Electrophilic Reactions at Single Bonds. VII.[1] Hydrogen–Deuterium Exchange Accompanying Protolysis (Deuterolysis) of the Borohydride and Aluminum Hydride Anions with Anhydrous Strong Acids. The Intermediacy of Pentahydroboron (BH_5) and Pentahydroaluminum (AlH_5) and Their Structural Relationship with the Methonium Ion (CH_5^+)

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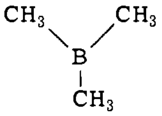
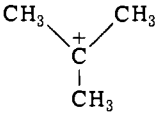
Abstract: Hydrogen–deuterium exchange accompanying protolysis (deuterolysis) of the borohydride (BH_4^-) and aluminum hydride (AlH_4^-) anions suggests the intermediacy of pentahydroboron (BH_5) and -aluminum (AlH_5). Pentahydroboron (BH_5) is both isoelectronic and isosteric with the methonium ion (CH_5^+). Theoretical calculations (CNDO/2 method) favor the BH_5 structure with C_s symmetry. These data suggest that the electrophilic attack on BH_4^- (AlH_4^-) is on the boron–hydrogen σ bond *via* the formation of a two-electron three-center bond and not through direct linear hydride ion transfer. In addition, trialkylboranes (alanes) and tetraalkylborates also undergo similar protolytic cleavage reaction with HF to give alkanes and BF_3 (AlF_3).

Borane (BH_3) and trialkylboranes, such as trimethylborane, are frequently used as isosteric model compounds for the carbenium ion (CH_3^+) and trialkylcarbenium ions, such as the trimethylcarbenium ion[2]

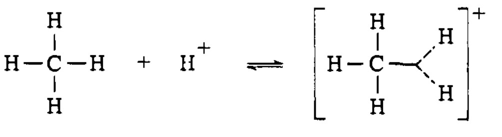


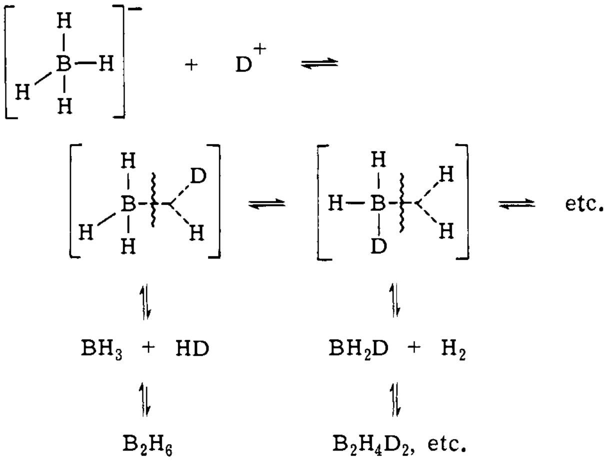


We would now like to suggest that not only do trivalent carbenium ions have their boron analogs but also pentacoordinated carbonium ions, of which CH_5^+ is parent,[3] find their isosteric hydroboron model compounds.

We reported in our preceding work both experimental evidence and theoretical calculations for pentacoordinated carbonium ions of the CH_5^+ type.[4] Our data indicated that the preferential structure of CH_5^+ is that of the C_s symmetry maintaining the carbon atom with approximately tetrahedral hybridization, with one of the sp[3] orbitals bound simultaneously to two hydrogen s orbitals. This structure represents "front side" protonation of methane, with the approaching proton forcing the electron pair of one of the C–H bonds into electron sharing *via* formation of a two-electron three-center bond.

The possible boron analog of CH_5^+ is BH_5.[3,5,6] Mesmer and Jolly,[7] studying the aqueous protolysis of borohydride, observed that if the reaction was carried out in deuterium oxide, besides HD as the main product, some H_2 (about 4%) was also formed. This observation pointed to the possibility that the attack of the deuteron is not collinear on one of hydrogens of BH_4^- but can involve the B–H bond itself, allowing subsequent scrambling in BH_4D prior to cleavage into HD and BH_3





The reversibility of the $BH_3 + H_2$ reaction is indicated by the work of Pitzer[5] who reported that B_2D_6, needed for his spectroscopic studies, was obtained by shaking B_2H_6 with D_2 at room temperature. The only reasonable mechanism we can envisage for the exchange reaction seems to be the insertion reaction of BH_3 into D_2, followed by bond-to-bond rearrangement.[2,8]

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[1] G. A. Olah, J. Shen, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **92**, 3831 (1970), is considered part VI. Part V: G. A. Olah and H. C. Lin, *ibid.*, **93**, 1259 (1971).

