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Reexamination of the Mechanism of Acid-Catalyzed Amine–Borane Hydrolysis. The Hydrolysis of NH₃·BH₃

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Studies of the acid-catalyzed hydrolysis of ammonia–borane confirm the trend $k_2(\mathrm{NH_3 \cdot BH_3}) > k_2(\mathrm{MeNH_2 \cdot BH_3}) > k_2(\mathrm{Me_2NH \cdot BH_3}) > k_2(\mathrm{Me_3N \cdot BH_3})$ where $k_2 = -(1/[\mathrm{H^+}])\, d \ln [\mathrm{R_3NBH_3}]/dt$. Unlike the behavior of $\mathrm{Me_3N \cdot BH_3}$, hydrolysis of $\mathrm{NH_3 \cdot BH_3}$ (at pH 4–5) is faster than boron-bonded hydrogen exchange. A comparison of rates in acetate and deuterated acetate buffer solutions shows a normal solution isotope effect $(k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}} \simeq 1.5)$. This is approximately the same as that observed for $\mathrm{Me_3N \cdot BH_3}$ $(\mathrm{Me_3N \cdot BD_3})$ in 0.29 M $\mathrm{H_2SO_4}$ $(\mathrm{D_2SO_4})$. Results are interpreted to be consistent with a previously suggested mechanism involving cis displacement of $\cdot\mathrm{BH_3}$ via electrophilic attack of the proton of a general acid at amino nitrogen (the nitrogen–boron electron pair). An alternative mechanism involving reversible protonation of substrate to a five-coordinate boron species with subsequent loss of $\mathrm{H_2}$ cannot be precluded, but difficulties persist in efforts to reconcile such a model with kinetic effects, particularly those of *N*-alkyl substitution and relative rates of hydrolysis and substrate–solvent hydrogen exchange.

Previous investigations have shown amine–boranes (BH₃ adducts of nitrogen bases) to undergo both uncatalyzed and acid-catalyzed solvolysis in mixed aqueous solvents.[1-3] Mechanistic models for both pathways have been proposed, that for the acid-dependent reaction involving rate-determining cis displacement of BH₃ via electrophilic attack by the proton of a general acid at amino nitrogen, i.e., at the nitrogen–boron electron pair. Various solvent and substituent effects observed for the hydrolysis of substituted phenylamine–boranes in aqueous dioxane as well as of alkylamine–boranes in water have been interpreted in terms of this mechanism.[1,4] More recently, and after extensive studies of the hydrolysis of tetrahydridoborate, $\mathrm{BH_4^-}$,[5-12] and cyanotrihydroborate, $\mathrm{BH_3CN^-}$, in which five-coordinate boron species $\mathrm{H_2BH_3}$ and $\mathrm{H_2BH_2CN}$ have been proposed as reaction intermediates, it has been suggested that analogous species are involved as intermediates in the hydrolysis of amine–boranes.[12,13] The present study of ammonia–borane, originally undertaken to provide additional data on effects of N-substitution on rates of amine–borane hydrolysis, provides an opportunity to reconsider both mechanistic models.

Experimental Section

Materials and Apparatus. Ammonia–borane was supplied by the Callery Chemical Co. Analysis was carried out by using hydrolytic and titrimetric procedures.[14] Anal. Calcd for NH₃·BH₃ (30.865): H⁻ (hydridic), 9.80; B, 35.02; N, 45.38. Found: H⁻ (hydridic), 9.9; B, 34.4; N, 44.8. The purity is improved through vacuum sublimation. Trimethylamine–borane was obtained from Aldrich Chemical Co. and sublimed in vacuo. Distilled deionized water was used to prepare all aqueous solutions. Deuterium oxide (99.8 atom % D) and deuteriosulfuric acid (>98% D₂SO₄ in D₂O) were obtained from Diaprep, Inc., and deuterium chloride was prepared according to the method of Brown and Groot.[15] Deuterated acetate buffer solutions were prepared through addition of deuterium oxide solutions of DCl to D₂O solutions of anhydrous sodium acetate. Infrared spectra were obtained by using a Beckman IR 4250 spectrophotometer. Kinetic studies were carried out by using Sargent Thermonitor and Freas Precision constant-temperature baths controlled to ±0.05 °C.

