CONTRIBUTION NO. 1528 FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

Studies of Boranes. XXVI. Preparation of Boron and Deuterium Isotopically Substituted *n*-Nonaborane-15 and Decaborane-14[1,2]

BY R. MARUCA, JEROME D. ODOM, AND RILEY SCHAEFFER

Received August 11, 1967

Reaction of octaborane-12 with liquid ^{10}B-diborane-6 at −30° formed a mono-^{10}B-labeled *n*-nonaborane-15 and a di-^{10}B-substituted decaborane-14. When the reaction was carried out using deuteriodiborane-6, nonspecifically deuterated *n*-nonaborane-15 and decaborane-14 were obtained. The reaction of *n*-nonaborane-15 with liquid ^{10}B-diborane-6 at room temperature gave products identical with those obtained from the reaction of octaborane-12 and ^{10}B-diborane-6. This result is consistent with the postulate of Ditter and Williams that *n*-nonaborane-15 dissociates at room temperature to yield octaborane-12 and diborane-6. The reaction of *n*-nonaborane-15 with liquid deuteriodiborane-6 at room temperature yields a nonspecifically deuterated decaborane-14 and a deuterio-*n*-nonaborane-15 with at least one terminal hydrogen site not deuterated. Hydrogen exchange did not occur at −30° between deuteriodiborane-6 and either isononaborane-15 or decaborane-14; however, the decaborane-14 obtained from the reaction of isononaborane-15 with deuteriodiborane-6 at −30° is extensively deuterated. Thus, hydrogen exchange must have occurred with some unstable intermediate in the formation of decaborane-14. Isononaborane-13, *n*-nonaborane-13, and a decaborane-16 are proposed as intermediates in this reaction Pentaborane-11 was shown to exchange boron completely with liquid ^{10}B diborane-6 at room temperature in 0.5 hr. The *n*-nonaborane-15 and decaborane-14 obtained from the reaction of pentaborane-11 and ^{10}B-diborane-6 at room temperature had the same ^{10}B/^{11}B ratio in all boron positions.

Introduction

Studies of interconversions of boranes have been of interest for many years and much work has been done with the lower boron hydrides to attempt to determine the mechanisms of interconversions. Since B_8H_{12} (octaborane-12), *n*-B_9H_{15} (normal nonaborane-15), and *i*-B_9H_{15} (isononaborane-15) have recently been prepared in sufficient quantities to allow further study of their chemistry,[3-5] it was possible to study these materials using isotopic substitution techniques to obtain information about the interconversions of the higher boron hydrides.

Reactions of B_8H_{12}, *n*-B_9H_{15}, and *i*-B_9H_{15} with B_2D_6 and $^{10}B_2H_6$ are reported in this paper. Mass spectral and ^{11}B nmr studies of the products of these reactions provide information about the mechanism for conversion of B_8H_{12} to *n*-B_9H_{15} and $B_{10}H_{14}$ and for the conversion of *n*-B_9H_{15} to $B_{10}H_{14}$. The recently postulated highly reactive intermediates *i*-B_9H_{13} and *n*-B_9H_{13}[6] have again proven useful in the interpretation of some of the isotopic studies.

The reaction of B_5H_{11} and B_2H_6 to yield other boron hydrides[7] was also studied with isotopically labeled materials to determine whether any specifically labeled compounds were formed.

Experimental Section

Methods.—Standard high-vacuum techniques were employed wherever possible throughout this investigation and have been treated elsewhere.[8,9]

Hydrogen–deuterium analyses of the partially deuterated boranes reported throughout this publication were obtained by pyrolyzing the boranes and analyzing the resulting hydrogen–deuterium mixtures mass spectrometrically. For mixtures of hydrogen and deuterium it was calculated and verified empirically that a plot of I_4/I_3 *vs.* (% D)/I_3 gives a straight line when $I_4 + I_3 + I_2 = 100$.[10]

In most of the reactions reported below liquid diborane is used as one of the reactants. Using vapor pressure–temperature data from the literature, the vapor pressure of liquid B_2H_6 at −30° is 11 atm and at room temperature it is approximately 50 atm. The vapor pressure of liquid B_2D_6 at room temperature appears to be in the neighborhood of 100 atm which is much higher than one calculates from a pressure–temperature relationship. Because of these pressures, *extreme caution* was used when these reactions were carried out in Pyrex bombs and medium-walled nmr tubes.

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 low-temperature spectra were obtained using standard Varian variable-temperature probe accessories. 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. Mass spectra were obtained with Consolidated Electrodynamics Corp. Model 21-620 and Associated Electrical Industries Model MS-9 mass spectrometers.

---

(1) For paper XXV of this series see D. B. MacLean, J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, **7**, 408 (1968).

(2) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

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

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

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

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

(7) J. F. Ditter, J. R. Spielman, and R. E. Williams, *ibid.*, **5**, 118 (1966).

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

(9) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(10) The relationship for % D as a function of mass spectrometric intensities (I) was derived from the equation

$$\%\ D_2 = \frac{(P_{D_2} + {}^1/_2 P_{HD})100}{P_{D_2} + P_{HD} + P_{H_2}}$$

where P = partial pressure of the hydrogen species specified in the total gas mixture. If one substitutes $P_{D_2} = C_1I_4$, $P_{HD} = C_2I_3$, and $P_{H_2} = C_3I_2$ into the above equation and simplifies, then one is left with the expression

$$\frac{\%D}{I_3} = C\frac{I_4}{I_3} + C'$$

I_4, I_3, and I_2 are the percentage mass spectral intensities of the m/e 4, 3, and 2 peaks, respectively, for the hydrogen–deuterium mixture and the C's are constants. The intensity of the m/e 1 peak was not observable and therefore was neglected.

Preparation of Starting Materials.—Sodium tetradeuterioborate, $NaBD_4$, was obtained from Metal Hydrides Inc. and was used without further purification. Deuteriodiborane-6 was prepared by the reaction of $NaBD_4$ with hot polyphosphoric acid. The B_8H_{12} used in this work was prepared by decomposition of i-B_9H_{15} as described elsewhere.[3] The n-B_9H_{15} was prepared by the reaction of B_2H_6 with B_8H_{12}.[5] All other reagents and the preparation of other starting materials used in this investigation are described elsewhere.[6]

Reaction of B_8H_{12} with Liquid $^{10}B_2H_6$.—A 1.9-mmole sample of B_8H_{12} and 11.0 mmoles of $^{10}B_2H_6$ (96% ^{10}B) were sealed in a 5-ml thick-walled Pyrex bomb equipped with a break-off tip. The bomb was placed in a −30° slush bath for 9 hr, quenched at −196°, and then connected to a high-vacuum system and opened. The volatile contents were fractionated through a −20, −78, and −196° trap system to separate the compounds $B_{10}H_{14}$, n-B_9H_{15}, and B_2H_6, respectively. A yellow solid, nonvolatile under high vacuum at 50°, remained in the reaction bomb. The yield of $B_{10}H_{14}$ was 0.53 mmole or 28% based on B_8H_{12}; the yield of n-B_9H_{15} was 1.0 mmole or 53% based on B_8H_{12}. Besides n-B_9H_{15} and $B_{10}H_{14}$, it is shown below that a trace of n-$B_{18}H_{22}$ can also be isolated from this experiment. The over-all 81+% conversion of B_8H_{12} to higher hydrides can be considered excellent for such an unstable species.

