It is interesting that octaborane-14 and isononaborane-15 appear to share an unusual structural feature; the ^{11}B nmr spectra suggest that in both these molecules the entire open periphery of the boron framework is B–H–B bridge bonded. This is a violation of topological principles based upon hydrogen atom crowding and perhaps explains the extreme ease with which these materials lose hydrogen.[24] It seems unlikely that the methods previously used in X-ray diffraction studies of other boranes will succeed with these materials. Final determination of the structures of such unstable materials may require the use of other structural methods.

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[24] See ref 19, p 52, rule 5, and p 60.

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Studies of Boranes. XXV. The Preparation of a Boron-Labeled Decaborane-14[1,2]

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Synthesis of decaborane by two different routes allows preparation of molecules labeled with a boron isotope in specific positions. Boron-11 nmr and mass spectra of the decaborane synthesized by reaction of nonaborohydride-12 with hydrogen chloride in the presence of diborane and of the product obtained by the decomposition of i-$^{10}B_9H_{15}$ in excess $^{11}B_2H_6$ as solvent indicates that decaborane has one isotopically labeled boron atom per molecule. Chemical and spectral evidence establish that the label is in the 6,9 and 5,7,8,10 positions. Partial conversion from an i-B_9H_{13} to a n-B_9H_{13} is postulated to account for labeling in the 5,7,8,10 position.

Introduction

The synthesis of boron hydrides with isotopic labels in specifically known positions is of current interest with respect to the implications concerning the mechanism of the route selected for synthesis whether or not a specific synthesis is achieved and also as a source of labeled molecules for possible use in the elucidation of the mechanisms of other reactions of boron hydrides. Various deuterium-labeled tetraboranes, pentaboranes, and decaboranes have been prepared by a number of workers.[3–7] The possible ready migration of hydrogen atoms at room temperature or below in the pure boranes or during the course of further reactions makes boron skeletal labeling of particular importance. The unselective methods generally used for preparation of boron hydrides makes the preparation of skeletally labeled boron hydrides a rather formidable task. The successful preparation of $^{11}B^{10}B_3H_{10}$ with the ^{11}B label in the 2,4 position from ^{10}B sodium triborohydride, hydrogen chloride, and normal diborane[8] suggested an analogous method of preparing specifically ^{10}B-labeled decaborane by the reaction of either tetramethylammonium nonaborohydride-12 or tetramethylammonium nonaborohydride-14 with hydrogen chloride and ^{10}B diborane. Decaborane was successfully prepared from either of the nonaborohydride anions and this is the first time in which the authors are aware that a higher boron hydride has been prepared from a planned synthesis. The 19.3-MHz ^{11}B nmr spectrum of the decaborane obtained from the reaction of either tetramethylammonium nonaborohydride-12 or terametyhlammonium nonaborohydride-14 with hydrogen chloride in the presence of $^{10}B_2H_6$ showed a small but reproducible reduction in the low-field peak of the decaborane spectrum. The value of the ratio of the intensity of the high-field peak of the triplet to that of the low-field peak was 1.15 ± 0.04 for the ^{10}B-labeled decaborane prepared from tetramethylammonium nonaborohydride-12 *vs.* the value of 1.03 ± 0.03 observed for normal decaborane. Since the low-field peak of the triplet arises from overlapping doublets of the 1,3 and 6,9 boron atoms, the boron label is in either the 1,3 or 6,9 positions.[9,10] *A priori*, it would seem more probable that the label is in the exterior 6,9 position rather than the interior 1,3 position.

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

Experimental Section

Spectroscopic Techniques.—The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates HA-60-IL high-resolution spectrometer operating at 19.3 MHz. The spectrum of $B_9H_{14}^-$ from the degradation of $^{11}B^{10}B_9H_{14}$ was obtained on the same instrument operating with a Varian C1024 time-averaging computer locked on $B(C_2H_5)_3$ in an internal capillary. A spectrum of $^{11}B^{10}B_9H_{14}$ was also obtained with a Varian Associates HA-100 high-resolution spectrometer operating in the HR

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[1] For paper XXIV of this series see J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

[2] Presented before the Inorganic Division at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

[3] A. D. Norman and R. Schaeffer, *Inorg. Chem.*, **4**, 1225 (1965).

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[5] T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 1754 (1963).

[6] J. A. DuPont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962).

