The triethyldiborane and tetraethyldiborane were not analyzed to prove their identities; however, their vapor pressures agree with those reported by Schlesinger[2] and they are expected decomposition products. Their infrared spectra contained the BHB bridge peak of diboranes. The triethyldiborane spectrum contains a BH peak at 3.9 μ, and the tetraethyldiborane spectrum has no BH peak, as would be expected from their structures.

This self-decomposition of *unsym*-diethyldiborane accounts for the continued formation of small amounts of ethyldiborane reported during the preparation of *unsym*-diethyldiborane. The stability study shows that the unsymmetrical diethyl derivative is significantly less stable than the symmetrical isomer which underwent no measurable amount of decomposition in 24 hr. It is interesting that very little, if any, of the *unsym*-diethyldiborane underwent a disproportionation to diborane and tetraethyldiborane analogous to the ethyldiborane reaction.

Experimental

The fractionation procedures were those generally used in high vacuum techniques (10^{-5} mm.) and were used for samples of approximately 100 cc. (gaseous) or less.

The diborane and ethyldiborane were obtained by fractionation of a mixture of ethyldiboranes supplied by the Callery Chemical Company.

Pure *unsym*-diethyldiborane was obtained from a mixture of diethyldiboranes by repeated expansion with diborane to remove the symmetrical isomer (see text), followed by the fractionation. The resulting diethyldiborane was the pure unsymmetrical isomer with a vapor pressure of 46 mm. at 0°. Previous literature[2] reported 42 mm. at 0°.

The *sym*-diethyldiborane was prepared by the disproportionation of ethyldiborane for 15–20 min. followed by separation of the diborane, ethyldiborane and *sym*-diethyldiborane. Disproportionation of the recovered ethyldiborane was repeated until sufficient product had been obtained. The diethyldiborane produced in this manner is the pure symmetrical isomer with a vapor pressure of 36 mm. at 0°. Other characterization data included a molecular weight measurement of 86.3 (calcd. 83.8) and an active hydrogen determination of 148 cc. (calcd. 132 cc.). on a 33-cc. sample. The compound did not decompose in 24 hr. at 25°. The infrared spectra were taken on a Perkin–Elmer Model 21 spectrometer with a 10-cm. gas cell. Sample sizes which resulted in approximately 35 mm. pressure were found to give the best results.

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CHICAGO, ILL.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Decaborane Grignard Reagents

BY BERNARD SIEGEL, JULIUS L. MACK, JAMES U. LOWE, JR., AND JOHN GALLAGHAN

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Inorganic Grignard reagents are formed when decaborane reacts with methylmagnesium iodide. Either $B_{10}H_{13}MgI$ or $B_{10}H_{12}(MgI)_2$ can be prepared. Upon hydrolysis of $B_{10}H_{13}MgI$, decaborane and MgIOH are formed. That a substituted decaborane could be formed by a Grignard condensation reaction was demonstrated by preparing benzyldecaborane, $B_{10}H_{13}CH_2C_6H_5$. In the latter, the benzyl group was shown to be bonded to a basal boron atom.

Introduction

Very few substituted decaboranes are known.[1] Because of the versatility of Grignard reactions it seemed that such reactions could be used to prepare substituted decaboranes if the decaboryl analog of the organic RMgX could be prepared. In attempts to prepare such a compound by treating iododecaborane with magnesium in various ether solutions, it was found that high temperatures were required for magnesium to be consumed; no reaction was observed at 68° and only a very slow reaction at 140°.[2] To avoid complicating side reactions at high temperatures a milder method for preparing a decaborane Grignard reagent was sought.

Although Wiberg[3] recently showed that diborane reacts with ethylmagnesium halides to form triethylboron and HMgX, we found that methane was formed when decaborane was treated with methylmagnesium iodide. Since this indicated that a decaborane Grignard reagent probably had been formed, a study of this reaction was initiated.