The ^{11}B nmr and mass spectra of the $B_{10}H_{14}$ and n-B_9H_{15} obtained from this reaction were recorded and are discussed in a later section.

The mass spectrum of recovered $^{10}B_2H_6$, 7.8 mmoles, gave a calculated 97% ^{10}B content in excellent agreement with the 96% value for the starting material.[11] From this it was concluded that under these conditions there was little, if any, boron exchange between the $^{10}B_2H_6$ and any species present.

This experiment was repeated using ^{11}B nmr to monitor the course of the reaction continuously. A 5-mm thick-walled nmr tube was charged with 1.0 mmole of B_8H_{12} and 2.0 mmoles of $^{10}B_2H_6$ (96% ^{10}B). The tube was sealed from the vacuum line, warmed to −78° in order to dissolve the B_8H_{12} in the liquid $^{10}B_2H_6$, and placed in the low-temperature nmr probe which had been precooled to −90°. The probe was slowly warmed and the ^{11}B nmr spectrum was repeatedly recorded. The B_8H_{12} was solid at −90°. It dissolved at approximately −80° and the spectrum obtained was that of B_8H_{12} and B_2H_6 which contained 4% ^{11}B. No change was observed in the spectrum until the probe was warmed to about −35° where the spectrum of n-B_9H_{15} started growing into those of B_8H_{12} and B_2H_6. After 2 hr at −32° the spectrum contained resonances for B_2H_6, B_8H_{12}, n-B_9H_{15}, and $B_{10}H_{14}$. After another 2 hr during which time the temperature warmed to −22°, the only resonances observable were those of B_2H_6, n-B_9H_{15}, and $B_{10}H_{14}$. At this time the sample was cooled to −196° and opened by a high-vacuum technique; the products were fractionated as outlined above. The n-$^{10}B^{n}B_8H_{15}$ obtained was shown by the ^{11}B nmr and mass spectrometry to be identical with that described above.

The Reaction of B_8H_{12} with Liquid B_2D_6.—A 6.5-ml thick-walled Pyrex bomb, fitted with a break-off tip, was charged with 2.0 mmoles of B_8H_{12} and 9.8 mmoles of B_2D_6 (92% deuterium). The tube was sealed and placed in a −30° slush bath. At the end of 6 hr the tube was cooled to −196° and opened; 1.0 mmole of hydrogen (shown to have 40% deuterium) was measured by means of a Toepler pump. The volatile materials were then fractionated as described in the above experiment to isolate various compounds including 0.8 mmole of n-$B_9H_nD_{15-n}$ of average composition $B_9H_{7.4}D_{7.6}$, 0.2 mmole of $B_{10}H_nD_{14-n}$ of average composition $B_{10}H_{4.3}D_{9.7}$, and 9.0 mmoles of $B_2H_nD_{6-n}$ which contained 81% deuterium.

The ^{11}B nmr spectra of the products were recorded and are discussed later.

In order to obtain information about the exchange taking place in the above reaction, it was repeated and monitored using ^{11}B nmr. A 0.55-mmole sample of B_8H_{12} and 2.7 mmoles of B_2D_6 (92% deuterium) were sealed in a 5-mm thick-walled nmr tube. The reaction mixture was warmed to −80°, shaken vigorously to dissolve the B_8H_{12} in the liquid B_2D_6, and then placed in the precooled low-temperature probe of the spectrometer. At −70° only the singlet of liquid B_2D_6 was observed. Upon warming to −47° the spectrum of B_8H_{12} also appeared. No change was observed in the spectrum until the sample was warmed to −34°. After 13 min at this temperature the low-field doublet of B_8H_{12} had collapsed to a singlet. After 19 min more, the high-field doublet of B_8H_{12} had become asymmetrical. After another 17 min, the spectrum of n-$B_9H_nD_{15-n}$ could be observed. At the end of 1.2 hr at −34°, the sample was cooled to −196° to stop the reaction so that unreacted, partially deuterated $B_8H_nD_{12-n}$ could be isolated. The reaction mixture was fractionated as described above except that a low-temperature fractionating column[12] had to be used to separate $B_8H_nD_{12-n}$ and n-$B_9H_nD_{15-n}$.

The $B_2H_nD_{6-n}$ isolated contained 86% deuterium. The $B_8H_nD_{12-n}$ obtained had the average composition $B_8H_{7.8}D_{4.2}$ while that of the n-$B_9H_nD_{15-n}$ was $B_9H_{9.1}D_{5.9}$. Only a trace of $B_{10}H_nD_{14-n}$ was recovered. The $B_8H_{7.8}D_{4.2}$ gave a ^{11}B nmr spectrum consisting of two equal singlets at −7.1 and 19.9 ppm in good agreement with the δ values of the two doublets of B_8H_{12}.[5] The ^{11}B nmr of the n-$B_9H_{9.1}D_{5.9}$ was similar to that of the n-$B_9H_nD_{15-n}$ described above (Figure 1(a)).

Isolation of n-$B_{18}H_{22}$ from the Reaction of B_8H_{12} with Liquid B_2H_6.—The reaction of B_8H_{12} with liquid B_2H_6 at −30° has been shown to yield good quantities of n-B_9H_{15} and $B_{10}H_{14}$.[5] A yellow polymeric mateial is also formed. Previous work on small quantities of this yellow solid failed to show the presence of volatile boron hydrides. However, when the reaction was repeated using 9.0 mmoles of B_8H_{12} and 11.7 mmoles of B_2H_6, a very small amount, approximately 0.05 mmole, of n-$B_{18}H_{22}$ was sublimed from the residue at 120°. The n-$B_{18}H_{22}$ was identified by its melting point of 175–177° (lit.[13] 177–178.5°) and by its ^{11}B nmr spectrum.[14]

Reaction of n-$^{n}B_9H_{15}$ with Liquid $^{10}B_2H_6$.—A 1.2-mmole sample of n-$^{n}B_9H_{15}$ and 5.5 mmoles of $^{10}B_2H_6$ (96% ^{10}B) were condensed into a 1.5-ml Pyrex bomb. The bomb was then sealed, allowed to stand at 27° for 2 hr, cooled to −196°, and opened; the contents were fractionated through a −78, −196° trap system. The mass spectra of the $^{10}B_2H_6$ and n-B_9H_{15} recovered were slightly different from those of the starting materials such that the $^{10}B_2H_6$ appears very slightly enriched in ^{11}B and the n-B_9H_{15} slightly enriched in ^{10}B. Since some exchange was indicated at 27° in 2 hr, the experiment was repeated allowing a much longer time for reaction to take place.

