The differences in the observed enthalpies of $Al(CH_3)_3$ and BCl_3 interactions with $(CH_2)_5S$ and $(CH_2)_4S$ suggest that ring-size effects are involved in the BCl_3 adducts. These ring-size effects are probably steric in nature. This type of effect has been established in BF_3 interactions with cyclic ethers where $(CH_2)_4O$ has a greater enthalpy of interaction than $(CH_2)_5O$.[20] If this effect in the sulfides were not steric, one would expect that trimethylalane should also differentiate the donor abilities of $(CH_2)_5S$ and $(CH_2)_4S$. These results are not inconsistent with other studies which have established that the steric requirements in alane adducts are much less severe than those in corresponding borane adducts. The 2,6-lutidine–trimethylalane adduct is quite stable[21] whereas the corresponding trimethylborane adduct does not exist, apparently for steric reasons.[22] The tetrahedral covalent radius of aluminum, which is approximately 43% larger than that of boron, apparently results in the formation of sufficiently long dative bonds so that the alane methyl groups are adequately removed from the sphere of steric influence of substituents on the donor atom.

The small differences in the observed solution enthalpies suggest that steric effects are minimal. The observed differences are probably best explained by considering the influence of inductive effects and ring strain upon the sulfur lone-pair availability.

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Reactions of Pentaborane(9) and Pentaborane Derivatives

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The preparations of a number of pentaborane derivatives are described and ^{11}B and ^{1}H nmr spectra recorded and correlated. Assessments of alternative preparative schemes are given. An extension of the apex to base rearrangement reaction to polyalkyl pentaboranes reveals the following trends: the rate of rearrangement decreases with increasing number of alkyl substituents on the pentaborane framework; the rate increases with the use of stronger and less sterically hindered bases. Mechanistic inferences are discussed.

Introduction

Although a number of reports on reactions of pentaborane and on the preparation of pentaborane derivatives appear in the literature,[1-24] there is a need for a study which correlates the reactivities and properties of such compounds. It is, in part, an attempt to pave the way for a systematized examination of this sort that accounts for the present work. The preparations of several new derivatives are described and assessments of presently known synthetic routes are made. In addition, both ^{1}H and ^{11}B nmr spectra are gathered and correlated.

Experimental Section

Materials.—Methyl chloride, ethylene, hydrogen chloride, and trimethylamine were obtained from The Matheson Co., Inc., and used without further purification. Chlorine (Matheson) was freed from HCl by a single distillation. Pentaborane and decaborane were obtained from Olin Mathieson Chemical Co., Inc., aluminum chloride from J. T. Baker Chemical Co., and metal hydrides from Metal Hydrides, Inc. Diglyme (Ansul), ethyl ether, and tetrahydrofuran were distilled from lithium aluminum hydride before use. 1-Methyl-,[3,4,8] 1-bromo-,[2,5,16] 2-bromo-,[17] 1-chloro-[25], and 2-chloropentaboranes[15,26] were pre-

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[26] If the product is not carefully fractionated, small amounts of 2-bromopentaborane[17] will be present.

pared using previously reported procedures. All chemicals were handled in standard high vacuum equipment.

Infrared spectra were recorded by a Beckman IR-5 instrument. All of the compounds were measured in the gas phase using pressures not exceeding 25 mm in a 10-cm length sodium chloride cell.

Nuclear Magnetic Resonance.—^{11}B nmr spectra (Table I) were obtained at 12.8 Mc with a Varian V-4300 high-resolution spectrometer. In addition, several of the compounds were recorded at 32.1 Mc by E. Pier of Varian Associates. ^1H nmr spectra (Table II) were obtained using a Varian A-60 spectrometer. ^{11}B decoupling experiments were performed at 19.2 Mc with an NMR Specialties Model HD-60 spin decoupler and Hewlett-Packard Model 200 CD wide-range oscillator.

Mass spectra were taken on a CEC 20-620 instrument.

Gas chromatography was used for final purification of most of the boron hydride derivatives. A 30% Kel-F on firebrick column[8] operated at temperatures no higher than 100° proved sufficient for most purposes.

TABLE I

^{11}B NMR CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS[a]

