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.

Acknowledgment.—The authors gratefully acknowledge the support of the National Science Foundation through Grant GP4944.

(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

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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 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]

$$B_2H_6 \rightleftarrows 2BH_3 \qquad (1)$$

$$B_2H_6 + BH_3 \rightleftarrows B_3H_9 \qquad (2)$$

$$B_3H_9 \rightleftarrows B_3H_7 + H_2 \qquad (3)$$

$$B_3H_7 + BH_3 \rightleftarrows B_4H_{10} \qquad (4)$$

$$B_4H_{10} \rightleftarrows B_4H_8 + H_2 \qquad (5)$$

$$B_4H_8 + BH_3 \rightleftarrows B_5H_{11} \qquad (6)$$

$$B_5H_{11} \rightleftarrows B_5H_9 + H_2 \qquad (7)$$

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

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[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).

described elsewhere.[7,8] The vacuum lines used were constructed so that all samples of unstable materials were transferred through as short a distance as possible in order to minimize decomposition.

Boron and hydrogen analyses were obtained by decomposing the samples to elemental boron and hydrogen in a hot quartz tube. The hydrogen was measured using a calibrated Toepler system. The boron was dissolved in hot nitric acid and titrated using the standard identical pH mannitol method.[9]

Nuclear magnetic resonance spectra were obtained using a Varian spectrometer operating at 32.1 MHz for ^{11}B and 100 MHz for ^{1}H. Low-temperature spectra were obtained with standard Varian 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. In general, the spectra reported were recorded between -20 and $-30°$ in order to avoid decomposition of the samples.

Mass spectra were obtained with Consolidated Electrodynamics Corp. Model 21-620 and Associated Electrical Industries Model MS-9 mass spectrometers. When the MS-9 was used to record spectra of unstable boranes, it was allowed to cool to room temperature overnight before the samples were admitted to the instrument, unless otherwise specified. The spectra were recorded before the instrument had time to warm to normal operating temperature. This procedure was shown to give spectra that contained fewer peaks arising from decomposition of the sample in and around the hot source. The relative intensities of the peaks obtained in this manner are probably affected somewhat by the continual warming of the source during the recording of the spectra. However, we believe that the decrease in sample decomposition outweighs the disadvantage of not having a constant-temperature source.

Infrared spectra were recorded with a Perkin-Elmer Model 137 Infracord. All spectra were taken of gas-phase samples in a 5-cm cell unless otherwise specified.

Gas-Phase Copyrolysis of B_2H_6 and B_5H_9.—The pyrolyses were carried out in a circulation system consisting of a circulating pump (rate estimated at 3–6 l./min at 0.5 atm) leading to a pyrolysis "U" trap maintained at 140° which was followed immediately by a quenching "U" trap cooled to $-20°$ by a salt–ice bath. The gas then flowed through a diborane ballast bulb and returned to the inlet of the circulating pump. The volume of the system was 2.2 l.; pressure was monitored by a mercury manometer. In a typical pyrolysis, the quenching trap was charged with 10–20 ml of liquid B_5H_9 and approximately 44 mmol of B_2H_6, the hot trap was heated to 140°, a salt–ice bath was placed around the quenching trap, and circulation commenced. During pyrolysis there was a negligible change in total pressure. After every 8–12 hr the quenching trap was cooled to $-196°$, circulation continued until all condensables were trapped out, and then hydrogen was removed and diborane was replenished as necessary to maintain a total pressure of about 0.5 atm. After 60 hr, during which time 78 mmol of hydrogen was formed and nearly the same amount of diborane was consumed, the pyrolysis was terminated.

Separation of Products.—Diborane, tetraborane(10), and most of the pentaborane(9) and pentaborane(11) were vacuum distilled from the product mixture cooled by a $-63°$ slush bath. When distillation had clearly ceased, the $-63°$ slush was replaced by a $-20°$ salt–ice bath and a further fraction was removed.

Products retained in the $-20°$ trap were subjected to a low-temperature crystallization at $-78°$ from *n*-pentane, *in vacuo*, and nearly pure n-B_9H_{15} crystals were obtained. The filtrate from this crystallization and the material which passed the $-20°$ trap were then fractionated using a low-temperature fractionating column.[10]

The products isolated during the first fractionation and the approximate temperatures at which they came off the column are as follows: B_5H_9 ($-85°$), B_5H_{11} ($-78°$), B_6H_{12} ($-72°$), B_6H_{10} ($-68°$), an unknown B_6 or B_7 hydride $-(68°)$, B_8H_{12} ($-50°$), an unknown mixture of B_8 hydrides ($-45°$), B_8H_{16} ($-40°$), $B_{10}H_{16}$ ($-38°$), n-B_9H_{15} ($-30°$), i-$B_{10}H_{16}$ ($-25°$). $B_{10}H_{18}$ ($-15°$), and $B_{10}H_{14}$ ($-5°$). Pentaborane(9), pentaborane(11), and hexaborane(12) were all obtained in a very pure state from the first fractionation; however, the rest of the materials required further purification, usually by repeated fractionations. The temperature at which any one material was removed from the column varied by as much as 10° from one fraction to another. The exact temperature of removal seemed to depend on the purity of sample as well as the pressure that was maintained during the fractionation.