[2] G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *ibid.*, **93**, 959 (1971), and references given therein.

[3] G. A. Olah, *ibid.*, **94**, 808 (1972).

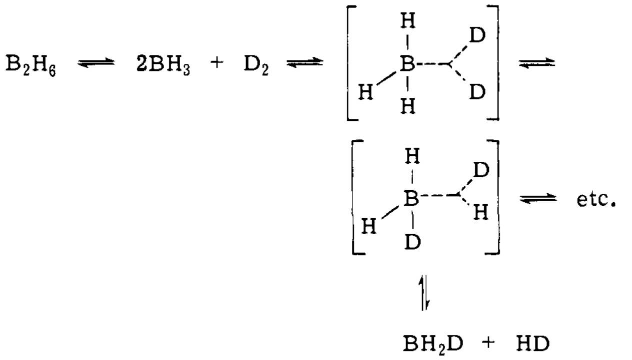
[4] G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969).

[5] A. N. Well, J. T. New, and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1964).

[6] After submission of this paper, we learned of the independent work of M. M. Kreevoy and J. E. C. Hutchins, *J. Amer. Chem. Soc.*, in press. Although the experimental approaches are different, conclusions reached relating to BH_5 are in good agreement.

[7] R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962).

[8] E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).



Results and Discussion

Protonation (Deuteronation) of the Borohydride Anion. We have studied the protolysis (deuterolysis) of the borohydride anion in anhydrous strong acids and found extensive hydrogen-deuterium exchange. When excess sodium borohydride is treated with 100% D_2SO_4 or DF (in a bomb), H_2 and HD (as well a trace amount of D_2) are formed (as analyzed by mass spectrometry) showing that extensive H-D scrambling takes place in accordance with the assumption that the reaction goes through BH_4D with subsequent bond-bond rearrangement[3] (statistical scrambling would give an H_2:HD ratio of 3:2).

That this, indeed, is the case is also shown when sodium borodeuteride is allowed to react with H_2SO_4 (or HF). The reaction produces HD and D_2 (with some H_2 also observed). Data of exchange reactions (summarized in Table I) thus strongly indicate formation of BH_5. We felt it of interest, therefore, to calculate the preferential structure of BH_5 and compare it with that previously found for CH_5^+.

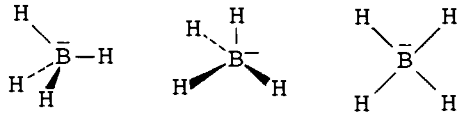
Table I. Typical Ratios of H_2, HD, and D_2 Obtained in the Protolysis (Deuterolysis) of Excess Sodium Borohydride (Deuteride) and Lithium Aluminum Hydride (Deuteride)[a] with Anhydrous Acids

Reaction system	H_2, %	HD, %	D_2, %
$NaBH_4 + D_2SO_4$	67.0	32.5	0.5
$NaBD_4 + H_2SO_4$	2.1	38.5	59.4
$NaBH_4 + DF$	57.7	39.6	2.7
$NaBD_4 + HF$	4.5	37.9	57.6
$LiAlH_4 + D_2SO_4$	68.8	28.1	3.1
$LiAlD_4 + H_2SO_4$	6.4	29.2	64.4
$LiAlH_4 + DF$	53.3	41.7	5.0
$LiAlD_4 + HF$	7.4	35.6	57.0

[a] Values obtained by mass spectrometry (see Experimental Section).

Theoretical Calculation. The PNDO (partial neglect of differential overlap) method,[9] used in our previous calculations of carbocation structures, cannot be used for BH_5 as it can deal only with hydrocarbons. The CNDO/2 method (complete neglect of differential overlap) of Pople[10] was, however, shown in similar cases to provide an adequate estimate of the geometrical constrains,[11] even though the total binding energies, in most cases, cannot be compared to actual experimental values. In order to test for the feasibility of CNDO/2 calculations for BH_5, we first determined with this method the geometry of the experimentally known structure of BH_4^-.

