Studies of Boranes. XXIX. Isotope Studies of Hexaborane(10)[1]

By JEROME DAVID ODOM and RILEY SCHAEFFER

The preparation of hexaborane(10) from octaborane(12) and deuterium oxide does not result in a molecule specifically labeled with deuterium. The hexaborane(10)–deuterium oxide exchange reaction results in a hexaborane(10) molecule almost completely substituted with deuterium in the bridge positions while the hexaborane(10)–deuteriodiborane(6) exchange reaction exclusively exchanges the basal terminal protons. The molecule which is substituted in the basal terminal positions was heated at 50° for 0.5 hr and did not undergo intramolecular exchange; however, it was found that hexaborane-(10) does undergo intermolecular exchange at room temperature involving only the basal terminal positions. A temperature dependency of the low-field doublet in the ^{11}B nmr spectrum of hexaborane(10) was found.

Introduction

Very little has appeared in the literature concerning B_6H_{10} primarily because of the difficulties encountered in obtaining reasonable quantities of the compound. Most of the publications have reported the preparation[2–5] or the physical properties and spectra[6,7] of hexaborane(10). Recent work in our laboratory has shown that octaborane(12) is nearly quantitatively converted to B_6H_{10} by limited hydrolysis[8] and since one can prepare B_8H_{12} in gram quantities it thus seemed opportune to begin an investigation of the former boron hydride. In the course of studying the interconversion reactions of boron hydrides in this laboratory, isotopically labeled hydrides have proven invaluable. Thus isotopic exchange and labeling studies were undertaken.

Experimental Section

Spectroscopic Techniques.—The ^{11}B nuclear magnetic resonance spectra were obtained with Varian Associates HA-60-IL and HA-100 high-resolution spectrometers operating at 19.3 and 32.1 MHz, respectively. Chemical shift values were determined by the external standard technique relative to boron trichloride and were converted to the boron trifluoride diethyl etherate scale by addition of −47.3 ppm. Proton nmr spectra were also recorded on the HA-100 instrument. The low-temperature spectra were obtained using standard Varian variable-temperature probe accessories. Mass spectra were obtained with Consolidated Electrodynamics Model 21-620 and Associated Electrical Industries Model MS-9 mass spectrometers. Exact mass determinations on the MS-9 instrument were made using perfluorotributylamine as the reference compound. Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer.

Deuterium Analyses.—Hydrogen–deuterium analyses of the partially deuterated hexaboranes were obtained by pyrolyzing the boranes and analyzing the resulting hydrogen–deuterium mixture mass spectrometrically as previously described.[9]

Preparation of Starting Materials.—Standard high-vacuum techniques were used throughout this investigation.[10] All

solvents employed were reagent grade and were dried before use. The octaborane(12) used in this work was prepared by decomposition of isononaborane(15) as described elsewhere.[11,12] Lithium aluminum hydride (Metal Hydrides, Inc.) and calcium fluoroborate (enriched to 96% ^{10}B by the Oak Ridge National Laboratories) were used without further purification. Calcium fluoroborate was converted to BF_3 by the procedure of Zedler.[13] Diborane enriched in the ^{10}B isotope was prepared by $LiAlH_4$ reduction of $^{10}BF_3 \cdot O(C_2H_5)_2$.[14] Sodium tetradeuterioborate, $NaBD_4$, was obtained from Metal Hydrides, Inc., and was used without further purification. Hexadeuteriodiborane(6) was prepared by the reaction of $NaBD_4$ with hot polyphosphoric acid. Deuterium chloride was prepared by treating PCl_3 with D_2O and purified by fractional distillation.

Nuclear Magnetic Resonance Spectra of B_6H_{10}.—The 100-MHz ^{1}H nmr spectrum of B_6H_{10} (Figure 1) consists of a downfield
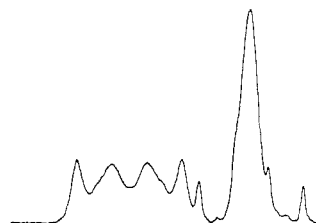
Figure 1.—The 100-MHz ^{1}H nmr spectrum of B_6H_{10}.

quartet and an upfield quartet superimposed over the bridge resonance. The ^{11}B and ^{1}H nuclear magnetic resonance spectra of B_6H_{10} at 19.3 and 32.1 MHz agree quite well with the published values[6,15] (we obtained a J value of 155 cps for the apex boron resonance).