A 2-ml Pyrex bomb, fitted with a break-off tip, was charged with 0.38 mmole of n-$^{n}B_9H_{15}$ and 4.94 mmoles of $^{10}B_2H_6$ (96% ^{10}B). The tube was sealed and left standing at 27° for 24 hr (*caveat emptor!*). The reaction was then quenched at −196°, the tube opened, and 0.36 mmole of hydrogen isolated. The volatile materials were then fractionated on a low-temperature fractionating column[12] yielding 4.78 mmoles of $^{10}B_2H_6$ (95% ^{10}B)[11], 0.11 mmole of n-B_9H_{15}, and 0.17 mmole of $B_{10}H_{14}$, a 63% yield. The n-B_9H_{15} and $B_{10}H_{14}$ recovered were shown by mass spectrometry and ^{11}B nmr to be identical with the same compounds formed by the reaction of B_8H_{12} with $^{10}B_2H_6$ (96% ^{10}B) which is described above.

Reaction of n-$^{n}B_9H_{15}$ with Liquid B_2D_6.—A reaction mixture containing 1.1 mmoles of n-B_9H_{15} and 5.6 mmoles of B_2D_6 (92% deuterium) was condensed into a 1.5-ml bomb which was then allowed to stand at 27° for 2 hr. The reaction was quenched at −196°, the tube was opened, and the contents were fractionated through a −78, −196° trap system which separated

---

(11) It was determined empirically from the mass spectra of diborane samples of known ^{10}B composition that

$$\%\ ^{10}B = \frac{I_{10}(100)}{I_{10} + (I_{11} - (0.41)I_{10})}$$

(12) J. Dobson and R. Schaeffer, to be published.

(13) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3218 (1962).

(14) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 147.

n-$B_9H_nD_{15-n}$ and B_2D_6 (90% deuterium). The n-$B_9H_nD_{15-n}$ had the average composition $B_9H_{13.4}D_{1.6}$. However, the ^{11}B nmr spectrum of this material appeared normal (Figure 1(b)). The mass spectrum had an m/e cutoff value of 120 with the most intense peaks in the B_9 and B_8 regions of 106 and 93, respectively, confirming that some exchange had occurred.

The n-$B_9H_{13.4}D_{1.6}$ was then resealed in a 1.5-ml Pyrex bomb with 8.4 mmoles of B_2D_6 (92% deuterium) and the reaction mixture was allowed to stand at 27° for 5 hr. The bomb was opened and fractionated as described above. The B_2D_6 had an average deuterium content of 91%. The ^{11}B nmr spectrum (Figure 1(c)) of the n-$B_9H_nD_{15-n}$, of average composition $B_9H_{11.9}D_{3.1}$, gave clear evidence that further exchange had taken place.

The n-$B_9H_{11.9}D_{3.1}$ was resealed in a 1.6-ml Pyrex bomb with 12.6 mmoles of B_2D_6 (91% deuterium). The mixture was warmed to 27° for 11.5 hr and then fractionated through a 0, −78, −196° trap system which separated $B_{10}H_nD_{14-n}$, n-$B_9H_nD_{15-n}$, and B_2D_6 (88% deuterium), respectively. The $B_{10}H_nD_{14-n}$ was accidentally lost in handling. However, the ^{11}B nmr spectrum of the n-$B_9H_nD_{15-n}$ (Figure 1(d)), with average composition $B_9H_{10.0}D_{5.0}$, was very different from that of the starting n-$B_9H_{11.9}D_{3.1}$. The low-field multiplet had collapsed to a large broad singlet with a low-field shoulder. The low-field doublet of the set of doublets had also become a singlet. From this set of experiments it appeared that n-B_9H_{15} was being selectively deuterated; thus, the reaction was repeated with a longer reaction time.

A 2-ml Pyrex bomb was charged with 0.66 mmole of n-B_9H_{15} and 15.6 mmoles of B_2D_6 (86% deuterium). The bomb was sealed and allowed to stand at 27° for 24 hr. The tube was cooled to −196° and opened; 0.32 mmole of hydrogen (73% deuterium) was obtained. The volatile materials were then fractionated through a −196, −78, −30, −20° trap system. The B_2D_6, 15.6 mmoles, isolated in the −196° trap had an average hydrogen composition of 84% deuterium. A trace of lower (B_4, B_5, or B_6) boron hydrides was obtained in the −78° trap. The −30° trap contained 0.31 mmole of n-$B_9H_nD_{15-n}$ with average composition $B_9H_{10.1}D_{4.9}$. The average composition of this material is almost the same as that isolated after the third exchange in the above reaction. Its ^{11}B nmr was also very similar (Figure 1(d)). The mass spectrum of the n-$B_9H_{10.1}D_{4.9}$ sample was similar to that recorded for the n-$B_9H_{7.4}D_{7.6}$ obtained when B_8H_{12} was allowed to react with B_2D_6.

A sample of $B_{10}H_nD_{14-n}$, 0.22 mmole, was obtained in the −20° trap and had an average composition of $B_{10}H_{7.5}D_{6.5}$. Its ^{11}B nmr spectrum (Figure 2(b)) also indicates that the molecule contains less deuterium than the $B_{10}H_{4.3}D_{9.7}$ obtained from the reaction of B_8H_{12} and B_2D_6.

No reaction or exchange of n-B_9H_{15} with B_2D_6 was found at 0°.

Reaction of n-B_9H_{15} with Gaseous B_2H_6.—After n-B_9H_{15} had been found to react with liquid diboranes at room temperature, the reaction of n-B_9H_{15} and gaseous B_2H_6 at elevated temperature was investigated. A 100-ml glass reaction vessel fitted with a break-off tip was charged with 1 mmole of n-B_9H_{15} and 2.2 mmoles of B_2H_6. The vessel was placed in an oven at 60° for 2 hr. The vessel was opened and 0.32 mmole of hydrogen measured. The rest of the volatile species were fractionated through a −20, −78, −135, −196° trap system which collected approximately 0.05 mmole of $B_{10}H_{14}$, 0.1 mmole of n-B_9H_{15}, 0.01 mmole of a mixture of boron hydrides which appear to have four or five boron atoms, and 2.1 mmoles of B_2H_6, respectively. A yellow residue, nonvolatile under vacuum at 120°, remained in the reaction vessel.

