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AROMATIC AMINE-HALOBORANES: EVIDENCE FOR TRIGONAL BORONIUM CATIONS

By

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B.S., University of Richmond, 1977

A Thesis

Submitted to the Graduate Faculty

of the University of Richmond

in Candidacy

for the degree of

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Richmond, Virginia

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Dedicated to my Lord and Savior
for His saving grace

and to Butch
for his constant support and understanding

Abstract of Thesis Submitted to the
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AROMATIC AMINE-HALOBORANES: EVIDENCE FOR TRIGONAL BORONIUM CATIONS

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The halogenation reactions of borane adducts of 2-methylpyridine, 2,6-dimethylpyridine, 3,5-dimethylpyridine, and 2,4,6-trimethylpyridine, were monitored by ^1H nmr. Signals due to both aromatic and aliphatic protons in the various adducts showed a downfield shift as size and/or number of halogens increased. These downfield shifts can be accounted for by a combination of steric compression and inductive effects. The last step of halogenation is accompanied by an upfield shift of the signals due to protons in the 2 or 6 positions of the pyridine ring, a further downfield shift of the signals due to protons in the 3, 4, or 5 positions of the ring, as well as by the appearance of conductivity in the solution. These observations are attributed to the formation in solution of trigonal boronium cations. These compounds have been isolated and characterized.

ACKNOWLEDGEMENTS

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INTRODUCTION

In the last twenty years Lewis adducts of boron trihalides and mixed boron trihalides have been examined using nuclear magnetic resonance spectroscopy. The donor to which the boron trihalide attaches has generally been some type of amine (strong donor), though oxygen, sulfur, phosphorous, and other donors have also been studied. The boron trihalide portion serves as the Lewis acid. Various nuclei (^{1}H, ^{13}C, ^{15}N, ^{11}B, ^{19}F) have been examined in such boron trihalide adducts and the general trend in signal position in all 5 nuclei observed is (in order of increasing downfield shift) $BF_3 < BCl_3 < BBr_3 < BI_3$.[1-5]

The acid strength of the boron trihalide has generally been assumed to be the principal factor determining this order and many physical studies confirm this order to be $BF_3 < BCl_3 < BBr_3 < BI_3$.[6-10] Three factors thought to affect Lewis acid strength of boron trihalides are the electronegativity of the halogens, the steric bulk of the halogens, and the ability of the halogens to pi-bond with the boron.[11]

The first factor, the electronegativity of the halogens was dismissed as the important influence causing this downfield shift because the order of electronegativity I<Br<Cl<F would predict an order of Lewis acidity which is the reverse of the order observed. The second factor affecting Lewis acidity,

steric bulk of the halogens, would introduce "front strain" into the adduct which would weaken the B-N bond as the bulkiness of the halogens on boron increased. Since the order of bulk is I>Br>Cl>F, one would predict the order of Lewis acid strength to be $BF_3>BCl_3>BBr_3>BI_3$, because BI_3 would be predicted on this basis to have the weakest bond to N and thus be the weakest Lewis acid. This was again the reverse of what was observed. The third factor was the ability of the halogens to pi-bond to the boron[1]. Pi-bonding exists in all boron trihalides, but much more so in the BF_3 than in BI_3.[12] The significance of the factor is affected by the size of the halogen orbitals and the electronegativity of the halogen. Fluorine, being the smallest in size, offers orbitals of pi symmetry which match well in size and energy with the pi bonding orbital of boron. Since this match is less favorable as the size of the halogen increases from F to I, consequently the extent of overlap and the extent of pi-bonding is progressively less as larger halogens are placed on boron. As a boron trihalide attaches to a Lewis base, any pi-bonding present must be at least partially destroyed in order to allow the new (sigma) bond with the Lewis base to form. More residual pi-bonding is present in boranes containing fluorine than in those containing iodine because there was more pi-bonding present initially in the fluorine cases. As the Lewis acid and base combine there is competition between the donor atom of the base and the halogen for the fourth boron orbital.[7] As the adduct forms, the boron rehybridizes from sp^2 to sp^3, the extent of that rehybridization depending on the types of halogen present. In the case of fluorine, less rehybridization occurs because fluorine is competing strongly for the orbital of the boron, so that it may retain some of its pi-bonding.[3,6]. In the case of iodine more rehybridization occurs because iodine, not only being less electronegative but also having less pi-bonding to start with, does not compete as well for the boron orbital. Consequently the bond length between donor atoms and boron is generally shorter in BI_3 adducts than in BF_3 adducts. The strong competition by fluorine for the orbital on boron weakens the donor-boron sigma bond to a much greater extent than does the competition by iodine. The donor atom however, in both cases remains bound to the boron. This argument is supported by crystal structures reported for $(CH_3)_3N$ adducts for which the B-N bond length was found to be 1.584 Å for the BI_3 adduct, 1.603 Å for the BBr_3 adduct, 1.610 Å for the BCl_3 adduct, and 1.64 Å for BF_3.[13]

The fact that BI_3 appears to be the strongest Lewis acid and BF_3 the weakest in the series of boron trihalides, and the fact that downfield shifts are observed in nmr spectra as larger halogens are introduced on boron in donor-trihaloborane molecules, implies that inductive effects are the principal causes of the trends in nmr spectral changes. However, this conclusion requires a discounting of the effects of halogen electronegativity, when, in the adduct, the effects of the pi-bonding should be minimized (since most of the pi-bonding is destroyed). Inductive effects certainly play a role but since the order of inductive effects is assumed to be in line with pi-bonding effects and since pi-bonding effects in the adducts are minimized, it seems resonable to consider the possibility of other factors also playing a role.

Myers, in his study of several series of aliphatic amine-haloboranes,[11] observed shifts in ^{1}H nmr signals which could not be adequately explained solely by an inductive effect but which could be explained on the basis of steric compression. His study of the effects of halogenation of trimethyl-, dimethyl-, (Figure 1) triethyl-, and diethylamine-boranes concluded that steric interference contributed in a major way to the shifts observed. There is precedence in the literature for steric compression causing downfield shifting on ^{1}H nmr signals.* Specifically for diethylamine-haloboranes the CH_2 protons should be identical as far as inductive effects are concerned because they are an equal distance from the boron through the bonds and thus would feel an equal increase in deshielding as the hydrogens on boron are replaced with halogens. This was not consistent

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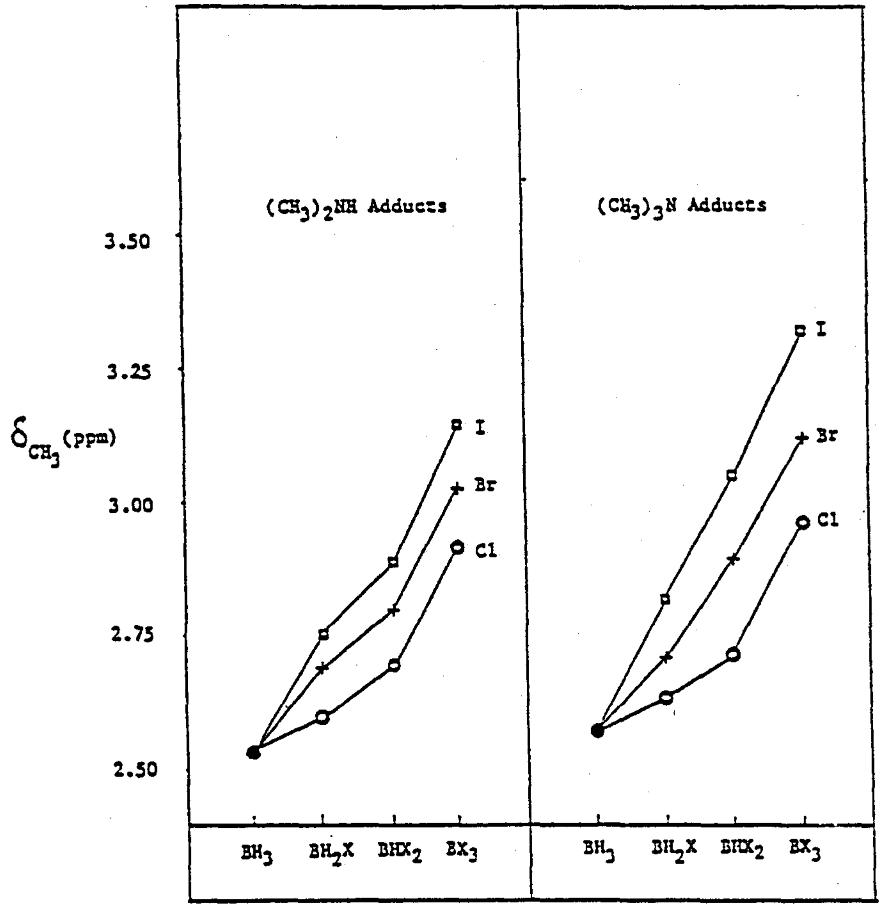
*This has been discussed in detail in reference 11.

Figure 1

^{1}H nmr Chemical Shifts of Dimethyl and Trimethylamine-Borane versus Degree of Halogenation



with the data observed during halogenation. There appeared instead to be two types of CH_2 protons in each molecule (H_a and H_b in Figure 2). Peaks representing protons labeled H_a experienced a large downfield shift as larger or additional halogens were added but the protons labeled H_b experienced at most only a small downfield shift (Figure 3). This difference in behavior observed between the two types of protons gave credence to the possibility of steric effects helping to cause the shifts of ^1H nmr signals.