Separation and purification of the products formed in the pyrolysis was indeed the most difficult part. As will be pointed out later, some of the compounds could not be purified even with repeated fractionations and attempted fractional crystallizations. Probably the main reason purification was so difficult is that for every 100 hr, or so, of pyrolysis most of the boron hydrides were present in 1–2-mmol quantities. This, along with the fact that all the compounds when not pure readily decomposed above $-20°$ restricted separation methods to relatively simple processes.

Identification of Products.—The well-characterized boron hydrides (B_5H_{11}, B_6H_{12}, B_6H_{10}, n-B_9H_{15}, and $B_{10}H_{14}$) were identified on the basis of volatility and their ^{11}B nmr spectra.[2,11] Tetraborane(10) was identified by its infrared spectrum.[12] The identification of the other products is given in more detail below.

(a) **Unknown B_6 or B_7 Hydride.**—A material left the low-temperature fractionating column at $-68°$ and in one instance was shown to be pure B_6H_{10}. In general, this material could never be satisfactorily purified and the ^{11}B nmr of the mixture consisted of a sharp doublet at -14.2 ppm, $J = 158$ cps, a second sharp doublet at 13.9 ppm, $J = 167$ cps, and a third doublet at 51.6 ppm, $J = 157$ cps. The sum of the intensity of the two doublets at -14.2 and 13.9 ppm was 5.06 times the intensity of the doublet at 51.6 ppm. In this sample the peak at -14.2 ppm was twice as intense as the one at 13.9 ppm. In a second sample where the resonance at 13.9 ppm was four times that at -14.2 ppm, the integration was 4.15. The only result of attempts to purify mixtures by repeated fractionation and fractional crystallization from *n*-pentane solution was a change in the ratio of intensities of the various peaks. When a sample of the mixture was allowed to warm to room temperature, it bubbled furiously and turned yellow. The doublet at -14.2 ppm in the ^{11}B nmr spectrum nearly disappeared after decomposition at room temperature for 15 min and the upfield doublet became asymmetrical with an increase in the intensity of the highest field member of the doublet. No other distinct new resonances were observed in the spectrum; however, a general rise in the base line was noted which may indicate one or more broad signals.

The mass spectrum of one sample of this mixture which had about equal intensities in the ^{11}B nmr peaks at -14.2 and 13.9 ppm gave a rather large B_2 region, a B_4 region one-fifth as large as the B_2, a B_5 region equal to the B_6 region which was roughly half the B_2 region, a B_7 region one-twentieth the B_2 region, and a very small B_8 region with a cutoff at m/e 100.

(b) **B_8H_{12}.**—This material is usually isolated with the mixture of unknown B_8 hydrides since B_8H_{12} is only slightly more volatile than the other products of this fraction: a very careful fractionation using the low-temperature column afforded nearly pure B_8H_{12} identified by its ^{11}B nmr spectrum and by converting it to $B_8H_{12}\cdot N(CH_3)_3$.[13]

(c) **Unknown B_8 Hydrides.**—The material remaining after the removal of B_8H_{12} could not be satisfactorily separated.

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

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

(9) J. R. Martin and J. R. Hages, *Anal. Chem.*, **24**, 182 (1952).

(10) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **8**, 2183 (1969).

(11) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **3**, 438 (1964).

(12) L. V. McCarty, G. C. Smith, and R. S. McDonald, *Anal. Chem.*, **26**, 1027 (1954).

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

Repeated attempts at fractionation as well as fractional recrystallization from *n*-pentane, propane, and methylene chloride failed to yield a product with a reproducible ^{11}B nmr spectrum. The ^{11}B nmr spectrum in general consisted of an intense doublet at 13.2 ppm, $J = 170$ cps, having a low-field shoulder, a much smaller doublet at 40 ppm, $J = 152$ cps, and a high-field singlet at about 59 ppm. The doublet at 13.2 ppm and the singlet at 59 ppm appeared to have a nearly constant relative intensity relationship. Likewise, the doublet at 40 ppm and the low-field shoulder on the doublet at 13.2 ppm appeared to go together. However, the relative intensity of the two sets of peaks changed so much with respect to each other that they appear to belong to different compounds.