Reaction of i-B_9H_{15} with B_2D_6.—A small (4.5-ml) thick-walled reaction vessel was charged with 1.0 mmole of KB_9H_{14}, attached to the vacuum line, and evacuated. A large excess of anhydrous hydrogen chloride was condensed into the vessel and reaction was allowed to proceed at −80°. After approximately 1 hr the HCl was removed and 20.0 mmoles of B_2D_6 (92% deuterium) was condensed into the tube at −196°. The vessel was sealed from the vacuum system and immersed in a −30° bath for 6 hr, then quenched in liquid nitrogen, and reattached to the vacuum system. Noncondensable gas, 1.1 mmoles, was removed and 18.9 mmoles of B_2D_6 was recovered. Subsequently, 0.0448 g (0.362 mmole) of decaborane was pumped from the vessel. Mass spectral analyses of the recovered B_2D_6 and the $B_{10}H_{14}$ obtained in this reaction showed 89.3 and 51.2% of deuterium, respectively. The mass spectrum of the $B_{10}H_nD_{14-n}$ species showed a cutoff at m/e 134. An analysis of the ^{11}B nmr spectrum of the recovered decaborane (Figure 2(b)) confirmed that extensive deuteration had taken place.

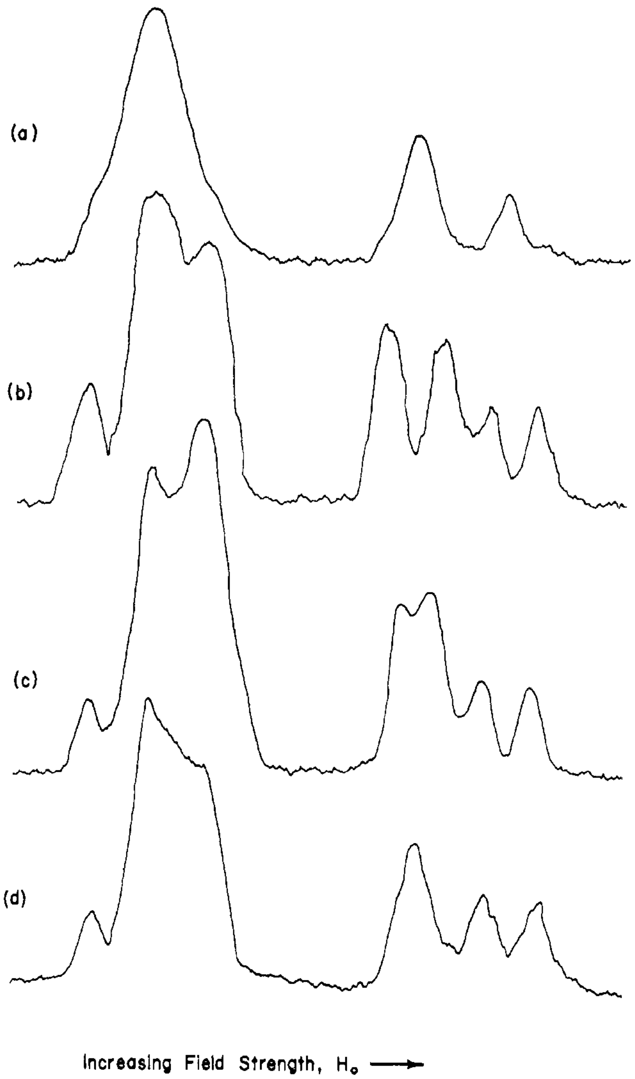

Figure 1.—Boron-11 nmr spectra of (a) n-$B_9H_{7.4}D_{7.6}$ obtained from the reaction of B_8H_{12} with B_2D_6, (b) n-$B_9H_{13.4}D_{1.6}$ obtained from the reaction of n-B_9H_{15} with B_2D_6 for 2 hr, (c) n-$B_9H_{11.9}D_{3.1}$ obtained from the reaction of n-B_9H_{15} with B_2D_6 for 7 hr, and (d) n-$B_9H_{10}D_5$ obtained from the reaction of n-B_9H_{15} with B_2D_6 for either 18 or 24 hr.

Attempted H–D Exchange of i-B_9H_{15} with B_2D_6.—i-B_9H_{15} was prepared in a manner identical with that in the preceding experiment starting with 0.5 mmole of KB_9H_{14}. A 10.0-mmole sample of B_2D_6 was condensed on the i-B_9H_{15} at −196° and the reaction vessel was sealed from the line. The vessel was allowed to stand at a temperature below the decomposition point of i-B_9H_{15} for approximately 6 hr. At this time the vessel was opened and infrared and mass spectra of the recovered B_2D_6 were obtained. Both spectra were identical with those taken before the experiment was performed. In a similar experiment, i-B_9H_{15} in liquid B_2D_6 was warmed for several minutes above the decomposition temperature of i-B_9H_{15}. The experiment was performed in a thick-walled 5-mm nmr tube using 0.5 mmole of i-B_9H_{15} and 2.0 mmoles of B_2D_6. The mass spectrum of B_2D_6 used (92% deuterium) ex-

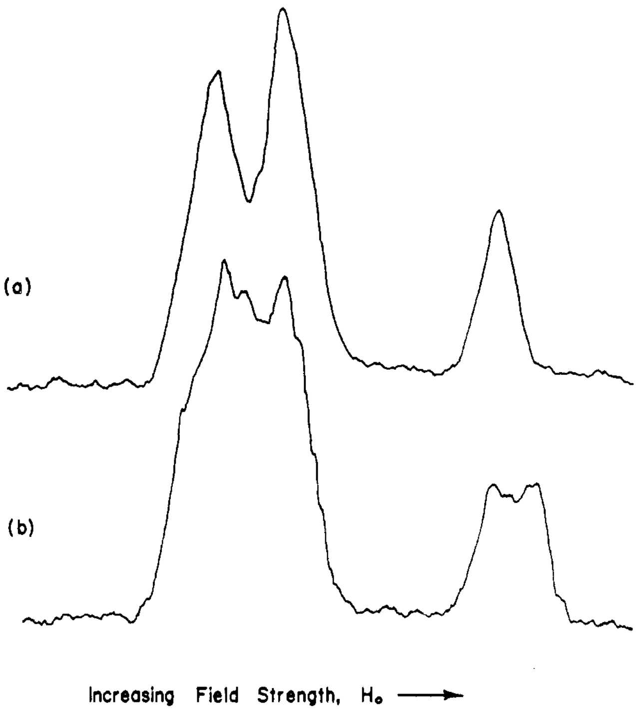

Figure 2.—Boron-11 nmr spectra of (a) $B_{10}H_{4.3}D_{9.7}$ obtained from the reaction of B_8H_{12} with B_2D_6 and (b) $B_{10}H_7D_7$ obtained from the reaction of either n-B_9H_{15} with B_2D_6 or i-B_9H_{15} with B_2D_6.

hibited its most intense peak at m/e 32. The mass spectrum of the B_2D_6 recovered after this experiment exhibited almost equal intensities for the m/e 31 and 32 peaks and the gas-phase infrared spectrum showed a small increase in the B–H terminal stretching mode.

