increased stability of the parent ion on increased methyl substitution could be attributed to the ability of the methyl group to release electron density into the borazine ring thus stabilizing the parent ion.

The general substituent effects on the relative stability of the parent ion observed for the B-substituted *N*-trimethylborazines also obtains for the B-substituted borazines. Mass spectral data available in the literature were analyzed by the method described here and the results summarized in Table X. The stability of the parent ion of B-monosubstituted borazines increases in the order $F < Cl < OCH_3 < CH_3 < Br$; for the known B-disubstituted derivatives the same order is observed. The results in both series of compounds are in general agreement with the data obtained for the corresponding *N*-trimethylborazine derivatives. A comparison of the results in Tables IV and VIII indicates that the loss of a hydrogen atom from an *N*-methyl group is more facile than from a *B*-methyl group, which is in agreement with the more ready formation of an immonium ion (II).

Registry No. $H_3N_3B_3H_3$, 6569-51-3; $H_3N_3B_3F_3$, 13779-24-3; $(CH_3)_3N_3B_3H_3$, 1004-35-9; $(CH_3)_3N_3B_3(CH_3)_3$, 877-07-6; $(CH_3)_3N_3B_3Cl_3$, 703-86-6; $(CH_3)_3N_3B_3(CH_3)_2C_6H_5$, 32386-02-0; $(CH_3)_3N_3B_3(CH_3)(C_6H_5)_2$, 28075-19-6; $(CH_3)_3N_3B_3(C_6H_5)_3$, 909-21-7; $H_3N_3B_3H_2Cl$, 15061-65-1; $H_3N_3B_3HCl_2$, 15259-40-2; $H_3N_3B_3Cl_3$, 933-18-6; $(CH_3)_3N_3B_3H_2Cl$, 13401-07-5; $(CH_3)_3N_3B_3HCl_2$, 13401-08-6; $(CH_3)_3N_3B_3H_2F$, 29812-74-6; $(CH_3)_3N_3B_3HF_2$, 29812-75-7; $(CH_3)_3N_3B_3H_2Br$, 13401-09-7; $(CH_3)_3N_3B_3HBr_2$, 13401-10-0; $(CH_3)_3N_3B_3Br_3$, 703-85-5; $(CH_3)_3N_3B_3H_2I$, 29812-76-8; $(CH_3)_3N_3B_3HI_2$, 29812-77-9; $(CH_3)_3N_3B_3Cl_2CH_3$, 7387-21-5; $(CH_3)_3N_3B_3Cl(CH_3)_2$, 13058-05-4; $(CH_3)_3N_3B_3Cl_2C_6H_5$, 36972-50-6; $(CH_3)_3N_3B_3Cl(C_6H_5)_2$, 36972-51-7; $(CH_3)_3N_3B_3C_6H_5ClCH_3$, 36972-52-8; $H_3N_3B_3H_2(OCH_3)$, 18277-68-4.

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Deprotonation of Tetraborane(10)

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The deprotonation of tetraborane(10) by methyllithium was found to proceed smoothly in ethyl ether at −78°. The reaction produced methane and the lithium salt of the nonahydrotetraborate(1−) ion. Reprotonation of the anion with HCl and DCl regenerated tetraborane(10) and monodeuterated tetraborane(10), respectively. The infrared spectrum of B_4H_9D indicated that the deuterium atom entered the bridge position only. The LiB_4H_9 was thermally unstable even for moderate periods of time at −78° and decomposed irreversibly at higher temperatures. Relative Bronsted acidities were determined by displacement reactions and found to increase in the order B_5H_9, B_4H_{10}, $B_{10}H_{14}$.

Introduction

The results of a study of the deprotonation of tetraborane(10) by $LiCH_3$ in ethyl ether have recently appeared in a brief report.[1] Both the Bronsted acidity of the tetraborane(10) and the reactivity of the product lithium nonahydrotetraborate(1−) were examined. At the same time Johnson and Shore[2] reported the results of a similar study using NH_3 and KH as deprotonating agents. Both of these studies confirm that tetraborane(10) is a Bronsted acid and forms the $B_4H_9^-$ anion intact at low temperatures. Previous studies had demonstrated that tetraborane(10) could be cleaved across the bridge bonds symmetrically yielding BH_3 and B_3H_7 generally as base adducts or asymmetrically in polar environments giving BH_2^+ and $B_3H_8^-$ fragments.[3]

In this article we present the experimental details of our study.