After closer examination, the complete ^1H nmr information for the diethylamine-haloboranes (Table I), shows that differences in coupling constants of H_a and H_b to the nitrogen hydrogen were observed. The value of the coupling constant for $J_{HNCH(A)}$ was and remained 4.5-5.0 Hz for all adducts whereas the coupling constant for $J_{HNCH(B)}$ was near zero after the first halogenation step. The Karplus rule in ^1H nmr spectroscopy for ethane-type systems[14] predicts that coupling constants for hydrogens on adjacent carbons will be at a minimum when the dihedral angle between the coupled protons is near 90°. This gave Myers some insight as to the structure in which the compounds exist.

The near zero HNCH(B) coupling constant combined with the small downfield shifts observed upon borane halogenation for H_b indicated that that proton was most likely at a near 90° dihedral angle with respect to the nitrogen hydrogen

Figure 2

Non-Equivalent Methylene Protons
For Diethylamine-Borane

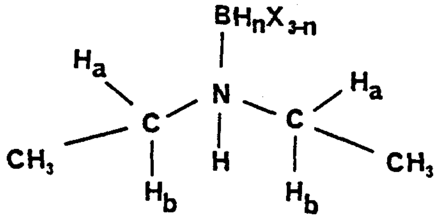


Figure 3

^{1}H nmr Chemical Shifts of H_a and H_b for Diethylamine-Borane versus Degree of Halogenation

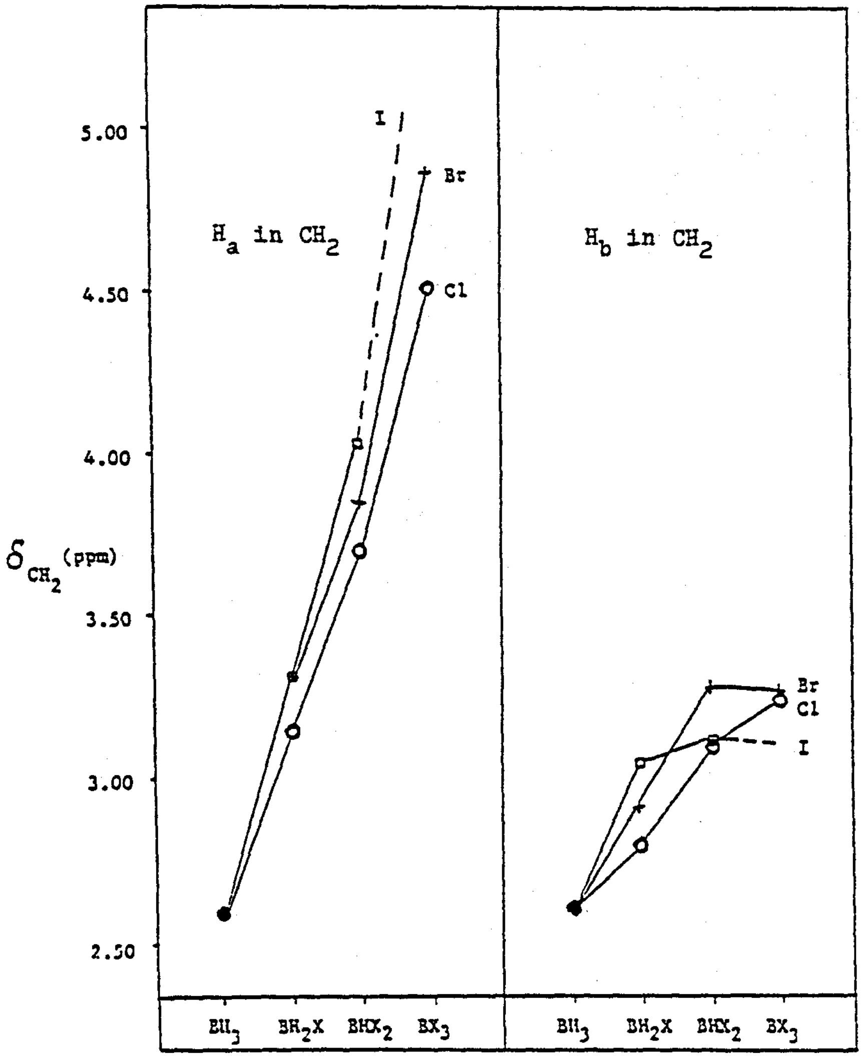


Table I

^{1}H nmr Data for $(CH_3CH_2)_2NH$ Adducts[*]

			CH_2(A)		CH_2(B)	
Borane	δ CH_3[a]	δ CH_2[a,b]	$J_{HNCH(A)}$[c]	δ CH_2(A)[a]	δ CH_2(B)[a]	$J_{HNCH(B)}$[c]
BH_3	1.233	2.800	7.0	2.800[d]	2.800[d]	7.0
BH_2Cl	1.255	2.983	5.3	3.070	2.895	5.7
BH_2Br	1.273	3.055	4.3	3.153	2.995	5.7
BH_2I	1.287	3.088	4.8	3.152	3.023	5.5
$BHCl_2$	1.335	3.203	4.8	3.347	3.043	-0.5
$BHBr_2$	1.373	3.278	4.6	3.418	3.137	-0.5
BHI_2	1.388	3.280	4.1	3.513	3.047	-0.2
BF_3	1.267	3.025	--[e]	--[e]	--[e]	--[e]
BCl_3	1.427	3.367	4.6	3.743	3.122	-0.2
BBr_3	1.437	3.530	4.6	3.928	3.130	-0.2

*taken from reference 11

[a] in ppm, downfield from internal tetramethylsilane in CH_2Cl_2 solvent

[b] average value for non-equivalent protons; actual values for each proton given in other columns

[c] in Hz

[d] poor resolution; non-equivalence not detectable

[e] multiplet structure not resolved; values not determinable

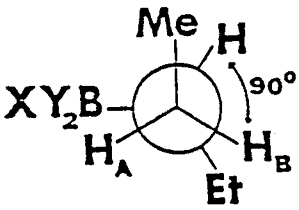
and at the same time insulated in the molecule from the borane group. Were H_b so isolated from the borane group, it would not have experienced any great steric compression. The other proton, H_a was observed to have large downfield shifts and therefore was most likely adjacent to the borane, consequently experiencing a significant steric compression.

Fischer projections (along one C-N bond) of the three possible rotamers of a diethylamine-haloborane are shown in Figure 4. Note that only rotamer 1 fulfills the requirements established by the observed data. Rotamer 2 can be eliminated because both H_a and H_b are adjacent to the borane group and would both experience large steric compression. Rotamer 3 can also be eliminated because the bulky groups are eclipsed, which would not be the most stable form. Myers concluded that if rotamer 1 was not the only form present, it was certainly present in much larger abundance than either of the other two.

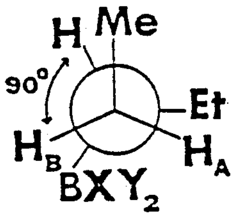
In summary, based on examination of the data collected on aliphatic amine-haloboranes, the downfield chemical shifts observed during halogenation of the BH_3 adducts were determined to have resulted from a combination of both steric and inductive effects with steric effects dominating in cases in which such effects oppose. Since 1975, Myers and his group have pursued the effects of steric interaction on ^1H nmr chemical shifts for various aromatic amine-boranes. Kegley and Tiedemann[15]

Figure 4

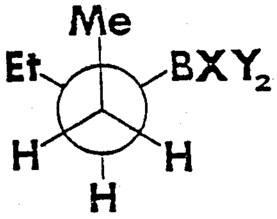
Fischer Projections of Diethylamine-Haloborane



I



II



III

prepared two aromatic amine-boranes, 2-methylpyridine-borane, and 2,6-dimethylpyridine-borane, and studied the halogenation of these amine-boranes via ^1H nmr spectroscopy. Downfield shifts were observed as larger or additional halogens were added for the peaks representing the protons at the 3, 4 and 5 positions on the pyridine ring for both compounds. Downfield shifts were also observed for protons at or in methyl groups at the 2 and 6 positions for the first two halogenation steps (i.e., for the formation of the BH_2X and BHX_2 adducts, X=halogen), but an upfield shift was observed for the peaks representing the 2 and 6 methyl protons in 2,6-dimethylpyridine-borane as a third halogen was added. An initial downfield shift was observed for the peaks representing the 2-methyl and 6-H in 2-methylpyridine-borane as a third halogen was added, but over time those peaks were observed to disappear as new peaks grew upfield. This appearance of peaks upfield indicated the trihalogenated species was converting to another, more stable form. The new structure was in both cases proposed to be a positively charged species (a trigonal boronium cation[16,17]) formed by the loss of a halide ion from the trihaloborane adduct, due to steric interference between substituents in the amine and halogens on boron. The formation of this positively charged species would be expected to deshield inductively the protons on the pyridine ring causing them to shift downfield, and this was observed for the 3, 4 and 5 protons. Protons at or in the methyl groups at the 2 and 6 positions would feel a combination of effects, increased deshielding due to the inductive effects of the formation of a positive charge combined with a release of steric compression creating an opposite result. Myers proposed that because the overall shift in ^{1}H nmr frequency was upfield at this point, the dominant effect was the relief of steric compression. Kegley and Tiedemann, however did not isolate the halogenated adducts nor obtain proof of the presence of ions in the last stages of the reaction, so the identity of proposed forms could not be confirmed.