Mass spectra of this mixture showed a definite cutoff at *m/e* 100 thus substantiating the belief, derived from volatilities, that it is a mixture of B_8 hydrides. The mass spectra, taken on both the MS-9 and the CEC Model 21-620 mass spectrometers, gave reasonable fragmentation envelopes for B_8 hydrides in the B_8, B_7, and B_6 regions. However, the B_5 and B_4 regions were of about equal intensity and were about twice as intense as the B_8 region. Also, there was a very large B_2 region.

(d) **B_8H_{16}.**—This new boron hydride appears to be a moderately unstable compound; it is probably more stable than B_8H_{12} but less stable than B_6H_{12} or *n*-B_9H_{15}. The material was observed to crystallize on the low-temperature column at −35° and was crystallized from propane at −126°; however, crystallization was not readily effected in isolated samples. As neither vapor pressure nor melting point could be used as a criterion for purity, the cleanness of its ^{11}B nmr spectrum was used. The ^{11}B nmr spectrum (Figure 1) consists of a broad singlet-like peak at 13.9 ppm with a high-field shoulder at 17.3 ppm, a poorly resolved structure which appears to have some doublet character at 44.5 ppm, and a well-resolved doublet at 56.8 ppm ($J =$ 180 cps) which slightly overlaps the resonance at 44.5 ppm. For several of the purest samples the integrated areas of low-field resonance to the combined high-field structures were in the ratios 1.70, 1.73, and 1.73 in good agreement with 1.67 expected for a 5–3 distribution in a B_8 hydride. In addition, the integrated areas of the structure at 44.5 ppm to the doublet at 56.8 ppm were 2.17 and 1.96, in good agreement with the assignment of three boron atoms to the total high-field structures.

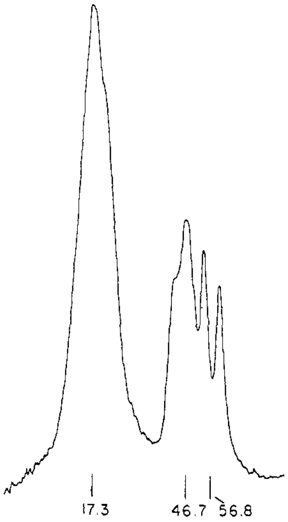

Figure 1.—The 32.1-MHz ^{11}B nmr spectrum of B_8H_{16}.

The 100-MHz ^1H nmr spectrum of B_8H_{16} is very uninformative. It consists of at least two-quartets which very badly overlap the bridge hydrogen resonance at 1.9 ppm. The overlap is so bad that a reasonable integration of the relative intensities of terminal protons to bridge protons could not be made.

Elemental analyses of five samples of the compound gave H/B ratios of 2.04, 1.94, 2.06, 1.99, and 1.98 in excellent agreement with the value of 2.00 expected for B_8H_{16}. The observed molecular weight, isopiestic *vs.* B_6H_{10} in approximately 1 mol % propane solution at −78°, was 101 (calculated for B_8H_{16} 102.4).

The mass spectra obtained using the MS-9 mass spectrometer and introducing the sample through the cold inlet system gave a cutoff at *m/e* 126. The B_{10} region of the spectrum was twice the B_9 region which was slightly larger than the B_8 region. The B_6 region was approximately equal to the B_{10} region while the B_5 region was at least 10 times the B_{10} region. A second spectrum was obtained using the MS-9 mass spectrometer except that the sample was introduced through a spiral adapter which fit into the duct inlet probe. The pressure of the sample had to be controlled by varying the temperature of a slush bath around the sample. Again, with this method of introducing the sample, the cutoff was at *m/e* 126. However, the relative intensities of the B_7, B_8, B_9, and B_{10} regions were all approximately equal. The B_6 region was at least 5 times as intense as the B_{10} while the B_5 region was very large. However, when the spectrum was recorded using the CEC Model 21-620 mass spectrometer, the apparent cutoff was *m/e* 100 with B_9 and B_{10} regions very small compared to the B_8 region. As with the MS-9 the B_6 and B_5 regions were exceptionally large when compared with the B_8 region.

(e) **$B_{10}H_{16}$.**—Very minor amounts of $B_{10}H_{16}$ were isolated during purification of B_8H_{16} and it was probably the major impurity in impure samples of B_8H_{16}. It was isolated nearly pure by very careful column purification of a large sample of B_8H_{16}. The product was further purified by recrystallization from *n*-pentane at −120°. The material thus isolated was a solid at room temperature and gave a mass spectrum consistent with the one published for the known $B_{10}H_{16}$.[14] The ^{11}B nmr spectrum of the material in *n*-pentane solution consisted of a doublet at 13.3 ppm, $J = 166$ cps, and a singlet at 57 ppm consistent with the ^{11}B nmr spectrum described by Lipscomb[2] for $B_{10}H_{16}$.

