondary products could not be assigned from their nmr spectra but appeared to be stable in the reaction mixture. The initial rate of hydrogen evolution, slightly more than 1 mole/mole of added water, suggested the first oxygen-containing product might have a composition of approximately B_2H_2O . It is interesting to note that the conversion of

octaborane-12 to hexaborane-10 was also a primary process in the gas-phase decomposition of octaborane-12 as was reported in the mass spectral study of the *n*-nonaborane-15 system.¹⁷ We have also observed this mode of decomposition in the mass spectrometer with pure samples of octaborane-12.

Octaborane-14.—The identification of this compound as an octaborane rests upon several points. First, the integrated area ratios of the ^{11}B nmr spectrum, 2:4:2 (or 1:2:1), requires a molecule with multiples of four boron atoms. Second, the composition established by analysis, B_4H_7 , limits these to the even multiples, *i.e.*, B_8H_{14} , $B_{16}H_{28}$, etc. Third, the volatility (slow distillation at -45°) is normal for an octaborane but is much too high for a hexadecaborane. Finally, the quantitative decomposition to octaborane-12 and hydrogen suggests an initial octaborane species. In view of these data and the anticipated difficulty of obtaining reliable molecular weight information for such an unstable material, the customary molecular weight determination was not attempted.

There appears to be only one reasonable structure consistent with the simplicity of the octaborane-14 nmr spectrum. The absence of triplet resonances strongly suggests that no BH_2 groups are present and therefore that the six extra hydrogens are present as B-H-B bridge groups, as shown in Figure 2-V. For this structure, the midfield doublet of intensity corresponding to four borons is assigned to the only set of four symmetry-equivalent borons, B-4,5,7,8. The remaining assignment of the B-1 and -2 borons to the highest field doublet may be tentatively suggested on the basis that resonance of apical borons is often at high field.

No single 6230 bond arrangement satisfying the connectivity rules of the topological theory set down by Lipscomb and Dickerson could be found;^{18,19} however, a 6230 "resonance hybrid" structure such as depicted in Figure 2-V would appear to be a satisfactory compromise. Considered separately, neither structure adequately connects all nearest neighbor borons but a hybrid structure would.

Two satisfactory 4412 structures, Figure 2-IV and one similar to 2-I but with an extra terminal hydrogen on both B-4 and B-5, have been proposed.^{20,21} They are much more difficult to reconcile with the ^{11}B nmr data, although it is possible that they might not exhibit the expected BH_2 triplet resonance in the event of a rapid hydrogen tautomerism equilibrating B-4,5,7,8 or if the BH_2 groups have a unique hydrogen which does not spin couple to boron as appears to be the case in the apical BH_2 resonance of pentaborane-11.^{22,23}

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It is interesting that octaborane-14 and nonaborane-15 appear to share an unusual structural feature; the ^{11}B nmr spectra suggest that in both these molecules the entire open periphery of the boron framework is B-H-B bridge bonded. This is a violation of topological principles based upon hydrogen atom crowding and perhaps explains the extreme ease with which these materials lose hydrogen.²⁴ It seems unlikely that the

methods previously used in X-ray diffraction studies of other boranes will succeed with these materials. Final determination of the structures of such unstable materials may require the use of other structural methods.

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(24) See ref 19, p 52, rule 5, and p 60.

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Studies of Boranes. XXV. The Preparation of a Boron-Labeled Decaborane-14^{1,2}

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Synthesis of decaborane by two different routes allows preparation of molecules labeled with a boron isotope in specific positions. Boron-11 nmr and mass spectra of the decaborane synthesized by reaction of nonaborohydride-12 with hydrogen chloride in the presence of diborane and of the product obtained by the decomposition of *i*- $^{10}\text{B}_9\text{H}_{13}$ in excess $^{11}\text{B}_2\text{H}_6$ as solvent indicates that decaborane has one isotopically labeled boron atom per molecule. Chemical and spectral evidence establish that the label is in the 6,9 and 5,7,8,10 positions. Partial conversion from an *i*- B_9H_{13} to a *n*- B_9H_{13} is postulated to account for labeling in the 5,7,8,10 position.

Introduction

The synthesis of boron hydrides with isotopic labels in specifically known positions is of current interest with respect to the implications concerning the mechanism of the route selected for synthesis whether or not a specific synthesis is achieved and also as a source of labeled molecules for possible use in the elucidation of the mechanisms of other reactions of boron hydrides. Various deuterium-labeled tetraboranes, pentaboranes, and decaboranes have been prepared by a number of workers.³⁻⁷ The possible ready migration of hydrogen atoms at room temperature or below in the pure boranes or during the course of further reactions makes boron skeletal labeling of particular importance. The unselective methods generally used for preparation of boron hydrides makes the preparation of skeletally labeled boron hydrides a rather formidable task. The successful preparation of $^{11}\text{B}^{10}\text{B}_3\text{H}_{10}$ with the ^{11}B label in the 2,4 position from ^{10}B sodium triborohydride, hydrogen chloride, and normal diborane⁸ suggested an analogous method of preparing specifically ^{10}B -labeled decaborane by the reaction of either tetramethylammonium nonaborohydride-12 or tetramethylammonium nonaborohydride-14 with hydrogen chloride and ^{10}B diborane. Decaborane was successfully prepared from either of the nonaborohydride anions and this is the first time in which the authors are aware that a higher

boron hydride has been prepared from a planned synthesis. The 19.3-MHz ^{11}B nmr spectrum of the decaborane obtained from the reaction of either tetramethylammonium nonaborohydride-12 or tetramethylammonium nonaborohydride-14 with hydrogen chloride in the presence of $^{10}\text{B}_2\text{H}_6$ showed a small but reproducible reduction in the low-field peak of the decaborane spectrum. The value of the ratio of the intensity of the high-field peak of the triplet to that of the low-field peak was 1.15 ± 0.04 for the ^{10}B -labeled decaborane prepared from tetramethylammonium nonaborohydride-12 *vs.* the value of 1.03 ± 0.03 observed for normal decaborane. Since the low-field peak of the triplet arises from overlapping doublets of the 1,3 and 6,9 boron atoms, the boron label is in either the 1,3 or 6,9 positions.^{9,10} *A priori*, it would seem more probable that the label is in the exterior 6,9 position rather than the interior 1,3 position.

Since the effect of a ^{10}B label on the ^{11}B spectrum of decaborane is rather small, a decaborane containing a ^{11}B label was synthesized to facilitate determination of the position of the label and to simplify study of the reactions of the labeled compounds.

Experimental Section

Spectroscopic Techniques.—The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates HA-60-IL high-resolution spectrometer operating at 19.3 MHz. The spectrum of $\text{B}_9\text{H}_{13}^-$ from the degradation of $^{11}\text{B}^{10}\text{B}_9\text{H}_{14}$ was obtained on the same instrument operating with a Varian C1024 time-averaging computer locked on $\text{B}(\text{C}_2\text{H}_5)_3$ in an internal capillary. A spectrum of $^{11}\text{B}^{10}\text{B}_9\text{H}_{14}$ was also obtained with a Varian Associates HA-100 high-resolution spectrometer operating in the HR

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