In the course of observing the ^{11}B nmr spectra of some of the deuterated derivatives of hexaborane(10) at low temperatures we observed partial collapse of the low-field doublet. When a temperature-dependent study was performed using normal B_6H_{10}, it was found that indeed the low-field doublet resonance showed a temperature dependency while the upfield doublet did not (Figure 2). The low-temperature spectra were run using neat B_6H_{10} and also at various concentrations of B_6H_{10} in *n*-pentane.

Preparation of B_6H_{10} from B_6H_{12} and D_2O.—In a typical reaction approximately 2 ml of diethyl ether was distilled from $LiAlH_4$ into an evacuated 150-ml bulb equipped with a Fisher–Porter stopcock. The bulb was removed from the vacuum line and weighed. After the bulb was attached to the apparatus

(1) Part XXVIII: A. L. Collins and R. Schaeffer, *Inorg. Chem.*, **9**, 2153 (1970).

(2) A. B. Burg and J. L. Boone, *J. Amer. Chem. Soc.*, **81**, 1766 (1959).

(3) J. L. Boone, U. S. Patents 3,109,710 and 3,110,565 (1963).

(4) P. L. Timms and C. S. G. Phillips, *Inorg. Chem.*, **3**, 297 (1964).

(5) W. N. Lipscomb and H. A. Beall, *ibid.*, **3**, 1783 (1964).

(6) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 333 (1959).

(7) S. G. Gibbins and I. Shapiro, *ibid.*, **30**, 1483 (1959).

(8) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

(9) R. Maruca, J. D. Odom, and R. Schaeffer, *ibid.*, **7**, 412 (1968).

(10) R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948.
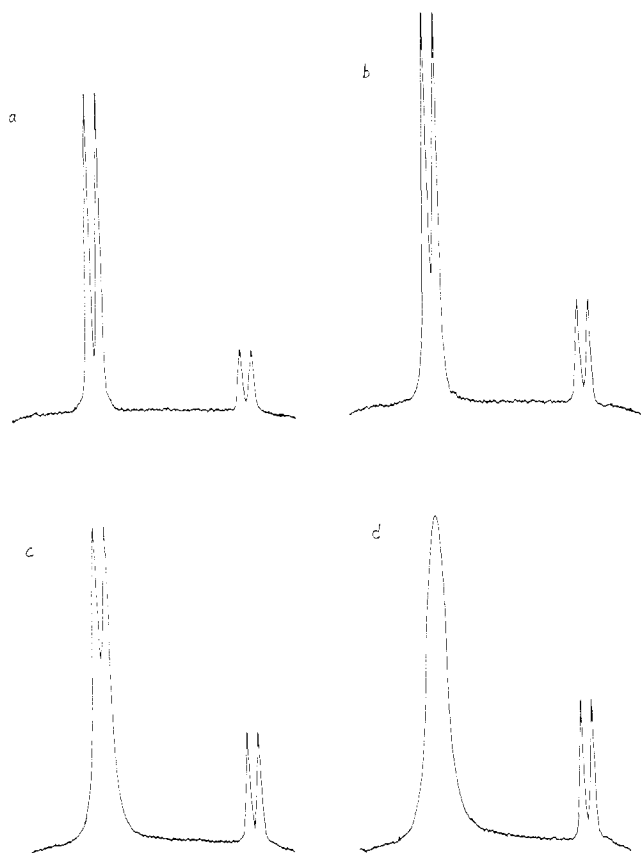
(11) J. Dobson, P. C. Keller, and R. Schaeffer, *J. Amer. Chem. Soc.*, **87**, 3522 (1965).

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

(13) R. E. Zedler and R. I. Luman, *Nucleonics*, **1**, 65 (1947).

(14) I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnick, and G. B. L. Smith, *J. Amer. Chem. Soc.*, **74**, 901 (1952).