(f) ***i*-$B_{10}H_{16}$.**—Very careful low-temperature column fractionation of the material with volatility between *n*-B_9H_{15} and $B_{10}H_{14}$ gave two distinct fractions. The most volatile, *i*-$B_{10}H_{16}$, distilled from the column at −25 to −30° and crystallized very readily while the second, $B_{10}H_{18}$, which could not be readily removed from the column below −15°, was never observed to crystallize. The ^{11}B nmr spectrum, Figure 2 of *i*-$B_{10}H_{16}$ had a doublet-like resonance at 12.4 ppm and a high-field slightly symmetrical doublet at 50.4 ppm, $J = 179$ cps. The integrated intensities of low-field to high-field resonances on three samples were 3.69, 3.72, or an average of 7.9:2.1 normalized to a ten-boron molecule.

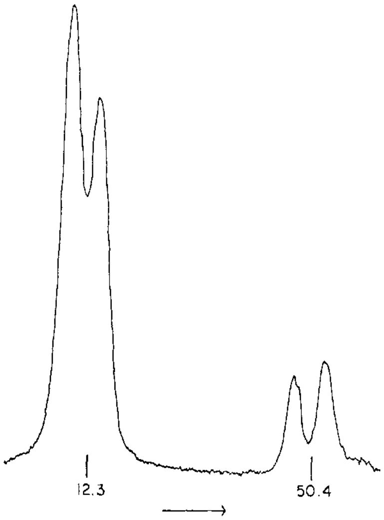

Figure 2.—The 32.1-MHz ^{11}B nmr spectrum of *i*-$B_{10}H_{16}$.

The ^1H nmr spectrum consists of two overlapping quartet

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[14] L. H. Hull, U. V. Subbanna, and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 3969 (1964).

resonances at low field, δ 2.4 ppm (J = 161 cps) and δ 0.5 ppm (J = 167 cps), arising from terminal protons and a broad bridge proton singlet at high field, δ 2.0 ppm.

The compound i-$B_{10}H_{16}$ does not inflame spontaneously in air as do most of the other materials studied. It also seems quite stable when pure and the infrared spectrum changed only slightly after remaining on AgCl plates for 18 hr at room temperature.

The mass spectrum recorded using the MS-9 had a cutoff at m/e 126. Even when the ionizing voltage was reduced to 8 V, where the spectrum completely disappeared, no higher peaks were observed. The mass spectral envelopes decrease in intensity down to the B_6 region as is expected for a B_{10} hydride.[15] However, the B_6 region is as intense as the B_7 region and the B_5 region is as intense as the B_{10} region. In fact, the spectrum from m/e 64 to 10 is in good agreement with that of B_5H_9.[15]

Analysis for hydrogen and boron gave H/B ratios of 1.71, 1.76, and 1.71 on the three samples. The composition $B_{10}H_{17}$ is not in accord with other data (nmr) and of the two possible formulas we prefer i-$B_{10}H_{16}$ to $B_{10}H_{18}$ on the basis of mass spectrometric studies. In any event, a complete single-crystal X-ray study has been undertaken.

(g) **$B_{10}H_{18}$.**—The ^{11}B nmr spectrum of this compound is shown in Figure 3. The integrated relative intensity of the low-field group of resonances to the high-field doublet is 4.09. The broad peak at −5.2 ppm appeared to change in intensity with respect to the doublet at 12.0 ppm even between samples that integrated and analyzed the same. Moreover, the relative intensities of these two resonances appeared to vary as a function of temperature increasing in intensity but decreasing in resolution as the sample was cooled. In contrast to this the highest field doublet increased greatly in resolution as the temperature of the sample was lowered.

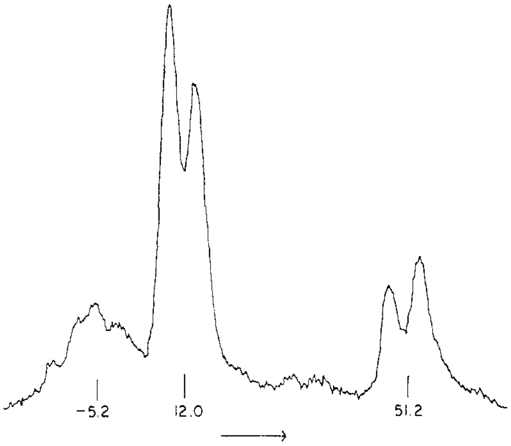

Figure 3.—The 32.1-MHz ^{11}B nmr spectrum of $B_{10}H_{18}$.

The ^1H nmr spectrum of $B_{10}H_{18}$ is rather nondescript. It consists of a quartet at −0.6 ppm, J = 169 cps, due to terminal hydrogens and a broad bridge hydrogen singlet at 2.1 ppm. In addition, there appear to be at least two more terminal hydrogen quartets badly overlapping the quartet at −0.6 ppm and the singlet at 2.1 ppm. Although an accurate integration could not be obtained for the ^1H spectrum because of the overlap of terminal and bridge resonances, a crude integration indicates that the ratio of terminal to bridge hydrogens is somewhat greater than 2.0.