Experimental

Decaborane-monomagnesium Iodide ($B_{10}H_{13}MgI$).—In a typical preparation, 0.057 mole of methylmagnesium iodide (free of methyl iodide) in dried diethyl ether solution was added rapidly to 0.075 mole of decaborane (purified by vacuum sublimation) also in dried diethyl ether solution. This was carried out in a conventional vacuum apparatus; the solutions were prepared in a dry box or under dry nitrogen. The solutions generally were added between 0–20°. An immediate reaction, liberating a gas, ensued. This reaction was completed in a few minutes. The gas was identified as methane by its infrared spectrum and by its vapor pressure of 10 mm. at −195°. The quantity of methane was determined by the usual *PVT* relationship and corresponded to 0.055 mole. After distilling the solvent, the unreacted decaborane was recovered by vacuum sublimation at 25–50°; it corresponded to 0.016 mole. After evacuation in a high vacuum apparatus for several days the residue was a viscous yellow liquid that had no detectable vapor pressure on a U-tube manometer. *Anal.* Calcd. for $C_4H_{23}OB_{10}IMg$: C, 13.9; H, 6.6; B, 31.2; I, 36.7; Mg, 7.2. Found: C, 16.3; H, 6.6; B, 30.3; I, 37.0; Mg, 6.8.[4]

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(1) Stock prepared $B_{10}H_{12}I_2$ and $B_{10}H_{12}Br_2$; A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933. Recently Schaeffer found that decaborane condensed with two molecules of acetonitrile; R. Schaeffer, THIS JOURNAL, **79**, 1006 (1957).

(2) Unpublished results of the present authors and J. T. MacQueen.

(3) E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

(4) The carbon values are slightly higher than theoretical for monoetherates and could be represented as 1.1–1.2 etherates, but considering how strongly ether is retained by these reagents and the viscosity of the preparations, calculating for a monoethereate is logical; the other analyses could fit a slightly higher fractional value.

After several runs it was found that the methane data were reproducible to within 1%. Subsequently the number of moles of methane liberated could be taken as equivalent to the number of moles of decaborane-monomagnesium iodide.

Number of Active Hydrogen Atoms on Decaborane.—Methylmagnesium iodide (0.068 mole) in dried diethyl ether was added to 0.00340 mole of decaborane in the same manner as above. Methane (0.00685 mole) was evolved. It was observed that a rapid immediate evolution of methane occurred that was followed by slow ebullition persisting 30–60 minutes. The ratio of moles of methane produced to moles of decaborane reacted was 2.02. The solvent was then distilled and replaced with dried *n*-butyl ether. This solution was heated at 100° for 1 hr. without further evolution of hydrocarbon gas.

Decaborane-dimagnesium Iodide ($B_{10}H_{12}(MgI)_2$).—In order to prepare decaborane-dimagnesium iodide, free of methylmagnesium iodide, 0.082 mole of methylmagnesium iodide was added to 0.082 mole of decaborane. An equivalent quantity of methane was generated within a few minutes. An additional 0.082 mole of methylmagnesium iodide was then added. After five minutes, 0.044 mole of methane was formed with vigorous ebullition. The vigorous ebullition persisted for a few additional minutes and then was followed by gentle ebullition. A second reading was taken after 30 minutes of reaction time and an additional 0.023 mole of methane was recorded, representing at this point a collective total of 81.7% reaction. Since ebullition of methane was very slow at this point, the solvent was distilled and the residue warmed to 50–60° to complete the reaction. The product was evacuated overnight in a high vacuum apparatus and then analyzed. *Anal.* Calcd. for $C_8H_{32}O_2B_{10}I_2Mg_2$: C, 16.8; H, 5.65; B, 19.0; I, 44.5; Mg, 8.5. Found: C, 19.3; H, 5.71; B, 18.1; I, 44.1; Mg, 8.1.[4]

Hydrolysis of Decaborane-monomagnesium Iodide.—When a large excess of water was added to decaborane-monomagnesium iodide, a vigorous reaction occurred with the liberation of bound diethyl ether and the formation of decaborane. Unfortunately the latter hydrolyzed so rapidly that only a small fraction was recovered.

However when a stoichiometric quantity of water was used, decaborane was recovered as a major product. Diethyl ether (266 cc.) containing 0.165% water was added to 0.0175 mole of decaborane-monomagnesium iodide at room temperature and the solution was stirred for 20 minutes. A precipitate had formed and was filtered; the latter was identified as MgIOH by elemental analysis and titration with HCl. After distilling the diethyl ether, decaborane was extracted with dry petroleum ether (b.p. 38–46°). The yields of decaborane and MgIOH correspond to approximately 80% of the theoretical amount for complete hydrolysis of decaborane-monomagnesium iodide.