(15) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

Figure 2.—The temperature dependency of the ^{11}B nmr spectrum of B_6H_{10}: (a) $30°$, (b) $-20°$, (c) $-40°$, (d) $-70°$.

used for preparing octaborane(12), B_8H_{12} was condensed from a $-15°$ bath (ice–salt) into the bulb. Preweighing the bulb showed that 2.67 mmol of B_8H_{12} had been added. Deuterium oxide, 8.01 mmol, was added to a small bulb and was then condensed into the bulb containing the B_8H_{12}. The bulb was removed from the vacuum apparatus and shaken for approximately 1 hr at $0°$. During this time a transient yellow color was noticed. The reaction bulb was then reattached to the vacuum system and placed in a liquid nitrogen bath, and the noncondensable gas was measured. The noncondensable gas, 7.0 mmol, was analyzed mass spectrometrically and contained approximately 43.2% deuterium. The bulb was shaken for another hour at $0°$ and 2.4 mmol of additional noncondensable gas having a deuterium content of 51.4% was evolved. The $B_8H_{10}-(C_2H_5)_2O$ mixture was pumped from the bulk at $0°$ and separated on a low-temperature fractionating column.[16]

The solid product obtained in this reaction was washed from the bulb with dry pentane, filtered, and dried, and the ir spectrum was taken in a KBr pellet. The spectrum was identical with that of boric acid, $B(OH)_3$.

The ^{11}B and ^1H nmr spectra at $0°$ were essentially those of normal hexaborane(10) with the exception that the bridge resonance in the proton spectrum appeared to be slightly less intense. The ir spectrum showed several changes: (1) there was a new absorption band at 1950 cm^{-1}; (2) the absorption at 1490 cm^{-1} was broadened with the shoulder at approximately 1560 cm^{-1} missing from the spectrum; (3) a new intense peak appeared at approximately 1125 cm^{-1}; (4) the very intense absorption at 880 cm^{-1} was considerably reduced in intensity. The mass spectrum had a cutoff value of m/e 82 corresponding to $^{11}B_6H_4D_6^+$. The most intense peak was m/e 73. High-resolution mass spectrometry showed that m/e 73 absorption consisted of three peaks. Exact mass determinations showed that the most intense of the three peaks corresponded to $^{10}B^{11}B_5H_4D_2^+$

(16) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).

while the second most intense peak corresponded to $^{11}B_6H_5D^+$ and the third peak matched well with $^{10}B_2^{11}B_4H_5D_2^+$. A small portion of the deuterated hexaborane(10) was pyrolyzed and the noncondensable gas was measured mass spectrometrically. The average composition of the deuterated species was calculated to be $B_6H_{7.3}D_{2.7}$.

$B_6H_{10}-D_2O$ Exchange.—A 100-ml reaction bulb equipped with a Fisher–Porter stopcock was charged with 0.360 ml (18 mmol) of D_2O. The bulb was placed in a liquid nitrogen bath and evacuated, and 0.69 mmol of B_6H_{10} was condensed in. Thus a 26:1 mole ratio of D_2O was used. The reaction mixture was shaken at room temperature for approximately 0.5 hr. Vigorous bubbling was observed throughout this period. The bulb was then reattached to the vacuum system, a liquid nitrogen bath was placed around it, and noncondensable gas, 1.48 mmol, was removed. The noncondensable gas was analyzed mass spectrometrically and contained 71.6% deuterium. The liquid nitrogen bath was replaced with a bromobenzene slush $(-30°)$ and all materials volatile at this temperature were pumped off and placed on the low-temperature fractionating column.[16] A very small amount of material distilled from the column at $-105°$. Its infrared spectrum was very similar to tetraborane-(10) and the mass spectrum had a cutoff peak at m/e 56 which would correspond to a deuterated B_4H_{10}. The hexaborane(10) distilled off the column at approximately $-80°$. The infrared spectrum was very similar to the spectrum of the deuterated hexaborane(10) obtained from the reaction of B_8H_{12} and D_2O with the exceptions that the band at 1950 cm^{-1} is markedly reduced in intensity although it still has a small shoulder at about 1885 cm^{-1} and the band at 1125 cm^{-1} was slightly more intense than the broad absorption which is now centered at 1460 cm^{-1}. The ^{11}B nmr spectrum was identical with that of normal B_6H_{10}. The 100-MHz ^1H nmr spectrum was normal except for a marked decrease in intensity of the bridge proton resonance (Figure 3). The mass spectrum of the compound had a cutoff
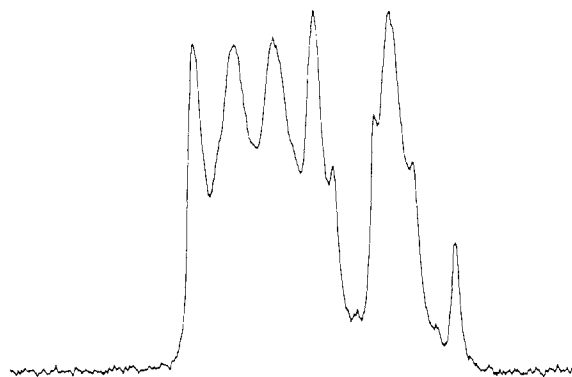