Experimental Section

Materials. All volatile compounds were handled using standard high vacuum procedures. Preparations of the nonahydrotetraborate(1−) anion and subsequent reactions were done in sealed tubes as shown in Figure 1. The capillary tubing on the side arms D provided a means of sealing off the reaction vessel under vacuum. The side arm could be fastened to a tube opener through a greaseless threaded adapter with a Viton O ring (Ace 5027-20). Sealed-tube reactions avoided contamination with stopcock grease and allowed reaction pressures of up to 5 atm.

Methyllithium [Alfa Inorganics], a 2.3 *M* solution in ethyl ether, was routinely diluted with ethyl ether in a syringe to avoid clogging the syringe needle and to provide additional solvent for the reaction. The bottle of $LiCH_3$ solution was always opened under a stream of dry nitrogen. B_4H_{10} was prepared by a modified method of Schaeffer and Tebbe[4] as described elsewhere.[5] Ethyl ether was distilled from sulfuric acid and stored in a dry nitrogen-filled bottle over molecular sieves (Linde 4A). The ether was checked periodically for peroxides.

A codistillation condensation column[5] was used to determine the purity of volatile compounds and, when possible, the composition of mixtures. All volatile starting materials were determined to be chromatographically pure by this method. Decaborane(14) was sublimed before use. Diborane(6) was prepared by adding an I_2 solution in diglyme to a $NaBH_4$–diglyme slurry.[6] Pentaborane(9) was prepared by the method of DeAcetis and Trotz.[7] Anhydrous aluminum chloride [Merck] was used as received. Boron trifluoride [Matheson] was taken from a tank directly into the vacuum line and purified. Both HCl and DCl gases [Stohler Isotopes] were prepared by pumping on their respective concentrated aqueous solutions through −78° traps.

All infrared spectra were taken on a Perkin-Elmer 521 grating spectrometer. Mass spectra were run on a double-focusing Hitachi Perkin-Elmer RMU-7 mass spectrometer.

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

(2) H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, 92, 7586 (1970).

(3) Considerable reference material may be found in ref 1 and 2.

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

(5) A. C. Bond and M. L. Pinsky, *J. Amer. Chem. Soc.*, 92, 32 (1970).

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(7) W. DeAcetis and S. J. Trotz, U. S. Patent 2,983,581 (May 9, 1961) [*cf. Chem. Abstr.*, 56, 2134e (1962)].

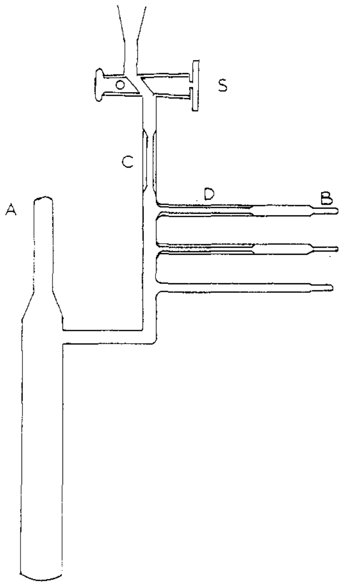

Figure 1. Reaction vessel: 10-mm tubing at A, capillary tubing at C and D for sealing the tube off under vacuum, vacuum stopcock S, and break tip B.

Preparation of LiB_4H_9. The reaction vessel (Figure 1) used in the preparation was flamed, evacuated to 10^{-6} Torr, and filled with dry nitrogen. The tube at A (Figure 1) was opened under a positive pressure of nitrogen and a long dry funnel was inserted. This funnel prevented contamination of the walls of the tube by the solution and directed the syringe needle to the bottom. Ethyl ether was taken into the syringe followed by the stock $LiCH_3$ solution. After introduction into the tube, the solution was frozen at −196°, the funnel was removed, and the tube was resealed under nitrogen at A. The vessel was evacuated and the previously measured B_4H_{10} was condensed into it. The vessel was sealed off from the line under a low pressure of 10^{-6} Torr at D and placed in a −78° bath. A moderate bubbling ensued. When the reaction was sampled, the solution was frozen at −196° and placed in the tube opener.[8] The tip on the side arm was broken at B after the system was evacuated. The resulting pressure in the system was 10.0 Torr. [The vapor pressure of CH_4 at −196° is 10.0 Torr.] The material volatile at −196° was pumped through a spiral trap at −196° into a calibrated gas buret by means of a Toepler pump. This material was identified as CH_4 by its infrared spectrum. The previously noted −196° vapor pressure excludes the presence of hydrogen. The yield of LiB_4H_9 was assumed to be approximated by dividing the moles of CH_4 produced by the moles of B_4H_{10} placed in the tube. All reaction conditions and yields are given in Table I. Fourteen reactions produced an average yield of 89.5%.