Compound	Boron environment	δ^b	J, cps
Pentaborane[c]	B(1)–H	51.8	178
	B(2,3,4,5)–H	12.5	161
1-Methylpentaborane	B(1)–CH_3	44.5	...
	B(2,3,4,5)–H	13.8	159
2-Methylpentaborane[d]	B(1)–H	50.4	176
	B(2)–CH_3	−2.2	...
	B(3,5)–H	12.7	*Ca.* 160
	B(4)–H	18.1	*Ca.* 160
1-Ethylpentaborane	B(1)–C_2H_5	42.5	...
	B(2,3,4,5)–H	14.2	160
2-Ethylpentaborane[d]	B(1)–H	51.4	173
	B(2)–C_2H_5	−4.2	...
	B(3,5)–H	13.4	*Ca.* 160
	B(4)–H	18.1	*Ca.* 160
1-Chloropentaborane	B(1)–Cl	30.6	...
	B(2,3,4,5)–H	14.5	*Ca.* 160
2-Chloropentaborane[d,e]	B(1)–H	51.0	179
	B(2)–Cl	−0.5	...
	B(3,5)–H	12.5	177
	B(4)–H	22.0	178
1-Bromopentaborane[c]	B(1)–Br	26.4	...
	B(2,3,4,5)–H	12.5	161
2-Bromopentaborane	B(1)–H	53.5	180
	B(2)–Br	11[f]	...
	B(3,5)–H	15[f]	*Ca.* 170
	B(4)–H	20[f]	*Ca.* 170
1-Iodopentaborane[c]	B(1)–I	55.0	...
	B(2,3,4,5)–H	11.8	160
1,2-Dimethylpentaborane	B(1)–CH_3	44.3	...
	B(2)–CH_3	0.8	...
	B(3,5)–H	15.3[f]	*Ca.* 160
	B(4)–H		
2,3-Dimethylpentaborane[g]	B(1)–H	50.4	178
	B(2,3)–CH_3	1.2	...
	B(4,5)–H	19.6	160
1-Bromo-2-methylpentaborane	B(1)–Br	34.0	...
	B(2)–CH_3	0.4	...
	B(3,5)–H	13.6[f]	173
	B(4)–H		
1,2,3-Trimethylpentaborane	B(1)–CH_3	43.6	...
	B(2,4 or 2,3)–CH_3	2.3	...
	B(3,5 or 4,5)–H	17.7	*Ca.* 160

[a] All spectra were taken at 12.8 Mc. Certain designated compounds were also run at 32.1 Mc. [b] δ, ppm relative to boron trifluoride ethyl etherate. [c] T. Onak, H. Landesman, H. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959). [d] Values also measured at 32.1 Mc. [e] Ref 15. [f] Represents an approximate value for the designated types of boron atoms. Overlap of resonances makes individual assignments difficult. [g] Ref 18.

1-Ethylpentaborane.—The adopted procedure for the preparation of 1-ethylpentaborane was the aluminum chloride catalyzed reaction between ethylene and pentaborane.[4,8,11] When ethyl chloride[11] was used instead of ethylene large amounts of boron trichloride, $C_2H_5BCl_2$, and $(C_2H_5)_2BCl$ (identified by infrared and ^{11}B nmr spectra) were also formed, thereby posing unnecessary separation problems. The purified 1-ethylpentaborane was identified by infrared and nmr spectra.[3]

2-Methylpentaborane.—A mixture of 6 ml of 2,6-lutidine[27] and 6.67 mmoles of 1-methylpentaborane was stirred at room temperature for 18 hr. Slow vacuum fractionation of the resulting orange-brown liquid gave 6.65 mmoles of crude product (trapped at −90°) from which 6.21 mmoles (93%) of glpc-purified 2-methylpentaborane was obtained. The product was identified by infrared,[17] ^{11}B nmr,[6] and mass spectra. The conditions required for rearrangement using bases other than 2,6-lutidine are given in Table III.

2-Ethylpentaborane.—Essentially the same procedure as described earlier[6] was employed. The addition of boron trifluoride ethyl etherate, however, was found unnecessary. Two or three careful fractionations through a trap at −35° removed the last traces of the solvent-catalyst, 2,6-lutidine. The infrared spectrum of the purified 2-ethylpentaborane exhibited bands at (cm^{-1}); 2965 s, 2915 ms, 2890 ms, sh, 2600 vs, 1815 m, 1610 w, 1462 ms, 1440 ms, 1397 s, 1390 s, 1315 m, sh, 1142 m, 1100 m, 1024 m, 980 m, 942 w, 889 s, 847 m, 768 w, 708 w, and 638 ms, broad.

1,2-Dimethylpentaborane was prepared from the aluminum chloride catalyzed reaction between 2-methylpentaborane and methyl chloride.[8] The yield (50%) was improved over the previously reported 20% by decreasing the reaction temperature from 100° to 50°. This reduces the formation of side products which are principally BCl_3 and $HBCl_2$, diborane, CH_3BCl_2, and $(CH_3)_2BCl$ (infrared and ^{11}B nmr analysis). The infrared spectrum of the glpc-purified[8] 1,2-dimethylpentaborane exhibits bands at (cm^{-1}): 2975 ms, 2940 s, 2865 m, 2610 vs, 1845 ms, 1790 m, 1630 w, 1446 s, 1387 vs, 1330 s, 1245 ms, 1145 w, 1115 ms, 1012 w, 917 s, 888 s, 798 w, 792 w, 752 w, and 677 ms.