The mass spectrum of the $B_{10}H_{18}$ had a cutoff at m/e 126. The spectrum was typical of a B_{10} hydride from the B_{10} region down to the B_6 region. However, as with all these compounds the B_5 region was about 1.5 times as intense as the B_{10} region. The molecular weight, determined on two samples by vapor pressure lowering of n-pentane, was between 121 and 125.

Analyses for hydrogen and boron on three different samples gave hydrogen to boron ratios of 1.85, 1.82, and 1.82.

Decomposition of $B_{10}H_{18}$.—During the workup of one of the pyrolyses, the less volatile products (those below n-B_9H_{15} in volatility) were accidently allowed to remain at room temperature for several hours. During this time considerable decomposition took place as indicated by formation of greenish yellow residue and considerable hydrogen evolution. No $B_{10}H_{18}$ was isolated when the decomposition mixture was fractionated. Instead, an abnormally large amount of i-$B_{10}H_{16}$ was isolated.

To study this decomposition more carefully, three samples of $B_{10}H_{18}$ were allowed to decompose at room temperature for periods of 5, 12, and 17 hr. The products and the range of mole per cent product isolated, based on $B_{10}H_{18}$ decomposed, are as follows: H_2, 10–40%; B_2H_6, 28%; B_5H_9, 43–55%; B_4H_{10}, <10%; n-B_9H_{15}, 10–50%; $B_{10}H_{16}$, 25–35%.

Pyrolyses under Different Conditions.—In the course of this investigation many pyrolyses were carried out under several different conditions. Basically, the copyrolysis described in the preceding section is representative. However, other reagents were present at times and in other reactions the temperature of the quenching "U" trap was changed. Variations on conditions and qualitative changes in product distribution for several reactions are noted below. It should be pointed out that no quantitative data of product yields were collected because of loss of products by decomposition during the workup.

(a) **Copyrolysis of B_2H_6 and B_5H_9 with B_5H_{11} Present.**—When the B_5H_9 recovered from the above described reaction was used for additional pyrolysis without careful purification, the concentration of B_5H_{11} increased until after some five 60-hr pyrolyses the recovered pentaborane was approximately a 50:50 mixture of B_5H_9–B_5H_{11}. The B_5H_{11} was probably formed by the pyrolysis of B_2H_6. As the concentration of B_5H_{11} increased the distribution of products changed considerably. B_6H_{12} was sharply increased; B_6H_{10} was not noticeably changed; the unknown B_6 or B_7 hydride decreased somewhat; B_8H_{12} increased sharply; the unknown mixture of B_8 hydrides was apparently unchanged; B_8H_{16} was only found when B_5H_{11} was present; $B_{10}H_{16}$ appeared unchanged; n-B_9H_{15} increased very sharply; i-$B_{10}H_{16}$ decreased sharply; $B_{10}H_{18}$ increased somewhat; and $B_{10}H_{14}$ did not change noticeably.

(b) **Copyrolysis of B_2H_6 and B_5H_9 with Quenching at 0°.**—This pyrolysis was carried out in exactly the same manner as the ones described above except the −20° salt–ice quenching bath was replaced with a 0° ice bath. The yields of n-B_9H_{15} and $B_{10}H_{14}$ increased very sharply. The unknown mixture of B_8's and B_8H_{16} were found in trace amounts while the other hydrides could not be isolated in identifiable quantities. The formation of hydrogen and the consumption of B_2H_6 also decreased to about 1 mmol/hr.

(c) **Copyrolysis of B_2H_6 and B_5H_9 with Quenching at −78°.**—In order to carry out this experiment the pyrolysis apparatus was modified such that the gas was made to pass through a B_5H_9 reservoir before reentering the circulating pump. At the start of pyrolysis the B_5H_9 was placed in the reservoir which was held at −20° and a −78° bath was placed around the quenching trap. Every 4–6 hr during the pyrolysis the B_5H_9 was fractionated from the other products in the quenching trap and condensed back into the reservoir. The pyrolysis was carried out for 21 hr during which time 23 mmol of hydrogen was formed. Upon separation of the products of this reaction, only a trace of material less volatile than B_5H_9 was found.

