weaker acid than $B_{10}H_{14}$ but stronger than B_2H_6 and B_5H_9.

Kodama[17] has recently indicated the presence of $B_4H_9^-$ in the diammoniate of pentaborane(11). Johnson and Shore[18] also report that they have prepared salts of $B_4H_9^-$ by a different method.

The details of our work will be described in a later publication.

Acknowledgment. Partial support of this work by the Rutgers Research Council is gratefully acknowledged.

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Deprotonation of Tetraborane(10) by Ammonia. The Temperature-Dependent Boron-11 Nuclear Magnetic Resonance Spectrum of $B_4H_9^-$

Sir:

It has been demonstrated that the bridge hydrogens of the intermediate boron hydrides, B_5H_9 and B_6H_{10}, can function as Brønsted acid sites in the presence of strongly basic anions.[1-4] We have recently reported that B_6H_{10} is deprotonated by NH_3,[5] thereby showing that the bridge acidity of this hydride is not restricted to reactions with strongly basic anions. At this time, we wish to report that in the initial reaction of tetraborane(10) with ammonia in ether at low temperature, the boron hydride is deprotonated. This observation is significant in that all previously reported reactions of tetraborane(10) with nucleophiles produced as the only identifiable products fragments which arise from bridge cleavage;[6] furthermore, it is in accord with the earlier suggestion of Parry and Edwards[7] that bridge hydrogens of the lower boron hydrides interact with ammonia.

$$B_4H_{10} + NH_3 \xrightleftharpoons{(C_2H_5)_2O} NH_4^+B_4H_9^- \qquad (1)$$

At −65°, $NH_4^+B_4H_9^-$ was observed exclusively in the initial boron-11 nmr spectrum of the sample. Upon standing, the bridge cleavage product, $BH_2(NH_3)_2^+$-$B_3H_8^-$, and B_4H_{10} appeared simultaneously in the spectrum. As the temperature was raised, reaction 2 accelerated and the $NH_4^+B_4H_9^-$ disappeared as the products of reaction 2 were formed. No H_2 formed.

$$B_4H_{10} + NH_3 \xrightarrow{(C_2H_5)_2O} {}^1/_2BH_2(NH_3)_2^+B_3H_8^- + {}^1/_2B_4H_{10} \qquad (2)$$

This result suggests the possibility of competing reactions involving ammonia and tetraborane(10): a rapid, reversible reaction in which the ammonium salt is formed through deprotonation of B_4H_{10} (eq 1); and a slower irreversible reaction in which bridge cleavage occurs (eq 2).

The $B_4H_9^-$ anion produced in reaction 1 was identified by its boron-11 nmr spectrum which was identical with that of KB_4H_9 prepared through the reaction of KH with B_4H_{10} in diethyl ether.[8] In addition, $(n\text{-}C_4H_9)_4$-NB_4H_9 was prepared from $NH_4^+B_4H_9^-$ through the following metathesis reaction and identified by boron-11 nmr.

$$NH_4^+B_4H_9^- + (n\text{-}C_4H_9)_4NI \xrightarrow[-78°]{CH_2Cl_2-(C_2H_5)_2O} (n\text{-}C_4H_9)_4NB_4H_9 + NH_4I\downarrow \qquad (3)$$

Also, $(n\text{-}B_4H_9)_4NB_4H_9$ was prepared from KB_4H_9.[10]

$$KB_4H_9 + (n\text{-}C_4H_9)NI \xrightarrow[-35°]{CH_2Cl_2-(C_2H_5)_2O} (n\text{-}C_4H_9)_4NB_4H_9 + KI\downarrow$$

The identity of the NH_4I and the KI produced in these reactions was established by X-ray powder diffraction. The product $BH_2(NH_3)_2^+B_3H_8^-$ from reaction 2 was identified from its boron-11 nmr spectrum and its X-ray powder diffraction pattern. Tetraborane(10) from reaction 2 was identified by its boron-11 nmr spectrum. The area ratios obtained from the boron-11 nmr spectrum and a mass balance of the products recovered from reaction 2 established the stoichiometry. For purposes of the nmr study, $B_4H_9^-$ was generated from the deprotonation of B_4H_{10} by KH in diethyl ether at −78°. Hydrogen evolution was rapid and nearly quantitative. At room temperature the solution deteriorated noticeably in 20–30 min; at −78° solutions appear to be stable indefinitely. The boron-11 nmr spectrum of the anion was studied over the temperature range −80° to ambient.

