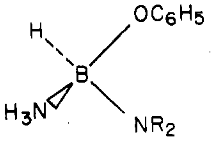
is important in the reactions of methylamine bases $[(CH_3)_nNH_{3-n}, n = 1-3]$ and the relatively small acid trimethylboron. The ambient-temperature proton magnetic resonance spectrum of the ammonia adduct of diisopropylaminohydridophenoxyborane (Figure 2B) is entirely consistent with free rotation about the boron–dialkylamino nitrogen bond. This is expected from coordinative saturation of the boron and sp^3 hybridization on boron in the adduct, i.e.



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Registry No. $BH_3·HN(C_2H_5)_2$, 2670-68-0; $BH_3·HN(n\text{-}C_4H_9)_2$, 55124-34-0; $BH_3·HN(i\text{-}C_3H_7)_2$, 55124-35-1; $BH_3·HN(CH_2C_6H_5)_2$, 55124-36-2; $BH_3·HNC_4H_8$, 55124-37-3; $BH_3·HNC_5H_{10}$, 4856-94-4; $BH_3·HN(CH_3)_2$, 74-94-2; $HBOC_6H_5N(CH_3)_2$, 55124-38-4; $HBOC_6H_5N(C_2H_5)_2$, 32015-64-8; $HBOC_6H_5N(i\text{-}C_3H_7)_2$, 32015-58-0; $HBOC_6H_5N(n\text{-}C_4H_9)_2$, 55124-39-5; $HBOC_6H_5N(CH_2C_6H_5)_2$, 55124-40-8; $HBOC_6H_5NC_4H_8$, 55124-41-9; $HBOC_6H_5NC_5H_{10}$, 55124-42-0; $HBOC_6H_5N(i\text{-}C_3H_7)_2·NH_3$, 55124-43-1; C_6H_5OH, 108-95-2.

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Reactions of Pentaborane(11) with Ethers

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Reactions of pentaborane(11) (B_5H_{11}) with ethers were studied at low temperatures by means of ^{11}B NMR spectroscopy. The reactions of B_5H_{11} with dimethyl and diethyl thioethers give the symmetrical cleavage products $R_2S·BH_3$ and $R_2S·B_4H_8$. Species that are produced in the reaction system of B_5H_{11} and oxoethers are very dependent upon the base strength of the ether. Strongly basic tetrahydrofuran can effect the unsymmetrical cleavage of B_5H_{11} to produce $H_2B(THF)_2{}^+B_4H_9{}^-$. Evidence for the formation of this cleavage product is based on the NMR spectral evidence and on the observed reaction products produced in the reaction of HCl with the B_5H_{11}–THF system. A second species is observable in the THF–B_5H_{11} system which is more predominant at higher temperatures. This species is assigned as the simple adduct $B_5H_{11}·THF$. Moderately basic ethers like dimethyl and diethyl ethers produce only one observable species which is considered to be $B_5H_{11}·OR_2$. Weakly basic diisopropyl ether does not react with B_5H_{11}. No direct evidence for the symmetrical cleavage of B_5H_{11} by oxoethers has been observed. The similarities and differences between these reactions and analogous B_4H_{10} reactions are discussed.

Introduction

The reactions of pentaborane(11) (B_5H_{11}) with some Lewis bases have been systematized in terms of symmetrical and unsymmetrical cleavage reactions. Symmetrical cleavage takes place with carbon monoxide and phosphines PF_2X (X = H, F, Cl, Br, I, $N(CH_3)_2$)[1]

$$B_5H_{11} + 2L \rightarrow H_3B·L + L·B_4H_8$$

where L represents the Lewis bases mentioned above. Unsymmetrical cleavage of B_5H_{11} has been found to occur in the reaction of the borane with ammonia[2]

$$B_5H_{11} + 2NH_3 \rightarrow H_2B(NH_3)_2{}^+B_4H_9{}^-$$

Reactions of ethers[3] and many amines[4] with B_5H_{11} are reported to give complex mixtures of borane derivatives and boranes. The boranes isolated from these reactions include diborane(6) (B_2H_6), tetraborane(10) (B_4H_{10}), pentaborane(9) (B_5H_9), hexaborane(10) (B_6H_{10}), and nonaborane(15) (B_9H_{15}). These boranes were speculated to be a result of the decomposition of the unstable ether adduct of tetraborane(8), $B_4H_8·OR_2$, which initially would have been formed in the symmetrical cleavage reaction of B_5H_{11}.[4] This speculation was apparently proposed on the basis of the known reactions of B_2H_6 and B_4H_{10} with ethers, which generally give the symmetrical cleavage products of the boranes, e.g.

$$B_4H_{10} + 2THF \rightarrow THF·BH_3 + THF·B_3H_7{}^5$$

Since none of the etherates of B_4H_8 have been isolated from the reactions of B_5H_{11} with ethers and the mechanism for the formation of the higher boranes from such reactions is not understood, the present investigation of B_5H_{11}–ether systems was undertaken. Observations of the systems were made by

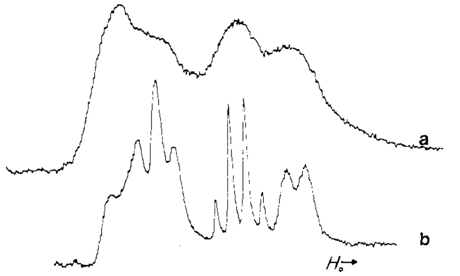


Figure 1. ^{11}B NMR spectra of a mixture of B_5H_{11} and $(C_2H_5)_2S$ in a 1:2 molar ratio in CH_2Cl_2: (a) −70°; (b) +13°.

means of ^{11}B NMR spectroscopy at low temperatures where the intermediate species might be stable.

Experimental Section

Standard high-vacuum techniques were used throughout for the handling of volatile compounds.

Chemicals. Pentaborane(11) was prepared from diborane(6) (Callery Chemical Co.) by the hot–cold reactor method.[6] The temperatures of outer and inner walls were maintained at −80 and +170°, respectively, for the preparation of most of the B_5H_{11} sample used in this work. The vapor pressure of the sample at 0° was 53.0 mmHg and no impurity was detected by either ^{11}B NMR or ir spectrum of the sample. A small portion of the B_5H_{11} sample used was prepared by heating the hot wall at 200–210°, and its ^{11}B NMR spectrum indicated the presence of pentaborane(9) in a small amount. The vapor pressure of the sample at 0°, however, was very close (53–54 mmHg) to that of the pure B_5H_{11} sample.

