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Evidence for the Nonsymmetrical Cleavage of Tetraborane by Ethers[1]

BY RILEY SCHAEFFER, FRED TEBBE, AND CARL PHILLIPS

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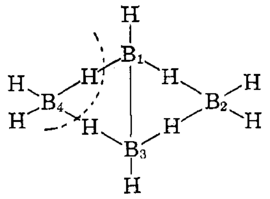
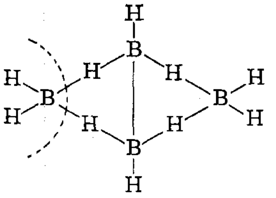
The ^{11}B n.m.r. spectra of solutions of tetraborane in tetrahydrofuran indicate that reaction takes place at $-53°$ to produce a material which has the spectral properties of the triborohydride ion. A signal attributable to the triborohydride ion also appears in tetraborane solutions of tetrahydropyran and ethylene glycol dimethyl ether but the material is less stable in the more weakly coordinating bases. The first detectable stage of the ether cleavage of tetraborane thus produces materials analogous to the products of the ammonia cleavage reaction which have previously been considered anomalous. A hydride ion from the triborohydride fragment apparently displaces an ether molecule from the $(ether)_2BH_2^+$ cation to yield the previously observed triborane-7 and borane derivatives. Unidentified intermediate species in the ammonia reaction suggest that cleavage of tetraborane to the diammoniate of tetraborane is itself a complex process which takes place by at least two steps.

Tetraborane reacts with a variety of Lewis bases which in general act to fragment the molecule into parts containing one and three borons.[2] With a series of amines and ethers the molecule is cleaved to produce triborane-7 derivatives of the respective bases and 0.5 mole of diborane[3] (complexed with base in some cases). By analogy with similar reactions of diborane, the reaction has been viewed in its over-all aspects as the removal of a 2(4) boron with three associated hydrogens in a symmetrical cleavage process.[2] Although the graphical representation of the cleavage process indicated in eq. 1 has occasionally been interpreted as a detailed mechanistic proposal, the formulation was originally advanced by Parry and Edwards as an operational classification of the reaction which was used in the development of a set of correlations of boron hydride reactions and to provide a basis for prediction and discussion of other reactions.[2] Among the ethers and amines thus far investigated, only ammonia has been found to react with tetraborane to produce the boron cation $(NH_3)_2BH_2^+$.[4–6] It has been suggested[2,4,6] that the ammonia reaction proceeds by the removal of a 2(4) boron with two associated hydrogens in what was classified as a nonsymmetrical cleavage process.



$$+ 2\ \text{base} \rightarrow \text{base}\cdot BH_3 + \text{base}\cdot B_3H_7 \qquad (1)$$



$$+ 2NH_3 \rightarrow (NH_3)_2BH_2^+ + B_3H_8^- \qquad (2)$$

It was of interest to determine to what extent the symmetrical and nonsymmetrical cleavage models are representative of actual mechanisms in some of the reactions of tetraborane. In the present study, nuclear magnetic resonance spectral examination of the course of tetraborane reactions with selected ethers suggests that the over-all symmetrical cleavage represented by eq. 1 takes place first by a nonsymmetrical cleavage process analogous to the ammonia reaction of eq. 2, which is then followed by transfer of a hydride ion from

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[1] Studies of Boranes. XIV. For part XIII see R. Schaeffer and F. Tebbe, *Inorg. Chem.*, **3**, 1638 (1964).

[2] Reactions of diborane and tetraborane with Lewis bases have been discussed by R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

[3] L. J. Edwards, W. V. Hough, and M. D. Ford, paper presented at the 16th International Congress of Pure and Applied Chemistry, Section on Inorganic Chemistry, Paris, 1957, p. 475.

[4] G. Kodama and R. W. Parry, paper presented at the 16th International Congress of Pure and Applied Chemistry, Section on Inorganic Chemistry, Paris, 1957, p. 483.

[5] G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **79**, 1007 (1957).

[6] G. Kodama and R. W. Parry, *ibid.*, **82**, 6250 (1960).