2,3-Dimethylpentaborane was prepared by the rearrangement of 1,2-dimethylpentaborane[18] using a variety of Lewis bases (Table III). The infrared spectrum of the glpc-purified product exhibits bands at (cm^{-1}): 2970 ms, 2935 m, 2855 w, 2610 vs, 1857 m, 1820 m, 1755 w, 1625 w, 1420 vs, broad, 1335 s, 1252 m, 1166 ms, 1120 s, 1040 w, 984 m, 912 s, 888 ms, 833 w, 780 w, 722 w, and 647 ms.

1-Bromo-2-methylpentaborane.—2-Methylpentaborane (10 mmoles) was added to 5 ml of a cooled (−190°) carbon disulfide solution containing bromine (9.5 mmoles) and a catalytic amount of aluminum chloride. The mixture was stirred first at −30° for 0.5 hr and then at room temperature for 1 hr. Fractional condensation gave 1.35 g (91%) of 1-bromo-2-methylpentaborane (mp −20.5 to −19°) which was trapped at −20°.

Anal. Calcd for $CH_{10}B_5Br$: Br, 51.2. Found: Br, 51.6.

1,2,3-Trimethylpentaborane.—A catalytic amount of aluminum chloride was sublimed into a 25-ml flask. After adding 2,3-dimethylpentaborane and methyl chloride (1.1 mmoles) the flask was sealed and allowed to stand at room temperature for 3 days. Fractional condensation removed about 0.6 mmole of a mixture of CH_3BCl_2 and $(CH_3)_2BCl$. Glpc of less volatile fractions gave 0.35 mmole (35%) of 1,2,3-$(CH_3)_3B_5H_6$ and 0.09 mmole of unreacted 2,3-$(CH_3)_2B_5H_7$.

Anal. Calcd for $C_3H_{15}B_5$: C, 35.9; H, 14.3. Found: C, 35.4; H, 14.1.

The infrared spectrum exhibited bands at (cm^{-1}): 2980 ms, 2940 ms, 2875 m, 2610 vs, 1845 m, broad, 1620 w, 1390 vs, broad, 1333 s, 1247 ms, 1148 m, sh, 1115 ms, 1020 w, 973 w, 912 s, 892 ms, sh, 854 m, 788 w, 725 w, and 674 ms.

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TABLE II

^{1}H NMR CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS

Compound	Proton environment[a]	τ[b]	J, cps[c]
Pentaborane	H–B(1)	9.05	173
	H–B(2,3,4,5)	7.45	168
	H_μ(2,3,4,5)	12.20	...[d]
1-Methylpentaborane	H–B(2,3,4,5)	7.55	165
	H_μ(2,3,4,5)	11.86	...[d]
	H–C	9.85	...
2-Methylpentaborane	H–B(1)	9.40	169
	H–B(3,5) H–B(4)	7.67[e]	163
	H_μ(2,5) H_μ(3,4)	12.25[f]	...[d]
	H–C	9.52	...
1-Ethylpentaborane	H–B(2,3,4,5)	7.47	162
	H_μ(2,3,4,5)	12.1	...[d]
	H–C(methyl) H–C(methylene)	9.06[f]	...
2-Ethylpentaborane	H–B(1)	9.42	170
	H–B(3,5) H–B(4)	7.65[e]	163
	H_μ(2,5) H_μ(3,4)	12.4[f]	...[d]
	H–C(methyl) H–C(methylene)	9.05[f]	...
1-Chloropentaborane	H–B(2,3,4,5)	7.23	165
	H_μ(2,3,4,5)	11.59	...[d]
2-Chloropentaborane	H–B(1)	9.21	175
	H–B(3,5) H–B(4)	7.54[f]	177
	H_μ(2,5 or 3,4)	10.60	...[d]
	H_μ(3,4 or 2,5)	12.17	...[d]
1-Bromopentaborane	H–B(2,3,4,5)	7.20	165
	H_μ(2,3,4,5)	11.50	...[d]
2-Bromopentaborane	H–B(1)	9.10	176
	H–B(3,5) H–B(4)	7.46[f]	166
	H_μ(2,5 or 3,4)	10.82	...[d]
	H_μ(3,4 or 2,5)	12.12	...[d]
1,2-Dimethylpentaborane	H–B(3,5) H–B(4)	7.66[f]	161
	H_μ(2,5) H_μ(3,4)	11.66[f]	...[d]
	H–C(1) H–C(2)	9.5–9.9[f]	...
2,3-Dimethylpentaborane	H–B(1)	9.37	167
	H–B(3,5 or 4,5)	7.73	162
	H_μ(2,3,4,5)	11.7	...[d]
	H–C	9.50	...
1-Bromo-2-methylpentaborane	H–B(3,5) H–B(4)	7.50[f]	168
	H_μ(2,5) H_μ(3,4)	11.6[f]	...[d]
	H–C	9.68	...
1,2,3-Trimethylpentaborane	H–B(3,5 or 4,5)	7.78	158
	H_μ(2,3,4,5)	11.51	...[d]
	H–C(1) H–C(2,4 or 2,3)	9.5–9.8[f]	...