(d) **Pyrolysis of B_2H_6.**—The pyrolysis of B_2H_6 using our trapping system afforded higher hydrides not previously reported as pyrolysis products of B_2H_6. In addition to the hydrides usually observed (B_4H_{10}, B_5H_9, B_5H_{11}, and $B_{10}H_{14}$), we were able to isolate and identify B_6H_{10} and n-B_9H_{15} when the quenching trap was maintained at 0°. When the pyrolysis was carried out holding the quenching trap at −20°, B_6H_{12} and the unknown mixture of B_8 hydrides was also isolated. The volume distribution of products from the latter pyrolysis was as follows: B_4H_{10}, 3%; B_5H_{11}, 46%; B_5H_9, 35%; B_6H_{10}, 3%; B_6H_{12}, 2%; unknown B_8 hydrides, 1%; B_8H_{16}, 1%; n-B_9H_{15}, 9%. No attempt was made to isolate $B_{10}H_{14}$ and the other higher boron hydrides were not

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[15] I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, *Advan. Chem. Ser.*, **No. 32**, 127 (1961).

formed in sufficient quantities to isolate. The amount of hydrogen formed did not appear to differ significantly from that formed when B_5H_9 was present.

(e) **Copyrolysis of $^{10}B_2H_6$ with $^{n}B_5H_9$.**[16]—The pyrolysis apparatus was charged with 36 mmol of $^{10}B_2H_6$, 96% ^{10}B,[17] and 26 mmol of $^{n}B_5H_9$. The pyrolysis was carried out as described above. A total of 75 mmol of $^{10}B_2H_6$ was added to the system during the pyrolysis which lasted 42 hr and 66 mmol of H_2 was formed. The diborane recovered, 9 mmol, gave a mass spectrum which was most consistent with the compound containing 91% ^{10}B.[4] Tetraborane, pentaborane(11), hexaborane(12), and octaborane(16) did not appear to be present. About 1 mmol each of the unknown B_6 or B_7 hydride and the unknown B_8 hydrides was obtained while only a trace of hexaborane(10) and octaborane(12) were found. A mixture of $B_{10}H_{16}$ and $B_{10}H_{18}$, approximately 0.5 mmol total, was collected but not separated.

Very pure pentaborane(9), 33 mmol, was isolated. The ^{11}B nmr spectrum of this material appeared perfectly normal yielding an integration of 3.74 for the ratio of the relative intensity of low-field doublet to high-field doublet. However, the mass spectrum of the sample was drastically changed from that of $^{n}B_5H_9$. When the m/e 59–64 region of the spectrum was stripped of contributions due to loss of hydrogen atoms,[18] relative parent ion contributions for the various combinations of ^{10}B and ^{11}B were as follows: $^{11}B_5H_9^+$, 21.8; $^{11}B_4{}^{10}BH_9^+$, 27.9; $^{11}B_3{}^{10}B_2H_9$, 16.1; $^{11}B_2{}^{10}B_3H_9^+$, 7.3; $^{11}B^{10}B_4H_9^+$, 8.8; $^{10}B_4H_9^+$, 18.1. This set of parent ion intensities indicates that the recovered pentaborane(9) contained 58% ^{11}B.

A sample containing 3.0 mmol of n-B_9H_{15} was isolated by low-temperature column fractionation and purified by two low-temperature recrystallizations from n-pentane solvent. The ^{11}B nmr spectrum (Figure 4) of the n-B_9H_{15} indicated that specific labeling had occurred. The relative integrated intensity ratios for the low-field multiplet to the midfield doublet to the high-field doublet are 4.5:0.65:1.0 (found for nonlabeled n-B_9H_{15} 6:2:1[1]). Likewise, the mass spectrum of the n-B_9H_{15} was very different from that of n-$^{n}B_9H_{15}$.[4] It had an apparent cutoff at m/e 111. The B_8 and B_9 regions were of about equal intensity with the largest peak in each region m/e 90 and 101, respectively. The decrease in the intensity from the B_7 region down through the B_2 region appeared perfectly normal for n-B_9H_{15}. Although this sample had been purified a number of times, a small but persistent set of peaks was found for a B_{10} hydride which just slightly overlapped the B_9 region of the n-B_9H_{15}. From the relative intensities obtained under high resolution, of the m/e 10 peak and the m/e 11 peak due only to ^{11}B, the recovered n-B_9H_{15} was calculated to contain 67% ^{10}B.[19]

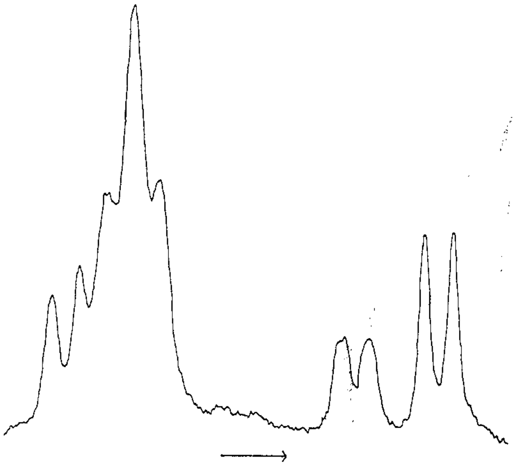

Figure 4.—The 32.1-MHz ^{11}B nmr spectrum of ^{10}B labeled n-B_9H_{15} from copyrolysis of $^{10}B_2H_6$ and $^{n}B_5H_9$.