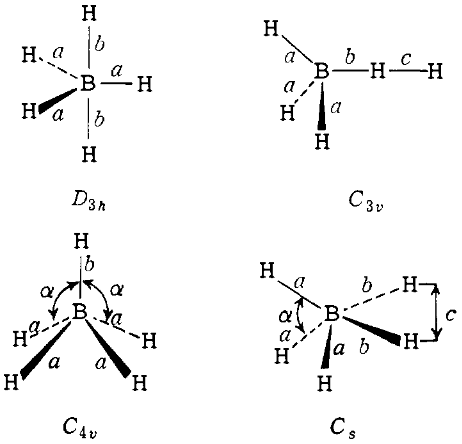
Three basic structures, T_d, C_{3v}, and D_{3h}, were considered as plausible and their relative energies were calculated. In these, the B-H bond distances were maintained arbitrarily at a value of 1.255 Å. The results indicate, in agreement with experimental data,



tetrahedral, T_d, −1.4185 au; trigonal pyramid, C_{3v}, −1.3613 au; square planar, D_{4h}, −1.1434 au

that the tetrahedral form is the most stable one. A symmetrical bond distance variation was then performed for the T_d structure. An energy minimum was found for a BH bond length of 1.21 ± 0.01 Å in reasonably good agreement with the experimentally determined value of 1.25 ± 0.02 Å.

These results encouraged us that the method was suitable to perform the calculations of hydroboron derivatives and in particular would lead to meaningful results for BH_5. Four basic geometries were considered in our attempt to determine the preferential structure of BH_5. These are depicted below



For each structure, a systematic and symmetrical variation of the geometry parameters (*a*–*c*) was performed until the energy minimum was found. The results are summarized in Table II, where for each structure the values given correspond to the energy minimum.

These calculations thus clearly favor the C_s symmetry structure for BH_5, where the central boron atom is practically tetrahedrally hybridized and one of the sp^3 hybrids is bonded symmetrically to two hydrogen s orbitals. This result is exactly analogous to that obtained for CH_5^+ and shows the apparent close similarity of BH_5 as an isosteric structure with CH_5^+.

Protolysis of Trialkylboranes and Tetralkylborates. Trialkylboranes react with anhydrous HF (in a bomb) to give alkanes and boron trifluoride

$$R_3B + 3HF \xrightarrow{\text{room temp}} BF_3 + 3RH$$

$$R = CH_3,\ C_2H_5,\ \text{and}\ i\text{-}C_4H_9$$

The reactions go to completion at room temperature. The product alkanes and BF_3 were analyzed by mass

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[9] M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

[10] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

[11] Relative energies of geometrical isomers.

Table II. Calculated Energy Minima of Possible Structures of BH_5

Structure	a, Å	b, Å	c, Å	α, deg	Binding energy au	Binding energy eV
D_{3h}	1.21 ± 0.01	1.21 ± 0.01			-1.501	-40.8
C_{3v}	1.21^{a}	1.23 ± 0.03	0.74 ± 0.05		-1.419^{b}	-38.6
C_{4v}	1.21 ± 0.005	1.20 ± 0.002		115 ± 0.5	-1.513	-41.1
C_s	1.200 ± 0.005	1.308 ± 0.005	0.92 ± 0.005	108 ± 0.5	-1.531	-41.6

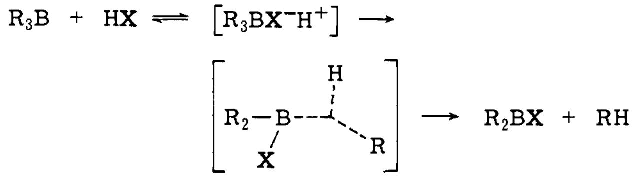
[a] Assumed. [b] Further minimization was considered superfluous as this structure was obviously less stable than the others.

spectrometry and nmr, respectively. In contrast, it should be noted that reaction of tri-*n*-butylborane with an excess of anhydrous HBr at 55–60° stops at di-*n*-butylboron bromide and *n*-butane[12a]

$$(n\text{-}C_4H_9)_3B + HBr \xrightarrow{55-60^\circ} (n\text{-}C_4H_9)_2BBr + n\text{-}C_4H_{10}$$

Thus a similarity with the electrophilic reactivity of the methyl halides seems to exist. In the case of methyl chloride, bromide, and iodide, electrophilic attack takes place preferentially on the halogen-unshared electron pairs, whereas in methyl fluoride, this is unfavorable, and C–H bond attack occurs.[13]

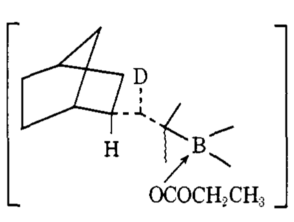
The mechanism of the protolysis of alkylboranes can be suggested to be similar to that of borane. Since trialkylboranes are strongly electron-deficient species, primary electrophilic attack on them is unlikely. Instead, the empty p orbital of the boron atom in alkylboranes will interact with the nucleophilic counterion to form the corresponding halotrialkylborates (R_3B---$X)^-$ or at least there will be some interaction between R_3B and X (the n-donor conjugate base)



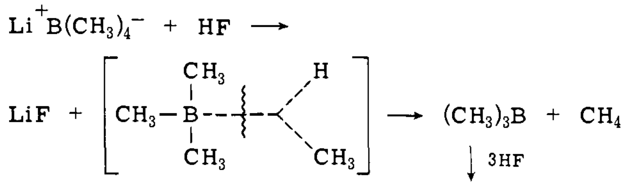
HX = HF, HBr, CH_3CH_2COOH, etc.