Kinetic Studies and Deuterium Exchange. Samples of NH₃·BH₃ (20–30 mg) and specific buffer solutions (100 mL) were brought to temperature equilibrium in separate flasks, and t_0 was taken at the

Table I. Rates of Hydrolysis of NH₃·BH₃, $\mu = 0.3$, $t = 25\ ^\circ\mathrm{C}$

pH[a]	pD[b]	$10^5 k_{\mathrm{obsd}}$[c]
4.30[d]		24.6
4.30[e]		24.2
4.30[f]		23.2
	4.40	16.9
4.6[g]		13.7
4.76		11.1
	4.82	7.58
4.92		6.37
	5.0[h]	3.6
	5.04	3.34
5.20		4.10
	5.20	2.84
	5.39	1.00
5.46		2.34
5.80		0.864
	5.90	0.883
6.10		0.553
		0.576[i]
		0.605[j]
		0.598[k]
	6.12	0.307

[a] HOAc/OAc⁻ buffer at pH 4.3–5.5; $\mathrm{H_2PO_4^-}$/$\mathrm{HPO_4^{2-}}$ buffer at pH 5.8–6.1. [b] DOAc/OAc⁻ buffer. [c] $k_{\mathrm{obsd}} \equiv -\mathrm{d} \ln [\mathrm{NH_3 \cdot BH_3}]/dt$. [d] [HOAc] = 0.3 M. [e] [HOAc] = 0.12 M. [f] [HOAc] = 0.03 M. [g] [HOAc] $\simeq$ [OAc⁻] $\simeq 0.3$ M ($\mu = 0.6$). [h] [DOAc] $\simeq$ [OAc] $\simeq 0.3$ M ($\mu = 0.6$). [i] [$\mathrm{H_2PO_4^-}$] = 0.053 M. [j] [$\mathrm{H_2PO_4^-}$] = 0.079 M. [k] [$\mathrm{H_2PO_4^-}$] = 0.105 M.

time of mixing. Solution of NH₃·BH₃ was complete within 3 s. At selected time intervals, 10-mL samples of hydrolysate were withdrawn and iodometrically analyzed for soluble hydride.[16] A similar procedure was employed for the study of trimethylamine–borane hydrolysis in H₂SO₄ and D₂SO₄. In separate experiments in which the extent of deuterium exchange in ammonia–borane was to be examined, a 280-mg sample of hydride was dissolved in 100 mL of deuterated acetate buffer (0.3 M DOAc, 0.3 M OAc⁻, pD 5). The course of hydrolysis was determined by periodic hydride analysis of 1-mL samples of hydrolysate. After about 23% hydrolysis, and again after 56% hydrolysis, a 40-mL sample was withdrawn and the reaction quenched by dropwise addition of 2 M NaOD (prepared by dissolving 4 g of NaOH in 50 mL of D₂O) to adjust pD $\simeq$ 8. The solution was then saturated with NaCl and extracted three times with 40-mL
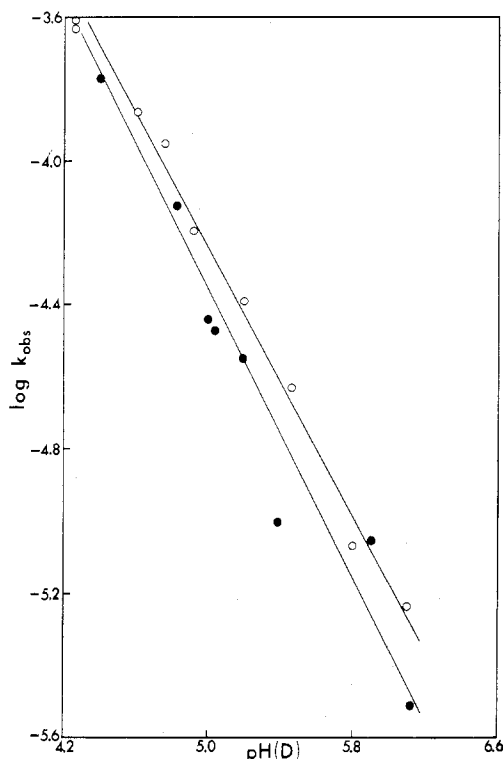
Figure 1. Rates of hydrolysis of $NH_3 \cdot BH_3$ in normal and deuterated buffer solutions at 25 °C: (O) HOAc/OAc⁻ in H_2O for pH 4.3–5.5, $H_2PO_4^-/HPO_4^{2-}$ in H_2O at pH 5.8–6.1, slope = –0.93, correlation coefficient = 0.997; (●) DOAc/OAc⁻ in D_2O, slope = –0.96, correlation coefficient = 0.972. $k_{obsd} \equiv -d \ln [NH_3 \cdot BH_3]/dt$.