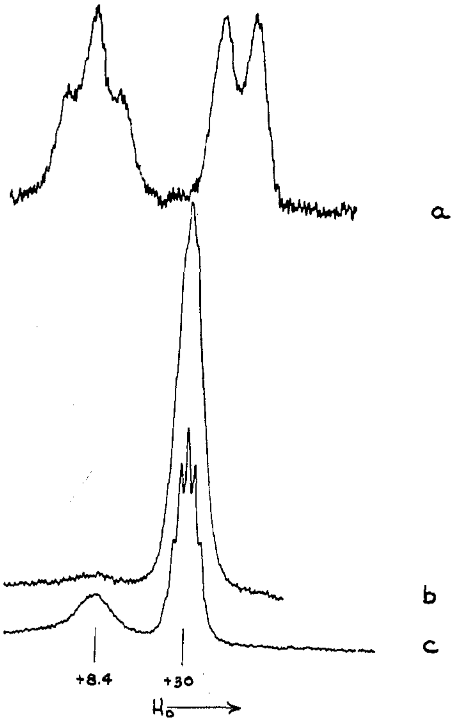

Fig. 1.—^{11}B n.m.r. spectra of tetraborane in tetrahydrofuran: a, −68°; b, −36°; c, −20°.

the triborohydride ion to the ether-coordinated BH_2^+ group to yield the previously observed products.

Experimental

Boron.—^{11}B n.m.r. spectra were obtained at 19.3 Mc. with a Varian Model 4300B spectrometer equipped with Varian low temperature accessories and a Model V3521 integrator and base-line stabilizer. All chemical shifts, including those drawn from the literature, are reported here in parts per million (p.p.m.) from boron trifluoride diethyl etherate = 0. The tetraborane was a Callery Chemical Company product, supplied through the courtesy of the U. S. Borax Research Corporation. Tetrahydrofuran (Baker, reagent grade), tetrahydropyran (K and K Laboratories), and ethylene glycol dimethyl ether (Ansul Ether 121) were distilled before use from lithium aluminum hydride. Tetraborane and the ether were condensed into an evacuated 5-mm. o.d. n.m.r. tube and were mixed at −80° prior to observation of the spectra by attaching the tube to the arm of a vibrating jig saw.

A sample of 1.10 mmoles of tetraborane dissolved in 4.50 mmoles of tetrahydrofuran exhibited a tetraborane-like ^{11}B n.m.r. spectrum at −68° (Fig. 1a). As the tube was allowed to warm from −68 to −53° in the spectrometer over a period of 12 min., the tetraborane signal intensity gradually diminished. (The decrease in signal intensity was attributed to an increase in solution viscosity as the reaction temperature was approached. A solution more concentrated in tetraborane, with a tetraborane:tetrahydrofuran ratio of 1:2, was observed to become nearly solid at the −53° reaction temperature.) At −53° a small peak appeared just below the low-field member of the tetraborane doublet; at −50° the tetraborane signal had disappeared, leaving only the weak line with a chemical shift of δ +30.1 ± 0.5 p.p.m. The intensity of the new peak increased as the temperature was allowed to rise and at −34° fine structure at the top of the peak was apparent (Fig. 1b). By the time the sample had reached −20° a seven-line multiplet with a coupling constant J = 33.2 ± 1 c.p.s. was detectable (Fig. 1c). Within experimental error the material giving rise to this multiplet has precisely the ^{11}B n.m.r. chemical shift and coupling constant of the triborohyride ion (δ +29.8 ± 0.5 p.p.m.; J = 33 c.p.s.[7]). The seven commonly observed[7,8] lines are apparent (Fig. 1c) and near the base of the set are suggested the two additional lines which the triborohydride ion is capable of displaying.[9] Chemically shifted below the multiplet there was a gradual rise on the order of 1–2 kc./sec. in width. The electronics of the V3521 accessory impose a ±2 kc./sec. inverted image of the signal (of about one-half the main band intensity) so that the broad low-field rise is reflected upside down on the high-field side of the triborohydride ion multiplet giving the base line a decided curvature throughout the entire spectrum (Fig. 2). As the formation of the triborohydride ion from tetraborane requires the presence of BH_2^+, the low-field rise in the spectrum is attributed to this cation. An additional unresolved peak in the spectrum centered at +8.4 ± 1.5 p.p.m. was barely evident at −34° (Fig. 1b), but it became more pronounced at −20° (Fig. 1c). At room temperature the +8.4 p.p.m. peak grew rapidly at the expense of the triborohydride multiplet and exhibited a poorly resolved structure with peak separations of 35 ± 5 c.p.s. From the method of preparation[8,10] and from the similarity of the n.m.r. data to that of diethyl ether triborane (δ +6.9 p.p.m.; J = 31 ± 5 c.p.s.[7]), the multiplet at +8.4 p.p.m. may be attributed to tetrahydrofuran triborane-7.