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[8] R. Schaeffer and F. Tebbe, *ibid.*, **84**, 3974 (1962).

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

[10] 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.

mode at 32.082 MHz, and this spectrum was used to obtain integrated intensities. Mass spectra were obtained with Consolidated Electrodynamics Corp. Model 21-610 and with Associated Electrical Industries Model MS-9 mass spectrometers.

Preparation of Starting Materials.—All operations and manipulations involving standard high-vacuum techniques in this investigation have been described elsewhere.[11,12]

All solvents employed were reagent grade and were carefully dried before use. 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] Deuterium chloride was prepared by the reaction of phosphorus trichloride with deuterium oxide and was purified by high-vacuum techniques.

Isotopically labeled diboranes, $^{10}B_2H_6$ and $^{11}B_2H_6$, were prepared by $LiAlH_4$ reduction of $^{10}BF_3 \cdot O(C_2H_5)_2$ and $^{11}BF_3 \cdot O(CH_3)_2$ (enriched to 98% ^{11}B by the Oak Ridge National Laboratories), respectively.[14] The 96% ^{10}B diborane was converted to decaborane, $^{10}B_{10}H_{14}$, in a hot–cold reactor in which the hot and cold surfaces were maintained at 180 ± 5 and 0°, respectively.[15]

Tetramethylammonium nonaborohydride-12 was prepared according to the method of Hawthorne and was dried under vacuum at room temperature.[16] The best yields of labeled decaborane were obtained from material which was not more than 1 week old. Tetramethylammonium nonaborohydride-14 was prepared by the method of Benjamin, *et al.*,[17] The preparation of the potassium salt of the nonaborane-14 anion, KB_9H_{14}, and isononaborane-15 has been described elsewhere.[18,19] Normal decaborane, $^{n}B_{10}H_{14}$, was obtained from a laboratory supply and was sublimed before use.[20]

Preparation of $B_{10}H_{14}$ from $(CH_3)_4NB_9H_{12}$, B_2H_6, and HCl in Monoglyme.—A reaction tube was charged with 0.54 mmole of $(CH_3)_4NB_9H_{12}$, attached to the vacuum line, and evacuated. Approximately 1.5 ml of monoglyme and 0.55 mmole of diborane were condensed into the tube. After 15 min at 0° little reaction was evident and the ^{11}B nmr spectrum corresponded to reactants only. After 54 hr at room temperature the ^{11}B nmr spectrum exhibited absorptions arising from the $B_{10}H_{13}^-$ and $B_{11}H_{14}^-$ ions. The reaction tube was opened to afford 0.65 mmole of noncondensable gas. Approximately 1.0 mmole of anhydrous HCl was condensed into the tube which was then resealed and allowed to react for 0.5 hr. The reaction tube was then opened, the materials were fractionated, and 0.278 mmole of $B_{10}H_{14}$ was isolated corresponding to a 52% yield based on the amount of $B_9H_{12}^-$ initially present. The $B_{10}H_{14}$ was identified by its ^{11}B nmr spectrum.

Preparation of $^{10}B^{n}B_9H_{14}$ from $(CH_3)_4N^{n}B_9H_{12}$, $^{10}B_2H_6$, and HCl.—A 250-ml flask containing 3.55 mmoles of $(CH_3)_4{}^{n}B_9H_{12}$ and assorted glass balls and chips was evacuated, and 7.3 mmoles of $^{10}B_2H_6$ and 14.0 mmoles of HCl were added by condensing the gases at −196°. The flask was sealed from the vacuum system, allowed to warm to room temperature, and rotated slowly for 6 hr to ensure mixing of the contents during reaction. During this time the solid became light yellow and appeared sticky. After 24 hr the flask was attached to the vacuum system and opened. Noncondensable gas, 9.75 mmoles, was removed; 7.4 mmoles of condensable gases with a vapor pressure of 218 mm at −112° was then removed from the system. Subsequently, 23 mg of a white solid was sublimed from the system. The ^{11}B nmr spectrum of this product was identical with that of $^{n}B_{10}H_{14}$ except that the low-field peak of the triplet was smaller in size relative to the high-field peak of the triplet than in $^{n}B_{10}H_{14}$. The condensable gases were replaced in the flask and the flask was again sealed off and left at room temperature for 4 more days with periodic slow rotation. During this period the solid became darker yellow and retained a sticky appearance. The flask was again opened as described above to afford 2.31 mmoles of noncondensable gases and 216 mg more of white sublimable solid, which was identified by nmr to be the solid previously obtained.