samples of Et_2O which had been freshly distilled from $LiAlH_4$. The combined ether extracts were dried overnight over anhydrous Na_2SO_4. Solvent was removed in vacuo following which infrared spectra were obtained on KBr wafers of the white solid residue.

Results and Discussion

In aqueous acetate or phosphate buffer, the hydrolysis of ammonia–borane is first order in substrate S. The observed first-order rate constant varies with pH (pD) as shown in Table I and Figure 1, leading to the expected second-order expression,[17] $-d[S]/dt = k_2[S][H^+]$. The reaction is subject to a small but measurable normal solvent isotope effect of k_2-$(H_2O)/k_2(D_2O) \simeq 1.5$. Rapid exchange of nitrogen-bonded hydrogen occurs but exchange of boron-bonded hydrogen is slow with respect to both N–H exchange and substrate hydrolysis. Thus, substrate recovered from a D_2O solution of pD $\simeq$ 5 at 25 °C after 23% hydrolysis showed only slight absorption in the N–H stretching region around 3300 cm⁻¹, disappearance of the N–H bending mode at 1600 cm⁻¹, and appearance of a strong sharp absorption band, attributed to ν_{N-D}, at 2480 cm⁻¹. Strong broad absorption characterizing B–H stretching modes centered between 2320 and 2340 cm⁻¹ remained prominent, and a weak band ν_{B-D} appeared at 1740 cm⁻¹ with a shoulder at 1690 cm⁻¹. After 56% hydrolysis, the spectrum of recovered substrate showed increased absorption at 1690 and 1740 cm⁻¹, but the intensity remained measurably weaker than that in the B–H stretching region. Thus, although exchange of boron-bonded hydrogen is measurable under these conditions, it is not rapid relative to hydrolysis.[18] For the solution isotope effect then, respective k_2 terms reflect hydrolysis of $NH_3 \cdot BH_3$ in aqueous solution containing hydronium ion and buffer acid of normal isotopic composition vs. that of $ND_3 \cdot BH_3$ (in early stages of reaction) in D_2O containing isotopically substituted buffer acid and D_3O^+.

In Table II the experimental value of k_2 for $NH_3 \cdot BH_3$ is compared to the corresponding second-order rate constants

**Table II.** Relative Rates of Amine–Borane Hydrolysis, t = 25 °C

substrate	$10^2 k_2$,[a] L mol⁻¹ s⁻¹
$NH_3 \cdot BH_3$	600,[b] 430[c]
$CH_3NH_2 \cdot BH_3$	35[1]
$(CH_3)_2NH \cdot BH_3$	0.97[1]
$(CH_3)_3N \cdot BH_3$	0.012,[d] 0.0074[e]

[a] $k_2 = k_{obsd}/[H^+] = (-1/[H^+])(d \ln [S]/dt)$. [b] Average of $k_{obsd}/[H^+]$ values from eight buffer solutions (Table I). [c] Average of $k_{obsd}/[D^+]$ values from eight buffer solutions (Table I). [d] From study at 0.29 M H_2SO_4 at 27.5 °C. [e] From study at 0.29 M D_2SO_4 (in D_2O) at 27.5 °C.