Optimum yields were obtained when no less than a 20% excess of methyllithium was used and when the reactants were dissolved in no less than a 40% additional volume of ether. Only occasional shaking of the dewar containing the tube was necessary for mixing. Large excesses of ether were avoided in order to facilitate its subsequent chemical separation from other volatile substances.

Attempts to isolate a dry solid at low temperatures proved unsuccessful. The LiB_4H_9 remained highly solvated by ethyl ether at temperatures approaching 0°.

An approximate rate of reaction was determined using reaction mixture 10 (Table I). The reaction at −78° was quenched at −196° and the methane was collected at three intervals. The reaction was 71.9% complete after 30 min, 90.0% complete after 60 min, and 95.1% complete after 90 min.

Since obtaining a solvent-free salt would have eliminated considerable experimental difficulties, a study of this reaction in the absence of solvent was tried. A solution containing 1.15 mmol of $LiCH_3$ was injected into the vessel. The tube was sealed under nitrogen as before and the ether was pumped out until the pressure in the tube reached 10^{-6} Torr. Next, B_4H_{10} (1.11 mmol) was condensed into the tube, followed by sealing off the tube under vacuum. The tube was placed in a −78° bath for 48 hr and kept at −45° for 1 hr and at 0° for 30 min. The volatile material recovered consisted of 0.970 mmol of boron trimethyl. The latter was identified by its mass spectrum.

Table I. Data on the Deprotonation of B_4H_{10}

Reaction no.	Amt, mmol B_4H_{10}	Amt, mmol $LiCH_3$	Ether added, ml	Reaction conditions Temp, °C	Reaction conditions Time, hr	% yield[a]	$LiCH_3$/B_4H_{10}
1	0.970	1.15	0.2	−78	17.5	89.0	1.19
				−45	3.5		
				0	0.5		
2	1.17	1.15	0.5	−78	41.7	81.4	0.983
				−45	1		
3	1.04	1.15	0.5	−78	21.5	94.4	1.11
4	1.02	1.15	0.4	−78	14.25	78.0	1.13
5	0.867	1.61	0.2	−78	15	89.3	1.86
6	0.915	1.38	0.3	−78	17	89.8	1.51
7	0.862	1.61	0.2	−78	15.3	98.0	1.87
8	1.11	1.84	0.2	−78	15.2	89.5	1.66
9	0.965	1.84	0.2	−78	16	88.4	1.91
10	0.906	1.84	0.2	−78	1.5	95.1	2.03
11	0.853	1.50	0.3	−78	3.25	92.7	1.76
12	0.790	1.61	0.3	−78	2.7	95.5	2.04
13	1.20	1.72	0.25	−78	16.25	91.5	1.43
				−63	2.2		
14	0.889	1.38	0.4	−78	3	79.9	1.55
						Av 89.5	

[a] Yield is based on methane collected divided by tetraborane(10) used.

Thus, only 12.5% of the B_4H_{10} reacted, and of this, 27% went by a different path to form $B(CH_3)_3$ and perhaps nonvolatile methylated boron hydrides.

Reaction of HCl and LiB_4H_9. Following the collection of CH_4 in reaction 5 (Table I), HCl (2.08 mmol) was condensed onto the frozen mixture in the tube. The side arm was sealed off under vacuum and the tube was immersed in a −112° (bromobutane) slush bath for 36 min and then in a −78° bath for 34 min. Noncondensable material (0.409 mmol) was recovered, half of which was CH_4 produced from HCl and unreacted $LiCH_3$. BF_3 (9.15 mmol) was next condensed into the vessel to complex the ether. The reaction proceeded in the sealed tube at −104° (cyclohexene) for 45 min. The volatile material was then pumped from the tube through a removable trap at −78° into the fractionating system. The −112° condensable fraction gave a single peak on the codistillation column. The peak was identified as tetraborane(10) by its infrared spectrum. The tetraborane(10) recovered (0.585 mmol) was 75.8% based on the initial CH_4 found.

Reaction of DCl and LiB_4H_9. After reaction 10 (Table I), a large excess of DCl was added and the above HCl procedure was followed exactly. A 76.7% yield of B_4H_9D was found. Mass spectra of normal B_4H_{10} and this B_4H_9D were run at 22- and 70-V ionizing voltage in the mass spectrometer. All heaters were off, and the chamber temperature was due only to the hot filament which was turned on just prior to scanning. The cutoff for B_4H_{10} was *m/e* 53 ($^{11}B_4H_9^+$) and that for B_4H_9D was *m/e* 54 ($^{11}B_4H_8D^+$) at both voltages. No ions arising from other neutral species were present in either spectrum.