Preparation of $^{10}B^{n}B_9H_{14}$ from $(CH_3)_4N^{n}B_9H_{14}$, $^{10}B_2H_6$, and HCl.—A 250-ml flask was charged with 3.4 mmoles of tetramethylammonium nonaborohydride-14 and a number of glass balls, and 13.1-mmoles of hydrogen chloride and 6.8 mmoles of $^{10}B_2H_6$ were added by condensation. The container was sealed from the vacuum line, allowed to warm to room temperature with agitation, and then slowly rotated for 66 hr to mix the contents and permit reaction. The apparatus was reattached to the vacuum manifold; 13 mmoles of noncondensable gases, 4.3 mmoles of condensable gases, and 1.68 mmoles of $^{10}B^{n}B_9H_{14}$ were removed. The 19.3-MHz ^{11}B nmr spectrum of the $^{10}B^{n}B_9H_{14}$ showed observable reduction in the size of the low-field peak of the triplet of decaborane similar to that described for the decaborane obtained from tetramethylammonium nonaborohydride-12.

Preparation of $^{10}B^{n}B_9H_{14}$ from *i*-B_9H_{15} and $^{10}B_2H_6$.—In a typical reaction 40 mmoles of $^{10}B_2H_6$ was condensed into a thick-walled glass reaction vessel containing approximately 2 mmoles of *i*-B_9H_{15}. The vessel was sealed from the vacuum system, placed in a −80° slush bath, and warmed slowly to −30° by using a series of consecutively warmer slush baths. The decomposition of *i*-B_9H_{15} was finally carried out at −30° for 4 hr, and at the end of this time the reaction was quenched by cooling the vessel with liquid nitrogen. The vessel was opened to the vacuum line and the diborane removed at −112°. A −20° bath was placed around the vessel in order to retain the decaborane and pumping was continued to remove any more volatile materials. A small amount of B_8H_{12} was recovered and identified by ^{11}B nmr. A warm water bath placed around the reaction vessel was then used to facilitate removal of decaborane from polymeric material that had formed during reaction. The decaborane was sublimed through a 0° bath, collected, and weighed. Based on the amount of *i*-B_9H_{15} initially present, the yield was approximately 50%. The preparation of $^{11}B^{10}B_9H_{14}$ was carried out in a similar manner. In each case, ^{11}B nmr demonstrated that the decaborane was specifically labeled and in the case of $^{10}B^{n}B_9H_{14}$ the spectrum was identical with that for the material obtained by the nonaborane ion–HCl routes.

Reaction of $^{10}B^{n}B_9H_{14}$ with NaH.—A vacuum filtration apparatus was equipped with a 100-ml bulb on one end and a 5-mm nmr tube on the other end. The bulb was charged with 0.56 mmole of $^{10}B^{n}B_9H_{14}$ and 2.3 mmoles of NaH (54% mineral oil dispersion); the apparatus was attached to the vacuum line and evacuated. Dry ether was condensed into the bulb and the solution was stirred for 2 hr at which time hydrogen evolution was complete. The solution was filtered into the nmr tube and frozen at −196°. Noncondensable gas, 0.60 mmole, was measured in a Toepler system. The solution was concentrated and the nmr tube was sealed from the apparatus. The ^{11}B nmr spectrum was very similar to the spectrum of normal $B_{10}H_{13}^-$. The nmr tube was reattached to the vacuum line, and approximately 1 mmole of anhydrous HCl was condensed in at −196°. The tube was resealed, shaken, and a ^{11}B nmr spectrum was obtained. The nmr spectrum of the regenerated $B_{10}H_{14}$ was identical with that of $^{n}B_{10}H_{14}$. The same experiment was performed using wet ether to remove any B_2H_6 that might be produced during the seal-off procedure since it has been determined that boron exchange occurs between B_2H_6 and $B_{10}H_{13}^-$.[21] The ^{11}B nmr spec-

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[11] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[12] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

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

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

[15] M. S. Klein, B. C. Harrison, and I. J. Solomon, *ibid.*, **80**, 4149 (1958).

[16] B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *ibid.*, **83**, 2669 (1961).

[17] L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *ibid.*, **85**, 2674 (1963).

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

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

[20] In this paper the superscript *n* refers to boron of normal isotopic distribution, 81.2% ^{11}B and 18.8% ^{10}B.