Attempted H–D Exchange of $B_{10}H_{14}$ with B_2D_6.—Previous experiments have shown that H–D exchange does take place between $B_{10}H_{14}$ and B_2D_6 at elevated temperatures;[15] however, low-temperature data were not available. In thick-walled reaction vessels H–D exchanges were attempted with $B_{10}H_{14}$ and large excesses of B_2D_6 (92% deuterium). Three exchange experiments were performed: (1) −30° for 6 hr, (2) room temperature for 18 hr, and (3) room temperature for 36 hr. The infrared spectra of the B_2D_6 obtained under identical conditions before and after the experiments and the ^{11}B nmr spectra of the $B_{10}H_{14}$ showed no evidence of exchange.

Reaction of $^{11}B_5H_{11}$ with $^{10}B_2H_6$.—An 11-ml glass bomb fitted with a break-off tip was charged with 2.0 mmoles of $^{11}B_5H_{11}$ (98% ^{11}B)[16] and 11.5 mmoles of $^{10}B_2H_6$ (96% ^{10}B). The tube was sealed, then warmed to 27°, and shaken for 5 hr. The calculated pressure of the B_2H_6 was 25 atm. Upon opening the tube and fractionating the contents through a −20, −45, −95, −135, −196° trap system, 0.1 mmole of $B_{10}H_{14}$, 0.4 mmole of n-B_9H_{15}, 0.5 mmole of B_5H_{11}, 0.2 mmole of B_4H_{10}, and 12.9 mmoles of B_2H_6 were isolated, respectively. From mass spectral data it was calculated that the B_2H_6 contained 73% ^{10}B and the B_5H_{11} contained 65% ^{10}B.[17] The value calculated for complete equilibration of all boron atoms was 68% ^{10}B. Integration of the ^{11}B nmr spectra of the n-B_9H_{15} and $B_{10}H_{14}$ obtained indicated that there was the same $^{10}B/^{11}B$ ratio in all positions in the molecules.

In an attempt to minimize boron exchange and still obtain isolable amounts of the higher boron hydrides from the reaction of $^{11}B_5H_{11}$ with $^{10}B_2H_6$, the reaction was repeated using liquid $^{10}B_2H_6$ but allowing only 0.5 hr for reaction. A Pyrex bomb was charged with 6.1 mmoles of $^{11}B_5H_{11}$ (98% ^{11}B) and 31.6 mmoles of $^{10}B_2H_6$ (96% ^{10}B), sealed, and warmed to 27° for 0.5 hr. It was then cooled to −196° and opened, and the contents were fractionated as in the above experiment. The recovered B_5H_{11} was shown by mass spectrometry to contain 65% ^{10}B as was the B_2H_6 recovered. This percentage is also the value calculated for complete equilibration of all boron atoms in both starting materials. No products were isolated in large enough quantities to obtain any information about them.

Discussion

The product distribution of the reaction of B_8H_{12} with B_2H_6 appears to be dependent on the ratio of the starting materials used. In previous work[5] where the mole ratio B_2H_6/B_8H_{12} was 18, n-B_9H_{15} and $B_{10}H_{14}$ were formed in yields of approximately 40% each. However, in this work where the mole ratio B_2H_6/B_8H_{12} was 5.8, the yield of n-B_9H_{15} was twice that of $B_{10}H_{14}$ with a total yield of 80%.

The ^{11}B nmr spectrum of the $B_{10}H_{14}$ obtained from the reaction of B_8H_{12} and $^{10}B_2H_6$ was very similar to that of normal $B_{10}H_{14}$ with one important difference: the area ratio of the triplet to doublet was not 4.00 as in normal $B_{10}H_{14}$. Ten spectra were carefully cut into the triplet and doublet portions and weighed. The average ratio of triplet to doublet was 3.12 ± 0.13. This indicates that within experimental error there are two less ^{11}B atoms contributing to the low-field triplet than for $^{n}B_{10}H_{14}$. This set of resonances in the spectrum of $B_{10}H_{14}$ has been assigned to the overlap of two doublets, one from 1,3,6,9 boron atoms and the other from the 5,7,8,10 boron atoms.[18,19] The low-field triplet of the labeled $B_{10}H_{14}$ is slightly asymmetrical. However, that portion of the triplet assigned to the 1,3,6,9 boron atoms appears to be only slightly less intense than the portion assigned to the 5,7,8,10 boron atoms. Therefore, we conclude that there are fewer ^{11}B atoms in both the 5,7,8,10 positions and the 6,9 or 1,3 positions. *A priori*, it would seem more probable that the ^{10}B label is in the exterior 6,9 positions rather than the interior 1,3 positions.

The mass spectrum of the $B_{10}H_{14}$ obtained is given in Table I. When this spectrum is compared with that of $^{n}B_{10}H_{14}$,[20] the parent peak appears to be m/e 122. A parent peak of m/e 122 agrees with the formula $^{10}B_2{}^{n}B_8H_{14}$ which is suggested by the analysis of the ^{11}B nmr data. Given that the two boron atoms added to the B_8 fragment from the $^{10}B_2H_6$ were 4% ^{11}B, it can be shown from probability calculations that the m/e 123 peak should be approximately 7.5% of the parent m/e 122 peak. The experimental spectrum shows the m/e 123 peak to be approximately 15% of the 122 peak. It is not unusual for the $P + 1$ peak to be more intense than that calculated from the parent peak;[21] however, the error here

---

[15] I. Shapiro and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 4787 (1959).

[16] The $^{11}B_5H_{11}$ was furnished by C. R. Phillips of this laboratory.

[17] It was determined empirically from the mass spectrum of $^{n}B_5H_{11}$ that

$$\% \, ^{10}B = \frac{I_{10}(100)}{I_{10} + (I_{11} - (0.19)I_{10})}$$

[18] R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

[19] The numbering system is that recommended for boron compounds in "Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds," available from Chemical Abstracts Service.

[20] I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 127.

[21] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 10.

TABLE I

MASS SPECTRUM OF THE B_{10} REGION OF THE DECABORANE OBTAINED FROM THE REACTION $^{10}B_2H_6 + {}^{n}B_8H_{12} \rightarrow {}^{10}B_2{}^{n}B_8H_{14}$

m/e	Rel intens (I/I_{118})	*m/e*	Rel intens (I/I_{118})
123	2.0	116	95.5
122	12.2	115	105.2
121	27.7	114	94.6
120	67.9	113	78.4
119	94.6	112	55.7
118	100.0	111	36.6
117	88.5	110	25.3

is probably too large to be explained by this reason alone and may indicate a higher ^{11}B content than expected. Still, the mass spectrum is consistent with the formulation $^{10}B_2{}^{n}B_8H_{14}$ for the $B_{10}H_{14}$ obtained from this reaction.