Figure 3.—The 100-MHz ^1H nmr spectrum of the hexaborane(10) obtained from the exchange with D_2O.

at m/e 82 corresponding to the species $^{11}B_6D_6H_4^+$ and the most intense peak was m/e 74, which under high resolution was a broad multiplet which was not very well resolved. Thus no exact mass determination was made.

$B_6H_{10}-B_2D_6$ Exchange.—Hexadeuteriodiborane(6) was decomposed by pyrolysis and it was determined mass spectrometrically that the deuterium content was 88%. Hexaborane-(10), 0.5 mmol, and B_2D_6, 5 mmol, were condensed into a thick-walled, 5-mm o.d. precision-bore nmr tube. The tube was placed in the 100-MHz nmr probe which had been cooled to $-80°$ and an attempt was made to follow the exchange in the nmr. At $-80°$ B_6H_{10} dissolves in liquid B_2D_6. There was almost a perfect overlap of the proton resonance of the 88% B_2D_6 with the quartet representing the basal terminal protons of the B_6H_{10} and thus the exchange could not be meaningfully followed by ^1H nmr. The experiment was repeated and the 32.1-MHz ^{11}B nmr was monitored. Since at low temperatures the downfield doublet of B_6H_{10} is collapsed, the nmr spectrum consisted of the

B_2D_6 singlet (under which lay the downfield doublet of B_6H_{10}) and the upfield doublet of B_6H_{10}. At $-65°$ there was discernible broadening of the upfield side of the B_2D_6 singlet and at $-45°$ the upfield portion of the low-field doublet of B_6H_{10} had completely separated from the B_2D_6 singlet. The probe was warmed to $-26°$ with no apparent change in the spectrum, but after 20 min at $-20°$ it was quite evident that exchange was taking place. After 1 hr at that temperature almost complete collapse had occurred and the spectrum again consisted of the B_2D_6 singlet and the upfield doublet of B_6H_{10}. The nmr tube was placed in a liquid nitrogen bath, attached to the vacuum system, and opened, and the B_2D_6 removed at $-131°$ (*n*-pentane slush). The tube was resealed and the ^{11}B, ^2H, and ^1H nmr spectra were obtained. The ^{11}B nmr spectrum consisted of a low-field singlet arising from the basal borons and an upfield doublet resulting from the resonance of the apical boron. The 15.3-MHz deuterium nmr spectrum resembled a poorly resolved doublet and was approximately 71 cps wide. The 100-MHz ^1H nmr spectrum (Figure 4)
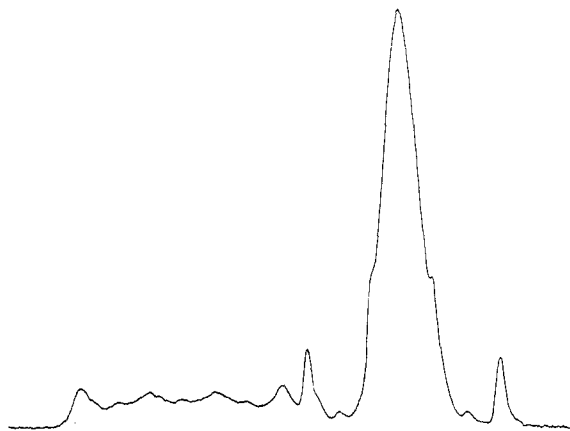

Figure 4.—The 100-MHz nmr spectrum of the hexaborane(10) obtained from the exchange with B_2D_6.

exhibited a marked decrease in intensity in the low-field quartet while the bridge hydrogen resonance and the upfield quartet appeared to be essentially unchanged.