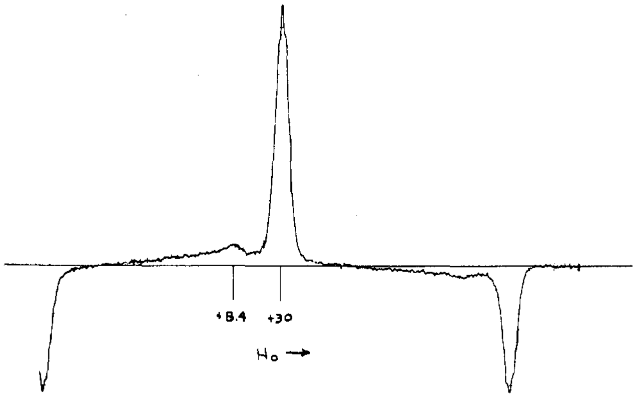

Fig. 2.—^{11}B n.m.r. spectrum of tetraborane in tetrahydrofuran solution at −24°, showing broad signal between the lower side band and the triborohydride ion peak at +30 p.p.m. The peak at +8.4 p.p.m. probably represents a small quantity of tetrahydrofuran triborane.

A peak attributable to triborohydride ion was also observed at low temperatures in solutions of tetraborane with tetrahydropyran and with ethylene glycol dimethyl ether. It was found by monitoring the ^{11}B n.m.r. spectrum that 1.06 mmoles of tetraborane, dissolved in 0.5 ml. of tetrahydropyran, reacted at −46° to yield two materials with chemical shifts of +7.0 ± 1.5 and +30 p.p.m., respectively. As in the tetrahydrofuran reaction, the +7.0 p.p.m. peak became resolved at higher temperatures and was assumed to arise from tetrahydropyran triborane-7.[10] The +30 p.p.m. peak did not form unaccompanied by tetrahydropyran triborane-7 and it did not exhibit the multiplet structure characteristic of a resolved triborohydride ion spectrum. On the basis of chemical shift and the expected similarity between tetrahydrofuran and tetrahydropyran behavior with tetraborane, however, the +30 p.p.m. peak may be assigned to the triborohydride ion. A spectrum of the material appearing in a 1:4 mixture of tetraborane in tetrahydropyran at −38° is illustrated in Fig. 3a. At comparable temperatures the spectrum of a solution of tetraborane in ethylene glycol dimethyl ether indicated only the presence of the tetraborane doublet (at high field in Fig. 3b) and a material in the triborane-7 etherate position. When the solution was cooled in the instrument to −56° over a period of

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(7) D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

(8) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(9) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

(10) G. Kodama, R. W. Parry, and J. C. Carter, *J. Am. Chem. Soc.*, **81**, 3534 (1959).