Tetrahydrofuran and diethyl ether (reagent grade) were stored over $LiAlH_4$. Dichloromethane (reagent grade) was stored over dried 5A molecular sieves. These liquids were distilled directly from their containers on the vacuum line. Dimethyl ether was obtained from an L.B. cylinder (Matheson Gas Products). Methyl sulfide and ethyl sulfide (Eastman Kodak Co.) were dried by passing the vapors through tubes containing P_4O_{10} powder in the vacuum line. Hydrogen chloride was generated from reagent grade concentrated hydrochloric acid by adding concentrated sulfuric acid to it and fractionated for purification in the vacuum line.

Measurements. Each sample tube (5-mm o.d., 0.75-mm wall thickness) for the studies of B_5H_{11}–ether systems contained 1 mmol of B_5H_{11} and 0.1 ml of CH_2Cl_2. First the measured amounts of B_5H_{11} and CH_2Cl_2 were condensed in the NMR sample tube and the tube was allowed to warm (about 0°) for a short time to prepare a uniform solution. The tube was frozen again with liquid nitrogen, a measured amount of ether was condensed in the tube, and the tube was sealed off from the vacuum line. The ether was mixed with the solution at −80° by turning the tube upside down several times in a container packed with Dry Ice powder or in a −80° freezer unit. The tube was then kept frozen in liquid nitrogen until the ^{11}B NMR spectra were taken. The ratios of the components are expressed in terms of mole ratios in this paper.

Samples for the systems that contained HCl were prepared in 10-mm o.d. sample tubes with attached stopcocks. Mixing of ethers into the B_5H_{11} solutions was accomplished easily for the tubes of this size. The tube was tilted and shaken gently with the end of the tube in a slush bath of desired temperature. HCl was then condensed into the tube and mixed with the solution in a like manner. Although 0.2–0.3-ml portions of CH_2Cl_2 were used, correspondingly increased amounts of B_5H_{11} were used so as to maintain the same molar concentrations of B_5H_{11} as described in preceding paragraph, unless stated otherwise in the Results.

^{11}B NMR spectra were recorded on a Varian XL-100-12 or XL-100-15 NMR spectrometer operating at 32.1 MHz. Chemical shifts are reported in parts per million from the $BF_3{\cdot}O(C_2H_5)_2$ signal.

Results

Systems of B_5H_{11} and Thioethers (Alkyl Sulfides). At −80° the ^{11}B NMR spectrum of a mixture of B_5H_{11} and ethyl sulfide in a 1:2 molar ratio in dichloromethane shows an overlap of four broad resonance signals. Upon raising of the temperature, each signal begins to sharpen to show its fine structure as illustrated in Figure 1. The reaction between B_5H_{11} and ethyl sulfide appears complete at −80° and no intermediate species could be detected. The reaction is

$$B_5H_{11} + 2(C_2H_5)_2S \rightarrow H_3B{\cdot}S(C_2H_5)_2 + (C_2H_5)_2S{\cdot}B_4H_8$$

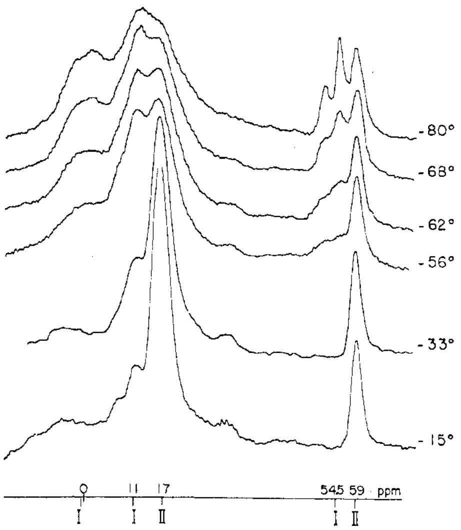


Figure 2. ^{11}B NMR spectra of a mixture of B_5H_{11} and tetrahydrofuran in a 1:2 molar ratio in CH_2Cl_2 (normal spectra).

The quartet at 23.3 ppm (J = 105 Hz) is due to $(C_2H_5)_2S{\cdot}BH_3$. Three other resonance peaks are assigned to B_3 (a doublet at −3.2 ppm, J = 100 Hz), B_2 and B_4 (a triplet at 5.2 ppm, J = 125 Hz), and B_1 (a doublet at 34.7 ppm, J = 125 Hz) atoms of diethyl sulfide–tetraborane(8). The extraordinary high appearance of the low-field (doublet) peak at −80° is attributed to the extreme broadness of the overlapping triplet signal at that temperature. The multiplet feature of each peak and an area ratio 1:2:1 for the three peaks have been confirmed on a proton spin decoupled spectrum.

The system of B_5H_{11} and methyl sulfide shows the same behavior as described above. $(CH_3)_2S{\cdot}BH_3$: a quartet at 20.2 ppm with J = 104 Hz (lit.[7] value 20.3 ppm, J = 104 Hz). $(CH_3)_2S{\cdot}B_4H_8$: a doublet at −2.0 ppm with J = 90 Hz for B_3, a triplet at 6.5 ppm with J = 125 Hz for B_2 and B_4, and a doublet at 33.3 ppm with J = 115 Hz for B_1.

Upon prolonged standing at room temperature, the solution containing the alkyl sulfide adducts of BH_3 and B_4H_8 undergoes a slow change, as evidenced by the growth of B_6H_{10} signals in its spectrum. Attempts to isolate the tetraborane(8) adducts of methyl and ethyl sulfide by means of a trap-to-trap fractionation are unsuccessful; as the solution becomes concentrated by the removal of solvent, the decomposition reaction becomes fast, and B_6H_{10} and $R_2S{\cdot}BH_3$ are separated as the major identifiable products.