Scheme I
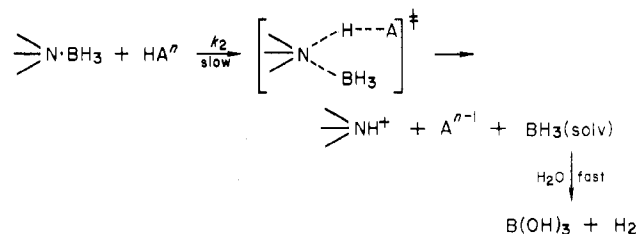
Scheme II
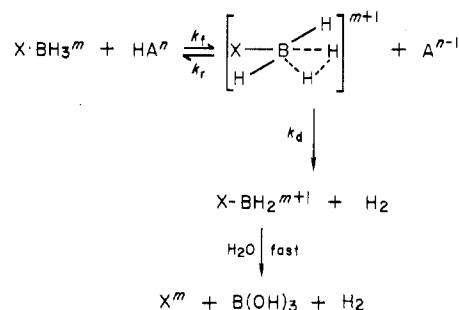
for mono-, di-, and trimethylamine–boranes. A normal solution isotope effect ($k_H/k_D \simeq 1.6$) is observed for trimethylamine–borane hydrolysis wherein the rate in 0.29 M H_2SO_4 (in H_2O) is compared to that in 0.29 M D_2SO_4 in deuterium oxide; however, any interpretation of this effect must take into consideration acid-catalyzed exchange of *boron*-bonded hydrogen with solvent which is known to be rapid relative to substrate hydrolysis.[19]

In the discussion to follow, two models are considered for the stoichiometric mechanism of acid-catalyzed amine–borane hydrolysis. Scheme I derives from earlier studies and may be regarded as a concerted electrophilic displacement or "associative interchange" reaction (I_a)[20] in which some degree of bonding of amino nitrogen to both entering (H^+) and leaving (BH_3) groups exists in the activated complex. General acid catalysis has been suggested for this reaction and is indicated below with species A^{n-1} denoting the conjugate base of acid HA^n. A solvated form of BH_3 is proposed as a highly reactive intermediate with is converted to product via a series of rapid steps following the rate-limiting step.

Scheme II represents a model based upon the studies of various workers on BH_4^- hydrolysis, a central feature of which is supposition of the existence of a distinct reaction intermediate involving five-coordinate boron.[8–12] For hydrolysis of BH_4^-, X = H^- and m = –1, for BH_3CN^-, X = CN^- and m = –1, and presumably, by analogy, for $R_yNH_{3-y}BH_3$, X = R_yNH_{3-y}, m = 0, and y = 0–3.

The intermediate is depicted as containing two equivalent boron-bonded hydrogens in each of two nonequivalent sets. This is based on a representation of "BH_5" proposed in consideration of the isotopic composition of hydrogen gas obtained on hydrolysis of tetrahydridoborate-d_4 in H_2O and

BH_4^- in D_2O.[7-9,12,21] Such nonequivalence of boron-bonded hydrogen also has been assumed for the proposed intermediate species BH_4CN.[13]