Reaction of Decaborane-monomagnesium Iodide with Benzyl Chloride.—Benzyl chloride (0.175 mole) was added to 0.0875 mole of decaborane-monomagnesium iodide in the vacuum apparatus. The latter immediately dissolved and a vigorous exothermic reaction ensued with heat persisting for 1 hr. After 2 hr. at ambient temperature, the reactor was heated at 50–60° for 1 hr. and then allowed to stand overnight at ambient temperature. The reaction contents were then diluted with dried petroleum ether and the insoluble material (ppt. A) was filtered; the latter was exhaustively washed with petroleum ether and the washings were added to the supernatant. After distilling the petroleum ether and unreacted benzyl chloride from the supernatant, the residue was fractionally distilled in a high vacuum distillation apparatus. Benzyl iodide (0.081 mole) was recovered as the first fraction. At approximately 100°, under a pressure of 10^{-5} mm., 8 g. of a viscous liquid (B) was collected. The undistilled residue was a dark sirup. After several distillations the viscous liquid (B) crystallized into a white solid. This material was recrystallized from petroleum ether until a sharply melting substance (m.p. 64.6°) was obtained. *Anal.* Calcd. for $C_7H_{20}B_{10}$: C, 39.6; H, 9.4; B, 50.9. Found: C, 39.8; H, 9.7; B, 50.3.

The molecular weight was determined to be 210 ± 5 by the freezing point depression method; decaborane was used as a standard to obtain the molal freezing point constant of 5.135 used in this determination. The infrared spectrum of the solid was recorded over the range 3–15 μ in a KBr-pressed disc; a double-beam spectrophotometer was used.

The petroleum ether-insoluble material (ppt. A) was extracted with benzene. After distilling the benzene a brown resinous solid (1.93 g.) was obtained. This fraction had an apparent molecular weight of 683 (freezing point depression method). Elemental analysis showed that its composition was 33.3% boron, 53% carbon, 7.7% hydrogen. After removal of the benzene-soluble material from ppt. A, the residue was water-soluble and was shown to consist of 0.079 mole of $MgCl_2$ by elemental analysis.

Discussion

Decaborane-mono- and Dimagnesium Iodides.—That decaborane Grignard reagents are formed when decaborane reacts with methylmagnesium iodide is indicated by the following evidence:

(a) When a slight excess of decaborane is used, the number of moles of methane formed is equal to the number of moles of methylmagnesium iodide added and also to the number of moles of decaborane consumed. The resulting product is an etherate, a property generally characteristic of Grignard reagents. It has the elemental composition corresponding to $B_{10}H_{13}MgI{-}OC_4H_{10}$. The formation of the latter is essentially quantitative and extremely rapid, according to the equation[5]

$$B_{10}H_{14} + CH_3MgI \longrightarrow B_{10}H_{13}MgI + CH_4 \cdot \quad (1)$$

(b) When decaborane-monomagnesium iodide is treated with methylmagnesium iodide in equimolar quantities reaction (2) takes place

$$B_{10}H_{13}MgI + CH_3MgI \longrightarrow B_{10}H_{12}(MgI)_2 + CH_4 \quad (2)$$

The resulting product is also an etherate, with an elemental composition corresponding to $B_{10}H_{12}(MgI)_2 \cdot (OC_4H_{10})_2$.