The low-temperature spectrum (−80 to −45°) may be assigned on the basis of the 2113 structure proposed by Lipscomb for this anion[11] (see Figure 1). Analogous assignments have been made for the boron-11 nmr spectra of the isoelectronic species B_4H_8L (L = CO,[12] PF_3,[12] $PF_2N(CH_3)_2$,[13] and PF_2H[13]); this type of structure for $B_4H_8PF_2N(CH_3)_2$ has been established by X-ray diffraction studies.[14] Thus, at −45° a triplet of relative intensity 1.0 is observed (δ 53.2 ppm relative to $BF_3 \cdot O(C_2H_5)_2$, J = 96 Hz), and two broad, unresolved resonances with a total combined relative intensity of 2.8 are also present (δ 9.7 and 0.4 ppm). The triplet may be assigned to B_1, the resonance at 9.7

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[6] See, for example, L. J. Edwards, W. V. Hough, and M. D. Ford, *Int. Congr. Pure Appl. Chem., 16th, 1957*, 475 (1957); G. Kodama, R. W. Parry, and J. C. Carter, *J. Amer. Chem. Soc.*, **81**, 3534 (1959); W. V. Hough and L. J. Edwards, *Advan. Chem. Series*, **No. 32**, 184 (1961); R. W. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

[7] R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959). A weak complex involving addition of ammonia to bridging hydrogens was proposed in this paper as a precursor to cleavage products.

[8] We have also deprotonated B_4H_{10} with $(n\text{-}C_4H_9)_4NB_5H_8$ and $(n\text{-}C_4H_9)_4NB_6H_9$ in dichloromethane. Bond and Pinsky, in an independent and concurrent investigation,[9] have prepared LiB_4H_9 by the reaction of B_4H_{10} with $LiCH_3$ and with LiB_5H_8, in diethyl ether.

[9] A. C. Bond and M. L. Pinsky, *J. Amer. Chem. Soc.*, **92**, 7585 (1970).

[10] The preparation of tetra-*n*-butylammonium salts of boron hydride anions from the corresponding potassium salts by metathesis with $(n\text{-}C_4H_9)_4NI$ in CH_2Cl_2–ether solvent mixtures at low temperature is a general reaction developed by Mr. Vincent Brice of this laboratory.

[11] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 218.

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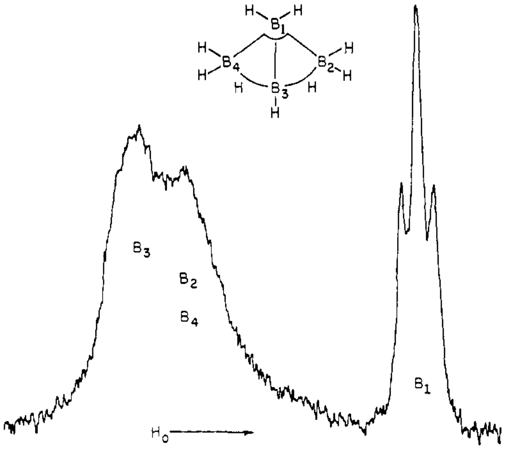

Figure 1. Boron-11 nmr spectrum of KB_4H_9 in $(C_2H_5)_2O$ at −45° (32.1 MHz).

ppm to B_2 and B_4, and the resonance at 0.4 ppm to B_3. At lower temperatures, the two resonances at low field are broader; the triplet is essentially unchanged.