The $B_{10}H_{14}$ isolated in this experiment gave a ^{11}B nmr spectrum which appeared normal but integrated with a low-field multiplet to high-field doublet ratio of 3.4 (expected $^{n}B_{10}H_{14}$ is 4.0[8]). The mass spectrum of the sample obtained with the MS-9 had a cutoff at m/e 121 with the most intense peak at m/e 112. From the relative intensities of the m/e 10 peak and the m/e 11 peak due to ^{11}B, the $B_{10}H_{14}$ was calculated to contain 73% ^{10}B.

Discussion

Let us first summarize what is known about the various new boron hydrides isolated in this work. A B_6 or B_7 hydride was obtained which apparently has volatility and solubility characteristics nearly identical with those of B_6H_{10}, as repeated column fractionation and attempted low-temperature crystallizations from n-pentane did not separate the two. The new B_6 or B_7 hydride was formed in very small yields. It also appears to be very unstable as decomposition residues were left behind when samples of the hydride were transferred in the vacuum system. The mass spectrum of a mixture of the unknown B_6 or B_7 hydride and B_6H_{10} also indicates the material is very unstable and that diborane is one of the products of decomposition. While the exact formula for this compound was not obtained, the rationale for calling it B_6 or B_7 hydride is based on volatility and the mass spectral data.

There were at least two and maybe three new B_8 hydrides formed during the pyrolyses. One compound obtained from the initial fractionation was fairly easily purified by refractionation and crystallization from n-pentane. A variety of data support the assigned formula B_8H_{16}. The other portion of this volatility fraction, however, could not be purified enough to allow a determination of the hydrogen to boron ratio. The mass spectrum of this impure hydride is typical of what would be expected for a B_8 hydride, except that there are very large B_5 and B_2 regions thus suggesting that the unknown B_8 hydride(s) decompose(s) to give diborane and one of the pentaboranes in the mass spectrometer. The conclusion that this portion is either one or two B_8 boron hydrides is based on the mass spectral and volatility data.

Two new boron hydrides were isolated from the copyrolyses with volatilities between n-B_9H_{15} and $B_{10}H_{14}$. The most volatile of the new hydrides is rather stable thermally and apparently does not react very rapidly with air. Arguments have been made in the Experimental Section for preferring the formula i-$B_{10}H_{16}$. The second new hydride in this volatility range is well characterized as $B_{10}H_{18}$.

The pyrolysis carried out where different hydrides were present initially indicates that all the hydrides isolated in this investigation did not come from diborane

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[16] The superscript n indicates normal boron distribution of 80% ^{11}B and 20% ^{10}B.

[17] The $^{10}B_2H_6$ was prepared by normal procedures from $CaF^{10}BF_4$ enriched to 96% ^{10}B by Oak Ridge National Laboratories.

[18] C. R. Phillips, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1967.

[19] Since the n-B_9H_{15} is specifically isotopically labeled, this method of calculating the per cent ^{10}B is not entirely correct, for it assumes that the probability to give B^+ and BH^+ is the same for every boron atom in the molecule. However, due to the small but persistent B_{10} impurity, it was not feasible to strip the spectrum by normal methods.

and pentaborane(9). In fact only when B_5H_{11} was present in considerable amounts at the beginning of the pyrolysis were isolable amounts of B_6H_{12}, B_8H_{12}, and B_8H_{16} obtained. Under these conditions the yield of n-B_9H_{15} also increased sharply. In contrast to this, only when B_5H_{11} was absent from the starting pentaborane was the first new $B_{10}H_{16}$ obtained in isolable quantities. The yield of the rest of the boron hydrides was rather independent of the presence of B_5H_{11} at the beginning of the pyrolysis. The product distribution probably depends on the relative concentration of B_5H_9 and B_5H_{11} in the hot zone during any given pyrolysis. The fact is that both species were undoubtedly present at all times as both are products of the thermal decomposition of B_2H_6. The product distribution changed with time indicating that some of the hydrides are formed from B_2H_6 and B_5H_9 while others are formed from B_2H_6 and B_5H_{11}.

The pyrolysis with ^{10}B labeled B_2H_6 and $^nB_5H_9$ was carried out to determine which products were coming from which pentaborane species. In order to avoid a large excess of either boron isotope, a much smaller amount of B_5H_9 was used during this pyrolysis than in the ones carried out where both B_2H_6 and B_5H_9 had normal isotopic distributions. Only B_2H_6, B_5H_9, n-B_9H_{15}, and $B_{10}H_{14}$ were obtained pure and in sufficient quantity after separation to allow a determination of the ratio of boron isotopes. The gross composition of the system corresponded to 61% ^{10}B and 39% ^{11}B. The B_2H_6 recovered was shown to be 91% ^{10}B. Thus while some exchange is indicated, complete scrambling did not occur.