[a] B(1) = apex of pentaborane pyrimid; B(2,3,4,5) = basal borons; H_μ = bridge hydrogens, $H_\mu(2)$ designates bridge hydrogen between boron atoms 2 and 3, etc. [b] In order to avoid negative values, τ (tetramethylsilane = 10.00) is used rather than δ. Most chemical shift values were confirmed with ^{11}B double resonance experiments. [c] Hydrogen–boron coupling constants refer to H–^{11}B coupling only. Most of the quartet peaks assigned to the ^{11}B-attached hydrogens are usually well defined, whereas the smaller septets of the ^{10}B (20% of the natural occurring boron, $I = 3$, magnetogyric ratio = 0.336^{11}B value) attached hydrogens are buried under the labyrinth of all other resonances. [d] Cannot be accurately determined because of lack of well-defined fine structure. However, from the peak width, bridge coupling to neighboring ^{11}B atoms in most pentaborane derivatives is estimated to be *ca.* 30–40 cps. [e] Some separation of the two kinds of basal H–B hydrogens is observed with ^{11}B decoupling experiments. However, there is still sufficient overlap to prevent individual τ assignments. The H–B(4) hydrogen does appear at slightly higher field than the H–B(3,5) hydrogens which is obvious from the peak shape of the decoupled spectrum. [f] Represents an approximate chemical shift for the designated types of hydrogens. Overlap of resonances makes individual assignments difficult.

Pentaborane and Sodium Hydride.—A mixture of pentaborane (1.0 mmole), 48.8 mg. of sodium hydride (50% mineral oil dispersion, 1.0 mmole of active hydride), and 1 ml of dry diglyme was stirred at room temperature for 10 hr. A measure of noncondensable gases gave 0.815 mmole of H_2. Vacuum fractionation gave diglyme (trapped at −60°) and only a trace quantity of a more volatile material.[28] A similar, but slower, process was observed in diethyl ether. Thus, 1.83 mmoles of NaH and 1.78 mmoles of B_5H_9 gave 0.301 mmole of H_2 after stirring for 3 days at room temperature. The reaction rate increases considerably on addition of tetrahydrofuran giving a total of 0.862 mmole of H_2 after another 16-hr period.

On adding dry hydrogen chloride (1.0 mmole) to the diglyme solution, hydrogen (0.825 mmole) was liberated. Fractional condensation of the diglyme solution yielded only a trace quantity of a material more volatile than diglyme. An additional millimole of hydrogen chloride liberated more hydrogen (0.9 mmole). Methyl chloride (0.3 mmole) was also isolated upon fractional condensation and identified by infrared spectra. The diethyl ether solution behaved similarly.

1-Methylpentaborane and Sodium Hydride.—A mixture of 1-methylpentaborane (1.0 mmole), 50.9 mg of sodium hydride (50% mineral oil dispersion, 1.06 mmoles of active hydride), and 1 ml of dry diglyme stirred at room temperature for 3 hr produced 0.817 mmole of H_2. No volatile substance other than diglyme was found on fractional condensation. Addition of decaborane (1.0 mmole) to a diglyme solution of the original mixture gave, after 2 hr stirring at room temperature, hydrogen (0.215 mmole), 2-methylpentaborane (0.036 mmole, 3.6%), diborane (0.15 mmole), and a trace of methyldiborane.

1-Ethylpentaborane and Sodium Hydride.—Essentially the same procedure was followed as described above for the 1-methyl derivative. A measure of noncondensable gases from the reaction between sodium hydride and 1-ethylpentaborane gave 0.82 mmole of hydrogen. Addition of an excess of decaborane gave off additional hydrogen but no B–H-containing volatile components.

1-Methylpentaborane and Trimethylamine.—In a 100-ml

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[28] In separate control experiments it was established that it is sufficient to distil off only about 50% of the diglyme to remove nearly all of the more volatile pertinent compounds (*i.e.*, diborane and pentaborane).

Table III

Conditions for Rearrangement[a] Using 4:1 Lewis Base:Substituted Pentaborane

	Substituted pentaborane				
Lewis base	1-D-	1-CH_3-	1,2-$(CH_3)_2$-	1,2,3-$(CH_3)_3$-	pK_a[b]
2,6-Lutidine	45 min, 25°	4 hr, 25°	5 days, 25°		6.75
2-Chloropyridine		30 min, 25°	20 hr, 25°	2 days, 80°	0.72
2-Bromopyridine		40 min, 25°	60 hr, 25°		0.90
N,N-Dimethylaniline		24 hr, 100°			5.06
N-Methyldiphenylamine		No rearrang. 150°, 24 hr			. . .
Trimethylamine	Complex[c]	Complex[c]	Complex[c]		9.80