System of B_5H_{11} and Tetrahydrofuran. The ^{11}B NMR spectra of a 1:2 mixture of B_5H_{11} and tetrahydrofuran in dichloromethane at various temperatures are given in Figure 2 (normal spectrum) and in Figure 3 (^{1}H spin decoupled spectrum). Inspection of the spectra reveals that two sets of resonance peaks are present at temperatures of −33° and below. One of the sets, due to the species I, consists of three peaks at −0.7, 11, and 54.5 ppm. The other set, due to species II, consists of two resonance peaks at 17 and 59 ppm, and these latter two peaks gain intensity as the temperature is raised. One of the peaks of I at 54.5 ppm is a well-resolved triplet at −80°, the high-field member of which is overlapped with one of the peaks of II at 59 ppm. As the temperature is raised, this triplet and the broad doublet at −0.7 ppm show broadening and weakening. The peak at 11 ppm does not become broad but appears to lose its intensity at the higher temperatures. These temperature effects on the resonance peaks of I are reversible to about −33°, at which temperature some irrev-

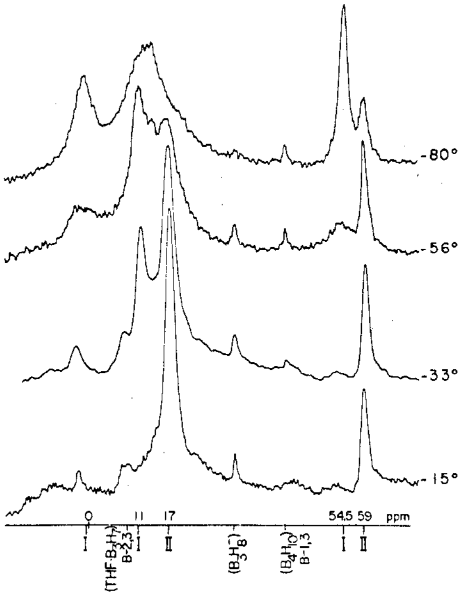


Figure 3. ^{11}B NMR spectra of a mixture of B_5H_{11} and tetrahydrofuran in a 1:2 molar ratio in CH_2Cl_2 (^1H spin decoupled spectra).

Table I. Comparison of ^{11}B NMR Data of $B_4H_9^-$ Salts

Compd	Peaks, ppm, at low temp	Peaks, ppm, at high temp
$K^+B_4H_9^-$ [a]	−45°: 0.4, 53.2 (triplet)	Ambient temp: both disappear; new peak at 26.5
	9.7	9.7
Species I	<−50°. −0.7, 54.5 (triplet)	~−30°: both disappear
	11	11
$H_2B(NH_3)_2^+B_4H_9^-$ [b]	−80°: −0.5, 54.5 (triplet)	>−40°: both disappear; new peak at 24.5
	10.5	10.5

[a] Reference 25. [b] Reference 2.

ersible reactions become detectable. At −33° and above, peaks due to B_2H_6, B_5H_9, B_6H_{10}, THF·BH_3, and THF·B_3H_7 begin to appear in the spectra, and eventually the original two sets of peaks assigned to I and II disappear.

Species I contains the tetraborohydride(9) ion $B_4H_9^-$. Table I shows the comparison of the data in this study and those reported in literature. Resemblances among one another are evident. The failure to observe, in this study, the higher temperature peak in the region of 24.5–26.5 ppm, which is due to the two equivalent boron atoms (B_1 and B_3) at the higher temperatures as seen for KB_4H_9 (26.5 ppm) and $H_2B(NH_3)_2^+B_4H_9^-$ (24.5 ppm), is attributed to the complex, further reactions that destroy the anion and also to the presence of a broad envelope of the 17-ppm peak, under which this weak signal of $B_4H_9^-$ might be hidden.

A 1:1 mixture of B_5H_{11} and tetrahydrofuran in dichloromethane at −80° gives a spectrum which indicates the presence of II, B_5H_{11}, and a small amount of $B_4H_9^-$.

The spectrum of a mixture of B_5H_{11} and tetrahydrofuran in a 1:5 ratio without the dichloromethane solvent at −70° is comparable to that of the 1:2 mixture described above. The reversible feature of the spectra at low temperatures is also observed.

System of B_5H_{11}, Tetrahydrofuran, and Hydrogen Chloride. A summary of results is compiled in Table II for the products resulting from different compositions of B_5H_{11}, THF, and HCl mixtures at various temperatures.

Table II. Reactions of B_5H_{11} with HCl in the Presence of Tetrahydrofuran

Compn B_5H_{11}:THF:HCl	Temp, °C	Major component identified (in the approx order of decreasing amt)
1:2:1	−60	B_4H_{10}, $B_3H_8^-$
	−20	$B_3H_8^-$, B_4H_{10}, B_3H_7·THF, II
	+10	B_3H_7·THF, $B_3H_8^-$, BH_2Cl·THF, B_4H_{10}, B_2H_6, II
1:3:2.5	+20	BH_2Cl·THF, B_3H_7·THF, small amt of $BHCl_2$·THF, very small amt of $B_3H_8^-$ and B_4H_{10} (H_2 gas evolved at −80°, very rapidly at −40°)

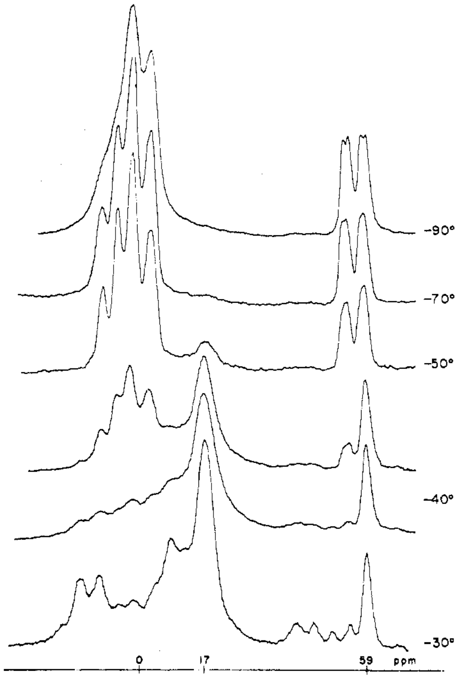


Figure 4. ^{11}B NMR spectra of a mixture of B_5H_{11} and diethyl ether in a 1:2 molar ratio in CH_2Cl_2.

System of B_5H_{11} and Diethyl Ether. At −90°, the ^{11}B NMR spectrum of a 1:2 mixture of B_5H_{11} and diethyl ether in dichloromethane solvent indicates only the presence of unchanged B_5H_{11}. The low-field triplet and doublet of B_5H_{11} are considerably broadened. The high-field doublet of B_5H_{11}, however, is indeed highly resolved, enough to give a doublet feature to each member of the upfield doublet (Figure 4). This observed fine splitting is attributed to coupling of the unique hydrogen attached to the apical boron. The separation of the fine splitting is measured to be 40 Hz, which compares with the value of the coupling constant $J = 51$ Hz reported by Schaeffer et al.,[8] based on the line-narrowing technique. Upon raising of the temperature to about −70°, two new peaks with an approximate intensity ratio 4:1 begin to appear at 17 and 59 ppm, respectively. It is noted that the same two peaks appeared also in the B_5H_{11}–THF system. The intensity of the two peaks increases at the expense of B_5H_{11} signals as the temperature is raised. The process is reversed upon lowering of the temperature; the B_5H_{11} signals again become intense at low temperatures accompanied by the disappearance of the resonance signals at 17 and 59 ppm. Upon warming of the system to −40° the B_5H_{11} resonance signals become very weak while the 17- and 59-ppm peaks become intense. While the temperature is maintained at −40°, signals due to other species (B_6H_{10}, B_5H_9, B_4H_{10}, and B_2H_6) begin to appear slowly. Upon warming of the sample to higher temperatures, these borane signals grow intense and the original two signals (17 and 59 ppm) disappear. This latter process is not reversible with temperature.