The ^{11}B nmr spectrum of the n-B_9H_{15} isolated from the reaction of B_8H_{12} with $^{10}B_2H_6$ has a multiplet with peaks at -21.2, -12.1, and -0.9 ppm and a set of two doublets at $+33.3$ and $+46.0$ ppm, respectively. The ratio of the relative intensity of the low-field multiplet to that of the high-field set of doublets is 1.67 ± 0.04. For n-$^{n}B_9H_{15}$ this ratio is 2.00. The chemical shifts of the peaks agree with those previously published for n-B_9H_{15}.[22] These results indicate that within experimental error there is one less ^{11}B atom represented in the low-field multiplet than there is in n-$^{n}B_9H_{15}$. The low-field multiplet has been tentatively assigned to the 1,4,5,6,7,9 boron atoms.[22–24]

The mass spectrum of the n-B_9H_{15} obtained in this experiment and that of n-$^{n}B_9H_{15}$ are given in Figure 3. The two spectra are nearly identical in the B_8 region whereas they differ considerably in the B_9 region.

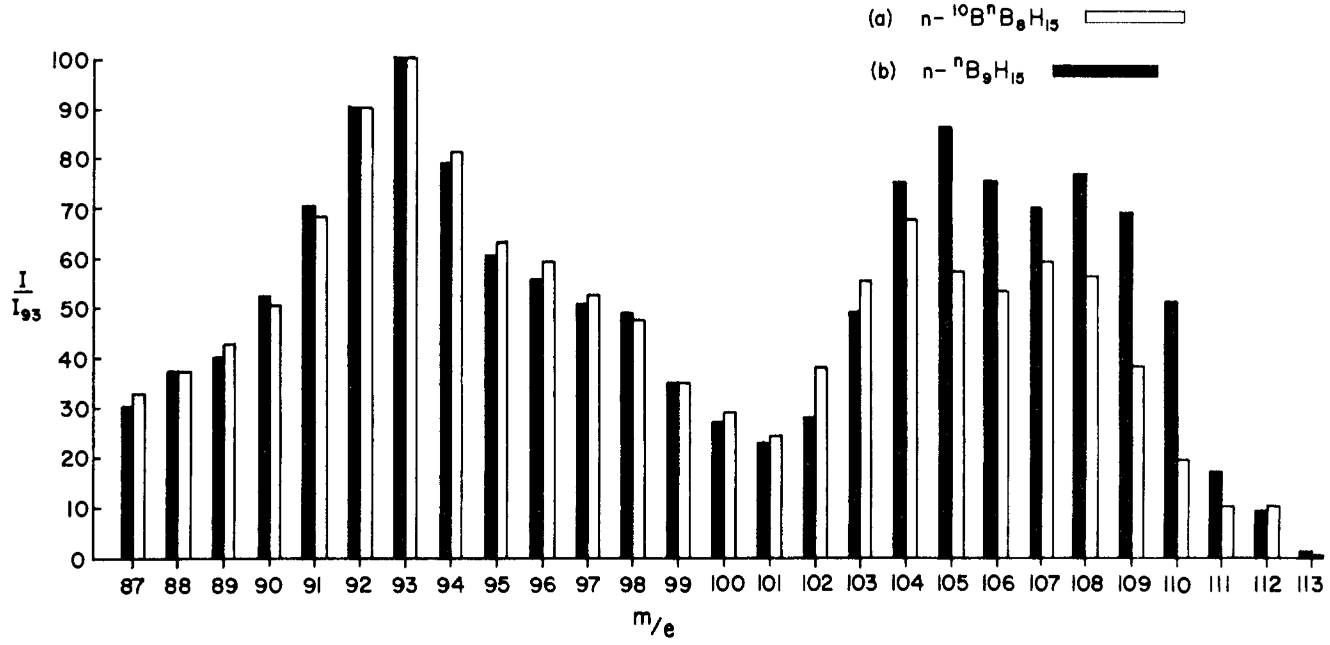

Figure 3.—Mass spectra of (a) n-$^{10}B^{n}B_8H_{15}$ and (b) n-$^{n}B_9H_{15}$.

However, the B_9 envelope of ^{10}B-labeled n-B_9H_{15} is nearly identical with the B_9 envelope for n-$^{n}B_9H_{15}$ except the former is displaced 1 mass unit lower (Figure 4). This analysis and the fact that the cutoff peak for n-$^{n}B_9H_{15}$ is 113 while that of the labeled n-B_9H_{15} is 112 indicate that the labeled n-B_9H_{15} has one extra ^{10}B atom per molecule. The ^{11}B nmr spectrum also agrees with the formulation n-$^{10}B^{n}B_8H_{15}$.

When the mass spectrum of n-$^{n}B_9H_{15}$ given by Ditter, Spielman, and Williams[7] is subtracted from our mass spectra of n-$^{n}B_9H_{15}$ and n-$^{10}B^{n}B_8H_{15}$, the residual intensities in the *m/e* 87–100 region agree very well with the mass spectrum of $^{n}B_8H_{12}$.[7] That the spectrum of B_8H_{12} is obtained is reasonable since Ditter, *et al.*,[7] have shown that a B_8 region larger than a B_9 region in the mass spectrum of n-B_9H_{15} is caused by the decomposition of n-B_9H_{15} to B_8H_{12} and B_2H_6 in the mass spectrometer. They also postulate that the BH_3 unit lost from n-B_9H_{15} comes from the 9 position. Since the B_8H_{12} formed when n-$^{10}B_8H_{15}$ decomposes appears to be n-^{10}B-$^{n}B_8H_{15}$, the one extra ^{10}B atom appears to be located in the 9 position in the labeled n-$^{10}B^{n}B_8H_{15}$ molecule.

The mechanism proposed to account for the products obtained from the reaction of $^{n}B_8H_{12}$ with $^{10}B_2H_6$ is given by the equations

$$
{}^{n}B_8H_{12} + {}^{1}/_{2}{}^{10}B_2H_6 \begin{array}{l} \nearrow n\text{-}{}^{10}B^{n}B_8H_{15} \\ \searrow i\text{-}{}^{10}B^{n}B_8H_{15} \end{array} \tag{1}
$$

$$
i\text{-}{}^{10}B^{n}B_8H_{15} \longrightarrow i\text{-}{}^{10}B^{n}B_8H_{13} + H_2 \tag{2}
$$

$$
i\text{-}{}^{10}B^{n}B_8H_{13} \longrightarrow n\text{-}{}^{10}B^{n}B_8H_{13} \tag{3}
$$

$$
i\text{-}{}^{10}B^{n}B_8H_{13} + {}^{1}/_{2}{}^{10}B_2H_6 \longrightarrow {}^{10}B_2{}^{n}B_8H_{16} \tag{4}
$$

$$
n\text{-}{}^{10}B^{n}B_8H_{13} + {}^{1}/_{2}{}^{10}B_2H_6 \longrightarrow {}^{10}B_2{}^{n}B_8H_{16} \tag{5}
$$

$$
{}^{10}B_2{}^{n}B_8H_{16} \longrightarrow {}^{10}B_2{}^{n}B_8H_{14} + H_2 \tag{6}
$$

Both B_9H_{15} species are postulated in step 1 since under the conditions of this experiment n-B_9H_{15} does

---

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

(23) P. C. Keller, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1966, p 51.