The ir spectrum of the deuterated B_6H_{10} did not show an absorption at 1125 cm^{-1} but the band at 1950 cm^{-1} (with a shoulder at 1890 cm^{-1}) had become as intense as the absorption at 2600 cm^{-1}. The mass spectrum had a cutoff at m/e 81 corresponding to $^{11}B_6D_5H_5{}^+$ and the most intense peak was m/e 73 which was a very poorly resolved triplet. Exact mass determination could not be made very accurately but the largest peak of the triplet correspond to either $^{10}B^{11}B_5H_4D_2{}^+$ or $^{10}B^{11}B_5H_2D_3{}^+$.

The B_2D_6 recovered from this exchange reaction was pyrolyzed and found to have a deuterium content of 83.5%. A small portion of the recovered B_6H_{10} was also pyrolyzed and the noncondensable gas had a deuterium content of approximately 30%. Thus the average deuterated hexaborane molecule had the formula $B_6H_7D_3$.

The remainder of the $B_6H_7D_3$ (which had been stored at or below $-15°$ during the above work) was allowed to warm to room temperature for 0.5 hr at which time the 100-MHz nmr spectrum showed no change. The sample was then heated to 50° in the nmr probe for 1 hr and there was still essentially no change in the proton nmr spectrum.

The B_6H_{10}–B_2D_6 exchange was repeated and the exchange was allowed to proceed at $-20°$ for 3 hr. The 100-MHz nmr was essentially identical with that described in the preceding experiment and again showed a small amount of hydrogen attached to the basal borons. Three millimoles of fresh 88% B_2D_6 was condensed into the nmr tube and the tube and contents were allowed to stand at room temperature for approximately 12 hr. The tube was opened and the B_2D_6 was removed at $-158°$. The 100-MHz nmr spectrum showed a slight decrease in intensity in the low-field quartet when compared to the deuterated B_6H_{10}

from the first exchange; however, there was no change in the upfield quartet or the bridge resonances. The ir spectrum was essentially identical with that of the deuterated hexaborane after the initial B_2D_6 exchange. The only notable change was the slight decrease in intensity of the absorption at 2600 cm^{-1} relative to the absorption peak and its accompanying shoulder at approximately 1990 cm^{-1}. In the preceding spectrum the two were equal in intensity but after the second B_2D_6 exchange the 2600-cm^{-1} absorption was not as intense. The mass spectrum of the compound had a cutoff m/e of 82 corresponding to $^{11}B_6H_4D_6{}^+$ and the most intense peak is m/e 74.

Attempted Boron Exchange of B_6H_{10} with $^{10}B_2H_6$.—Hexaborane(10), 1 mmol, and $^{10}B_2H_6$ (96% ^{10}B, 10 mmol) were condensed into a thick-walled glass bomb which was then sealed from the vacuum system. Two exchange experiments were performed: (1) $-30°$ for 15 hr and (2) room temperature for 24 hr. In each case the ir and mass spectra of the reactants and products were identical. There was no evidence of reaction and very little decomposition had occurred.

Intermolecular Exchange Study.—Identical amounts of deuterated hexaborane (10) which had undergone two exchanges with B_2D_6 (described above) and normal hexaborane(10) were condensed into a small volume where they would exist in the liquid phase. The mass spectrum of the mixture was obtained and had a cutoff at m/e 82. The mass spectra were obtained at intervals over a 13.5-hr period. After 0.5 hr the m/e 82 peak had completely disappeared and in the remaining 13 hr the relative intensities showed small changes. The m/e 66, 67, 73, 74, and 76–79 peaks increased in relative intensity, while the m/e 68–72 and the m/e 75, 80, and 81 peaks decreased in intensity. Thus the cutoff of the mixture after 13.5 hr was m/e 81. The ir spectrum of the mixture exhibited no band at 1125 cm^{-1} after 13 hr and the 100-MHz nmr spectrum was normal except for decreased intensity of the resonance arising from the basal terminal hydrogens. The downfield doublet of the ^{11}B nmr spectrum appears to be a doublet with a superimposed singlet. The upfield peak is the normal doublet of B_6H_{10}.