[a] Minimum conditions for the reaction to proceed to 95+% completion. [b] See D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965; and A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, for leading references. For most bases pK_a values are only approximate and may well deviate from the actual value by *ca.* ±0.2 pK_a. [c] The complex is formed almost immediately at room temperature. The rearranged substituted pentaborane is obtained by decomposing the complex with an appropriate Lewis acid.[10,14]

flask was condensed 3.33 mmoles of trimethylamine and 0.935 mmole of pentaborane. Over a period of 3 hr the mixture was slowly warmed from −190° to room temperature. At about −10° the solution became a viscous oil which, for the most part, turned to an opaque white solid by the time room temperature had been reached. The mixture, which was now rather slushy in behavior, was stirred for 1 hr at room temperature. During this time a light yellow oil began to develop. Fractional condensation removed 41.1 mg of white sublimable crystals (trapped at −90°) which infrared analysis indicated to be mostly trimethylamine borane (0.56 mmole). Trapped at −190° was 1.03 mmoles of unused trimethylamine. Addition of decaborane (1.0 mmole) to the nonvolatile residue gave 0.06 mmole (*ca.* 6%) of 2-methylpentaborane.

Trimethylamine and Excess Pentaborane.—Pentaborane (3.46 mmoles) and 1.99 mmoles of $(CH_3)_3N$ were kept at −78° for 16 hr. The excess B_5H_9 was distilled out first at −78°, then with slow warming to −29° over a period of 3 days. The purity of the recovered B_5H_9 (2.43 mmoles) was established by its vapor pressure at 0° and ^1H nmr spectrum (which is sensitive to CH_3–N compounds). The ratio of $(CH_3)_3N$ to B_5H_9 in the residue is 1.93.

1-Ethylpentaborane and Trimethylamine.—In a 100-ml flask was condensed at −190° trimethylamine (4.60 mmoles) and 1-ethylpentaborane (1.51 mmoles). The mixture was stored at −60° for 16 hr, during which white crystalline material formed on the walls of the flask. The crystals gradually changed to a light yellow oil after about 10 min at room temperature. After stirring for 2 hr the flask was cooled to −40° and the excess trimethylamine (0.74 mmole) removed. To the residue was added a solution of 500 mg (4.1 mmoles) of decaborane in 4 ml of ethyl ether, and the resulting mixture was stirred for 1 hr at room temperature. Fractional condensation gave 0.58 mmole (38%) of 2-ethylpentaborane (identified by infrared and ^{11}B nmr).

In another experiment a mixture of trimethylamine (3.04 mmoles) and 1-ethylpentaborane (0.88 mmole) was raised from −190° to room temperature over a period of 45 min. Immediate fractionation removed 1.21 mmoles of trimethylamine, leaving a nonvolatile residue with an ethylpentaborane:trimethylamine ratio of 1:2.08.

Discussion

Formation of Pentaborane Derivatives.—Nearly all substitutions at the apex of pentaborane have been effected using conditions[2–5,7,8,11,13,16,21–24] generally reminiscent of aromatic electrophilic substitution reactions. It is observed that both the reactivity toward apical substitution and the susceptibility of the pentaborane skeleton to fragment under Friedel–Crafts conditions appear to be enhanced with substitution in the base. Whereas methylation of pentaborane takes place at *ca.* 100° with only small amounts of side products produced, 2,3-dimethylpentaborane reacts at room temperature to give significant quantities of monoboron side products as well as the desired trimethylpentaborane. 2-Methylpentaborane is intermediate in behavior.

To avoid side products such as $RBCl_2$, R_2BCl, BCl_3, etc., we have found alkenes to be preferred over alkyl halides for the preparation of alkylpentaboranes (with the obvious exception of 1-methylpentaborane). It is possible that the buildup of large amounts of hydrogen chloride is largely responsible for the side products when alkyl halides are used.[11] This suspicion receives some support in a separate deuteration study. The reaction of deuterium chloride with pentaborane in the presence of small amounts of aluminum chloride at the higher temperatures used in the alkylation experiments resulted in slow decomposition to give BCl_3, $HBCl_2$, B_2H_5Cl, B_2H_6, and corresponding deuterated derivatives. This is in contrast to the rather selective (and nondestructive) monodeuteration of the apical boron under ambient conditions.[7]

Although some 2-substituted pentaboranes can be obtained directly from pentaborane,[8,12] the base-catalyzed rearrangement of the corresponding 1-substituted derivative is to be preferred for most preparative purposes,[6,10,17] for although one extra step is required, the over-all yield of product is significantly higher.

Reactions of Pentaborane with Metal Hydrides.—The previously reported chemistry of pentaborane with metal hydrides is in need of clarification. Hough and Edwards[29] found that sodium hydride does not react with pentaborane(9) at room temperature using diethyl ether as a solvent. In contrast, Schlesinger and co-workers reported a reaction using lithium hydride which appears to follow the stoichiometry.[30]

$$B_5H_9 + 2LiH \xrightarrow{(C_2H_5)_2O} [Li_2B_5H_{11}] \longrightarrow LiBH_4 + [LiB_4H_7]$$

We find that both sodium hydride and lithium hydride react with pentaborane(9) in a variety of ethers (in-

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(29) W. V. Hough and L. J. Edwards in "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 184; M. D. Ford, W. V. Hough, and L. J. Edwards, *Nucl. Sci. Abstr.*, **11**, Abstract No. 6233 (1957).