(24) The numbering system for n-B_9H_{15} is that given by W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 7.

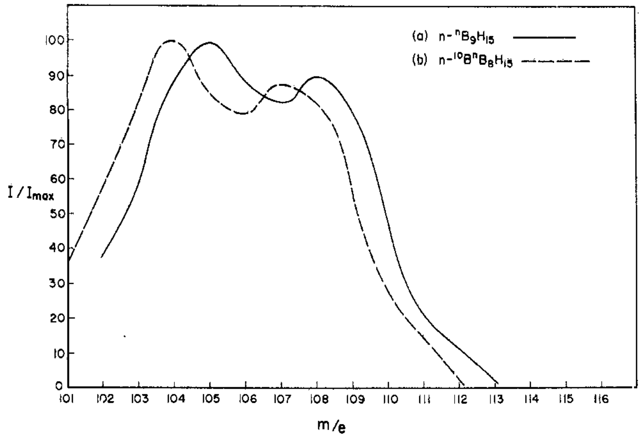

Figure 4.—Comparison of the B_9 region of the mass spectra of (a) n-$^{n}B_9H_{15}$ with that of (b) n-$^{10}B^{n}B_8H_{15}$.

not react with B_2H_6 to give $B_{10}H_{14}$ and under identical conditions i-B_9H_{15} has been shown to react with B_2H_6 to yield $B_{10}H_{14}$ but not n-B_9H_{15}.[6] The isolation of n-$B_{18}H_{22}$ from the residue of the reaction of B_8H_{12} with B_2H_6 suggests that i-B_9H_{15} is an intermediate in the reaction since n-$B_{18}H_{22}$ has been shown to be a decomposition product of i-B_9H_{15}.[3] We also postulate that $B_{10}H_{14}$ is formed by the insertion of a BH_3 unit into a B_9 unit rather than the simultaneous insertion of two BH_x units into a B_8 unit which has no precedence in borane interconversions. Steps 2 through 6 are the same as those reported in an accompanying paper for the reaction of i-B_9H_{15} with B_2H_6.[6]

The reaction of $^{n}B_8H_{12}$ with $^{10}B_2H_6$ was repeated using ^{11}B nmr to monitor the course of the reaction to search for direct evidence for the formation of i-B_9H_{15} as a reactive intermediate. That the spectrum of i-B_9H_{15} is not observed does not mean it is not an intermediate. It may simply mean that either the i-B_9H_{15} concentration is too low to be detected by the nmr instrument or if, a detectable concentration is formed, its resonances are obscured by those of the other species. The monitoring of this reaction also indicated that below about $-40°$ the rate is very slow and that between -40 and $-30°$ the rate increases sufficiently for the reaction to be useful in preparing higher hydrides.

The reaction of B_8H_{12} with liquid B_2D_6 yields n-B_9H_{15} and $B_{10}H_{14}$ which appear to have undergone extensive deuteration. The ^{11}B nmr spectrum (Figure 2(a)) of the $B_{10}H_{4.3}D_{9.7}$ consisted of a low-field doublet where the 1,3,6,9 and 5,7,8,10 overlapping doublets normally appear and a singlet where the 2,4 doublet normally appears in $B_{10}H_{14}$. The ^{11}B nmr spectrum of the n-$B_9H_{7.4}D_{7.6}$ (Figure 1(a)) contained a singlet at -4.1 ppm with a shoulder at -16.3 ppm and singlets at 33.1 and 47.2 ppm. All of these absorptions occur where there are doublets and multiplets in the spectrum of n-B_9H_{15}. From the ^{11}B nmr spectra of the n-$B_9H_nD_{15-n}$ and $B_{10}H_nD_{14-n}$, no specific deuterium labeling is apparent.

When the reaction was monitored by ^{11}B nmr, it was shown that B_8H_{12} first exchanges hydrogen for deuterium with B_2D_6 (eq 7). Then the $B_8H_nD_{12-n}$ reacts more slowly with the B_2D_6 to give n-$B_9H_nD_{14-n}$ and $B_{10}H_nD_{14-n}$ according to the mechanism proposed above. From the $B_8H_nD_{12-n}$ recovered from this experiment it appears that there are five or six hydrogen positions in B_8H_{12} that are taking part in the exchange. It is interesting to note that deuterium exchange takes place without boron exchange in the B_8H_{12}–B_2D_6 reaction. Such is also the case in the B_5H_9–B_2D_6 exchange reaction[25-27] although in that reaction all terminal hydrogens have been found to exchange. Since only five or six hydrogens were found to exchange in B_8H_{12}, the B_8H_{12} may react with B_2D_6 to produce higher hydrides before the exchange reaction reaches complete equilibration.

$$B_8H_{12} + B_2D_6 \longrightarrow B_8H_nD_{12-n} + B_2H_nD_{6-n} \qquad (7)$$

The n-$^{10}B^{n}B_8H_{15}$ and $^{10}B_2{}^{n}B_8H_{14}$ obtained when n-$^{n}B_9H_{15}$ was allowed to react with liquid $^{10}B_2H_6$ at 27° were identical within experimental error with the respective compounds formed by the reaction of $^{n}B_8H_{12}$ and $^{10}B_2H_6$ at $-30°$. In order to explain these results we accept the Ditter–Williams postulate that at room temperature n-$^{n}B_9H_{15}$ decomposes to give $^{n}B_8H_{12}$ and $^{1}/_{2}{}^{n}B_2H_6$ (eq 8). A rate constant for this decomposition,

$$n\text{-}^{n}B_9H_{15} \longrightarrow {}^{n}B_8H_{12} + {}^{1}/_{2}{}^{n}B_2H_6 \qquad (8)$$

in the absence of B_2H_6, has been measured previously.[7] The $^{n}B_8H_{12}$ formed by this reaction then reacts with the large excess of $^{10}B_2H_6$ according to the mechanism proposed in steps 1 through 6 to form n-$^{10}B^{n}B_8H_{15}$ and $^{10}B_2{}^{n}B_8H_{14}$. The $^{10}B_2H_6$ recovered from the reaction of n-B_9H_{15} with $^{10}B_2H_6$ contained 95% ^{10}B. The expected value, calculated from the quantities of reagents and according to the reaction given in eq 8, is 94% ^{10}B.