Present work seeks to confirm the proposed model in five ways:

1. To isolate and characterize each of the complexes thought to be present in the systems studied by Kegley and Tiedemann.

2. To confirm observations concerning the shifting of ^{1}H nmr signals due to the protons at or in methyl groups at the 2 and 6 positions upon trihalogenation of 2-methyl- and 2,6-dimethylpyridine-borane.

3. To study conductivity changes during those reactions so as to confirm the presence of ions at the end of the reaction sequence.

4. To determine the behavior of protons in

the 3, 4 and 5 positions in 2-methyl and 2,6-dimethylpyridine-borane to confirm the expectation of downfield shifts being observed at all stages of halogenation.

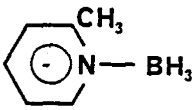
5. To study two other systems related to the two already studied, 2,4,6-trimethylpyridine-borane and 3,5-dimethylpyridine-borane, seeking further confirmation from the behavior observed there. These compounds were chosen because this ^1H nmr spectra were expected to be very simple in both the aromatic region and the aliphatic region.

The overall group of compounds studied offer a variety of steric interactions around the N-B bond (Figure 5). The strategically placed methyls allow not only the different steric possibilities but also a variety of ^1H nmr results ranging from extremely complex coupling occurring with the aromatic protons of 2-methylpyridine-borane to the simple singlets observed for 2,4,6-trimethylpyridine-borane.

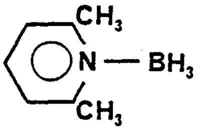
Figure 5

CHEMICAL STRUCTURES

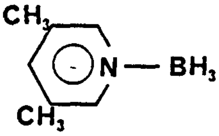
2-Methylpyridine-Borane



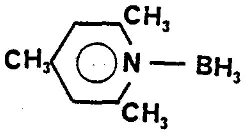
2,6-Dimethylpyridine-Borane



3,5-Dimethylpyridine-Borane



2,4,6-Trimethylpyridine-Borane



EXPERIMENTAL

I. Equations and Reactions

The syntheses of the aromatic amine-boranes used as precursors in this study were carried out by following the procedure of Nainan and Ryschkewitsch[18] (equation 1).

(1) $2NaBH_4 + 2R_nC_5H_{5-n}N + I_2 \dashrightarrow 2NaI + 2R_nC_5H_{5-n}NBH_3 + H_2$

The derivative compounds were isolated and characterized after preliminary halogenation reactions of these aromatic amine-boranes were run using chlorine, bromine, or iodine as the halogenating agent. Equations (2) - (5) account for the formation of the various products observed in the halogenation of aliphatic amine-boranes.[19]

(2) $R_3NBH_3 + HX \dashrightarrow R_3NBH_2X + H_2$ (X=Cl,Br)
(3) $R_3NBH_3 + 1/2X_2 \dashrightarrow R_3NBH_2X + 1/2H_2$ (X=Cl,Br,I)
(4) $R_3NBH_3 + 3/2X_2 \dashrightarrow R_3NBHX_2 + 1/2H_2 + HX$ (X=Cl,Br,I)
(5) $R_3NBH_3 + 5/2X_2 \dashrightarrow R_3NBX_3 + 1/2H_2 + 2HX$ (X=Cl,Br,I)

Equations (6) - (9) were expected to occur in the halogenation of aromatic amine-boranes.

(6) $R_nC_5H_{5-n}NBH_3 + HX \dashrightarrow R_nC_5H_{5-n}NBH_2X + H_2$ (X=Cl,Br)
(7) $R_nC_5H_{5-n}NBH_3 + 1/2X_2 \dashrightarrow R_nC_5H_{5-n}NBH_2X + 1/2H_2$ (X=I)
(8) $R_nC_5H_{5-n}NBH_3 + 3/2X_2 \dashrightarrow R_nC_5H_{5-n}NBHX_2 + 1/2H_2 + HX$ (X=Cl,Br,I)
(9) $R_nC_5H_{5-n}NBH_3 + 5/2X_2 \dashrightarrow R_nC_5H_{5-n}NBX_3 + 1/2H_2 + 2HX$ (X=Cl,Br,I)

Preliminary reactions supplied information concerning reactivity and the means for identifying each species produced by its chemical shifts. Quantitative reactions were then performed in the isolation of the mono-, di- and trihalogenated adducts of each compound.

It was observed generally that of the four parent compounds (precursors) 3,5-dimethylpyridine-borane was the most reactive, followed in order of decreasing reactivity by 2-methylpyridine-borane, 2,6-dimethylpyridine-borane and 2,4,6-trimethylpyridine-borane. The order of reactivity observed is consistent with the order predicted from a consideration of relative steric crowding in the molecule, more specifically, steric crowding around the N-B bond. The observed reactivity of the different halogenating agents with a given amine-borane was related to the size of the halogen, chlorine being the most reactive followed in order of decreasing reactivity by bromine, and iodine. When using the gaseous halogens, HCl gas was more reactive than HBr.

II. Reagents

Sodium borohydride, 3,5-dimethylpyridine, 2-methylpyridine, 2,4,6-trimethylpyridine, iodine and bromine were obtained from commercial sources as were the gases HCl, HBr and Cl_2. Aldrich Chemical Co. supplied 2,6-dimethylpyridine-borane in good purity (98%), although this amine-borane (as the three synthesized amine-boranes) was observed to decompose slowly with gas build up.* All solvents were reagent grade and were used as such without any purification other than drying over molecular sieves.

III. Instrumentation

Proton nmr spectra were obtained at ambient temperature on a Hitachi Perkin Elmer R-24A 60MHz spectrometer. Typically a 0.75mL sample was used of a 0.20M solution in CH_2Cl_2. Spectra are reported in ppm relative to tetramethylsilane.

Conductivity measurements were made on a Markson model 4503 SelectroMark Analyzer with a dedicated conductivity cell for which a direct reading of specific conductance was obtained. The specific conductances of CH_2Cl_2 solutions of bis(triphenylphosphine)iminium halides,[20] $(\emptyset_3P)_2N^+X^-$ (X=Cl,Br,I), were measured at various concentrations for comparison purposes (see Table II). In all cases the conductivity appeared to be a linear function of concentration up to about 0.025M. Above 0.025M the rise in conductivity was less than would be expected from linear behavior, the difference being larger at larger concentrations.

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*The amine-borane was easily repurified since the byproduct was insoluble in CH_2Cl_2. Thus extracting with CH_2Cl_2 and evaporating solvent gave pure product again. The identity of the byproduct is not known, but the buildup of pressure and the insolubility in CH_2Cl_2 suggests that B-H bonds are reacting with traces of H_2O to give B-OH and H_2 gas.

Table II

Conductivity of Some Standard Solutions

Solute	Concentration in CH_2Cl_2(M)	Conductance(μohm^{-1}cm^{-1})
A. $(Ph_3P)_2N^+Cl^-$	0	0.53
	0.0109	469
	0.0217	910
	0.0435	1770
	0.0869	3560
	0.1739	6340
	0.3477	10,170
B. $(Ph_3P)_2N^+Br^-$	0	0.82
	0.00385	197.4
	0.00770	362
	0.0154	684
	0.0308	1292
	0.0616	2480
	0.1232	4550
C. $(Ph_3P)_2N^+I^-$	0	0.63
	0.00419	205
	0.00839	394
	0.0168	738
	0.0335	1370
	0.0671	2650
	0.1342	4780

Melting points were recorded on a Thomas Hoover Unimelt apparatus and are uncorrected.

Infrared spectra were run on a Perkin Elmer 397 or a Nicolet 5DX-FTIR spectrometer. Samples were prepared as KBr pellets using 2mg sample to 200mg KBr.

Electron impact mass spectra were recorded on a Hitachi Perkin Elmer RMU-6H spectrometer using 0.5mg of sample in a direct probe.

IV. General Procedure for Preparation of Amine-Boranes

A nitrogen-flushed, one-neck round bottom flask was fitted with a pressure-equalized dropping funnel. The system was kept under a nitrogen blanket and vented to a bubbler. A solution of iodine in 1,2-dimethoxyethane (monoglyme) was prepared and added dropwise to a stirred solution of sodium borohydride (20% excess) and the desired amine (10% excess). Molar quantities were calculated on the basis of equation 1.

A. 3,5-Dimethylpyridine-Borane.--$NaBH_4$ (2.85 g, 75.4 mmol) was added to a stirred solution of 3,5-dimethylpyridine (7.17 g, 6.70 mmol) in monoglyme (80 mL) under a nitrogen blanket. A solution of iodine (7.74 g, 30.4 mmol) in monoglyme (80 mL) was added dropwise over a period of one hour. During that time bubbling and fizzing occurred. The solution was then evaporated on a rotary evaporator to dryness. To the resulting solid, was added cyclohexane (180 mL) to extract the soluble amine-borane from the insoluble product NaI, and unreacted $NaBH_4$. The insoluble material was filtered and isolated (113.5 g) and the filtrate was evaporated on a rotary evaporator. The resulting solid was left under vacuum for several days to ensure dryness. The solid was then redissolved in methylene chloride, and the resulting solution filtered. The methylene chloride was evaporated on a rotary evaporator leaving a fine, white powder ($3,5\text{-}(CH_3)_2C_5H_3NBH_3$, 5.93 g, 73.2% yield, melting point 102.5-105.4°C, ir: 3090,3030(s),2920(s),2460-2200(b),1600, 1470,1200,1170,980,920,650(s)cm^{-1}).