The spectra of mixtures of B_5H_{11} and diethyl ether in a 1:1 ratio and in a 1:3.7 ratio are essentially the same as that described above, except that the decomposition reaction yielding various boranes proceeds much faster in the 1:3.7 mixture above −40°.

System of B_5H_{11}, Diethyl Ether, and Hydrogen Chloride. ^{11}B NMR spectra of a 1:2:2 mixture of B_5H_{11}, diethyl ether, and hydrogen chloride in dichloromethane solvent indicate only the resonance peaks of B_5H_{11} in the temperature interval −80 to −45°. At −45°, very weak B_4H_{10} signals become apparent. The intensity of the B_4H_{10} signals increases at the expense of the B_5H_{11} signals as the temperature is raised further. Diborane(6) first appears as a weak signal at −25°. At 0°, B_5H_{11} signals are no longer detectable, the B_4H_{10} signals are strong, and the signals of B_2H_6 are seen clearly. In addition, present in the spectrum at 0° are a triplet at −5.5 ppm with $J = 140$ Hz and a doublet at −8.0 ppm with $J = 150$ Hz. These two peaks are attributed to $BH_2Cl{\cdot}O(C_2H_5)_2$ and $BHCl_2{\cdot}O(C_2H_5)_2$, respectively. A chemical shift value of −7.9 ppm has been reported for the latter compound.[9]

When the three components were mixed in a ratio 1:2:1 (B_5H_{11}:$(C_2H_5)_2O$:HCl), spectra of the solution were the same as described for the 1:2:2 mixture at lower temperatures. At −20° a difference was noted in that the two resonance peaks at 17 and 59 ppm began to appear.

System of B_5H_{11} and Dimethyl Ether. At lower temperatures the spectral features of a 1:2 mixture of B_5H_{11} and dimethyl ether in dichloromethane are similar to those of the B_5H_{11}–diethyl ether system. No signals of $B_4H_9^-$ ion could be detected. In this system, however, the two peaks at 17 and 59 ppm were already detectable at −80°. Irreversible reactions take place above −40° as evidenced by the appearance of B_6H_{10} and $B_3H_7{\cdot}O(CH_3)_2$ signals (peak maximum at 7.0 ppm) along with weak B_2H_6 and B_4H_{10} signals.

System of B_5H_{11} and Diisopropyl Ether. A 1:2 mixture of B_5H_{11} and diisopropyl ether in dichloromethane gives exclusively the spectrum of B_5H_{11} at all temperatures (−96 to +23°).

Discussion

The observations presented in the foregoing section indicate that the type of interaction between pentaborane(11) and ether depends upon the nature of the individual ether.

Alkyl sulfides, or *thio*ethers, effect the symmetrical cleavage of B_5H_{11}

$$B_5H_{11} + 2R_2S \rightarrow R_2S{\cdot}BH_3 + R_2S{\cdot}B_4H_8$$

This reaction is analogous to the previously reported reactions of B_2H_6 and B_4H_{10} with thioethers

$$B_2H_6 + 2R_2S \rightarrow 2R_2S{\cdot}BH_3\ ^{10}$$

$$B_4H_{10} + 2R_2S \rightarrow R_2S{\cdot}BH_3 + R_2S{\cdot}B_3H_7\ ^{5}$$

The latter reaction which was confirmed in the course of this study takes place at −80°, at which temperature no intermediate species could be detected under the conditions employed.[11]

Unlike thioethers, *oxo*ethers do not bring about the symmetrical cleavage of B_5H_{11}. The species that are observed in the systems of B_5H_{11} and oxoethers at low temperatures depend upon the base strength of the interacting ether. Tetrahydrofuran, the strongest base among those tested in this study, reacts with B_5H_{11} to produce two species, namely I and II, which are in equilibrium with each other. The more weakly basic dimethyl ether produces only one species which is identified by its characteristic ^{11}B NMR peaks (at 17 and 59 ppm) that are identical with those of species II in the B_5H_{11}–tetrahydrofuran system. Diethyl ether, a weaker base than dimethyl ether, also produces only one species which also has the same two peaks in its ^{11}B NMR spectrum, but a higher temperature is required for its formation than those for the dimethyl ether and tetrahydrofuran reactions. Diisopropyl ether, the weakest base among those tested, does not react with B_5H_{11}.

Species I in the tetrahydrofuran system contains $B_4H_9^-$ ion (vide ante) and is considered to be the product of the unsymmetrical cleavage of B_5H_{11}

$$B_5H_{11} + 2THF \rightarrow H_2B(THF)_2^+B_4H_9^-$$

Failure to observe the ^{11}B NMR signal for the cation $H_2B(THF)_2^+$ must be due to the broadness of the resonance peak. Indeed, in our study of the B_4H_{10}–THF system the signal of the cation in $H_2B(THF)_2^+B_3H_8^-$ could be observed as a broad hump only in proton spin decoupled spectra.[12b]

The study of the reaction of HCl with a mixture of B_5H_{11} and tetrahydrofuran provides additional evidence supporting the assignment of species I as $H_2B(THF)_2^+B_4H_9^-$. The reaction of $B_4H_9^-$ with HCl in ether is known to give B_4H_{10} at a temperature as low as −80°[2,13]

$$B_4H_9^- + HCl \rightarrow B_4H_{10} + Cl^-$$

Upon addition of HCl to a 1:2 mixture of B_5H_{11} and tetrahydrofuran, species I would be consumed by the above reaction. Since I is in equilibrium with II, the reaction would continue until all the original B_5H_{11} would have been converted to B_4H_{10} and $H_2BCl{\cdot}THF$

$$H_2B(THF)_2^+B_4H_9^- + HCl \rightarrow H_2BCl{\cdot}THF + B_4H_{10} + THF$$

The B_4H_{10} produced would react with tetrahydrofuran to give $H_2B(THF)_2^+B_3H_8^-$

$$B_4H_{10} + 2THF \rightarrow H_2B(THF)_2^+B_3H_8^-\ ^{12}$$

Thus, the overall reaction would be

$$B_5H_{11} + 2THF + HCl \rightarrow {}^1/_2B_4H_{10} + H_2BCl{\cdot}THF + {}^1/_2H_2B(THF)_2^+B_3H_8^-$$