(c) To show further that a Grignard reagent had been formed, decaborane-monomagnesium iodide was hydrolyzed. The expected products were obtained according to the equation

$$B_{10}H_{13}MgI + H_2O \longrightarrow B_{10}H_{14} + MgIOH \quad (3)$$

Additional proof was obtained by condensing decaborane-monomagnesium iodide with benzyl chloride[6] to form benzyldecaborane according to the equation

$$B_{10}H_{13}MgI + 2C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2B_{10}H_{13} + MgCl_2 + C_6H_5CH_2I \quad (4)$$

Benzyldecaborane.—Although benzyldecaborane is a new substituted decaborane and has not been previously characterized, the evidence for its formation is substantial. In addition to its elemental composition and molecular weight, the infrared spectrum of this material is consistent with the expected spectrum. The analysis of the latter is shown in Fig 1. The bands at 7.97 and 9.18 μ do not appear in the decaborane spectrum. Starting with the band at 9.95 μ the unlabeled bands do appear in the decaborane spectrum, in the region

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(5) The formula $B_{10}H_{13}MgI$ is used for convenience; actually the empirical formula RMgX has been shown to represent a complex equilibrium; see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Chapter IV, Prentice-Hall, New York, N. Y., 1954.

(6) For a discussion of Grignard condensation reactions see ref. 5, chapter 16.

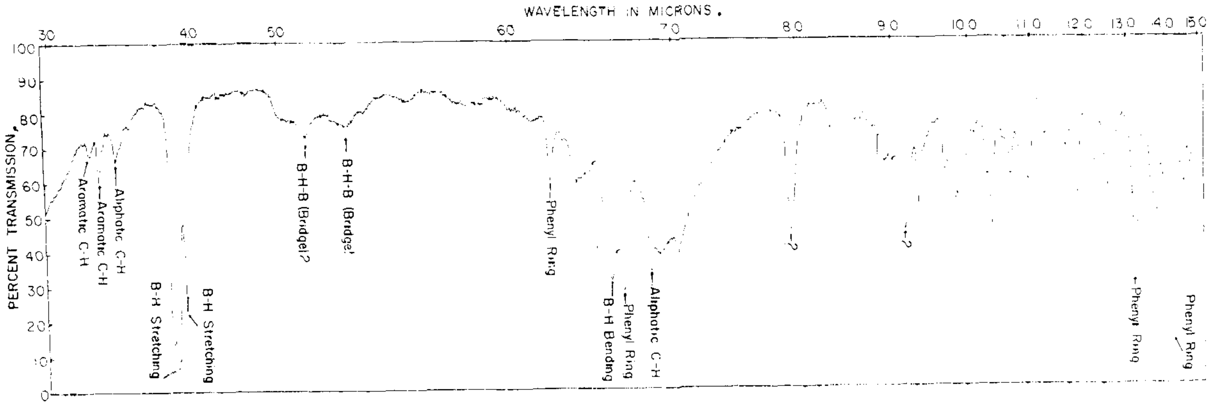

Fig. 1.—Infrared spectrum of benzyldecaborane.

generally assigned to B–B skeletal stretching and B–H bending.[7]

Nuclear Magnetic Resonance Spectra.—Previous studies of the nuclear magnetic resonance signals in boranes[8] have shown this technique to be capable of providing directly interpretable information about their structures. With the hope of settling the question of the position of substitution the B^{11} spectra of decaborane and benzyldecaborane in benzene solution were obtained at 16.192 mc. in a field of 11,840 gauss. Unfortunately it was not possible to determine the spectra of the Grignard reagents because of high viscosity and limited solubility. The instrument used was a Varian Associates V-4300-B High Resolution Spectrometer and the compounds were studied in 15 mm. Pyrex cylindrical sample cells.

The following interpretation of the spectra has been provided by Dr. J. N. Shoolery and L. F. Johnson of Varian Associates.

The spectrum of decaborane, shown in Fig 2, consists of a large triplet and a small doublet, the latter arising from the apical boron atoms and the former from all the remaining B^{11} nuclei. Two similar groups of lines arise in the spectrum of benzyl decaborane, Fig. 2b, and are assigned in the same way. Although the two apical nuclei are identical, the resonance in decaborane is a doublet. This is due to the spin-spin coupling with the directly attached proton. Each apical B^{11} resonance is split into a doublet and the resonances from the two apical boron nuclei superimpose exactly.

If the assumption is made that benzyldecaborane is substituted at one of the apical positions, the doublet due to that B^{11} will be expected to collapse to a single line. At the same time a chemical shift may occur. If none of the resulting lines superimpose, the resonance would display multiplet character with intensities 2:1:1, 1:2:1 or 1:1:2, depending on the direction and magnitude of the chemical shift due to the substitution of the benzyl group for a proton. If accidental superposition occurs, the resulting doublet could have relative intensities 1:3 or 3:1. These latter two possibilities both have been observed[8d] in $B_{10}H_{13}I$ and $B_{10}H_{13}Br$. The spectrum of benzyldecaborane, however, does not agree even in a qualitative way with any of these predictions.