The infrared spectrum of 3,5-dimethylpyridine-borane (Figure 6) was characterized by a broad band at 2460 to 2200 cm^{-1} assigned to B-H stretching.

The ^1H nmr spectrum (Figure 7) is characterized by three singlets, one singlet in the aliphatic region from protons in the methyl groups at the 3 and 5 positions on the ring and two singlets in the aromatic region, one from the proton at the 4 position and the other from the protons at the 2 and 6 positions on the ring. The integrated intensities of these singlets are 6:1:2 respectively. The chemical shifts are given in Table III (see pages 33-36).

B. <u>2-Methylpyridine-Borane</u>.--The apparatus used and

Figure 6

Infrared Spectrum of

$3,5\text{-}(CH_3)_2C_5H_3NBH_3$

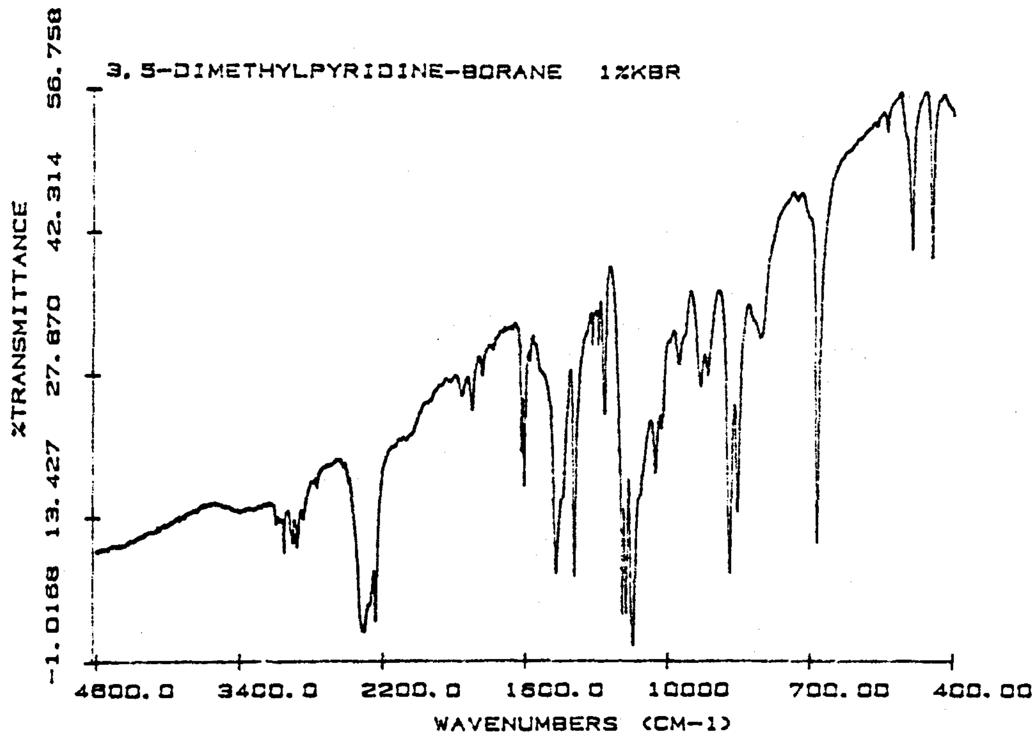
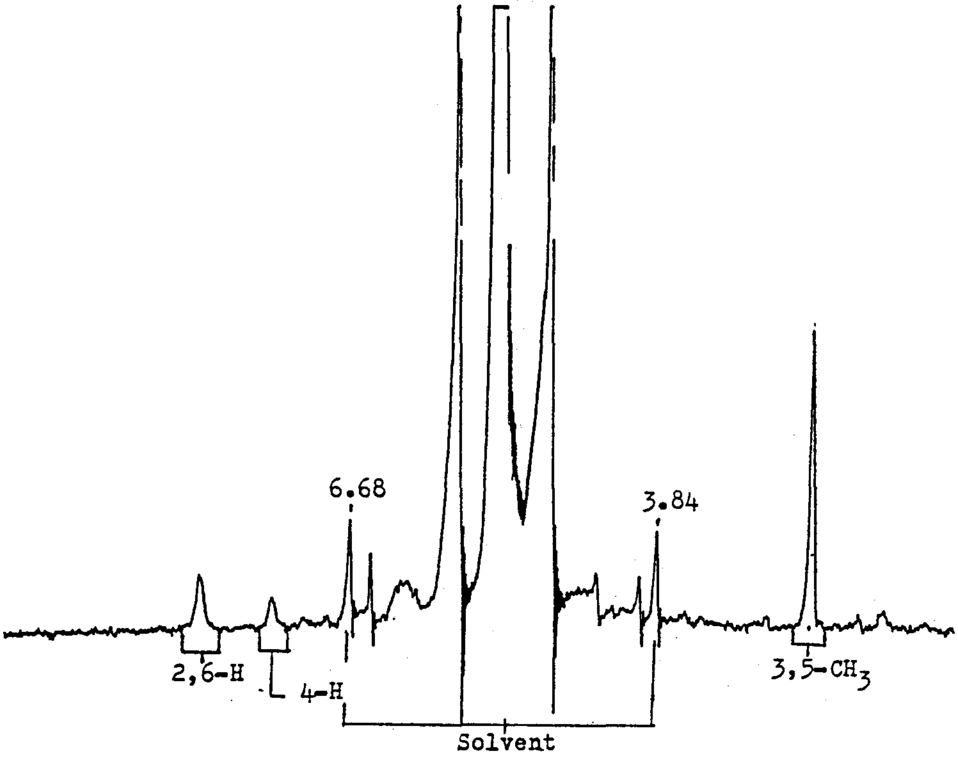


Figure 7

^{1}H nmr Spectrum of

$3,5\text{-}(CH_3)_2C_5H_3NBH_3$



the procedure followed were similar to that in the synthesis of 3,5-dimethylpyridine-borane, varying only the molar amounts used. To a stirred solution of 2-methylpyridine (6.00 g, 62.5 mmol) and $NaBH_4$ (2.90 g, 76.8 mmol) in monoglyme (80 mL), a solution of iodine (7.81 g, 30.7 mmol) in monoglyme (80 mL) was added over a period of one hour. Bubbling and fizzing occurred as the iodine was added, and the solution turned pale yellow. After the addition was completed, the solvent was stripped and the resulting solids were extracted with cyclohexane. After filtration and evaporation of cyclohexane, the resulting solid was dissolved in methylene chloride, the solution filtered, and the solvent removed by evaporation. The resulting product was left under vacuum for one week to ensure dryness. The product was a coarse, white powder ($2\text{-}CH_3C_5H_4NBH_3$, 4.58 g, 42.8 mmol, 68.4% yield, melting point 49.5-52.3°C, Literature[18] 45.0-46.5°C, ir: 3120,3080, 2990(s),2470-2160(vb),1575,1500,1425(s),1200(m),1090(s), 920(s),770,700(m)cm^{-1}).

The infrared spectrum of 2-methylpyridine-borane (Figure 8) was also characterized by a broad band at 2470 to 2160 cm^{-1} which was assigned to B-H stretching.

The ^1H nmr spectrum (Figure 9) is characterized in increasing downfield order by a singlet in the aliphatic region from the protons in the methyl group at the 2 position on the ring, two aromatic multiplets from the protons at