Experimentally the system containing B_5H_{11}, tetrahydrofuran, and HCl in a 1:2:1 molar ratio gave B_4H_{10} and $B_3H_8^-$ ion in about equimolar quantities (Table II). The $H_2BCl{\cdot}THF$ signal was apparently hidden as a broad hump under the broad envelope of the low-field signal of B_4H_{10}. At 10°, the triplet peak of $H_2BCl{\cdot}THF$ was seen clearly along with the signals of $THF{\cdot}B_3H_7$ and B_2H_6 which were formed by the conversion of $H_2B(THF)_2^+B_3H_8^-$ [12]

$$H_2B(THF)_2^+B_3H_8^- \rightarrow THF{\cdot}B_3H_7 + THF{\cdot}BH_3 \rightarrow THF{\cdot}B_3H_7 + {}^1/_2B_2H_6 + THF$$

Thus, the experimental result is consistent with that expected for the reaction of $H_2B(THF)_2^+B_4H_9^-$ with 1 equiv of HCl.

When the ratio B_5H_{11}:THF:HCl was 1:3:2, the $B_3H_8^-$ ion, which was produced in the above reaction, would undergo a further reaction with the excess of HCl to give $THF{\cdot}B_3H_7$ and H_2 at low temperatures[14]

$$H_2B(THF)_2^+B_3H_8^- + HCl \rightarrow THF{\cdot}B_3H_7 + H_2BCl{\cdot}THF + H_2$$

Or, at higher temperatures, the reaction between $THF{\cdot}BH_3$ and HCl would proceed, i.e.

$$B_4H_{10} + 2THF + HCl \rightarrow THF{\cdot}B_3H_7 + THF{\cdot}BH_3 + HCl \rightarrow THF{\cdot}B_3H_7 + H_2BCl{\cdot}THF + H_2$$

Therefore, the final products at room temperature from either reaction involving the 1:3:2 ratio should be $THF{\cdot}B_3H_7$ and $H_2BCl{\cdot}THF$ regardless of reaction pathway. The overall reaction is

$$B_5H_{11} + 3THF + 2HCl \rightarrow 2H_2BCl{\cdot}THF + THF{\cdot}B_3H_7 + H_2$$

The experimental result shown in Table II for the system containing B_5H_{11}, tetrahydrofuran, and HCl in a 1:3:2.5 ratio is consistent with that expected above. The presence of a small amount of $HBCl_2{\cdot}THF$ in the products is attributed to the use of excess HCl, which causes a further reaction

$$H_2BCl{\cdot}THF + HCl \rightarrow HBCl_2{\cdot}THF + H_2$$

to proceed at room temperature.

The equilibrium between I, which is $H_2B(THF)_2{}^+B_4H_9{}^-$, and II shifts in favor of the formation of II when the amount of tetrahydrofuran in the mixture is decreased, as seen in the study of a 1:1 mixture of B_5H_{11} and tetrahydrofuran. Since 2 mol of tetrahydrofuran/mol of B_5H_{11} is involved in the formation of I, the observed equilibrium shift suggests that less than 2 mol of tetrahydrofuran is involved per mole of B_5H_{11} in the formation of II. The most likely formula suggested for this species would be a 1:1 adduct $B_5H_{11}{\cdot}THF$ and the reactions of B_5H_{11} with tetrahydrofuran at the low temperatures are summarized as

$$B_5H_{11} + 2THF \rightleftarrows B_5H_{11}{\cdot}THF + THF \rightleftarrows H_2B(THF)_2{}^+B_4H_9{}^-$$

Similarity between the tetrahydrofuran reaction of B_5H_{11} and that of B_4H_{10} is apparent here in that the unsymmetrical cleavage of the boranes takes place in both cases.[12] Differences, however, are also observed between the two systems. The 1:1 adduct $B_5H_{11}{\cdot}THF$ has certain stability, whereas the corresponding adduct for B_4H_{10}, $B_4H_{10}{\cdot}THF$, apparently does not have a comparable stability to permit its detection in the NMR spectrum. In the B_4H_{10}–tetrahydrofuran system the unsymmetrical cleavage product, $H_2B(THF)_2{}^+B_3H_8{}^-$, is in equilibrium with the symmetrical cleavage products, $THF{\cdot}BH_3$ and $THF{\cdot}B_3H_7$. Higher temperatures favor the symmetrical cleavage[12]

$$H_2B(THF)_2{}^+B_3H_8{}^- \rightleftarrows THF{\cdot}BH_3 + THF{\cdot}B_3H_7$$

The formation of the corresponding symmetrical cleavage products of B_5H_{11}, however, could not be observed in the present study. Instability of the B_5H_{11} symmetrical cleavage product, $THF{\cdot}B_4H_8$, at the higher temperatures and the unique stability of $B_5H_{11}{\cdot}THF$ appear to be responsible for our not observing a perfect analogy between the two systems.

It was reported that the ability of ethers to cleave B_4H_{10} unsymmetrically parallels with the base strength of ethers;[12a] tetrahydrofuran produces $H_2B(THF)_2{}^+B_3H_8{}^-$ readily at low temperatures upon reacting with B_4H_{10}, and tetrahydropyran does the same, but less extensively than tetrahydrofuran, whereas diethyl ether does not react with B_4H_{10} under comparable conditions. The same tendency is observed in the present study for the systems of B_5H_{11} and ethers; only the strongly basic tetrahydrofuran causes the unsymmetrical cleavage of B_5H_{11}.

The significant and characteristic feature of the B_5H_{11} reactions with dimethyl and diethyl ethers is the formation of the species that show two ^{11}B NMR signals at 17 and 59 ppm in a 4:1 intensity ratio. It is noted earlier in this paper that these two signals are identical with those of species II in the B_5H_{11}–tetrahydrofuran system. The structure of the species formed in dimethyl and diethyl ether systems, therefore, must be very closely related to II. Accordingly, formulas $B_5H_{11}{\cdot}O(CH_3)_2$ and $B_5H_{11}{\cdot}O(C_2H_5)_2$ are considered to be appropriate for these species.