In terms of Scheme I, the magnitude of the k_2 term for $NH_3 \cdot BH_3$ is consistent with expectations based on trends established with *N*-alkylamine–boranes,[1] the increase in rate with decreasing *N*-methyl substitution being attributed to a commensurate decrease in steric hindrance to approach of general acid and proton transfer to nitrogen.[22] In view of the rapid exchange of nitrogen-bonded hydrogen in D_2O, a firm interpretative statement of the solvent isotope effect is probably unwarranted (though in Scheme I this would be expected to produce at most a secondary effect). The overall isotope effect, though in the direction expected (normal by about 50%), is perhaps smaller than what might be anticipated for the mechanism depicted in Scheme I. On the other hand, the acid-catalyzed hydrolysis of *p*-toluidine–borane in 50% aqueous dioxane[1] shows $k_{H_2O}/k_{D_2O} \simeq 2$, and the small magnitude in both cases may simply reflect relatively unsymmetrical transition states with respect to proton transfer. Perhaps equally significant, and a factor which bears on the feasibility of Scheme II as a mechanistic model, is the absence of an *inverse* solution isotope effect for either *p*-toluidine–borane, $NH_3 \cdot BH_3$, or, particularly, $Me_3N \cdot BH_3$. Scheme I does not address the question of the mechanism of acid-catalyzed boron-bonded hydrogen exchange which may be regarded as a parallel reaction of the substrate.

In order to apply Scheme II to the interpretation of experimental data for amine–borane hydrolysis, it is necessary to consider results of studies of hydrolysis and hydrogen exchange on tetrahydridoborate and cyanotrihydridoborate ions. Acid-catalyzed hydrolysis of BH_4^- occurs more rapidly than substrate–solvent hydrogen exchange,[8] while the reverse is true for BH_3CN^-.[13] The hydrolysis of BD_4^- in H_2O and of BH_4^- in D_2O leads almost exclusively to HD with very little H_2 or D_2 evolved in either case.[20] Second-order rate constants for BH_4^- hydrolysis are faster in normal water and hydronium ion than in D_2O and D_3O^+, while the reverse is true for BH_3CN^- where $k_H/k_D \simeq 0.7$. In the interpretation, it has been assumed that, for BH_4^- hydrolysis, the formation of BH_5 is rate determining (k_f slow; $k_d > k_r$), whereas, for BH_3CN^-, prior equilibrium is established relatively rapidly and the rate-limiting step is the dissociation of BH_4CN ($k_d < k_r$).[12,13] The relative rates of hydrolysis (BH_4^- faster than BH_3CN^-) and the relative magnitudes of acid-catalyzed hydrolysis and hydrogen exchange are explained by assuming that in the transition state for hydrolysis an electron pair is being completely removed while for exchange it is only undergoing protonation; thus, while the *electron-withdrawing* CN^- group should *lower* the rates of both reactions, it will be expected to exert a greater influence in reducing the rate of hydrolysis than the rate of exchange.[13]

Some difficulties are encountered in attempting to apply this scheme to amine–borane hydrolysis wherein rates are *lowered* with increasing substitution of *electron-releasing* (methyl) groups at nitrogen. Further, in trimethylamine–borane, acid-catalyzed hydrogen exchange at boron is more *rapid* than hydrolysis (this has led to a convenient synthesis of $Me_3N \cdot BD_3$),[19] whereas in ammonia–borane the reverse appears to be true. In terms of Scheme II, this would require the reversible formation of intermediate to be rapid and k_d to be rate limiting for $Me_3N \cdot BH_3$ hydrolysis but a different kinetic pattern to prevail for $NH_3 \cdot BH_3$, e.g., k_f rate limiting with k_d somewhat but not overwhelmingly greater than k_r. This would reconcile the observed solvent isotope effect for $NH_3 \cdot BH_3$ and accomodate the fact that boron-bonded hydrogen exchange in this substrate is measurable but slower than hydrolysis; however, it would require k_d for $Me_3N \cdot BH_3$

to be less than k_d for $NH_3 \cdot BH_3$, and such a pattern is not expected on the basis of interpretations of relative rates of hydrolysis and those of hydrolysis vs. hydrogen exchange in BH_4^- and BH_3CN^- in terms of electronic release and withdrawal.[13] Also since hydrolytic decomposition of intermediate via k_d is presumed to lead to a reduction in coordination number at boron, it would not be anticipated, from steric considerations, that this step should be slower for a five-coordinate intermediate derived from the tertiary amine adduct than for one derived from $NH_3 \cdot BH_3$.