[21] R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **85**, 2020 (1963).

trum of the regenerated $B_{10}H_{14}$ again was almost identical with the spectrum of $^nB_{10}H_{14}$.

Reaction of $^{11}B^{10}B_9H_{14}$ with NaOH (Aqueous).—Into a 5-mm nmr tube charged with 0.163 mmole of $^{11}B^{10}B_9H_{14}$, 0.08 ml of 2.5 *N* NaOH was added. The solution immediately turned yellow, and hydrogen evolution occurred. Because of the small amount of sample used a time-averaging computer was employed with the nmr spectrometer. By the time adjustments had been made and a sufficient number of sweeps recorded to obtain the spectrum (a period of several hours) the $B_{10}H_{13}^-$ ion had been degraded to $B_9H_{14}^-$.[17] The ^{11}B nmr spectrum consisted of a low-field doublet and an asymmetric high-field doublet suggesting that an impurity was present. Chemical shift and coupling constant values corresponded to those of $^nB_9H_{14}^-$ although the relative intensities did not correspond.

Results

The ^{11}B nmr spectrum of $^{10}B^nB_9N_{14}$ obtained by the *i*-B_9N_{15} route was integrated both by the spectrometer-integrating system and by carefully cutting the spectrum into the triplet and doublet portions and weighing each separately. Forty-two values were obtained by machine integration and were subjected to a statistical analysis; the triplet to doublet ratio was 3.50 ± 0.20 and 40 values lie within the 95% confidence interval of this ratio. Nine spectra were integrated by cutting and weighing; all nine values lie within the 95% confidence interval of a triplet:doublet ratio of 3.61 ± 0.13. The mass spectrum of the $^{10}B_2H_6$ recovered from the reaction was unchanged showing that an exchange process had not taken place. These facts strongly suggest that the decaborane formed contains a predominance of molecules with one excess ^{10}B and that this atom is not in the 2,4 position.

The ^{11}B nmr spectrum of $^{11}B^nB_9H_{14}$ shows that specific labeling has taken place but is not as revealing as the ^{11}B nmr spectrum of $^{11}B^{10}B_9H_{14}$. The 19.3-MHz ^{11}B nmr spectrum (Figure 1a) of $^{11}B^{10}B_9H_{14}$ showed a large doublet for the 1,3, 6,9 signal, but substantial absorption arising from the 5,7,8,10 positions showed that ^{11}B was also in those positions to a greater extent than that unavoidably introduced from the 4% ^{11}B present in the starting materials. The resonance arising from the 2,4 borons shows only the approximately 4% ^{11}B introduced from the ^{10}B-labeled nonaborane-14 salt. A mass spectrum of the $^{11}B_2H_6$ recovered from the reaction showed no change from the 98% ^{11}B initially present. A mass spectrum of the $^{11}B^{10}B_9H_{14}$ shows a strong parent peak P, *m/e* 115, and P + 1, P + 2, and P + 3 peaks which can be accounted for by the presence of 4% ^{11}B statistically distributed in the remainder of the molecule.

To determine whether the ^{11}B was primarily in the 1,3 or 6,9 position, the $^{11}B^{10}B_9H_{14}$ was deuterated in the 1,2,3,4 positions.[6] The only change in the nmr spectrum (Figure 1b) was the collapse to a singlet of the doublet arising from the resonance of the 2,4 borons. Thus negligible labeling in a 1,3 position had occurred.

The 32.1-MHz nmr spectrum of $^{11}B^{10}B_9H_{14}$ (Figure 1c) was integrated by carefully cutting out the three doublets and weighing them. Of the total spectrum, the doublet representing the 1,3, 6,9 positions contributes 68.9%, the 5,7,8,10 doublet contributes 24.6%, and the 2,4 doublet 6.52%. Since the deuteration experiment demonstrates that the label is in the 6,9 position, we assumed that the 1,3 position contains the same amount of ^{11}B as that of the 2,4 position and subtracted that amount to give a total of 62.4% ^{11}B in the 6,9 position.