The formula $B_5H_{11}{\cdot}O(CH_3)_2$, in particular, receives support from an experimental observation reported by Burg and Kratzer.[15] They treated B_5H_{11} with dimethyl ether at −78° and isolated a residue with an apparent composition $B_5H_{11}{\cdot}1.50(CH_3)_2O$ at −78°. Upon pumping on this residue at −78° for 3 hr, more dimethyl ether was removed and the composition of the remainder became $B_5H_{11}{\cdot}1.45(CH_3)_2O$, suggesting solid–solution effects in the retention of dimethyl ether beyond the 1:1 ratio. It is also described in the same report that the residue was not a mixture of $(CH_3)_2O{\cdot}BH_3$ with some kind of etherated B_4H_8.

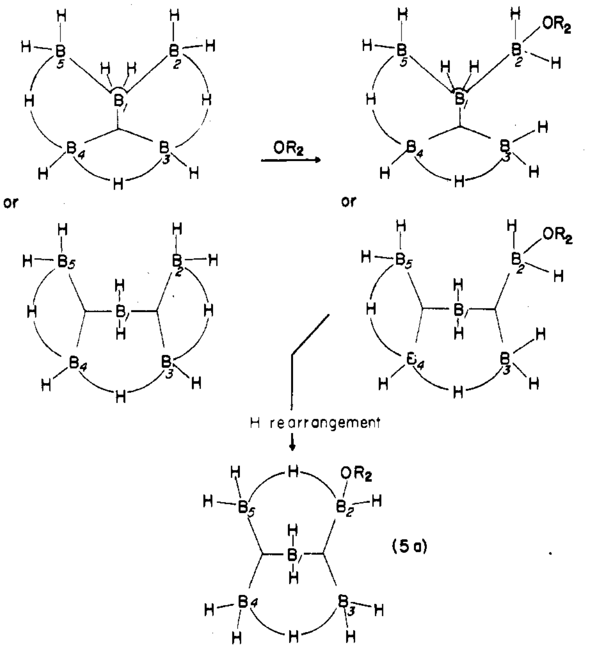


Figure 5. Formation of $B_5H_{11}{\cdot}OR_2$ indicating a possible structure for the 1:1 adduct.

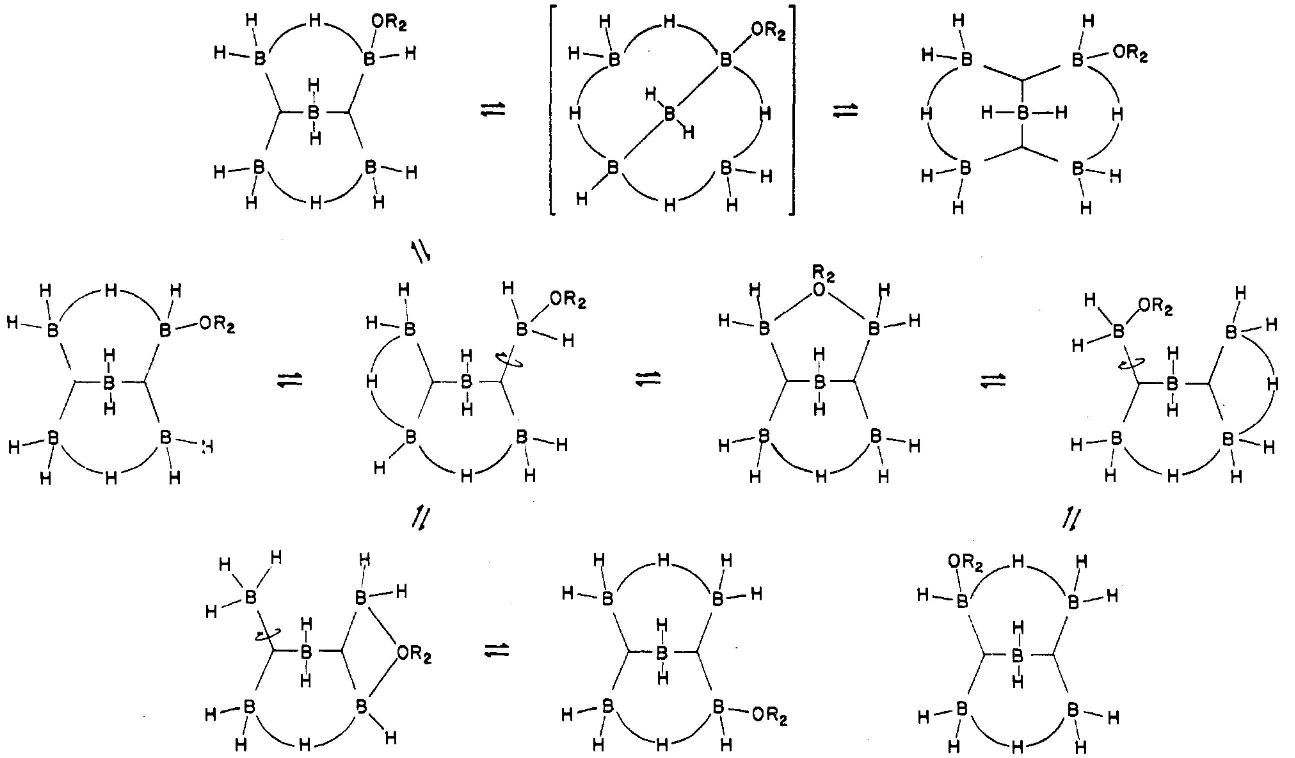
A possible bonding structure analogous to the $B_5H_{12}{}^-$ ion 2205 structure[16] is drawn for the 1:1 adduct $B_5H_{11}{\cdot}OR_2$ in Figure 5a. The coordination of an ether molecule on the B_2 atom, cleaving a B–H–B bridge bond, followed by a slight rearrangement of hydrogen atoms, would result in the structure of Figure 5a. This reaction path is indicated in Figure 5 for both possible bonding structures of B_5H_{11}.[17]

The ^{11}B NMR spectra of $B_5H_{11}{\cdot}OR_2$, which consists of two resonance peaks at 17 and 59 ppm in an area ratio 4:1, may be explained by assuming a rapid migration of the ligand ether within the molecule and a rapid hydrogen tautomerism,[18] as illustrated in Chart I. Such migration and tautomerism would make the four basal boron atoms equivalent.