Figure 8

Infrared Spectrum of

$2\text{-}CH_3C_5H_4NBH_3$

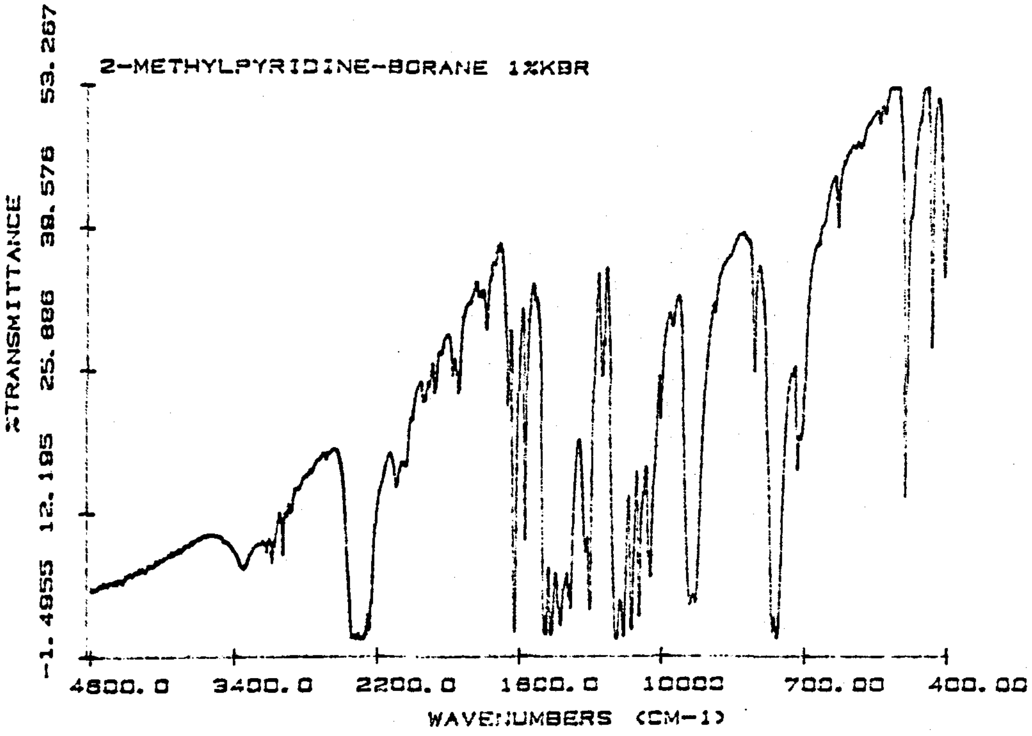
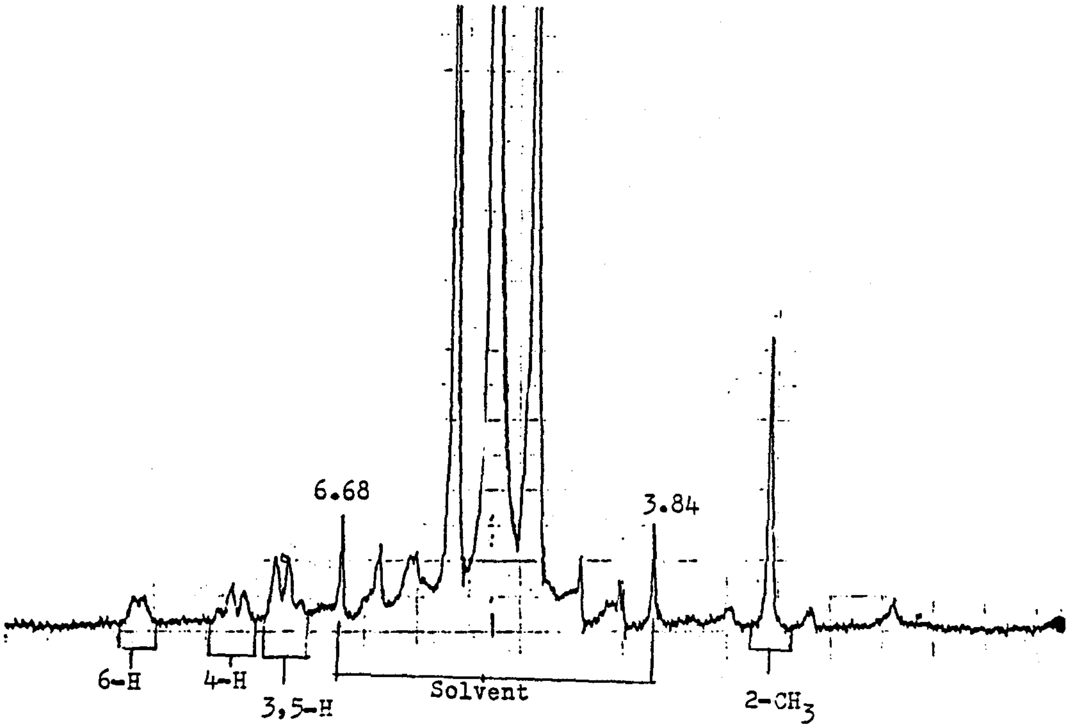


Figure 9

^{1}H nmr spectrum of

$2\text{-}CH_3C_5H_4NBH_3$



the 3,5 and 4 positions on the ring respectively and one aromatic doublet from the protons at the 6 position on the ring. The integrated intensities observed were 3:2:1:1 respectively.* The chemical shifts are listed in Table III (see pages 33-36).

C. <u>2.4.6-Trimethylpyridine-Borane</u>.--Using the apparatus and procedure as described for 3,5-dimethylpyridine-borane, a solution of 2,4,6-trimethylpyridine (8.10 g, 66.8 mmol) and $NaBH_4$ (2.75 g, 72.8 mmol) in monoglyme (70 mL) was prepared, and a solution of iodine (7.71 g, 30.3 mmol) in monoglyme (80 mL) was added dropwise over a period of 1-1/2 hours. Again fizzing and bubbling occurred as the iodine was added. The procedure followed in isolation of product was as before. After 5 days under vacuum the white crystals were still slightly oily ($2,4,6\text{-}(CH_3)_3C_5H_2NBH_3$, 6.76 g, 50.1 mmol, 74.9% yield, mp** 96.5-99.2°C. Literature[18] 96.0-97.0°C crude, ir: 3040(s),2980(s),2440-2250(vb),1640(s),1170,1140,860(m), 830(m)cm^{-1}).

The infrared spectrum of 2,4,6-trimethylpyridine-borane (Figure 10) was poorly resolved. A broad band at 2440 to 2250 cm^{-1} was assigned to B-H stretching.

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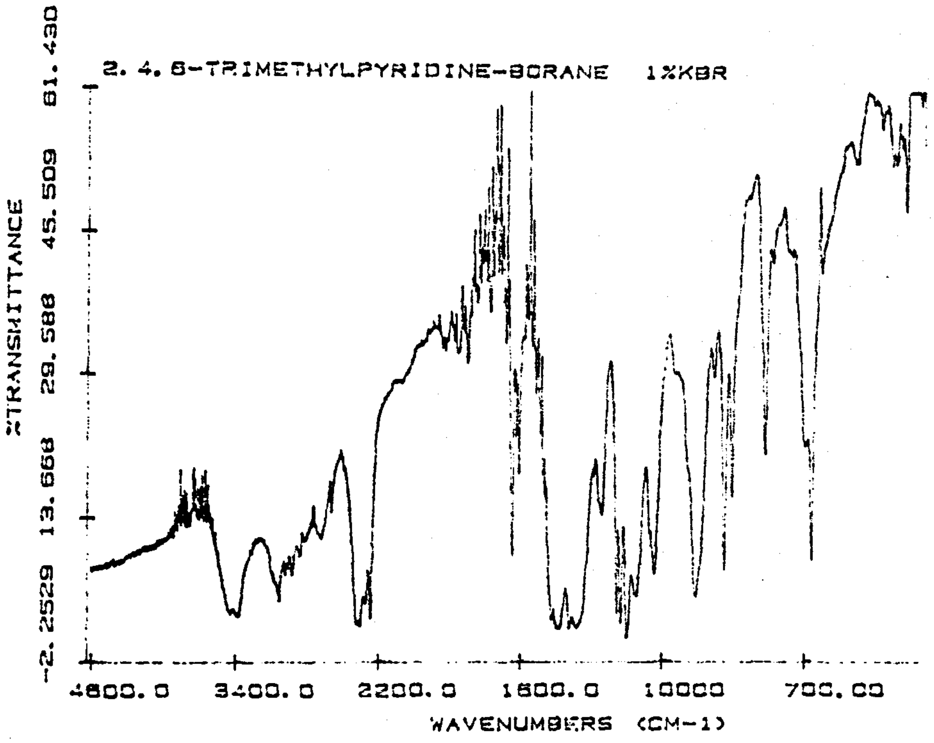
*The aromatic signals are actually a complex ABCD pattern,[21] but these approximate assignments are being made until a detailed analysis can be conducted.

**This same procedure was repeated many times. The humidity and room temperature seemed to affect crystal stability. Storage life as a rule was very short.

Figure 10

Infrared Spectrum of

$2,4,6\text{-}(CH_3)_3C_5H_2NBH_3$



The ^1H nmr spectrum (Figure 11) is characterized by three singlets, two in the aliphatic region from protons in the methyl groups at the 4 and 2,6 positions of the ring and one in the aromatic region from protons at the 3 and 5 positions of the ring. The three singlets were in an intensity ratio of 3:6:2. The chemical shifts are given in Table III (see pages 33-36)

D. 2,6-Dimethylpyridine-Borane.--The compound was used as obtained from Aldirch Chemical Company but was characterized by its infrared spectrum (3060,2990(m),2500-2240(vb),1610, 1570(s),1475,1385,1170(s),800(s),530(s)cm^{-1}) and ^1H nmr spectrum.

The infrared spectrum of 2,6-dimethylpyridine-borane (Figure 12) was characterized by a broad band assigned to B-H stretching between 2200 and 2400 cm^{-1}.

The ^1H nmr spectrum of 2,6-dimethylpyridine-borane (Figure 13) was characterized by a singlet in the aliphatic region from protons in the methyl groups at the 2 and 6 positions on the ring, and two multiplets resembling a triplet and quartet in the aromatic region from protons at the 3,5 and 4 positions on the ring respectively. The observed intensities were 6:2:1.* The chemical shifts are given in Table III (see pages 33-36).

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*The aromatic signals are actually a complex ABB' pattern,[21] but these approximate assignments are being made until a detailed analysis of the pattern can be conducted.