On warming the nmr sample from −45 to 0°, the triplet first loses resolution, then broadens, and disappears as the peak at 0.4 ppm also broadens and disappears and the peak at 9.7 ppm becomes sharper. At 0°, a very broad new peak is visible, and as the temperature is raised this peak becomes more intense and progressively sharper until at room temperature (see Figure 2), it has become a doublet (δ 26.5 ppm, J = 105 Hz). The ratio of the areas of the two resonances at room temperature is 1.0:1.0. The doublet can be attributed to B_1 and B_3 which have become equivalent on the nmr time scale due to a rapid tautomerism. The chemical shift of this doublet is equal to the arithmetic mean of separate resonances observed at low temperature and recooling the sample regenerates the original low temperature spectrum.

The competing reactions described here involving NH_3 and B_4H_{10} (deprotonation and unsymmetrical cleavage) appear to occur in the reaction of NH_3 with B_6H_{10}.[5,15] A recent report has been made of the reaction of pentaborane(11) with ammonia to give a diammoniate salt,[16] $BH_2(NH_3)_2^+B_4H_9^-$. It is of interest to note that we have evidence for the deprotonation of B_5H_{11} by NH_3. Ammonia was frozen at −196° above a dimethyl ether solution of B_5H_{11} in an nmr tube (mole ratio 2:1). The sample was warmed to −100° in the nmr machine and the spectrum was recorded at intervals as the temperature was slowly raised to −80° At this point the spectrum of B_5H_{11} had completely disappeared but the high-field triplet characteristic of $B_4H_9^-$ was not present. The spectrum was very similar to that of KB_5H_{10} prepared from KH and B_5H_{11}. Furthermore, in a reaction analogous to (3) described above, NH_4I was produced and identified by X-ray powder diffraction.

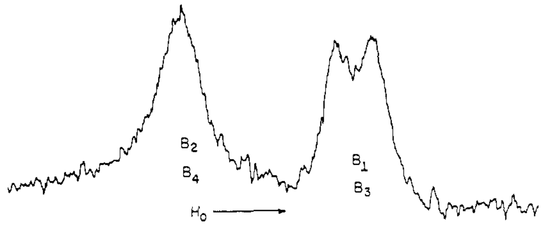

Figure 2. Boron-11 nmr spectrum of KB_4H_9 in $(C_2H_5)_2O$ at ambient temperature (32.1 MHz).

The following reaction is proposed.

$$B_5H_{11} + NH_3 + (n\text{-}C_4H_9)_4NI \xrightarrow[-97°]{CH_2Cl_2} (n\text{-}C_4H_9)_4NB_5H_{10} + NH_4I\downarrow$$

It is possible that deprotonation of the boron hydrides by ammonia is a general reaction. We are continuing to explore this possibility.

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[15] A preliminary report on the unsymmetrical cleavage of B_6H_{10} was presented by G. Kodama at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract INOR 10.

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Reactive Species Mutually Isolated on Insoluble Polymeric Carriers. I. The Directed Monoacylation of Esters

Sir:

When molecules of a substance, A, are bound to an insoluble, cross-linked polymer, their free motion will be restricted due to the relative rigidity of the polymeric lattice. If the molecules are bound at the appropriate mutual distances, a situation approaching infinite dilution can thus be obtained, while actual "concentration" may still be relatively high. In this manner intermolecular reactions between the molecules of A (or reactive intermediates derived therefrom) are minimized, and, depending on the case, these molecules can be made to react either with a soluble reagent, B, or intramolecularly to give cyclic compounds.

This concept of "immobilization-on-polymer" has recently been used in the synthesis of cyclic peptides.[1–4] In this communication we wish to illustrate the general applicability of this novel approach by reporting on the directed monoacylation of polymer-bound ester enolates.

When attempting to acylate esters having more than one α-hydrogen by treating the corresponding enolate with an acyl halide, two competing reactions are reported to occur: self-condensation of the ester to be acylated and diacylation due to proton transfer from the monoacylated ester to still unreacted enolate.[5,6]

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