Subsequent protonation of the B–C bond *via* two-electron three-center bond formation then leads to alkane cleavage.

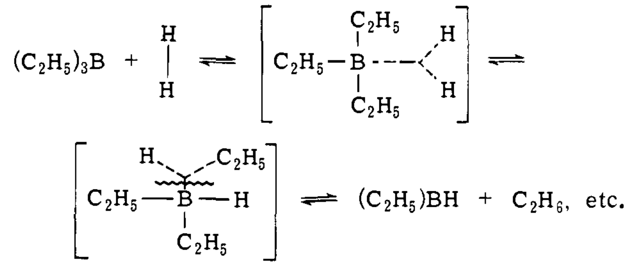
In addition, the retention of configuration in the protolysis (deuterolysis) of tri-2-norbornylborane as observed by Brown and Murray[12b] indicates the front-side protolytic attack on the B–C bond.



Similar to the protolytic behavior of borohydrides and trialkylboranes is the protolysis of tetraalkylborates, such as tetramethylborate, yielding alkanes (*i.e.*, methane). These reactions also indicate protolytic attack on the B–C bond *via* two-electron three-center bond formation.



Hydrogenation of trialkylboranes at 140–160° and 200–300 atm of pressure yields alkanes,[14] in a reaction analogous to the observed reaction of borane with deuterium. The reaction is considered to involve the interaction of $B(C_2H_5)_3$ with hydrogen *via* two-electron three-center bond formation forming the pentacoordinated boron intermediate which undergoes bond-to-bond rearrangement and finally cleaves to the products, ethane and borane.



Comparison of Protolysis of Aluminum Hydride and Trialkylalanes with that of Borohydrides and Trialkylboranes. In the hydrolysis of lithium aluminum hydride with heavy water, besides HD as the main product, formation of H_2 (and a trace of D_2) is also observed.[15] Whereas this result was explained either by the presence of impurities or due to the shifting of equilibrium $H_2 + D_2 \rightleftharpoons HD$, we felt that the real reason probably is an intramolecular exchange process. When $LiAlH_4$ was treated with D_2SO_4 (or DF) under conditions similar to those used in the case of borohydride, H_2 and HD (with a small amount of D_2) were formed (see Table I). Based on data we suggest that intermediary AlH_4D is formed *via* deuteration of the Al–H bond, followed by bond-to-bond rearrangement resulting in hydrogen–deuterium scrambling and subsequent cleavage to HD and H_2, respectively.

When lithium aluminum deuteride was allowed to react with H_2SO_4 (or HF), HD and D_2 were obtained (with some H_2) further substantiating the intermediacy of pentahydroaluminum.

Trialkylalanes (such as trimethyl- and triethylalanes) also cleave readily with HF yielding alkanes (methane and ethane, respectively) and AlF_3 as the final products. The mechanism for these protolyses is again suggested

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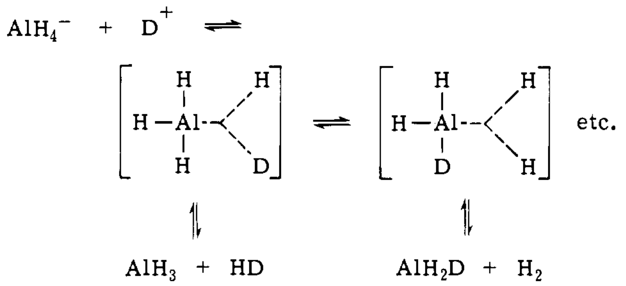
(12) (a) For a review, see H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, p 63; (b) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).

(13) G. A. Olah, John R. DeMember, R. H. Schlosberg, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 156 (1972).

(14) R. Köster, *Angew. Chem.*, **69**, 94 (1957).