The formation of $B_5H_{11}{\cdot}OR_2$ from B_5H_{11} and ether is endothermic as indicated by the observed positive temperature dependence of the equilibrium constant of formation. In the formation of $B_5H_{11}{\cdot}OR_2$ the energy of the B–O bond resulting from the coordination of ether does not exceed the sum of the energies that are required to cleave a B–H–B bridge bond and to reorganize bonds in the molecule. Therefore, a positive entropy change in the formation of the B_5H_{11} adduct would have to be provided by some sort of intramolecular disorder like that illustrated above.[19] If one accepts such a stabilization effect due to entropy increase, the aforementioned difference between B_4H_{10} and B_5H_{11} in the ability of forming 1:1 adducts may be attributed to the intrinsic inability of $B_4H_{10}{\cdot}OR_2$ to have an extensive intramolecular disorder comparable to that in $B_5H_{11}{\cdot}OR_2$. It is pointed out that $B_3H_8{}^-$ ion and B_3H_7 etherates, which are the cleavage products of B_4H_{10}, have the stabilization due to the scrambling of hydrogen atoms[20] around boron atoms.

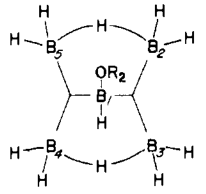
The magnitude of the equilibrium constant observed for the reaction $B_5H_{11} + R_2O \rightleftarrows B_5H_{11}{\cdot}OR_2$ decreases going from the tetrahydrofuran system to the diisopropyl ether system, or in the order of decreasing base strengths of the ethers. This trend is naturally expected as due to the more negative enthalpy of formation for the more strongly basic ether.

Chart I



The ^{11}B NMR chemical shift values of the two peaks for the 1:1 adducts $B_5H_{11}\cdot OR_2$ are unique in that they are the same for all three ether adducts. Moreover, the reported chemical shift values of the two peaks for $B_5H_{12}^-$ ion are 16.6 and 58.6 ppm with an intensity ratio 3.9:1.0;[21] they are identical, within experimental error, with the values for the species being discussed here. These values contrast the reported values for the adducts of BH_3 and B_3H_7; reported are −2.3, 0.8, and 38 ppm for $(CH_3)_2O\cdot BH_3$, $THF\cdot BH_3$, and BH_4^-, respectively,[22] and 6.9 and 11.3, 8.5 and 12.7, and 30 ppm for $(C_2H_5)_2O\cdot B_3H_7$, $THF\cdot B_3H_7$,[23] and $B_3H_8^-$,[22] respectively.

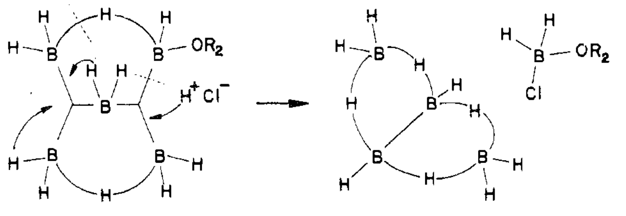
A different structure (displayed) for the adduct $B_5H_{11}\cdot OR_2$, in which the ether ligand is attached to the apical boron atom, satisfies the equivalency of four basal boron atoms without ether migrating among the basal positions. This structure



is thought to be unlikely because of the following arguments. Since the ether molecule is bonded to a single boron atom to which a single hydrogen atom is bonded, one would expect, contrary to our observation, to observe a distinct chemical shift value for the apical boron for each different ligand attached to it. The formation of the unsymmetrical cleavage product, $H_2B(OR_2)_2^+B_4H_9^-$, can be visualized readily as the result of another ether coordination on the B_2 atom (Figure 5a), whereas the apically substituted structure requires complicated reaction pathways to produce the same product. Charge distribution in B_5H_{11}[24] suggests also that the basal boron atoms are the preferred sites of nucleophilic attack compared to the apical boron atom.

The ammonia reaction of B_5H_{11}, which produces an unsymmetrical cleavage product, $H_2B(NH_3)_2^+B_4H_9^-$, would involve the formation of a 1:1 molecular adduct as an intermediate,[25] as described previously.[2] The structure of the adduct may well be similar to the one proposed here for the ether adducts. Since ammonia is a stronger base than ethers, equilibrium in the ammonia reaction would be shifted more toward the formation of the unsymmetrical cleavage product than that in the tetrahydrofuran–B_5H_{11} system. Thus the observations on the reaction system of B_5H_{11} with ammonia can be interpreted as an extension of the B_5H_{11}–ether reactions. Other factors are also involved in determining a reaction pathway in cleavage reactions.[26] The different behavior of thioethers toward B_5H_{11} has been demonstrated already in this study. The enhanced stability of thioether adducts of B_4H_8 relative to that of oxoether adducts[27] is partly responsible for the difference. An analogous difference in stability is noted for the amine and phosphine adducts of B_4H_8; while several stable phosphine adducts have been reported,[1] amine adducts have not.

Diethyl ether plays an essential role in the reaction between B_5H_{11} and hydrogen chloride at −45° to produce B_4H_{10}. This is demonstrated by the fact that B_5H_{11} does not react with hydrogen chloride until the temperature is raised to −30°. Even at this temperature only a trace quantity of B_4H_{10} is detected in the ^{11}B NMR spectrum. In the THF–HCl–B_5H_{11} system, the reacting species to produce B_4H_{10} is the $B_4H_9^-$ ion that had been produced by the unsymmetrical cleavage of B_5H_{11}. Although the reaction of HCl with B_5H_{11} in the diethyl ether system may be looked upon as a reaction of HCl with the $B_4H_9^-$ ion that might have been produced in a minute quantity by unsymmetrical cleavage of B_5H_{11}, a more favored reaction path is proposed, as shown.



This reaction sequence involving the $B_5H_{11}\cdot O(C_2H_5)_2$ adduct is favored because of the following experimental observations. The formation of B_4H_{10} occurs above −45° in the diethyl ether system and not at lower temperatures where the formation of unsymmetrical cleavage product, if any, would be more favorable than at higher temperatures. In contrast, the THF–B_5H_{11} system gives complete reaction with HCl at the significantly lower temperature of −80°.

Summary

Similarity between the reactions of B_5H_{11} and B_4H_{10} is noted in that both boranes react with thioethers to produce symmetrical cleavage products and react with strong oxoethers, tetrahydrofuran in particular, to form unsymmetrical cleavage products at low temperatures.

Differences also occur in the behavior of the two boranes. Although B_5H_{11} reacts with oxoethers to form 1:1 adducts, B_4H_{10} does not. Reactions of B_4H_{10} with oxoethers produce symmetrical cleavage products at higher temperatures whereas no evidence for the formation of symmetrical cleavage products could be obtained in the reactions of B_5H_{11} with oxoethers. These differences are interpreted as due to the unique stability of the 1:1 adduct $B_5H_{11}{\cdot}OR_2$ and the instability of the symmetrical cleavage product $B_4H_8{\cdot}OR_2$.