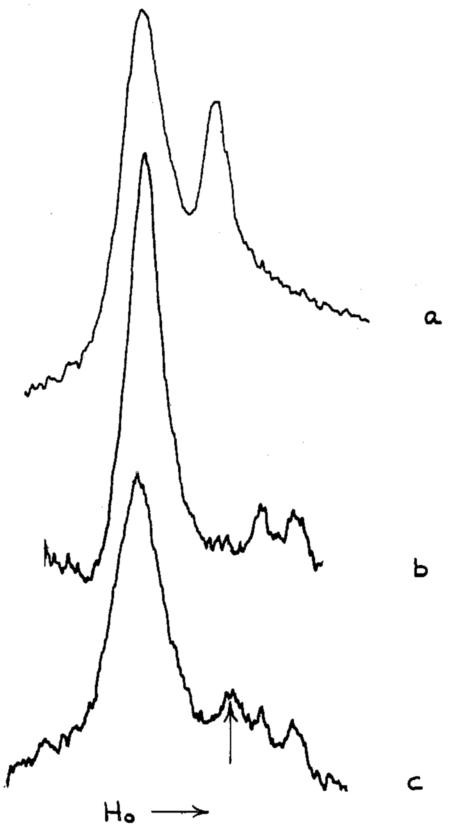

Fig. 3.—^{11}B n.m.r. spectra of solutions of tetraborane in tetrahydropyran and in ethylene glycol dimethyl ether. The peak at lower field in each spectrum is in the triborane etherate region. (a) Tetrahydropyran solution of tetraborane at −38°. The peak at higher field is at 30 p.p.m., which corresponds to the triborohydride ion position. (b) Ethylene glycol dimethyl ether solution of tetraborane at −32°. The doublet at higher field is assignable to undecomposed tetraborane. No signal at the triborohydride ion position is apparent. (c) The small indicated peak at 30 p.p.m. grew into the spectrum as the temperature of the ethylene glycol dimethyl ether solution was lowered to −56°. The chemical shift of the new peak again suggests the presence of the triborohydride ion.

about 10 min., a small, unresolved peak appeared in the triborohydride ion region (Fig. 3c).

The spectrum of a previously unwarmed mixture of 0.985 mmole of tetraborane and 1.95 mmoles of ammonia in 0.4 ml. of diethyl ether at −66° indicated the presence of unreacted tetraborane and material producing a triplet of relative intensities approximately in the ratio 1:2:1 with peak separations of 96 ± 5 c.p.s., centered at about 12 p.p.m. above the tetraborane doublet. At −54° the disappearance of the tetraborane signal was rapid, but the materials which were produced could be stabilized long enough for study by lowering the temperature to −80°. The −80° spectrum of the sample treated in this fashion consisted of a broad unresolved band centered below the triborohydride region and the relatively sharply defined triplet, centered above the triborohydride region. Ultimately, at room temperature, the spectrum consisted primarily of the expected[4-6,11] triborohydride ion signal.

The sodium triborohydride used for spectral comparison with the tetraborane cleavage products had been prepared in the course of other work from reaction of diborane (enriched to 98% ^{11}B) with sodium amalgam in the presence of diethyl ether.[12]

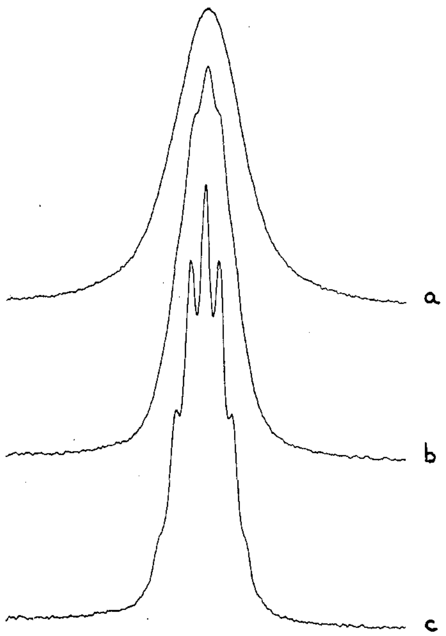

Fig. 4.—^{11}B n.m.r. spectra of sodium triborohydride: a, −29°; b, −6°; c, 15°.