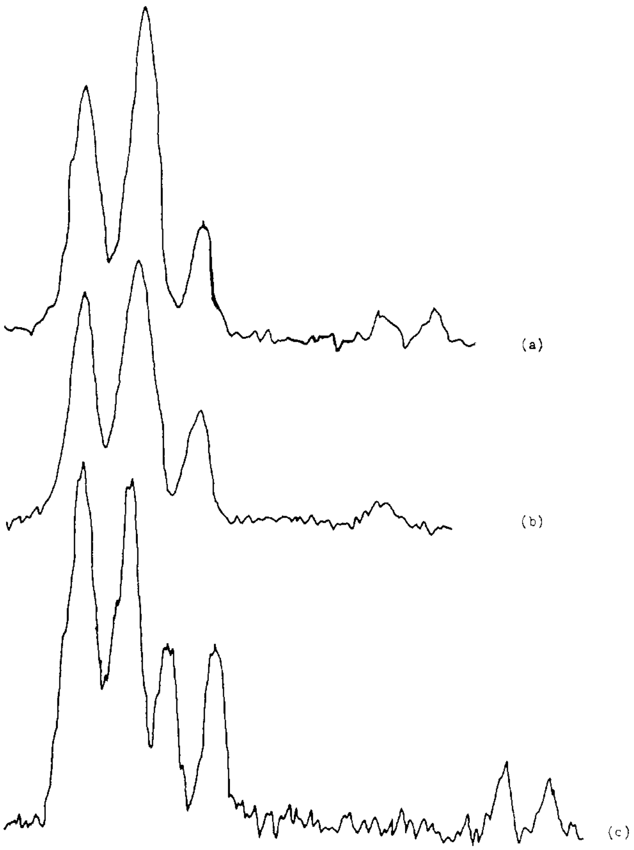

Figure 1.—Boron-11 nmr spectra of ^{11}B-labeled decaborane: (a) $^{11}B^{10}B_9H_{14}$ (19.3 MHz); (b) 1,2,3,4-$^{11}B^{10}B_9H_{10}D_4$ (19.3 MHz); (c) $^{11}B^{10}B_9H_{14}$ (32.1 MHz).

Discussion

This reaction is probably best viewed as the decomposition of *i*-$^{10}B_9H_{15}$ to *i*-$^{10}B_9H_{13}$ followed by attack of $^{11}B_2H_6$, acting as a base, to form a $^{11}B^{10}B_9H_{16}$ species which loses hydrogen to form $^{11}B^{10}B_9H_{14}$. Earlier studies of the decomposition of *i*-B_9H_{15} have led to the suggestion that the intermediate *i*-B_9H_{13} is the first decomposition product;[19] and indeed Lipscomb has predicted the existence of a neutral B_9H_{13} in an evironment free of electron-donating ligands.[22] From the structure proposed for *i*-B_9H_{13},[22] it is not difficult to visualize labeling in the 6,9 position of decaborane by BH_3 insertion. However, no simple pathway has been devised to account for 24.6% ^{11}B in the 5,7,8,10 positions. There are several pathways by which one might possibly explain the presence of ^{11}B in these positions if only *i*-B_9H_{13} is involved

$$B_9H_n \xrightarrow{-x^{10}B} B_{9-x}H_z \xrightarrow{x^{11}B} B_9H_n \qquad (1)$$

$$B_9H_n \xrightarrow{x^{11}B} B_{9+x}H_z \xrightarrow{-x^{10}B} B_9H_n \qquad (2)$$

$$B_9H_n \xrightarrow{^{11}B} {}^{11}B^{10}B_9H_{14} \xrightarrow{\text{migration}} B_{10}H_{14} \qquad (3)$$

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

$$B_9H_n \xrightarrow{^{11}B} B_{10}H_y \xrightarrow{\text{migration}} {}^{11}B^{10}B_9H_{14} \qquad (4)$$

Pathway 1 represents the loss of ^{10}B to form an intermediate of less than nine borons followed by addition of ^{11}B to re-form a B_9 species. In the opposite sense, pathway 2 represents addition of ^{11}B to form an intermediate which contains more than nine borons followed by loss of ^{10}B to form the B_9 species again. Both pathways 1 and 2 would involve exchange and labeling at the B_9H_n stage. Pathway 3 is self-explanatory. Pathway 4 is seen as addition of a ^{11}B atom to form a species containing ten boron atoms which subsequently goes to $^{11}B^{10}B_9H_{14}$ with migration in the latter step.