Figure 11

^1H nmr spectrum of

$2,4,6\text{-}(CH_3)_3C_5H_2NBH_3$

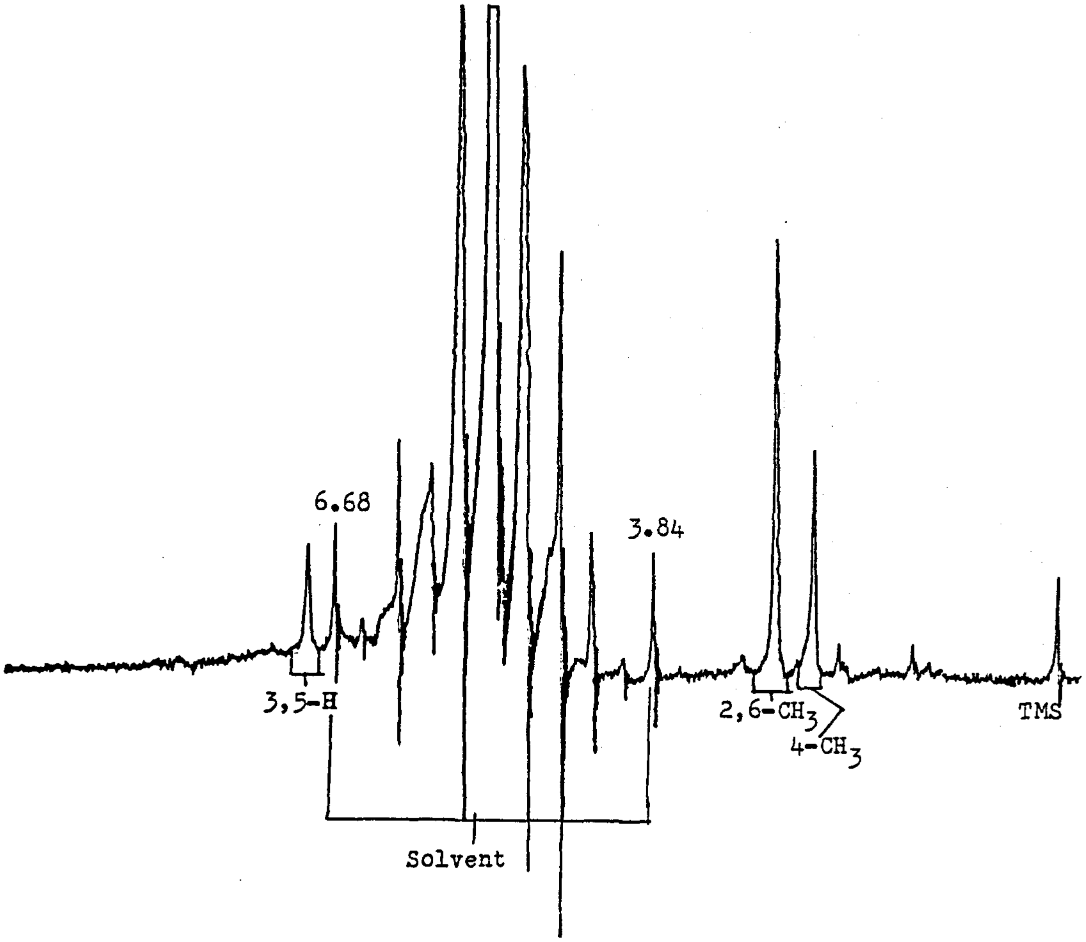

Figure 12

Infrared Spectrum of

$2,6\text{-}(CH_3)_2C_5H_3NBH_3$

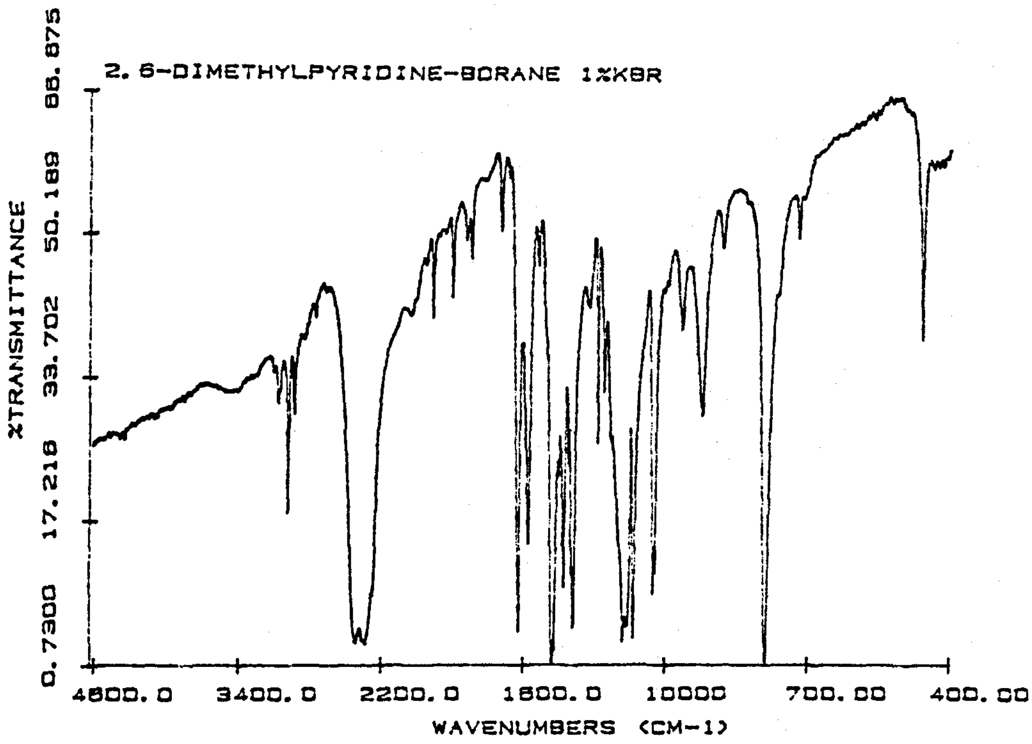

Figure 13

^{1}H nmr spectrum of

$2,6\text{-}(CH_3)_2C_5H_3NBH_3$

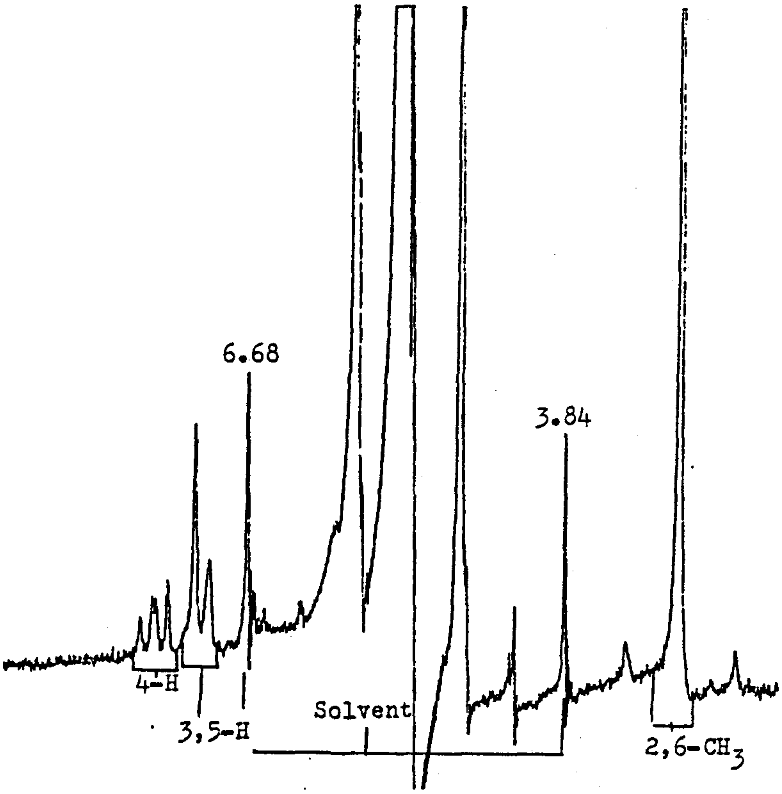

Table III

Summary of ^{1}H nmr Chemical Shifts

of Aromatic Amine-Haloboranes

a. 3,5-$(CH_3)_2C_5H_3NBH_3$

COMPOUND	δ^a 3,5-CH_3	δ^a 4-H	δ^a 2,6-H
3,5$(CH_3)_2C_5H_3NBH_3$	2.36	7.58	8.26
CHLORO			
3,5$(CH_3)_2C_5H_3NBH_2Cl$	2.43	7.73	8.38
3,5$(CH_3)_2C_5H_3NBHCl_2$	2.46	7.89	8.58
3,5$(CH_3)_2C_5H_3NBCl_3$	2.48	7.94	9.03
BROMO			
3,5$(CH_3)_2C_5H_3NBH_2Br$	2.43	7.78	8.44
3,5$(CH_3)_2C_5H_3NBHBr_2$	2.46	7.88	8.63
3,5$(CH_3)_2C_5H_3NBBr_3$	2.54	7.91	9.22
IODO			
3,5$(CH_3)_2C_5H_3NBH_2I$	2.43	7.79	8.48
3,5$(CH_3)_2C_5H_3NBHI_2$	2.48	8.04	8.63
3,5$(CH_3)_2C_5H_3NBI_3$	2.56	8.33	8.78
3,5$(CH_3)_2C_5H_3NBI_2^+I^-$	2.61	8.33	8.59