Discussion

A somewhat surprising result of our work with hexaborane(10) was the temperature dependence of the low-field doublet. The crystal structure[17–19] shows a six-boron atom icosahedral fragment arrangement with six terminal hydrogen atoms and four bridge hydrogen atoms. Thus there is a B–B bond in the base of the molecule and four different types of boron in the molecule. The ^{11}B nmr spectrum which consists of two doublets with area ratios of 5:1 is not consistent with the crystal structure unless complete accidental overlap occurs. A more popularly invoked explanation for the nmr spectrum is a rapid tautomeric shift[20–22] which cannot mix bridge and terminal hydrogens since the proton nmr shows different resonances for the two types. The broadening and collapse of the base boron nmr signal in hexaborane at low temperature, without a corresponding collapse of the apex signals, is due in large part to the shorter ^{11}B relaxation time of the base borons.[23a] On the basis of recent relaxation time measurements,[23b] it is possible to predict minimum boron

(17) K. Eriks, W. N. Lipscomb, and R. Schaeffer, *J. Chem. Phys.*, **22**, 754 (1954).

(18) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, and W. N. Lipscomb, *ibid.*, **28**, 56 (1958).

(19) M. G. Rassman, R. A. Jacobson, F. L. Hirshfeld, and W. N. Lipscomb, *Acta Crystallogr.*, **12**, 530 (1959).

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

(21) W. N. Lipscomb, *J. Phys. Chem.*, **65**, 1064 (1961).

(22) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(23) (a) A. Allerhand, J. D. Odom, and R. E. Moll, to be published; (b) A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, **50**, 5037 (1969).

nmr line widths in hexaborane, that is, the absence of such broadening effects as unresolved splittings and tautomerism. Typical values are given in Table I. Results for pentaborane are included for comparison purposes.[23]

TABLE I
CALCULATED LOWER LIMIT ^{11}B LINE WIDTH (Hz)

Temp, °C	Hexaborane(10)		Pentaborane(9)	
	Base	Apex	Base	Apex
30	12	2.7	4.7	0.53
−50	51	14	12	1.5

At room temperature, the experimentally observed line widths are much greater than the calculated lower limit values given in Table I. This broadening is most likely determined by unresolved splittings due to long-range coupling. At −50° long-range coupling effects are still the most predominant factor in causing the observed line widths of the pentaborane(9) nmr signals to be much broader than the lower limit line widths calculated from relaxation time measurements. This is equally true for the apex boron nmr signal in hexaborane(10). However, the lower limit value of the line width of the nmr signal of the base boron at −50° approaches the experimentally observed line width and thus relaxation effects must be making a significant contribution to the broadening of this particular nmr signal. The observed broadening is somewhat greater than that expected solely on the basis of relaxation, so that tautomerism effects at low temperature cannot be totally excluded as a possibility. Further work is indicated.

From an examination of the infrared spectra of the various deuterated species, it appears that Gibbins and Shapiro were correct in the assignment of the B–H$_t$ and B–H$_b$ stretching frequencies.[7] Unfortunately, the band at 1125 cm^{-1} is the only B–D stretch that is not obscured by a B–H stretch. The B–D$_t$ and the first B–D$_b$ absorptions are very nearly superimposed on the two B–H$_b$ bands. Thus the band at 1125 cm^{-1} correlates well with the expected frequency ratio BH/BD = 1.33.

The preparation of B$_6$H$_{10}$ from B$_6$H$_{12}$ and D$_2$O does not result in a specifically labeled molecule. The ir spectrum exhibited both B–D$_t$ and B–D$_b$ absorption peaks. No mechanism for the formation has been determined experimentally but the observation of a transient yellow color suggests the formation of at least one ionic intermediate which may be more susceptible to hydrogen scrambling than a neutral boron hydride. The change with time in the per cent D evolved also leads one to believe that there is more than one step in the mechanism. Besides the potential for scrambling in an ionic intermediate, exchange may well have taken place between the B$_6$H$_{10}$ which was formed and the D$_2$O still present before the reaction was complete. There was no indication of deuterium attached to the apex boron.