The first three possible pathways can be eliminated. From the fact that mass spectral evidence shows the $^{11}B_2H_6$ remained essentially 98% ^{11}B after reaction, pathways 1 and 2 can be ruled out. Pathway 3 can be eliminated since the stability of $B_{10}H_{14}$ is well-known, and CS_2 solutions of the $^{10}B^{n}B_9H_{14}$ have stood at room temperature for several months with no change in their nmr spectrum. If a $^{11}B^{10}B_9H_{16}$ species is formed, pathway 4 may give exchange in the formation of $^{11}B^{10}B_9H_{16}$, in $^{11}B^{10}B_9H_{16}$ itself, or in hydrogen loss to form $^{11}B^{10}B_9H_{14}$ and cannot be eliminated.

A mechanism which accounts for the presence of ^{11}B in a 5,7,8,10 position and is more structurally pleasing to the authors is a postulated conversion of i-B_9H_{13} to n-B_9H_{13}. This may well be reversible and sufficiently rapid so that an equilibrium is reached between the normal and iso forms. It can be shown by models that there are three locations in i-B_9H_{13} where a BH_3 addition would give a 6,9-labeled decaborane. Likewise, there are two locations in n-B_9H_{13} where BH_3 addition may occur to give a 5,7,8,10-labeled decaborane. If this suggestion is correct, the experimentally observed nmr integrations may be used to get a measure of the probability of a ^{11}B traveling each pathway

Position	Relative integrated intensity
2,4	0.065
5,7,8,10	0.246
6,9	0.624

$$\begin{tikzcd} i\text{-}B_9H_{13} \arrow[rr, shift left] \arrow[d, "p"] & & n\text{-}B_9H_{13} \arrow[ll, shift left] \arrow[d, "1-p"] \\ 6{,}9\text{-}{}^{11}B^{10}B_9H_{14} & & 5{,}7{,}8{,}10\text{-}{}^{11}B^{10}B_9H_{14} \end{tikzcd}$$

p = probability of ^{11}B entering a 6,9 position

total ^{11}B atoms per $B_{10}H_{14}$ unit $= (0.04 \times 9) + 0.98 = 1.34$

5,7,8,10 label: $1.34 \times 0.246 = 0.98(1 - p) + (0.065/2) + p(0.065/2) \quad p = 0.789$

6,9 label: $1.34 \times 0.624 = 0.98p + (0.065/2) + (1 - p)(0.065/2) \quad p = 0.814$

The 2.5% difference between the calculated probability values for the two routes is well within the experimental error involved in integrating the nmr spectra. Thus there is approximately an 80% probability of the $^{11}BH_3$ addition to give a 6,9-labeled molecule which may arise from either kinetic or equilibrium causes. That equilibrium may favor i-B_9H_{13} receives some support from the preliminary observation that reaction of n-B_9H_{15} with diethyl ether yields $B_9H_{13} \cdot O(C_2H_5)_2$ which appears to be identical with the $B_9H_{13} \cdot O(C_2H_5)_2$ formed in the decomposition of i-B_9H_{15} in the presence of diethyl ether.[23] It would be of interest to attempt to obtain more concrete evidence for the formation of n-B_9H_{13} and further study is in progress with this goal in mind.

No explanation can be offered at this time concerning the randomization of the label when $^{10}B^{n}B_9H_{14}$ is converted to $B_{10}H_{13}^-$ and $B_{10}H_{14}$ is subsequently regenerated with acid. The label is apparently not completely randomized since the ratio of the high-field portion of the triplet to that of the low-field portion in the ^{11}B nmr spectrum gave a value of 1.07 ± 0.02 compared to a value of 1.03 ± 0.03 for normal decaborane observed at the same time under identical conditions. The ^{10}B-labeled $B_{10}H_{14}$ gave a value of 1.15 ± 0.04 for the same ratio. It is indeed unfortunate that the identical reaction was not accomplished with $^{11}B^{10}B_9H_{14}$. In the normal ^{11}B nmr spectrum of the $B_9H_{14}^-$ ion, which exhibits two doublets with area ratios of 1:2, absorptions have been assigned on the basis of deuterium labeling.[24] In the spectrum obtained in this experiment six integrations give an average value for the ratio of the high-field doublet to the low-field doublet of 4.07 ± 0.12. However, it appears that there is another absorption under the high-field doublet so it would be idle speculation to attempt to draw conclusions concerning randomization from this spectrum, but the results are sufficiently promising to warrant further study.

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[23] J. Dobson, personal communication.

[24] P. C. Keller, Ph.D. Thesis, Indiana University, 1966.