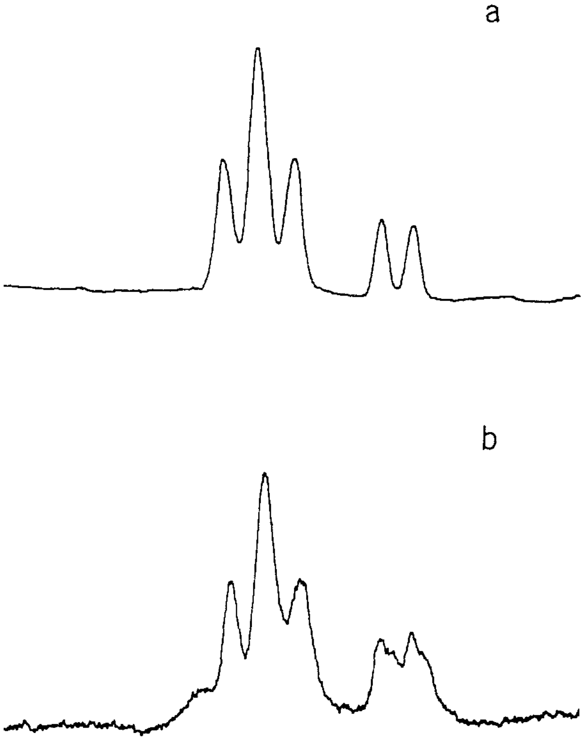

Fig. 2.—B^{11} magnetic resonance spectra: (a) decaborane; (b) benzylborane.

If, on the other hand, the assumption is made that benzyldecaborane is not substituted at one of the apical positions, neither doublet due to the apical borons will collapse but, due to the destruction of the symmetry of the molecule, the doublet from one of the apical borons may shift slightly relative to the other. The observed spectrum exhibits a shifted doublet structure which most nearly fits this prediction. One pair of lines appears broader than the other and this may be due to the lower symmetry of the molecule and consequent greater electric quadrupole relaxation of one of the

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(7) W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).

(8) (a) J. N. Shoolery, *Disc. Faraday Soc.*, **19**, 215 (1955); (b) R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954); (c) R. Schaeffer, J. N. Shoolery and R. Jones, THIS JOURNAL, **79**, 4606 (1957); (d) **80**, 2670 (1958).

apical nuclei. The large triplet in benzyldecaborane shows a considerable perturbation which also points to the direct substitution by the benzyl group of one of the protons attached to a basal boron atom. These data, therefore, strongly suggest that benzyldecaborane is substituted at a basal boron atom.

Acknowledgments.—The authors are indebted to Dr. George Wilmot for the infrared spectrum of benzyldecaborane, Mrs. Phyllis Wheeler for the elemental analyses and Dr. Sol Skolnik for valuable advice. LeRoy Johnson of Varian Associates obtained the nuclear magnetic resonance spectra.

INDIAN HEAD, MARYLAND

[CONTRIBUTION NO. 423 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Reactions of Hydrogen Fluoride with Some Boron–Oxygen Compounds

BY EARL L. MUETTERTIES

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Advantage has been taken of the facile cleavage of the boron–oxygen bond by hydrogen fluoride to prepare boron trifluoride–oxygen base complexes. The alcohol complexes of boron trifluoride, $2ROH\cdot BF_3$, formed essentially quantitatively in the reaction of trialkyl borates with hydrogen fluoride at 30°. Similarly, $2CH_3COOH\cdot BF_3$ was obtained in good yield from boric oxide, acetic anhydride and hydrogen fluoride. Attempts to extend these syntheses to organoboron fluoride complexes were unsuccessful. In reactions of such compounds as $C_6H_5B(OC_2H_5)_2$ and $ClC_3H_6B(OH)_2$ with hydrogen fluoride, there was not only cleavage of boron–oxygen bonds but also extensive cleavage of the boron–carbon bonds.