Hexaborane(10) is relatively stable toward water and in the exchange experiment between B$_6$H$_{10}$ and D$_2$O

extensive exchange occurred. The rate of exchange is much faster in the bridge positions than in the basal terminal hydrogens and actually the only indication that terminal deuterium is present comes from a small shoulder in the infrared spectrum. Judging from the ^{1}H and ^{11}B nmr the hydrogen on the apical boron does not appear to exchange at all. No definitive statement can be made concerning the mechanism of exchange and the competitive hydrolysis reaction would make kinetic studies exceedingly difficult. It is interesting to speculate that an intermediate in this exchange might well be the B$_6$H$_{11}^+$ ion[24] predicted by Lipscomb to be stable. Loss of a proton from any of the five equivalent bridge positions would then lead to a bridge labeled species. However, this would not explain the possible presence of deuterium in the terminal positions. The tautomeric shift required to interpret the nuclear magnetic resonance spectrum must occur on a lifetime short with respect to the nmr experiment and a migration even several orders of magnitude slower would suffice to explain the possible presence of label in the terminal positions. However, this too seems unlikely from results obtained in an intramolecular exchange experiment (*vide infra*).

The hexaborane(10)–hexadeuteriodiborane(6) exchange provided a molecule specifically labeled in the basal terminal hydrogen positions. The exchange was fairly rapid as the downfield doublet had completely collapsed in slightly more than 1 hr at −20°. The infrared spectrum showed that there was no deuterium in the bridge positions and within the limits of the method the ^{11}B nmr spectrum indicated that there was no deuterium attached to the apical boron. An earlier report indicated that the bridge hydrogens also exchanged with B$_2$D$_6$[6] but we found no evidence of this even with vigorous conditions (liquid B$_2$D$_6$, room temperature, 12 hr). However, no experimental conditions were reported in the earlier publication and a catalyst or higher temperatures may have been used. The 15.3-MHz deuterium nmr spectrum also indicated that deuterium was contained in the basal terminal hydrogens. As a general rule deuterium nmr spectra of deuterated boranes are not very well resolved and the spectrum which we obtained is approximately the correct width for a quartet with J values one-sixth that of the B–H coupling constant.

The activation energy required to interconvert the bridge and basal terminal hydrogens must be rather large. After 0.5 hr at room temperature followed by 0.5 hr at 50° the infrared and nmr spectra still showed no evidence of bridge deuterium.

Intermolecular exchange occurs at room temperature in hexaborane(10). The infrared and nuclear magnetic resonance spectra indicate that only the basal terminal protons take part in the exchange. This type of exchange whereby only certain terminal hydrogens exchange intermolecularly is unprecedented in boron hydrides and not enough is known to make a definitive statement about the mechanism involved.

(24) W. N. Lipscomb, *J. Chem. Phys.*, **28**, 170 (1958).

In this study of isotopic exchanges with B_6H_{10}, we have succeeded in defining routes whereby we could prepare several specifically labeled hexaborane(10) molecules. We can now prepare a molecule labeled with deuterium in the basal terminal positions or labeled almost completely in the bridge positions. Also by two consecutive labeling reactions a hexaborane molecule can be prepared with deuterium in every position except the apical boron. Alternatively, by starting with $B_{10}D_{14}$ and degrading to B_6D_{10}, a hexaborane molecule could be prepared which is labeled with deuterium attached specifically to the apical boron.

Thus far, the apical proton has been inert to isotopic exchanges. However, this may only mean that the right set of conditions has not been used. Various other substitution reactions may well involve the apical position and indeed calculated charge densities[25] indicate that this particular position should be more susceptible to electrophilic substitution reactions.

Further research should also involve the general investigation of the chemistry of B_6H_{10}. The deuterium labels provide a handle on the molecule which should enable one to learn a great deal more about the mechanisms of reaction of B_6H_{10}. Work is under way in this laboratory with this aim in mind.

(25) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 110.