It seemed essential to attempt to obtain chemical confirmation of the triborohydride ion. Consequently, a sample of 4.47 mmoles of tetraborane-10 was mixed with about 2 ml. of THF and allowed to remain at −80° for 1 hr. The solution was then warmed to −45° for an additional hour to allow reaction to occur and frozen at −196°, and 9 mmoles of trimethylamine was added. The reaction mixture was sealed from the line, warmed to −80° for 2 hr., to −63° for a few minutes, to −45° for 20 min., and finally to −30° for 1 hr. The mixture did not melt until it was warmed in the −45° bath and gave a clear solution at all higher temperatures. The ^{11}B n.m.r. spectrum showed a multiplet at δ 29.8 p.p.m. with a coupling constant of 31.0 c.p.s. The mixture was subsequently allowed to remain at room temperature for 11 days and apparently underwent slight decomposition since a quartet appeared in the n.m.r. spectrum somewhat downfield from the triborohydride multiplet. After 30 days at room temperature the tube was opened and the contents poured into 5 ml. of tetramethylammonium hydroxide. A white precipitate formed immediately but there were no other visible signs of reaction and in particular no apparent signs of hydrolysis. The white precipitate was collected, washed with water and with ether, and dried under vacuum. It was identified as tetramethylammonium triborohydride by its infrared spectrum. During recrystallization from methanol a major fraction of the material was lost but 0.84 mmole of recrystallized triborohydride salt was recovered corresponding to a 19% yield.

Discussion

The reaction of tetraborane with tetrahydrofuran at −53° produced a material which at higher temperatures had the ^{11}B n.m.r. chemical shift, coupling constant, and number of lines (Fig. 1c) characteristic of the triborohydride ion (Fig. 4). At −34° the signal differed from an idealized triborohydride spectrum in that the seven easily visible lines did not have the intensity ratios 8:28:56:70:56:28:8 expected for the central lines of a nonet. The observed ratios 14.6:32.8:57.6:70:57.6:32.8:14.6 are closer to those expected for the central seven lines of an eleven-line spectrum (12.5:33.4:58.4:70:58.4:33.4:12.5) but are also consistent with and closer to the intensities 14:33:58:70:58:33:14 obtained from the sample of

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(11) The ionic structure of the diammoniate of tetraborane has been confirmed by an X-ray diffraction study: C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, **82**, 5758 (1960).

(12) W. V. Hough, L. J. Edwards, and A. D. McElroy, *ibid.*, **80**, 1828 (1958).

authentic sodium triborohydride at 15°. The ^{11}B n.m.r. spectrum of sodium triborohydride has been reported[8] to be independent of temperature to $-60°$, and the collapse of the nonet at lower temperatures (Fig. 4) observed in this study was not expected. The solution of sodium triborohydride contained about three equivalents of the triborohydride ion in four of diethyl ether, and in the case of the tetraborane cleavage experiment, the triborohydride to tetrahydrofuran ratio, assuming the presence of the $(C_4H_8O)_2BH_2^+$ cation, was 1:2:1. Both the tetraborane and the authentic triborohydride solutions were thus highly concentrated, and it is quite possible that they were too viscous at lower temperatures to produce sharply resolved spectra. The low temperature behavior of sodium triborohydride observed in the present work is consistent with the behavior of the tetraborane cleavage product. The correspondence of all ^{11}B n.m.r. spectral properties of the cleavage product to those of the triborohydride ion provides strong evidence of identity.

The ^{11}B n.m.r. spectrum[13] of the diammoniate of diborane shows a resolved triplet at +14.6 p.p.m. assigned[12] to the $(NH_3)_2BH_2^+$ cation. The tetrahydrofuran analog of the amine-coordinated ion may thus be expected to appear well below the triborohydride ion.[14] In the low temperature solutions of tetraborane in tetrahydrofuran, no species was detected which could be identified as a 1:2:1 triplet from the BH_2^+ ion, but the broad rise of 1–2 kc./sec. width on the low-field side of the triborohydride ion signal (Fig. 2) requires the presence of additional boron and is assumed to arise from a very much broadened $(C_4H_8O)_2BH_2^+$ ion signal.[15]

The nuclear magnetic resonance data themselves constitute strong evidence for the cleavage of tetraborane to a triborohydride salt. Their weakness rests in the inability to detect the remaining boron atom and the possible discrepancy in relative intensity measurements. In particular it seems necessary to consider the possibility that only a single bridge bond has broken in the intermediate, resulting in a structure in which a borane group is still coordinated to a triborane fragment. On the grounds of the n.m.r. data alone this interpretation appears unlikely. The closest analogy for such an intermediate would appear to be the diborohydride ion, in which the coordinated borane group appears as a broadened but readily visible quartet. It is by no means evident that a simple mechanism exists for rapid interchange of the borane protons with those in the remainder of the molecule which could lead to the observed multiplet; furthermore, the fact that triborohydride rapidly disappears from the tetrahydrofuran solution but remains indefinitely if trimethylamine is added would be most difficult to explain if some four-boron intermediate were present.