(30) H. I. Schlesinger, Final Report, Contract N6 ori-20, T.O.X., June 30, 1951, p 7; also Progress Report 41, March 31, 1951.

cluding diethyl ether, although slowly), and nearly every attempt performed with a 1:1 ratio of reactants proceeds to give about 80% of the hydrogen expected for

$$\mathrm{MH} + \mathrm{B_5H_9} \xrightarrow{\text{diglyme}} \mathrm{H_2} + [\mathrm{MB_5H_8}] \quad (\mathrm{M = Li, Na})$$

The resulting material, which has the composition MB_5H_8, might be expected to behave like the proposed ion intermediate[10] in the amine-catalyzed rearrangement of 1-alkylpentaboranes. However, this is not the case; for addition of proton donors does not result in the recovery of pentaborane in significant yield. This is in contrast to $B_{10}H_{13}^-$ [31] and $C_2B_4H_7^-$,[32] which give $B_{10}H_{14}$ and $C_2B_4H_8$, respectively. Unfortunately, attempts to prepare tetramethylammonium salts of the ion product, $B_5H_8^-$, resulted in a degradation to give substantial amounts of $(CH_3)_4N^+B_3H_8^-$ and some $(CH_3)_4NBH_4$. It is unlikely that either of the ions, $B_3H_8^-$ or BH_4^-, is present as disproportionated products of the $B_5H_8^-$ ion for the addition of HCl to the ion solution would be expected to give rise to a significant yield of B_2H_6.[33] This was not observed. Furthermore, BH_4^- could not be observed in the ^{11}B nmr spectrum of the MB_5H_8 solution.

The ^{11}B nmr spectrum (12.8 Mc) consists of three broad partly overlapping peaks at δ ($BF_3 \cdot (C_2H_5)_2O$ = 0.0) +4, +16.5, and +27.5 with an estimated area ratio of 0.9:2.4:1.7. Assuming appropriate overlap of resonances this observed ratio is within reason for both a 2221 (calcd ratio 0.75:2.50:1.75) and a 3130 (calcd ratio 1.0:2.50:1.50) $B_5H_8^-$ structure.[34]

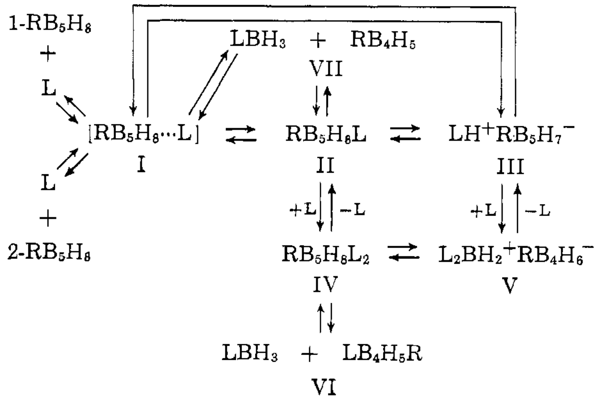
Mechanism of Rearrangement.—That the known 2-substituted pentaboranes are more thermodynamically stable than the corresponding 1-substituted derivatives is little questioned.[6,8,10,17–20,35] As might be expected from the limited information available, however, the mechanistic pathway for the base-catalyzed rearrangement of the apically-substituted to the basal-substituted isomer has been open to considerable speculation.[6,9,10,14,18,19,36–38]

To summarize pertinent observations: (1) A "sufficiently" strong Lewis base is necessary for a catalyst. (2) It appears impossible to draw a correlation between the catalytic activity of the base and Brønsted–Lowry base strength (Table III). In some cases a weaker but less sterically hindered base is more effective than a stronger but bulky base. (3) Increasing the number of alkyl groups on the pentaborane framework results in a decrease in rearrangement rate.

Although (3) is not inconsistent with a mechanism which involves ion formation,[10] both (1) and (2) provide compelling reasons to include the base in the transition state. Obviously, it would be most desirable to make a detailed and quantitative study of the rate dependence on base concentration. Thus far, attempts to carry out such a study have been discouraging due to inadequate means of following the reaction in dilute solutions.

A mechanism which takes into account most reasonable intermediates and the necessary transition state I is outlined in Scheme I. Such a scheme does not attempt to indicate all possible position isomers. Also, beyond the first intermediate little justice is done to all possible equilibria. A prior proton dissociation of the boron hydride followed by base capture is regarded as unimportant since it ignores the catalytic effect of the base. For the moment it is sufficient to regard all of the species (II–VII) as potential intermediates in the rearrangement reaction.