CONTRIBUTION NO. 1844 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

Studies of Boranes. XXX. Reaction of Pentaborane(9) with Diborane(6). Isolation of Several New Boron Hydrides[1]
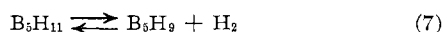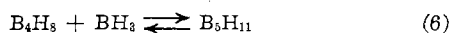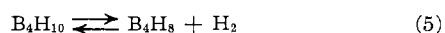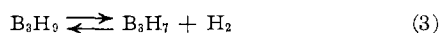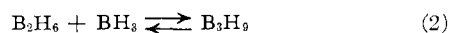
BY J. DOBSON, R. MARUCA, AND R. SCHAEFFER

The reaction of B_5H_9 with B_2H_6 has been studied at elevated temperatures in a flow–quench system. Three new boranes have been isolated: B_8H_{16}, $B_{10}H_{18}$, and what is probably $B_{10}H_{16}$. In addition, evidence suggests that a new B_{6-7} hydride and a second new B_8 hydride are probably formed but these could not be obtained sufficiently pure to characterize. Evidence is presented that in part B_5H_{11} plays a role in the synthesis of the new hydrides. Isotopic tracer studies of the reaction produce some specific labeling, particularly of n-B_9H_{15}. Nmr and mass spectra are reported for the new compounds.

Introduction

For many years the thermal decomposition of diborane has been used as a means of preparing tetraborane, pentaborane(9), pentaborane(11), and decaborane(14). Recently, much interest has been shown in the detailed mechanism by which diborane forms the higher hydrides and ultimately goes to the thermally more stable state of elemental boron and hydrogen gas. Many investigators have shown that the formations of B_4H_{10}, B_5H_{11}, and B_5H_9 are consistent with a mechanism which involves borane addition followed by hydrogen loss (eq 1–7).[2,3] Recently, in this laboratory it has

$$B_2H_6 \rightleftharpoons 2BH_3 \tag{1}$$

$$B_2H_6 + BH_3 \rightleftharpoons B_3H_9 \tag{2}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{3}$$

$$B_3H_7 + BH_3 \rightleftharpoons B_4H_{10} \tag{4}$$

$$B_4H_{10} \rightleftharpoons B_4H_8 + H_2 \tag{5}$$

$$B_4H_8 + BH_3 \rightleftharpoons B_5H_{11} \tag{6}$$

$$B_5H_{11} \rightleftharpoons B_5H_9 + H_2 \tag{7}$$

been shown that the conversions of B_8H_{12} to n-B_9H_{15} and $B_{10}H_{14}$ and of i-B_9H_{15} to $B_{10}H_{14}$ are consistent with the same type mechanism, that is, borane addition followed by hydrogen loss.[4,5]

The labeling work by Hillman, Mangold, and Norman[6] has shown that B_5H_9 reacts with B_2H_6 to form $B_{10}H_{14}$ and also that five boron atoms come from the B_5H_9 and five come from B_2H_6. In an attempt to learn more about the mechanism of $B_{10}H_{14}$ formation from B_5H_9 and B_2H_6, we have carried out the copyrolysis of these two hydrides in a circulating pyrolysis system consisting of a hot pyrolysis zone immediately followed by a cold quenching trap, thus allowing us effectively to trap out unstable higher hydrides. Using this trapping technique, at least 14 different boron hydrides have been isolated of which five or more are new compounds not previously reported.

Experimental Section

Methods.—Standard high-vacuum techniques were employed wherever possible throughout this investigation and have been

---

(1) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968. Part XXIX: J. D. Odom and R. Schaeffer, *Inorg. Chem.*, **9**, 2157 (1970).

(2) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 154 ff.

(3) M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 223 ff.

(4) R. Maruca, J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).

(5) D. B. MacLean, J. D. Odom, and R. Schaeffer, *ibid.*, **7**, 408 (1968).

(6) (a) M. Hillman, D. J. Mangold, and J. H. Norman, *J. Inorg. Nucl. Chem.*, **24**, 1565 (1962); (b) M. Hillman, D. J. Mangold, and J. H. Norman, *Advan. Chem. Ser.*, **No. 32**, 151 (1961).