The B_4H_9D was condensed into a gas infrared cell (13-cm path length) to give approximately 300 Torr pressure and the cell was placed in one beam of the infrared spectrometer. Only the range 2000-1500 cm^{-1} was scanned so that the initial position of the deuterium could be reliably determined. Group frequencies of B_4H_{10} have been assigned by Dahl.[9] The interpretation of this spectrum will be discussed later.

Reaction of $B_{10}H_{14}$ and LiB_4H_9. After reaction 6 (Table I), with the vessel in the tube opener at −196°, the top at A (Figure 1) was opened under a positive pressure of dry nitrogen and the $B_{10}H_{14}$ was added through a dry funnel. The top was resealed, and the vessel was evacuated and sealed from the line at D (Figure 1). The reactants were warmed and a pale yellow color formed as the solution melted. The tube was immersed in a −78° bath and shaken. Bubbling began and the solution frothed. After 1 hr, the solution was an intense lemon yellow indicative of the $B_{10}H_{13}^-$ anion. After complexing the ether with BF_3, the volatile material was recovered. No noncondensable (at −196°) material was found. B_4H_{10} (0.322 mmol) was collected giving a 39.6% yield based on the initial CH_4 formed.

B_5H_9 and LiB_4H_9. Two reactions of B_5H_9 and LiB_4H_9 were attempted. After reactions 2 and 14 (Table I), excess pentaborane(9)

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[8] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948.

[9] A. J. Dahl, Ph.D. Thesis, University of Michigan, 1963 [*cf. Diss. Abstr.*, 25, 2252 (1964)].

was condensed into the vessel. The conditions used were −78° for 18.5 hr for the first and −45 and −23° for 32 min each for the second. After reaction 2, the ether was separated from the volatile mixture by condensing the mixture on $AlCl_3$. The $AlCl_3$ complexed the ether. The bulk of the B_5H_9 was recovered. After reaction 14, BF_3 was used as the ether-complexing agent. The unreacted B_5H_9 remained in the −78° traps with the $BF_3 \cdot OEt_2$. A trace of unreacted B_4H_{10} was also recovered.

Reaction of B_4H_{10} and LiB_5H_8. The deprotonation of B_5H_9[10] was carried out in a sealed tube similar to those used above. $LiCH_3$ (1.27 mmol), ethyl ether (0.2 ml), and B_5H_9 (0.575 mmol) were condensed together, kept at −78° for 15 hr and then at −23° for 90 min with occasional shaking. The only noncondensable (−196°) material found was CH_4 (0.575 mmol) which resulted in 100% yield. B_4H_{10} (1.01 mmol) was condensed into the vessel and it was again sealed off and placed in a −78° bath for 4.5 hr. After this time the solution appeared to be mostly liquid. The vessel was then immersed in a −63° bath for 100 min. At this point, the solution was so viscous that tilting the tube caused no liquid flow. The tube was opened and CH_4 (0.361 mmol) was collected again. The CH_4 was produced by the deprotonation of some B_4H_{10} by excess $LiCH_3$. The ether was condensed with $AlCl_3$ and the volatile material measured. The infrared spectrum of a sample of the −95° condensate was identical with that of B_5H_9. The mass spectrum of this material showed a sharp cutoff at *m/e* 64 ($^{11}B_5H_9^+$). The yield of B_5H_9 (0.297 mmol) was 51.6% based on initial CH_4 collected.

B_2H_6 and LiB_4H_9. After reaction 7 (Table I) diborane(6) (1.44 mmol) was condensed into the tube. After 1 hr of contact of B_2H_6 at −78° the recovered volatile fraction contained diborane(6) (1.41 mmol) for a 97.4% return. Essentially no reaction had occurred.

CH_3Cl, CH_3I, and LiB_4H_9. Attempts to methylate the $B_4H_9^-$ by treating it with CH_3Cl and CH_3I were unsuccessful. Conditions of −73° for 100 min and −63° for 35 min with CH_3Cl and −78° for 13.5 hr and −63° for 2 hr with one CH_3I attempt gave no volatile products. Only traces of unreacted B_4H_{10} were found along with the bulk of unreacted CH_3Cl and CH_3I.