Since n-B_9H_{15} does not exchange hydrogen for deuterium in B_2D_6 at 0° but does at 27° and since both $^{10}B_2H_6$ and B_2D_6 exchange boron and deuterium, respectively, with n-B_9H_{15} at 27°, we postulate that n-B_9H_{15} is not the species which exchanges with B_2D_6 and $^{10}B_2H_6$, but that the n-B_9H_{15} dissociates according to eq 8 and the B_8H_{12} thus formed exchanges and reacts with the B_2D_6 according to equations similar to (1) through (7). The n-$B_9H_nD_{15-n}$ and $B_{10}H_nD_{14-n}$ obtained from the reaction of n-B_9H_{15} with B_2D_6 at 27° both contain less deuterium than the respective compounds obtained from the reaction of B_8H_{12} with B_2D_6 at $-30°$. This is explained by assuming that, at 27°, the rate of reaction of B_8H_{12} with B_2D_6 (eq 1) is faster than the rate of exchange of B_8H_{12} with B_2D_6 (eq 7). To explain the results of the reaction of B_8H_{12} with B_2D_6 at $-30°$ we postulated that the opposite was true and that the reaction given by eq 7 was faster than that represented by eq 1. To attempt to justify the apparent discrepancy we suggest that the two reaction rates have a different temperature dependency.

The reactions of n-B_9H_{15} and B_2D_6 at 27° which were carried out for different lengths of time show that the n-$B_9H_nD_{15-n}$ obtains a constant deuterium content

---

(25) W. S. Koski, J. J. Kaufman, L. Friedman, and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

(26) J. J. Kaufman and W. S. Koski, *ibid.*, **24**, 403 (1956).

(27) W. S. Koski, J. J. Kaufman, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **79**, 2382 (1957).

only after about 18 hr. Since B_8H_{12} has been shown to react and exchange much faster than this even at −30°, the rate of decomposition of n-B_9H_{15} to B_8H_{12} and $^1/_2B_2H_6$ (eq 8) must be rather slow. This is also supported by the results of the reaction of $^{10}B_2H_6$ with n-B_9H_{15} at 27°. The ^{11}B nmr spectrum of the n-$B_9H_nD_{15-n}$ obtained form the reaction of n-B_9H_{15} with B_2D_6 (Figure 1(d)) indicates that there is specific labeling in the molecule. However, since the ^{11}B nmr spectrum of n-B_9H_{15} has not been unambiguously assigned, the positions of the deuterium labeling cannot be assigned. The ^{11}B nmr spectrum of the $B_{10}H_nD_{14-n}$ obtained (Figure 2(b)) indicates only that there is less deuterium present than in the $B_{10}H_nD_{14-n}$ recovered from the reaction of B_8H_{12} with B_2D_6 at −30° and does not necessarily indicate any specific labeling.

In the reaction of i-B_9H_{15} with excess B_2D_6, the ^{11}B nmr spectrum of the decaborane recovered was considerably different from the normal spectrum of $B_{10}H_{14}$. The downfield triplet collapsed to a poorly resolved broadened doublet. The upfield doublet collapsed to a singlet. Thus, it appears that the decaborane has undergone extensive deuteration in almost all positions. Mass spectral analysis of the hydrogen–deuterium mixture obtained from the pyrolysis of the $B_{10}H_{14}$ showed that the average composition of the molecule was $B_{10}H_{6.8}D_{7.2}$. Exchange experiments involving $B_{10}H_{14}$ and i-B_9H_{15} with B_2D_6 under the same conditions showed that neither of the species exchanged deuterium with B_2D_6.

In an attempt to monitor the reaction by ^{11}B nmr, i-B_9H_{15} and B_2D_6 were sealed in an nmr tube, but no signal was obtained for i-B_9H_{15}. This is attributed to the low solubility of i-B_9H_{15} in B_2D_6 at or below −30° which is the decomposition temperature of i-B_9H_{15}. When the nmr tube was warmed slightly above −30° to allow the i-B_9H_{15} to melt in the B_2D_6, melting was not observed but slight decomposition of the solid was noticed. The mass spectrum of the recovered B_2D_6 showed a small but significant change in the relative amplitudes of the m/e 31 and 32 peaks as compared to the spectrum of the starting B_2D_6 indicating that a small amount of exchange had taken place.

The results of this experiment are quite surprising in view of the fact that previous work with the same reaction under the same conditions but using $^{10}B_2H_6$ instead of B_2D_6 resulted in a decaborane molecule specifically labeled in the 6,9 and 5,7,8,10 positions. Since under the experimental conditions neither i-B_9H_{15} nor $B_{10}H_{14}$ undergoes deuterium exchange, an intermediate in the reaction must be exchanging with the B_2D_6. The intermediates which have been postulated for this reaction are i-B_9H_{13}, n-B_9H_{13}, and a $B_{10}H_{16}$ species, none of which can definitely be established as the exchanging species; and, indeed, one or all of these species may be exchanging.

A B_9H_{13} species has been postulated to exist in an environment free of electron-donating ligands[28] and has recently been postulated as an unstable intermediate in the conversion of $B_9H_{13}S(CH_3)_2$ to $B_{10}H_{14}$ and $B_{18}H_{22}$.[29] The conversion of an i-B_9H_{13} species to an n-B_9H_{13} species with the possibility of an equilibrium existing has been postulated from previous work in this laboratory.[6] In the reaction of B_8H_{12} with $^{10}B_2H_6$, mass spectra combined with integrations of the ^{11}B nmr spectra of the decaborane obtained indicated that there was little or no ^{10}B in the 2,4 positions. However, the decaborane obtained from the reaction of B_8H_{12} with B_2D_6 was extensively deuterated in the 2,4 positions (Figure 2(b)). These observations lead us to believe that there is not a rapid equilibrium established between i-B_9H_{13} and n-B_9H_{13} since this would lead to a migration of boron atoms throughout the B_9 structure and would necessarily incorporate ^{10}B into the 2,4 positions of the decaborane formed. The B_9H_{13} species could have open-orbital structures which would account for the ease of exchange of hydrogen and deuterium and for the presence of deuterium throughout the decaborane molecule.

Acknowledgment.—We gratefully acknowledge the support of the National Science Foundation through Grant GP4944 and the Public Health Service for a postdoctoral fellowship to R. M.

---

[28] W. N. Lipscomb, *Inorg. Chem.*, **3**, 1683 (1964).

[29] J. Plesek, S. Hermanek, B. Stibr, and F. Hanousek, *Collection Czech. Chem. Commun.*, **32**, 1095 (1967).