In any event, the chemical isolation of triborohydride from the solution conclusively eliminates this interpretation. It is significant to observe that the cleavage products obtained with trimethylamine are derivatives of borane and triborane and not of triborohydride. Consequently, generation of triborohydride ion must be a consequence of the presence of the ether rather than of the amine.

The intermediate which was detected in the reaction of tetraborane with tetrahydropyran also had the chemical shift of triborohydride ion, but it was not formed free of the triborane-7 end product. The intermediate was present in small quantities in the ethylene glycol dimethyl ether solution only after the system had been rapidly cooled below the temperature at which conversion from tetraborane to triborane-7 was taking place (Fig. 3b,c). Although the spectra of the intermediate formed in these ethers did not have the triborohydride ion fine structure, the chemical shift of the material suggests that the tetrahydropyran and the ethylene glycol dimethyl ether reactions are analogous to the tetrahydrofuran reaction.

The ease with which the triborohydride ion formed free of the triborane-7 end product was dependent on the base used in the cleavage reaction and decreased in the order: ammonia, tetrahydrofuran, tetrahydropyran, ethylene glycol dimethyl ether. The order of the first three bases is also that determined[10] for decreasing stability of base–triborane-7 adducts and is that generally expected for decreasing base strength in boron hydride systems where adduct formation or cleavage reactions take place. In the present study this trend is consistent with the initial formation of the salt $(base)_2BH_2^+B_3H_8^-$, which is more or less stable depending upon the ease with which a hydride ion from the triborohydride fragment may displace one of the molecules of base coordinated with the cation.

The examination of the initial stages of the reaction between ammonia and tetraborane in diethyl ether solution indicated the presence of intermediate species which could not be assigned to any of the known cleavage products of tetraborane. The existence of at least one step prior to the formation of the known diammoniate of tetraborane salt makes it tempting to speculate that the reaction takes place by a stepwise displacement of bridge hydrogens with base. The first material formed could perhaps be $NH_3B_4H_{10}$.

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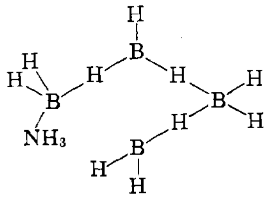
[13] T. P. Onak and I. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960).

[14] The $(C_4H_8)_2OBH_2^+$ cation may actually be centered below $(NH_3)_2BH_2^+$. In known cases, ether-coordinated boron hydrides occur at lower chemical shift positions than analogous amine coordinated hydrides.[7] For example, tetrahydrofuran borane (δ 0.9 p.p.m.[7]) appears at significantly lower field than ammonia borane (δ 23.8 p.p.m., determined by D. F. Gaines in this laboratory) and the di- and trimethylamine boranes.[7] Tetrahydrofuran triborane-7 appears about 10 p.p.m. below trimethylamine triborane (δ 18.6 ± 0.5 p.p.m.; $J = 35.0 \pm 1$ c.p.s. determined in other phases of this work).

[15] In connection with the postulate of a broadened BH_2^+ ion signal, it may be mentioned that B–H spin–spin splitting in the ^{11}B n.m.r. spectra of tetrahydrofuran derivatives of borane and triborane-7 is more poorly resolved than is the splitting obtained from the corresponding amine adduct. In spectra obtained in this laboratory the first and fourth members of the tetrahydrofuran borane quartet have appeared as unresolved shoulders on the central lines whereas the base line is nearly recovered between the peaks in the spectrum of trimethylamine borane. As the coupling constant for the tetrahydrofuran adduct is greater by 6 c.p.s.,[8] the difference in resolution must reflect a line-broadening effect by the ether.