Boron-11 Nmr. Boron-11 nmr spectra were taken of LiB_4H_9 at −63° and at warmer temperatures. While a definite change in appearance of the spectra occurred as the sample was warmed, the 19.3-MHz spectra were too broad to allow a unique interpretation.[11] Higher resolution spectra are needed to determine whether the Li^+ ion contributed to this broadening by interacting strongly with the $B_4H_9^-$ in the environment of the missing hydrogen atom.

Results and Discussion

Deprotonation of Tetraborane(10). The deprotonation of B_4H_{10} by $LiCH_3$ proceeded smoothly at −78° in ethyl ether. The reaction

$$B_4H_{10} + LiCH_3 \rightarrow LiB_4H_9 + CH_4$$

gave yields as high as 98.0%. The highest yields were obtained when sufficient ether was present to solvate the reactants and products. In the absence of solvent, the deprotonation was slower and was accompanied by a second reaction to produce $B(CH_3)_3$.

Structure of $B_4H_9^-$. When the $B_4H_9^-$ was reprotonated using HCl, high yields of B_4H_{10} were returned.

When DCl was substituted for HCl, B_4H_9D was formed. The initial infrared scan between 2000 and 1500 cm^{-1} gave a strong absorption at 1583 cm^{-1}, due to a bridge deuterium stretch. The sample was transparent between 2000 and 1910 cm^{-1}. The terminal B-D stretch for B_4D_{10} occurs at 1946 cm^{-1}. The 1583-cm^{-1} band intensity decreased and a new band at 1946 cm^{-1} appeared and grew more intense with time. The change of intensity was due to intramolecular exchange of hydrogen and deuterium atoms. This exchange was previously observed by Norman and Schaeffer.[12] The deuterium atom had formed a three-center bridge bond rather than a single terminal B-D bond. So unless rearrangement occurred after deprotonation, the structure of $B_4H_9^-$ resembled that of the parent B_4H_{10}, but missing the bridge proton.[2]

Stability of LiB_4H_9. The stability of LiB_4H_9 was confirmed by chemical means. In those HCl reprotonation reactions in which methods for removing the ether were being developed, it was found that the longer the salt was kept at temperatures above −78°, the less B_4H_{10} and more hydrogen were recovered. Recooling to −78° or lower did not improve the yields of recovered B_4H_{10}. This indicated that the anion decomposed irreversibly to at least one compound containing hydridic hydrogen atoms. No noncondensable (−196°) material was produced during its decomposition.

The relative stability of the boron hydride anions derived from neutral boron hydrides in ether solvents and similar cations appears to be $B_{10}H_{13}^-$ [13] $>$ $B_6H_9^-$ [14] $>$ $B_5H_8^-$ [14] $>$ $B_4H_9^-$ and KB_4H_9[2] is thermally more stable than LiB_4H_9.

Bronsted Acidity of B_4H_{10}. The fact that B_4H_{10} reacted with LiB_5H_8 to give B_4H_9 and that no reaction occurred between B_5H_9 and LiB_4H_9 showed that B_4H_{10} is a stronger Bronsted acid than B_5H_9. $B_{10}H_{14}$ easily protonated $B_4H_9^-$ to produce B_4H_{10} and $B_{10}H_{13}^-$. The two reactions can be written as

$$B_4H_{10} + LiB_5H_8 \xrightarrow{Et_2O} LiB_4H_9 + B_5H_9$$

$$B_{10}H_{14} + LiB_4H_9 \xrightarrow{Et_2O} LiB_{10}H_{13} + B_4H_{10}$$

The relative Bronsted acidity of boron hydrides cannot be correlated with their dipole moments or their charge distribution about the bridge atoms from recent calculations.[15] It appears that a more detailed theoretical approach is needed to describe charge distributions and predict bridge and terminal hydrogen atom reactivities in these boron hydrides.

Lewis Base Strength of $B_4H_9^-$. The observation that B_2H_6 did not react with LiB_4H_9 while in another study[10] unsymmetrical cleavage products of B_2H_6 were formed in the presence of $B_5H_8^-$ is important. In the latter study, *i*-B_6H_{10} was produced by insertion of BH_2^+ into the basal plane of $B_5H_8^-$ in place of the missing bridge proton under similar conditions. Thus, $B_5H_8^-$ may be a stronger Lewis base than $B_4H_9^-$ because the B_2H_6 was not cleaved in the present study.

Registry No. $LiCH_3$, 917-54-4; B_4H_{10}, 18283-93-7; LiB_4H_9, 30284-67-4; LiB_5H_8, 12447-54-0; $B_{10}H_{14}$, 17702-41-9; B_4H_9D, 37474-12-7.

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