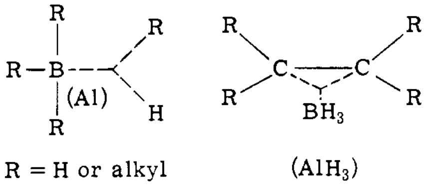
(15) I. Wender, R. A. Friedel, and M. Orchin, *J. Amer. Chem. Soc.*, 71, 1140 (1949).



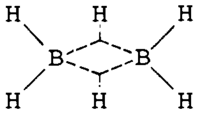
to be similar to that discussed previously for similar cleavages of trialkylboranes and involves pentacoordinated aluminum intermediates.

Conclusion

The intermediacy of BH_5 and AlH_5 is indicated by extensive hydrogen–deuterium exchange of borohydrides and aluminum hydrides in strong anhydrous acids. The species must exist as intermediates with finite lifetimes in order to explain the exchange results. Theoretical calculation (CNDO/2 method) favors the C_s symmetry structure for BH_5, which thus is isosteric with CH_5^+. Trialkylboranes (alanes) are suggested to undergo protolytic cleavage through similar pentacoordinated intermediates. Finally it should be mentioned that related pentacoordinated boron and aluminum bridged transition states were suggested[16] for the Brown hydroboration[12] and Ziegler hydroalanation[17] reactions.



Diborane itself is, of course, also a pentacoordinated boron compound in which, however, each boron is involved in forming two three-center bonds.



Experimental Section

Materials. $NaBH_4$, $NaBD_4$, $LiAlH_4$, $LiAlD_4$, $(CH_3)_3B$, $(C_2H_5)_3$, and $(i\text{-}C_4H_9)_3B$ were obtained from Alfa Inorganics, Inc. $Al(CH_3)_3$ and $Al(C_2H_5)_3$ were obtained from Ethyl Corp. D_2SO_4 was obtained from Merck Sharp and Dohme of Canada, Limited. DF was prepared from the reaction of CaF_2 with D_2SO_4 in a bomb. $LiB(CH_3)_4$ was prepared from CH_3Li and $B(CH_3)_3$.[15]

General Procedure of Protolysis. (a) In a stainless steel bomb 0.02 mol of D_2SO_4 (H_2SO_4) or DF (HF) was cooled at −78°. $NaBH_4$ ($NaBD_4$) or $LiAlH_4$ ($LiAlD_4$) (0.05 mol) contained in a small test tube (extending above the level of acid) was placed in the bomb, which was then degassed and sealed. By shaking, the borohydride (or aluminum hydride) was introduced into the acid. The reaction was completed by continued shaking for 30 min. The gaseous products, H_2, HD, and D_2, were analyzed by mass spectrometry using a Consolidated Engineering Corp. Model 21-620 mass spectrometer. The results are shown in Table I.

(b) Trialkylboranes (alanes), such as trimethyl, triethyl, and triisobutyl, and $LiB(CH_3)_4$ were introduced into a bomb containing liquid HF at −78°. The reaction was completed in 10 min at room temperature. The product alkanes were analyzed by mass spectrometry and gas–liquid chromatography.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

(16) G. A. Olah, *Angew. Chem.*, in press.

(17) For a review, see H. Lehmsuhl and K. Ziegler in "Houben-Weyl Methoden der Organischen Chemie," Vol. 13, 4th ed, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1970.

Reaction of Diatomic Carbon with Alkanes and Ethers. Trapping of Alkylcarbenes by Vinylidene

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Abstract: Singlet-state C_2, produced in a carbon arc under high vacuum, reacts with alkanes and ethers, RCH_3, at a liquid-nitrogen cooled surface to give allenes, $RCH{=}C{=}CH_2$, as well as the acetylene previously reported from reaction with other substrates. A typical reaction proceeds through an alkylcarbene–vinylidene pair, with product formation arising from coupling of the vinylidene with the alkylcarbene.

Previous reports have shown that C_2 reacts with alcohols[1] and carbonyl compounds[2,3] to produce acetylene as the major product. Two electronic states of C_2, the singlet $(X^1\Sigma_g^+)$[4] ground state and the long-lived triplet $(X'^3\pi_u)$[4] state, have been suggested as those responsible for acetylene formation from reaction with acetone.[2,3] This paper presents data concerning the reaction of singlet C_2 with alkanes and ethers. While acetylene is still the major product, there occurs an apparent insertion of C_2 into carbon–hydrogen bonds, which is of considerable mechanistic interest.

(1) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

(2) P. S. Skell, J. H. Plonka, and R. F. Harris, *Chem. Commun.*, 689 (1970).

(3) P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 5620 (1970).

(4) E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 61, 84 (1963).