Parry and Shore[16] have discussed the possibility of a diborane analog of this molecule, and other studies have indicated that base displacement of a bridge hydrogen can occur before cleavage takes place in reactions of diborane with trimethylamine[17] and with ethers.[18]

In addition to yielding mechanistic information about the reaction of tetraborane with tetrahydrofuran, the formation of $(C_4H_8O)_2BH_2^+$ provides a reactive boron hydride cation which may have synthetic utility.

Acknowledgment.—This work was supported by the National Science Foundation under Grant NSF-G-14595.

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[16] R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

[17] S. H. Bauer and J. V. Martinez, paper presented at the International Symposium on Boron–Nitrogen Chemistry, Duke University, Durham, N. C., April 23–25, 1963, p. 338.

[18] D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

A Tracer Study of the Reaction between Tetraborane and Sodium Tetradeuterioborate(III)

BY R. W. PARRY, R. W. RUDOLPH, AND D. F. SHRIVER

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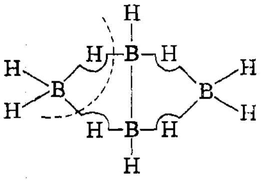
Tetraborane (B_4H_{10}) and sodium tetradeuterioborate(III) ($NaBD_4$) were allowed to react in ethylene glycol dimethyl ether at −45°. The resulting diborane and sodium triborohydride (NaB_3H_8) were analyzed for deuterium. The data clearly indicate that under the conditions used in this study a BH_3 group is split from the tetraborane and a deuteride ion is transferred from the BD_4^- to the resulting B_3H_7 to give as final products NaB_3H_7D and a mixture of diborane molecules whose over-all composition is consistent with the formula $B_2H_3D_3$.

It has been convenient to describe much of the chemistry of diborane and tetraborane in terms of symmetrical and nonsymmetrical cleavage of the double hydrogen bridge bonds.[1,2] Symmetrical cleavage of B_4H_{10} gives products which may be formally derived from BH_3 and B_3H_7 fragments while nonsymmetrical cleavage gives products derived from H_2B^+ and $B_3H_8^-$. While identification of reaction products usually provides a firm basis for reaction classification, it does not provide definite evidence about reaction mechanism. Indeed, in several cases it has not even been possible to classify the cleavage process on the basis of product identification. For example, the reaction between B_4H_{10} and $NaBH_4$, first described by Hough and Edwards,[3] can be given by the equation

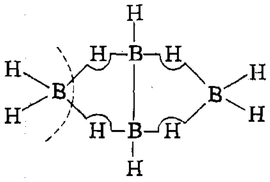
$$NaBH_4 + B_4H_{10} \longrightarrow NaB_3H_8 + B_2H_6$$

The NaB_3H_8 and B_2H_6 could arise from BH_3 and B_3H_7 fragments of tetraborane formed by symmetrical cleavage or from BH_2^+ and $B_3H_8^-$ fragments formed by nonsymmetrical cleavage. Direct information on the nature of the reaction process can be obtained from a tracer study using $NaBD_4$ and B_4H_{10} as indicated below.



$$+ NaBD_4 \longrightarrow \underset{12\%\ D}{NaB_3H_7D} + \underset{50\%\ D}{B_2H_3D_3}$$

symmetrical cleavage



$$+ NaBD_4 \longrightarrow \underset{0\%\ D}{NaB_3H_8} + \underset{67\%\ D}{B_2H_2D_4}$$

unsymmetrical cleavage

The results of the study described herein indicate clearly that a symmetrical cleavage process is involved. The observations are also consistent with the boron labeling experiments of Schaeffer and Tebbe,[4] who synthesized tetraborane with a known boron isotope located in the 4-position. The B_4H_{10} synthesis involved the reaction of B^{10}-enriched NaB_3H_8 with HCl and normal B_2H_6. The boron position indicated addition of a boron to the three-boron cluster in the expected fashion but did not differentiate between possible addition of BH_3 to B_3H_7 or of BH_2^+ to $B_3H_8^-$. The tracer result on the reverse process described below

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[1] R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

[2] G. Kodama and R. W. Parry, *ibid.*, **81**, 3534 (1960); *ibid.*, **82**, 6250 (1960).

[3] W. V. Hough and L. J. Edwards, "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p. 190.

[4] R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).