The observed normal solution isotope effect for trimethylamine–borane ($k_H/k_D \simeq 1.6$) reflects the relative rates of $Me_3N \cdot BH_3$ hydrolysis in normal sulfuric acid and $Me_3N \cdot BD_3$ hydrolysis in D_2SO_4 and, therefore, is not amenable to simple interpretation. In terms of Scheme II, an *inverse* solvent isotope effect common to reactions proceeding via A-1 mechanisms[23] might be anticipated. It is possible that secondary substrate effects are contributing. Otherwise it would seem that the k_H/k_D ratio could be reconciled with Scheme II only by invoking a normal-isotope effect for k_d, involving elimination of H_2 (vs. D_2) from the respective intermediate, of greater magnitude than the inverse effect accompanying substrate protonation. On the other hand, the observed isotope effect, comparable to normal effects observed for *p*-toluidine–borane and $NH_3 \cdot BH_3$, is quite consistent with the mechanism depicted in Scheme I.

It is interesting to consider a modification of Scheme I where, for the intermediate in question, an amine molecule rather than a second hydrogen atom is proposed to occupy a site in the coordination sphere of boron comparable to that of the entering proton (III). This modification loses what

III
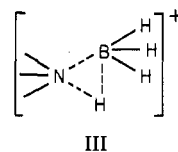
some may consider to be an appeal of Scheme II in providing a single mechanistic framework for hydrolysis and hydrogen exchange. Conceptually, such a model differs from Scheme I, first, in the supposition of bond formation between boron and the entering proton and, second, in terms of III being a molecular intermediate rather than an activated complex. At present, there is no independent evidence for such an intermediate, and if it is suggested that III is very short-lived, then in spite of the conceptual distinction it becomes questionable as to whether there is a kinetically operational distinction between this modification and an electrophilic interchange mechanism.[19,24]

Although the foregoing considerations do not preclude the existence of an intermediate more or less analogous to those proposed for BH_4^- and BH_3CN^- hydrolysis, such a mechanism does not appear to offer obvious advantages over that depicted in Scheme I. At present, electrophilic interchange seems to be at least equally attractive as a model for the stoichiometric mechanism of hydrolysis of amine–boranes. In spite of obvious difficulties associated with substrate–solvent hydrogen exchange, additional studies of solution isotope effects in selected amine–boranes are being conducted, and results may prove useful in further examination of these models.

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Rearrangement of Mono- and Poly-*B*-methyl Derivatives of 2,4-*closo*-Dicarbaheptaborane, 2,4-C₂B₅H₇

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An equilibrium can be established between $(B\text{-}CH_3)_x\text{-}2,4\text{-}C_2B_5H_{7-x}$ (x = 1, 2, 3, or 4) isomers at 300 °C; and it is evident, after statistical corrections, that the methyl positional preference follows the order 3 > 1, 7 > 5, 6. The mechanism of isomer interconversions most likely does not involve substituent migration from boron to boron but instead either a dsd (diamond–square–diamond) or a triangle rotation cage rearrangement. Within presumed energy-preferred dsd conversions of one 2,4-cage isomer to another 2,4-cage isomer, the allowed equilibria for interconversion of $B,B'\text{-}Me_2\text{-}2,4\text{-}C_2B_5H_5$ isomers are 5,6-Me₂-2,4-C₂B₅H₅ ⇌ 1,5- ⇌ 3,5- ⇌ 1,7-; and 1,5- ⇌ 1,3-. In a carefully controlled thermal rearrangement of 5,6-(CH₃)₂-2,4-C₂B₅H₅, the 1,5-dimethyl isomer is observed to form prior to the production of the 1,3-, 3,5-, and 1,7-(CH₃)₂-2,4-C₂B₅H₅ isomers. Furthermore, the rate of 3,5-isomer production from the 1,5-isomer exceeds that of the 1,3-isomer formation from the 1,5-isomer although the 1,3-isomer is more stable. A significant increase in separation of *B*-Me groups in the transition state could account for the high rate of 1,5- to 3,5-Me₂-C₂B₅H₅ conversion. The methyl group positional preference trend observed in this thermal rearrangement study is exactly the opposite of that observed in the obviously kinetically controlled "electrophilic" methylation of the C₂B₅H₇ carborane, the latter reaction showing the following overall positional preference of boron methylation: 5, 6 > 1, 7 > 3. It is advanced that increased *B*-methyl positional stability, under equilibrium conditions, involves a simple electrostatic polarization model in which the methyl group is more effective in dispersing the charge when located on the more positively charged boron atoms.