The study of the mechanistic aspect of the formation of higher boranes, which was one of the motives for initiating this work, is in progress and will be described elsewhere upon its completion.

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Registry No. B_5H_{11}, 18433-84-6; $(C_2H_5)_2S$, 352-93-2; methyl sulfide, 75-18-3; tetrahydrofuran, 109-99-9; HCl, 7647-01-0; dimethyl ether, 115-10-6; $H_3B{\cdot}S(C_2H_5)_2$, 55606-71-8; $(C_2H_5)_2S{\cdot}B_4H_8$, 55669-44-8; $(CH_3)_2S{\cdot}BH_3$, 13292-87-0; $(CH_3)_2S{\cdot}B_4H_8$, 55669-43-7; B_5H_9, 19624-22-7; THF·BH_3, 14044-65-6; $(C_2H_5)_2O{\cdot}B_3H_7$, 52842-97-4; $H_2B(THF)_2{}^+B_4H_9{}^-$, 55669-07-3; B_4H_{10}, 18283-93-7; $H_2B(THF)_2{}^+B_3H_8{}^-$, 55669-45-9; B_3H_7·THF, 52842-96-3; BH_2Cl·THF, 55606-72-9; B_2H_6, 19287-45-7; $BH_2Cl{\cdot}O(C_2H_5)_2$, 36594-41-9; $BHCl_2{\cdot}O(C_2H_5)_2$, 41156-66-5; B_6H_{10}, 23777-80-2; $B_3H_7{\cdot}O(CH_3)_2$, 12347-17-0; $B_5H_{11}{\cdot}O(CH_3)_2$, 55648-92-5; $B_5H_{11}{\cdot}O(C_2H_5)_2$, 55606-73-0.

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(11) Chemical shift values for the triborane adducts were determined at +10°: 29.6 (B_1) and 11.1 ppm (B_2, B_3) for $(CH_3)_2S{\cdot}B_3H_7$; 32.8 (B_1) and 11.7 ppm (B_2, B_3) for $(C_2H_5)_2S{\cdot}B_3H_7$. The peaks are all broad. The multiplet feature could be recognized as very slight shoulders on the B_2 and B_3 peaks. Apparently the multiplet consists of an even number of peaks; six peaks could be detected out of presumably eight peaks.

(12) (a) R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964). (b) During the course of this study, the system of B_4H_{10} and THF was reexamined. The results reported by Schaeffer et al.[12a] were reproducible. Additional observations relevant to the discussion in this paper are reported below. (i) A mixture of B_4H_{10} and THF in a molar ratio 1:1 in CH_2Cl_2 solution gave a spectrum that contains the signals of B_4H_{10} and $B_3H_8{}^-$ (in about a 1:1 *molar* ratio) at −30°. At higher temperatures signals due to THF·B_3H_7, THF·BH_3, and B_2H_6 grow at the expense of the B_4H_{10} signal intensity. This observation supports the reaction stoichiometry 1:2 for the B_4H_{10}–THF system. (ii) The resonance signal that can be attributed to $H_2B(THF)_2{}^+$ ion could be detected as a broad peak at −8.5 ppm in proton spin decoupled spectra. (iii) The equilibrium $H_2B(THF)_2{}^+B_3H_8{}^- \rightleftarrows$ THF·BH_3 + THF·B_3H_7 at a temperature range of −40 to −10° was confirmed; lowering of temperature and adding of B_2H_6 to the system both shift the equilibrium toward the left. The detailed discussion will be presented elsewhere.

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(16) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963, p 46.

(17) In view of the low electron density on the B_3 atom, the coordination of ether may take place at the B_3 position. The resulting configuration, however, would be identical with that shown in Figure 5a except for the numbering of basal boron atoms; B_2–H–B_3 and B_4–H–B_5 bonds would be broken and the B_2–H–B_5 bond would be formed. Presently available experimental data do not permit us to differentiate the two reaction paths.

(18) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds", W. A. Benjamin, New York, N.Y., 1969, p 553.

(19) If one assumes that, in the $B_5H_{11}{\cdot}OR_2$ molecule as shown in Figure 5a, the ether ligand can be attached to any one of the four basal boron atoms, nine basal hydrogen atoms can scramble among nine possible positions, two sets of B–H–B bond arrangements (B_2–H–B_5, B_3–H–B_4 and B_2–H–B_3, B_4–H–B_5) are possible, and the two apically attached hydrogen atoms can exchange positions with each other, the number of possible configurations is calculated to be 5.8×10^6, which gives an entropy value 31 eu for the disorder. Thus, contribution to the free energy change amounts to 6.0 and 7.5 kcal at −80 and −30°, respectively. In view of the apparent closeness of the energies involved in cleavages of B–H–B and R_2O–B bonds as suggested from the reactions of ethers with B_2H_6 and with B_4H_{10}, the amounts of energy estimated above, which probably represent minimal figures, are considered to have a significant effect on the formation of the 1:1 adduct $B_5H_{11}{\cdot}OR_2$.

(20) Reference 16, p 127.

(21) H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **93**, 3798 (1971).

(22) Reference 18, pp 58 and 436.

(23) G. Kodama, *Inorg. Chem.*, **14**, 452 (1975).

(24) Reference 16, p 110.

(25) The intermediate considered here is a 1:1 molecular adduct and not the deprotonation product of B_5H_{11}, $NH_4{}^+B_5H_{10}{}^-$, which is reported by H. D. Johnson and S. G. Shore, *J. Am. Chem. Soc.*, **92**, 7586 (1970). The latter compound converts, in the presence of excess NH_3, to the diammoniate of B_5H_{11}. The 1:1 molecular adduct is thought to be an intermediate in this conversion process.

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(27) It was thought previously in our study that the decomposition of $B_5H_{11}{\cdot}O(C_2H_5)_2$ proceeded through the formation of $B_4H_8{\cdot}O(C_2H_5)_2$ [Abstracts, 2nd International Meeting on Boron Chemistry, Leeds, England, March 1974, Paper No. 22]. However, it is clear now that the ^{11}B NMR signals which were thought to be attributable to the B_4H_8 etherate [Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, No. INOR 85] are due to the other borane decomposition products. The diethyl etherate of B_4H_8 prepared by the reaction of $B_5H_9{\cdot}2NH_3$ with HCl in diethyl ether [G. Kodama, U. Engelhardt, C. Lafrenz, and R. W. Parry, *J. Am. Chem. Soc.*, **94**, 407 (1972)] appears stable only at lower temperatures.