Table III (continued)

b. $2\text{-}CH_3C_5H_4NBH_3$

COMPOUND	δ^{a} $2\text{-}CH_3$	$\delta^{a,b}$ 3,5-H	$\delta^{a,b}$ 4-H	$\delta^{a,b}$ 6-H
$2\text{-}CH_3C_5H_4NBH_3$	2.71	7.32	7.87	8.75
CHLORO				
$2\text{-}CH_3C_5H_4NBH_2Cl$	2.89	7.49	8.04	8.80
$2\text{-}CH_3C_5H_4NBHCl_2$	2.94	7.62	8.05	9.23
$2\text{-}CH_3C_5H_4NBCl_3$	3.24	7.70	8.20	9.75
$2\text{-}CH_3C_5H_4NBCl_2^+Cl^-$	2.94	7.94	8.61	8.76
BROMO				
$2\text{-}CH_3C_5H_4NBH_2Br$	2.88	7.47	7.98	8.76
$2\text{-}CH_3C_5H_4NBHBr_2$	2.88	7.66	8.16	9.50
$2\text{-}CH_3C_5H_4NBBr_3$	3.34	7.67	8.23	10.14
$2\text{-}CH_3C_5H_4NBBr_2^+Br^-$	2.98	7.94	8.63	8.75
IODO				
$2\text{-}CH_3C_5H_4NBH_2I$	2.84	7.54	8.09	8.82
$2\text{-}CH_3C_5H_4NBHI_2$	2.84	7.60	8.06	9.61
$2\text{-}CH_3C_5H_4NBI_3$	3.09	8.55	8.90	8.90
$2\text{-}CH_3C_5H_4NBI_2^+I^-$	3.01	7.97	8.60	8.59

Table III (continued)

c. $2,6\text{-}(CH_3)_2C_5H_3NBH_3$

COMPOUND	δ^{a} 2,6-CH_3	$\delta^{a,c}$ 3,5-H	$\delta^{a,c}$ 4-H
$2,6\text{-}(CH_3)_2C_5H_3NBH_3$	2.76	7.27	7.68
CHLORO			
$2,6\text{-}(CH_3)_2C_5H_3NBH_2Cl$	2.88	7.40	7.88
$2,6\text{-}(CH_3)_2C_5H_3NBHCl_2$	3.04	7.59	8.26
$2,6\text{-}(CH_3)_2C_5H_3NBCl_2^+Cl^-$	2.94	7.59	8.31
BROMO			
$2,6\text{-}(CH_3)_2C_5H_3NBH_2Br$	2.94	7.36	7.85
$2,6\text{-}(CH_3)_2C_5H_3NBHBr_2$	3.11	7.45	7.91
$2,6\text{-}(CH_3)_2C_5H_3NBr_2^+Br^-$	2.98	7.68	8.36
IODO			
$2,6\text{-}(CH_3)_2C_5H_3NBH_2I$	2.88	7.37	7.90
$2,6\text{-}(CH_3)_2C_5H_3NBHI_2$	3.36	7.47	7.98
$2,6\text{-}(CH_3)_2C_5H_3NBI_2^+I^-$	2.94	7.69	8.38

Table III (continued)

d. $2,4,6\text{-}(CH_3)_3C_5H_2NBH_3$

COMPOUND	δ^{a} 4-CH_3	δ^{a} 2,6-CH_3	δ^{a} 3,5-H
$2,4,6\text{-}(CH_3)_3C_5H_2NBH_3$	2.34	2.69	7.06
CHLORO			
$2,4,6\text{-}(CH_3)_3C_5H_2NBH_2Cl$	2.38	2.83	7.16
$2,4,6\text{-}(CH_3)_3C_5H_2NBHCl_2$	2.51	3.31	7.27
$2,4,6\text{-}(CH_3)_3C_5H_2NBCl_2^+Cl^-$	2.58	2.84	7.36
BROMO			
$2,4,6\text{-}(CH_3)_3C_5H_2NBH_2Br$	2.39	2.83	7.14
$2,4,6\text{-}(CH_3)_3C_5H_2NBHBr_2$	2.43	3.04	7.28
$2,4,6\text{-}(CH_3)_3C_5H_2NBBr_2^+Br^-$	2.61	2.91	7.41
IODO			
$2,4,6\text{-}(CH_3)_3C_5H_2NBH_2I$	2.41	2.83	7.16
$2,4,6\text{-}(CH_3)_3C_5H_2NBHI_2$	2.56	2.98	7.28
$2,4,6\text{-}(CH_3)_3C_5H_2NBI_2^+I^-$	2.63	2.91	7.48

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[a] in ppm downfield from TMS in CH_2Cl_2 solution

[b] center of region of complex patterns due to those protons. Aromatic region appears as an ABCD pattern; See Footnote 21

[c] center of region of complex pattern due to these protons. Aromatic region appears in an ABB' pattern; See Footnote 21

V. Preliminary Survey of the Halogenation of Methylpyridine-Boranes

A. General Procedure.--A three-neck, 100 mL Schlenk tube was fitted with a nitrogen blanket, vented into a hood. To a stirred amine-borane solution was added a halogenating agent in small increments in solid form (I_2), in liquid form (Br_2 in methylene chloride) or in gaseous form (Cl_2, HCl, HBr). The halogen gases were bubbled into the solution through a long pasteur pipette. After each addition, a 0.75mL aliquot was removed and its ^1H nmr spectrum taken in order to trace the progress of the reaction. Special care was taken to remove all unreacted halogen and hydrogen halide from the reaction mixture by bubbling nitrogen through the solution for 10 to 15 minutes before any aliquot was removed for a ^1H nmr analysis. Spectra were taken of starting material as well as the final isolated product. Molar quantities involved in the isolation of the mono-, di-, and trihalogenated products were calculated on the basis of equations (6), (7), (8) and (9). A summary of those spectra and of the infrared spectra obtained is given in Tables II and III.

B. Halogenation Reactions of 3,5-Dimethylpyridine-Borane. Chlorination.--The reaction of 3,5-dimethylpyridine-borane and chlorine (Cl_2) was examined by monitoring the changes in the ^1H nmr spectrum of a solution of 3,5-dimethylpyridine-borane in CH_2Cl_2 (0.20M) as chlorine was added. The original pattern of 3,5-dimethylpyridine-borane (Figure 7) consists of three singlets, which, as chlorine was added, were observed to diminish in intensity as a new set of peaks (three singlets) grew downfield from the first set. The reaction solution bubbled and fizzed as the second set of peaks formed. The second set of peaks grew to a maximum and then began to diminish as a third set of peaks (three singlets) grew downfield from the second set. All gas evolution had stopped by this time. This new set of peaks grew to a maximum and then began to disappear as a fourth set of peaks (three singlets) began to grow further downfield eventually to a maximum. By that time all other peaks had disappeared and the spectrum remained unchanged with further addition of chlorine. The solution at this point was pale yellow. The reaction of 3,5-dimethylpyridine-borane and chlorine was so rapid that it was necessary to run the reaction at $-55^{\circ}C$ in order to see the three new sets of peaks sequentially. When the reaction was carried out at room temperature all four sets of peaks were observed from the first addition of chlorine, although the final pattern was the same. These observations are explained on the basis of a stepwise chlorination of 3,5-dimethylpyridine-borane producing, successively, 3,5-dimethylpyridine-monochloroborane, 3,5-dimethylpyridine-dichloroborane, and 3,5-dimethylpyridine-trichloroborane.

Bromination.--The reaction of 3,5-dimethylpyridine-borane and bromine (Br_2) was examined by monitoring the changes in the ^1H nmr spectrum of a solution of 3,5-dimethylpyridine-borane in CH_2Cl_2 (0.20M) as bromine was added. This reactiton was run at -55°C as well, due to the reactive nature of 3,5-dimethylpyridine-borane with bromine. The reaction proceeded as did chlorine as 1/2 mole-equivalent was added, in that again a set of three singlets appeared downfield as the peaks representing the starting material diminished. Gas evolution was observed as this set of singlets grew which stopped as they reached to a maximum, the first set having disappeared. As another 1 mole-equivalent of bromine was added these singlets were replaced by a third set of three singlets each further downfield, but at -55°C, the reaction stopped at this point (presumably $BHBr_2$ adduct). The reaction solution at this point was pale yellow. In order for the reaction to proceed to completion another 1 mole-equivalent of bromine was added and the solution was warmed to room temperature. In so doing the third set of peaks (three singlets) disappeared completely, a fourth set of three peaks grew to a maximum, and the solution turned dark orange. Only these three singlets (fourth set) were observed, with no further changes observed in the spectra as an additional 1/2 mole-equivalent of bromine was added. These observations can be explained on the basis of a stepwise bromination of 3,5-dimethylpyridine-borane producing, successively, 3,5-dimethylpyridine-monobromoborane, 3,5-dimethlypyridine-dibromoborane and 3,5-dimethylpyridine-tribromoborane.