It was calculated that the B_5H_9 contains 58% ^{11}B. However, it is apparent from the parent ion intensities calculated that the recovered B_5H_9 was not a mixture of molecules containing a statistical distribution of 58% ^{11}B and 42% ^{10}B. In fact, the parent ion intensities can be mathematically reproduced fairly well by assuming the recovered B_5H_9 is made up of a mixture of pentaborane(9), 65% of which is starting pentaborane(9), $^nB_5H_9$, and 35% of which is $^{10}B_5H_9$ containing 91% ^{10}B. The isotopic ratio in the B_5H_9 made from the $^{10}B_2H_6$ reagent would be expected to be about 94% ^{10}B (the average ^{10}B composition of starting and recovered $^{10}B_2H_6$). However, the average composition of the B_2H_6 may well have been a function of time.

The n-B_9H_{15} isolated from the pyrolysis of $^{10}B_2H_6$ and $^nB_5H_9$ was at least partially specifically labeled as is indicated by its ^{11}B nmr spectrum, Figure 4. Since the n-B_9H_{15} is specifically labeled, some n-B_9H_{15} must come from the reaction of $^nB_5H_9$ and $^{10}B_2H_6$ where at least partial isotopic integrity is retained by the boron atoms which come from the B_5H_9. If one assumes that when B_5H_9 reacts with diborane to give n-B_9H_{15}, five boron atoms come from the B_5H_9[20] and four from the B_2H_6, then by simple calculations involving the relative percentages of ^{10}B and ^{11}B in the species under consideration, one can show that 64% of the n-B_9H_{15} came from starting $^nB_5H_9$ and that 36% was formed from species which were made from the $^{10}B_2H_6$ during pyrolysis. Both pentaboranes, B_5H_9 and B_5H_{11}, must now be considered as intermediates in the formation of n-B_9H_{15} by the thermal decomposition of B_2H_6. That B_5H_9 is an intermediate is shown by the above labeling work. That B_5H_{11} is an intermediate is strongly indicated by the fact that much larger yields of n-B_9H_{15} were obtained in the pyrolyses where the starting pentaborane contained B_5H_{11} than were obtained when B_5H_{11} was absent.[21] In addition it has been reported that the reaction of B_5H_{11} and B_2H_6 yields n-B_9H_{15} at temperatures too low for the pyrolysis of B_2H_6 to take place at an appreciable rate.[22]

According to the ^{11}B nmr spectrum of the $B_{10}H_{14}$ isolated from the pyrolysis of $^nB_5H_9$ and $^{10}B_2H_6$, there is a slightly lower percentage of ^{10}B in the 2,4 positions than in the remainder. Using the percentage ^{10}B in the entire molecule (73% ^{10}B) and the integrated area ratio of the low-field multiplet to high-field doublet (3.4), it can be calculated that the per cent ^{10}B in the 2,4 positions of the $B_{10}H_{14}$ is 69 while that in the other positions is 74. These figures indicate that for all practical purposes the $B_{10}H_{14}$ has a random distribution of ^{10}B and ^{11}B throughout the molecule unlike the n-B_9H_{15} which showed specific labeling.

All the boron hydrides mentioned above have three properties in common: (1) they all have a higher than usual hydrogen to boron ratio; (2) they all have large B_5 regions in their mass spectra (often the B_5 region is many times as intense as the parent region); and (3) they all have rather simple ^{11}B nmr spectra. The ^{11}B spectra usually consist of a low-field asymmetrical multiplet centered near where the basal borons of B_5H_9 appear and a much smaller upfield doublet or doublets centered about where the apical boron of B_5H_9 resonance occurs. One mechanism which might account for these facts is that B_5H_9 or B_5H_{11} couples with small, hydrogen rich, icosahedral fragments. The small icosahedral fragments could be formed by the decomposition of diborane. For example, B_5H_9 might react with the previously postulated B_3H_7 to give B_8H_{16}. Structures suggested by this approach could be used to interpret nmr data but such idle speculation is resisted except to note that $B_{10}H_{16}$ could be interpreted on the basis of two B_5H_8 groups linked in the 2,2′ positions. Crystallographic studies are currently under way in this laboratory.

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[20] This assumption is based on the results given in ref 6.

[21] Although quantitative yield data were not obtained, the yield of n-B_9H_{15} was estimated to be about 20% of the volatile products when no B_5H_{11} was present in the starting B_5H_9. However, in the pyrolysis where the starting pentaborane was approximately a 50:50 mixture of B_5H_9 and B_5H_{11}, the yield of n-B_9H_{15} was estimated to be about 70% of the volatile products. The total yield of volatile products was approximately the same in all pyrolyses.

[22] J. F. Ditter, J. R. Spielman, and R. E. Williams, *Inorg. Chem.*, **5**, 118 (1966).