Introduction and Discussion

Complexes of boron trifluoride with organic oxygen compounds such as ethers, alcohols, esters and acids are a well established class of compounds.[1] Usually these compounds are prepared by the reaction of boron trifluoride or its etherate with the organic base.[1] Because boron–oxygen bonds are easily cleaved by hydrogen fluoride, we have explored the reactions of various boron–oxygen compounds with hydrogen fluoride as direct routes to boron trifluoride complexes.

Hydrogen fluoride converted trialkyl borates rapidly and cleanly to the dialcoholates

$$B(OR)_3 + 3HF \longrightarrow ROH + 2ROH\cdot BF_3$$

These dialcoholates were purified readily provided that the amount of hydrogen fluoride used was not in excess of the amount required to convert the borate to the complex (it was found difficult to free the dialcoholates of excess hydrogen fluoride). Triphenyl borate appeared to behave similarly to the alkyl borates, but a rigorous purification of the product was not achieved. Trimethoxyboroxine, $(CH_3OBO)_3$, was converted by hydrogen fluoride to a product that could not be vacuum distilled without decomposition and that appeared to be a labile mixture of $2CH_3OH\cdot BF_3$, $2H_2O\cdot BF_3$ and possibly $H_2O\cdot CH_3OH\cdot BF_3$. Several attempts were made to modify the borate reactions in order to obtain other boron trifluoride complexes. Acid anhydrides were employed here as alcohol acceptors, and the idealized reactions were represented in the two equations

$$B(OCH_3)_3 + 3(C_2H_5CO)_2O + 3HF \longrightarrow 2C_2H_5COOCH_3 + 3C_2H_5COOH + C_2H_5COOCH_3\cdot BF_3$$

$$B(OCH_3)_3 + 3(CF_3CO)_2O + 3HF + (C_2H_5)_2O \longrightarrow 3CF_3COOH + 3CF_3COOCH_3 + (C_2H_5)_2O\cdot BF_3$$

In these two systems, the reactions were apparently more complex than indicated in the equations, and only low yields of the desired addition compounds were realized.

The 1:2 boron trifluoride complex with acetic acid formed directly and in good yield from the reaction of boric oxide, hydrogen fluoride and excess acetic anhydride

$$^1/_2B_2O_3 + {}^3/_2(CH_3CO)_2O + 3HF \longrightarrow CH_3COOH + 2CH_3COOH\cdot BF_3$$

Use of tetraacetyl diborate, $(CH_3COO)_4B_2O$, in place of the boric oxide–acetic anhydride mixture led to products that, like those from the methoxyboroxine, were not purified readily.

Both trimethoxyboroxine[2,3] and tetraacetyl diborate[4,5] have boron–oxygen–boron bonds, and consequently, in the reactions of these compounds with hydrogen fluoride, water must in effect be formed. This water would emerge from the reaction as some type of boron trifluoride hydrate. For example, the boroxine might be expected to form the dialcoholate and the dihydrate

$$^2/_3(CH_3OBO)_3 + 6HF \longrightarrow 2CH_3OH\cdot BF_3 + 2H_2O\cdot BF_3$$

However, if such a mixture were obtained and if there were no strong interactions between the components, distillation should permit isolation of the dialcoholate. Low molecular weight dialcoholates, as demonstrated in this work, can be *vacuum* distilled without significant decomposition but the hydrates cannot be distilled.[6] However, in the case of the products from the boroxine and the tetraacetyl diborate reactions, temperatures (∼25-38°)

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[1] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 61-74.

[2] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **77**, 1578 (1955).

[3] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **267** (1951).

[4] R. G. Hayter, A. W. Laubengayer and P. G. Thompson, THIS JOURNAL, **79**, 4243 (1957).

[5] The contrasting behavior of tetraacetyl diborate and the boric oxide–excess acetic anhydride in the hydrogen fluoride reaction appears to be further evidence that "boron acetate" is $(CH_3COO)_4B_2O$ and not $(CH_3COO)_3B$.

[6] J. S. McGrath, G. G. Stack and P. A. McCusker, THIS JOURNAL, **66**, 1263 (1944).