Introduction

Most carborane skeletal rearrangements have involved the net movement of two cage carbon atoms to positions of increased mutual separation. Examples include the thermal conversion of 1,2-C₂B₁₀H₁₂ to 1,7-C₂B₁₀H₁₂ and then to 1,12-C₂B₁₀H₁₂[2] and of 1,6-C₂B₈H₁₀ to 1,10-C₂B₈H₁₀[3] and the rearrangement of 1,2-C₂B₄H₆ to 1,6-C₂B₄H₆.[4] In this regard it is not surprising that there have been no reports of the parent 2,4-C₂B₅H₇ rearrangement, for the two carbons in this cage carborane are already at maximum separation among the predicted stable[5] low-coordination equatorial sites. However, attachment of a group onto the 5-position of *closo*-2,4-C₂B₅H₇[6,7] allows for the possibility of observing rearrangement in this cage system without forcing the carbons to occupy positions in the D_{5h} structural framework of the product isomers other than the stable 2,4-positions.

Experimental Section

Nuclear Magnetic Resonance. Proton spectra were recorded on Varian A-60 and HA-100 spectrometers. The boron-11 spectra were obtained at 32.1 MHz by using the Varian HA-100 instrument. Boron-11-decoupled proton spectra at 100 MHz were observed while

irradiation was done at 32.1 MHz by using a General Radio Model 1061 frequency synthesizer with power booster provided by an Electronic Navigation Industries Model 320L RD power amplifier. Proton-decoupled ¹¹B spectra at 32.1 MHz were observed while irradiation was done at 100 MHz by using the above-mentioned system. Boron-11-decoupled ¹H NMR spectra were also obtained by using a FT-Bruker WP-60 instrument equipped with a Fluka 6160B frequency synthesizer and the ENI-320L amplifier.

The boron-11 chemical shift data (Table I) are reported relative to boron trifluoride ethyl etherate and were obtained by using boron trichloride (δ = –46.8) as a secondary external standard. The proton chemical shifts are reported relative to internal tetramethylsilane (τ = 10.00). In addition to the proton data given in Table II, 3-CH₃-2,4-C₂B₅H₆ exhibited ¹¹B-decoupled proton resonances at τ = 6.00 (H–B(5,6)), 9.83 (H–B(1,7)), and 4.77 (H–C(2,4)); also J-(H$_C$–H$_{B(5)}$) $\simeq$ 7 Hz. For 1,5-(CH₃)₂-2,4-C₂B₅H₅, τ = 5.19 (H–B(3)), 6.13 (H–B(6)), 10.01 (H–B(7)), 4.61 (H–C(2)), and 4.85 (H–C(4)); J(H$_{C(2)}$–H$_{B(3)}$) $\simeq$ 6.5 Hz. For 3,5-(CH₃)₂-2,4-C₂B₅H₅, τ = 5.28 (H–B(6)), 9.75 (H–B(1,7)), 4.8–5.0 (H–C(2)), and 5.14 (H–C(4)).

The gas-phase infrared spectra were recorded on a Beckman Acculab 3 spectrometer.

Mass spectra were recorded on a Varian CH-5 high-resolution mass spectrometer and GLC–MS data were gathered by using a Varian Mat 111 equipped with 10% Kel-F grease on a 60/80 mesh Chro-