SCHEME I



With the use of weak or sterically hindered bases these intermediates may be present in only very small concentrations at any time. This is consistent with ^{11}B nmr observations which show, with 2,6-lutidine, the slow disappearance of 1-alkylpentaborane and concurrent appearance of the 2 isomer. No other boron resonances are apparent during the course of the rearrangement. With stronger and less sterically hindered bases there is the possibility of isolating one or more of the intermediate complexes. Isolation of the ion III has been reported and thought to be the key intermediate for the isomerization.[10] Unfortunately, we have not been successful in obtaining this same ion (*e.g.*, $(CH_3)_3NH^+RB_5H_7^-$) for further studies.[39] Even with excess boron hydride we find a ratio of 1:2 alkylpentaborane to trimethylamine. The latter observation, incidentally, is consistent with related work carried out on the parent compound, pentaborane.[14,40–45]

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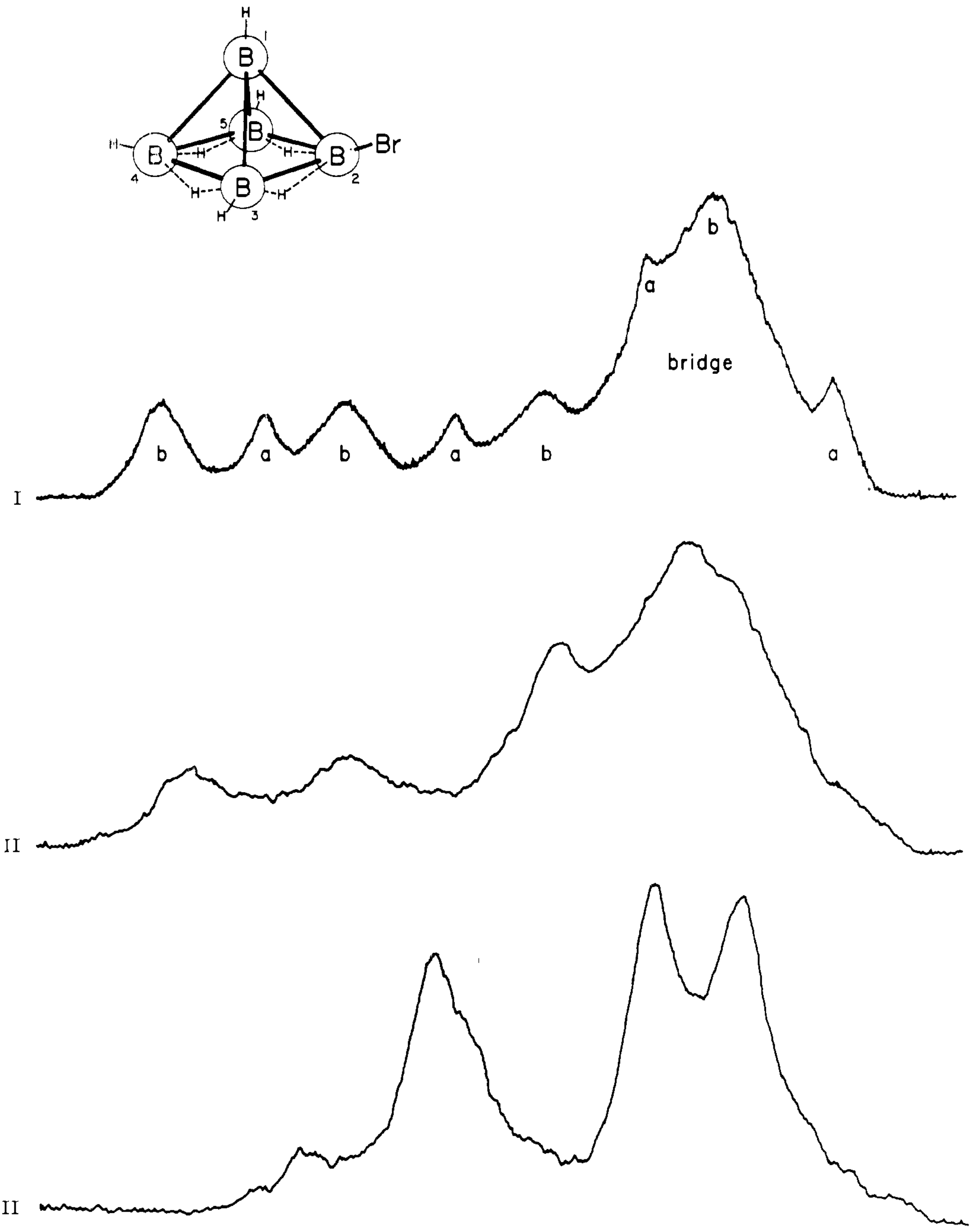

Figure 1.—Proton nmr spectra (60 Mc) of 2-bromopentaborane: I, no applied decoupling; II, decoupling of apical ^{11}B at 19.2 Mc; III, decoupling of basal ^{11}B at 19.2 Mc.

An alternate preparation of the ion III and the unsubstituted counterpart was attempted with the action of metal hydrides on pentaborane and alkylpentaborane (*vide supra*). The boron hydride ion from this reaction, however, did not give significant amounts of the (rearranged) product on adding proton donors.

There appears to be no compelling evidence, therefore, to regard ion formation as a *necessary* requirement in the base-catalyzed rearrangement. And, although, we find that the diamine adduct will lead to the isomerized pentaborane derivative, there is, again, no compelling evidence to regard this adduct as *necessary* to the rearrangement. And since there is evidence to show that the isomerization is intramolecular[37] with respect to all B, H, and C atoms in the pentaborane derivative, both VI and VII are regarded as unimportant intermediates.[46] It is then encouraged that II, which is the result of a simple association, be given greater consideration as the likely candidate for the necessary intermediate. This intermediate is also attractive from the standpoint of a solid surface catalyzed rearrangement,[17] in that exposure of an isolated unshared pair of electrons would undoubtedly promote necessary tautomeric shifts within an attached boron hydride.

^{11}B Nmr (Table I).—Substitution at the apex or base

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[46] Also, unless III and V are present as tight ion pairs it is possible to totally disregard these from further consideration.

of pentaborane generally results in a downfield chemical shift of the attached boron. The only known exception is that of 1-iodopentaborane. The magnitude of the shift for various directly attached substituents is not unusual when compared to other boron systems.[47–52] The upfield shift of the boron diagonally opposite the substituent is mildly surprising, however. It is tempting to attribute this to long-range resonance effects such as are found in substituted benzenes. But considering the complexities inherent in rationalizing chemical shifts in boron compounds,[53] other factors may well be contributing to the observed shift.

^{1}H Nmr (Table II).—The proton magnetic resonance spectra of various substituted pentaboranes reveal several trends: (a) The proton bonded to the apical boron is shifted upfield upon basal substitution, alkyl groups being more effective than the known halogen derivatives. (b) Although it is not possible to resolve all the various kinds of basal terminal hydrogens in certain derivatives, the effect of neighboring substituents is very roughly additive. (c) Upon substitution at the apex the basal protons shift slightly to higher field with alkyl derivatives and slightly to lower field with halogen derivatives. (d) Methyl hydrogens are shifted to lower field in going from an apex to a basal position. All methyl and methylene groups bonded to boron are observed at higher field than in alkanes. This is consistent with observations made on other boron systems.[54–56]

Double resonance of the ^{11}B nuclei resolves the two types of bridge hydrogens in 2-chloro- and 2-bromopentaborane (Figure 1), but because the number of each kind is identical, an absolute assignment is not possible. There are certain inconsistencies in J_{H-B} and J_{B-H} for given boron–hydrogen bonds. This is not totally unexpected, since other nuclei in the molecule will couple weakly but with different magnitude to the two nuclei of a given B–H bond.[57]

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The Crystal Structure of Neodymium Monotellurooxide—Nd_2O_2Te

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The crystal structure of Nd_2O_2Te has been determined and refined from powder X-ray diffraction intensity data. The unit cell possesses body-centered tetragonal symmetry with two molecules per unit cell. The lattice parameters are a_0 = 4.032 A and c_0 = 12.80 A. The three crystallographically independent atoms are located in the following positions of space group I4/mmm: 4(e) ±(0, 0, *z*), *z* = 0.341 (Nd); 4(d) (0, $^1/_4$, $^1/_4$; $^1/_2$, 0, $^1/_4$ (O); and 2(a) (0, 0, 0) (Te), all plus body-centering translations. One significant feature of this structure is the ninefold coordination exhibited by the lanthanide ion. The magnetic susceptibility measured as a function of temperature gave μ_{eff} = 3.62 BM.

Introduction

The preparation of a family of lanthanide compounds of the general formula R_2O_2Te, in which R is a lanthanide element, has been reported [2–4] Although they listed lattice parameters, they did not report a structure. We suggest a structure compatible with the observed X-ray powder data.

Experimental Section

The olive-green sample we used was prepared by the reaction of calcined sesquioxide with hydrogen and tellurium according to the procedure described by Kent and Eick.[2] From its loss in mass upon oxidation to the sesquioxide, according to

$$Nd_2O_2Te(s) + {}^1/_2O_2(g) \longrightarrow Nd_2O_3(s) + Te(g) \qquad (1)$$

the composition of the oxytelluride was determined to be $NdOTe_{0.50\pm0.01}$.

The density was determined pycnometrically in phenyl chloride, with relatively large quantities of powder. A value of ρ = 7.2 ± 0.1 g/cm^3 was observed and is in good agreement with the theoretical value of 7.15 g/cm^3 and also with the previously re[2]ported[4] value of 6.98 g/cm^3. The result of Kent and Eick (5.17 g/cm^3), which was deduced reproducibly from volume and weight measurements of a compacted cylindrical sample, is in-

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(1) (a) Operated with support from the U. S. Air Force; (b) to whom correspondence should be addressed at Massachusetts Institute of Technology; (c) Michigan State University.

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