Iodination.--The reaction of 3,5-dimethylpyridine-borane and iodine (I_2) was also examined by monitoring the change in ^1H nmr spectrum of a solution of 3,5-dimethylpyridine-borane in CH_2Cl_2 (0.20M) as iodine was added. A total of 3 mole-equivalents of iodine were added in 1/2 mole-equivalent portions. After the first addition of iodine (1/2 mole-equivalent), a new set of three singlets (second set) appeared downfield from the first set of peaks (starting material). Great care was taken when adding I_2 initially due to vigorous bubbling and fizzing which occurred as the second set of peaks grew. Another portion of I_2 (1/2 mole-equivalent) was added and the second set of peaks grew as did a third set of three peaks still further downfield, while the peaks due to starting material (first set) diminished. Another portion of I_2 (1/2 mole-equivalent) was added and the solution refluxed, in an attempt to force all unreacted iodine into solution. The first set of peaks (starting material) were no longer present and the second and third set of peaks were observed to have grown considerably in intensity. In addition, a fourth set of peaks (three singlets) had appeared further downfield from the third set. After an additional 1/2 mole-equivalent of iodine was added with reflux, the fourth set of peaks grew to a maximum as the second set diminished and the third set remained unchanged. As the reflux continued a fifth set of peaks (three singlets) appeared. The two singlet peaks from the methyl groups in the 3 and 5 positions and from the proton at the 4 position of the pyridine ring appeared further downfield from their corresponding peaks in set four while the singlet peak from the protons at the 2 and 6 positions appeared far upfield from its corresponding peak in the fourth set. After another addition of 1/2 mole-equivalent of iodine and after 1-1/2 hours of refluxing, only two sets of peaks remained, the fourth and fifth set of peaks. An additional 1/2 mole equivalent of iodine was added and the solution allowed to stand overnight after which only three singlets were observed (the fifth set). With continued refluxing the solution turned a clear dark violet. It is interesting to note that five sets of peaks were observed in the iodination of 3,5-dimethylpyridine-borane, but only four sets in the chlorination and bromination reactions. These observations are explained on the basis of a stepwise iodination of 3,5-dimethylpyridine-borane producing, successively, 3,5-dimethylpyridine-monoiodoborane, 3,5-dimethylpyridine-diiodoborane, and finally 3,5-dimethylpyridine-triiodoborane, with the triiodoborane adduct decomposing to a trigonal boronium cation by loss of I-. The specific conductance during the course of the reaction ranged from 15 μmhos/cm for the solution of starting material to 138 μmhos/cm for the solution after 2 mole-equivalents of iodine were added (mixture of di, tri and cation/I$^-$) to 177 μmhos/cm for the solution after 2-1/2 mole-equivalents were added (mixture of tri and cation/I$^-$), to 927 μmhos/cm for the final ionic solution after 3 mole-equivalents of iodine had been added and the contents stirred overnight.

C. Halogenation Reactions of 2-Methylpyridine-Borane. Chlorination.--The reaction of 2-methylpyridine-borane and chlorine (Cl_2) was examined by monitoring the change in the ^1H nmr spectrum of a solution of 2-methylpyridine-borane in CH_2Cl_2 (0.23M) as chlorine was added. It was necessary to run the reaction at -55°C due to the reactivity of 2-methylpyridine-borane and chlorine. The original pattern of 2-methylpyridine-borane (Figure 9), a singlet in the aliphatic region, and three multiplets in the aromatic region was observed to diminish as another similar set of peaks appeared further downfield. Gas evolved rapidly during the formation of the second set of peaks. With further addition of chlorine a third set appeared downfield and grew to a maximum as all other peaks disappeared and the solution turned slightly yellow. The addition of chlorine was stopped at this point, all excess chlorine and HCl was removed with a nitrogen purge at -55°C and an aliquot was taken for ^1H nmr. Only the third set of peaks were observed in this spectrum. As still more chlorine was added at -55° C (the reaction was still very rapid) a fourth set of peaks began to grow downfield from the third set of peaks. The reaction seemed to slow down considerably at this point so the solution was taken out of the -55°C bath and allowed to warm to room temperature at which time the reaction became more vigorous and the fourth set of peaks grew more in intensity as the third set rapidly disappeared. The fourth set of peaks was far downfield from the first three sets. After the solution had warmed to room temperature a fifth set of peaks appeared, an aliphatic singlet <u>upfield</u> from the aliphatic singlet in set four, one aromatic multiplet <u>upfield</u> from the corresponding multiplet in set four, and two aromatic multiplets downfield from the corresponding multiplets in set four. The reaction was allowed to stir at room temperature in the presence of excess chlorine for 24 hours after which time the fifth set of peaks had grown to a maximum and all other peaks had disappeared. These observations are explained as resulting from the stepwise chlorination of 2-methylpyridine-borane producing, successively, 2-methylpyridine-monochloroborane, 2-methylpyridine-dichloroborane, and 2-methylpyridine-trichloroborane, which slowly decomposed to a trigonal boronium cation and Cl^-. The conductivity was observed to increase from 15 μmhos/cm for the starting solution to 26 μmhos/cm for the trichloroborane adduct solution and to 1490 μmhos/cm for the final ionic solution.

Bromination.--The reaction of 2-methylpyridine-borane and bromine was also examined by monitoring the changes in the ^1H nmr spectrum of a solution of 2-methylpyridine-borane in CH_2Cl_2 (0.23M) as bromine was added in 1/2 mole-equivalent portions. The reaction was run at room temperature because the bromine was not as reactive as was chlorine with 2-methylpyridine-borane. The reaction proceeded as with chlorine, producing a new set of peaks downfield from those of the starting material as the first portion of bromine was added. Again gas was evolved during this first reaction but not as vigorously as in the chlorination reaction. With the addition of more portions of bromine, this set diminished as a third set appeared and grew to a maximum. As the third set diminished a fourth set of peaks appeared again downfield from the previous set of peaks. The reaction at this point seemed sluggish so the solution was refluxed and as more bromine was added the fourth set of peaks grew to a maximum and then diminished as a fifth set of peaks, (aliphatic singlet upfield from the aliphatic singlet in the fourth set, one aromatic multiplet upfield from the corresponding multiplet in the fourth set, and the other two aromatic multiplets downfield from the multiplets in the fourth set) appeared. The solution was allowed to stir for 48 hours during which time the fifth set of peaks grew to a maximum and all other peaks disappeared. These observations are explained as resulting from a stepwise bromination of 2-methylpyridine-borane producing, successively, 2-methylpyridine-monobromoborane, 2-methylpyridine-dibromoborane, and 2-methylpyridine-tribromoborane, which slowly decomposed to a trigonal boronium cation and Br^-. The conductivity was observed to increase from 15 μmhos/cm for the starting solution to 49 μmhos/cm for the 2-methylpyridine-tribromoborane solution, and as the fifth set of peaks grew to a maximum the conductivity increased to 834 μmhos/cm for the final solution.

Iodination.--The reaction of 2-methylpyridine-borane and iodine was also examined by monitoring the changes in the ^1H nmr spectrum of a solution of 2-methylpyridine-borane in CH_2Cl_2 (0.23M) as iodine was added in 1/2 mole-equivalent portions. As the first portion of iodine was added to the solution of starting material, vigorous gas evolution occured and a second set of peaks was observed slightly downfield from those of the starting material. As a second portion of iodine was added, the solution turned orange and a third set of peaks appeared downfield from those of the second set. The reaction however, was at this point very sluggish so the solution was refluxed and two more portions of iodine were added. A fourth set of peaks was observed far downfield from the third set with visible broadening of the aromatic multiplet from the proton in the 6 position on the ring. With extensive refluxing the fourth set was observed to grow to a maximum very slowly as all other peaks disappeared. Over a period of several days without reflux and with no additional iodine added, a fifth set of peaks was observed, an aliphatic singlet upfield from the singlet in set four, two aromatic multiplets downfield from aromatic multiplets in set four, and one aromatic multiplet upfield from an aromatic multiplet in set four. The fourth set of peaks was observed to diminish very slowly, but after five days of stirring at room temperature only the fifth set of peaks remained. These observation are explained on the basis of the stepwise iodination of 2-methylpyridine-borane to give, successively, 2-methylpyridine-monoiodoborane, 2-methylpyridine-diiodoborane, and 2-methylpyridine-triiodoborane, which slowly decomposed to a trigonal boronium cation and I^-. The conductivity was observed to increase from 21 μmhos/cm for the solution containing the mono adduct to 39 μmhos/cm for the solution containing 2-methylpyridine-triiodoborane, and, as the fifth set of peaks grew to a maximum, the conductivity increased to 482 μmhos/cm for the final solution.

D. Halogenation Reactions of 2,6-Dimethylpyridine-Borane.

Chlorination.--The reaction of 2,6-dimethylpyridine-borane and chlorine (Cl_2) was examined by monitoring the changes in the ^1H nmr spectrum of a solution of 2,6-dimethylpyridine-borane (0.20 M) in CH_2Cl_2 as chlorine was added. The original pattern of 2,6-dimethylpyridine-borane (Figure

13), consisted of, in increasing downfield order, an aliphatic singlet, and two multiplets in the aromatic region. This set of peaks was observed to diminish as chlorine was added. A new, similar set of peaks appeared downfield of the peaks in the first set, growing to a maximum as the peaks due to starting material disappeared. Large amounts of gas evolved from the solution during this reaction. As additional chlorine was added, a third set of peaks (aliphatic singlet, two aromatic multiplets) appeared downfield from the peaks of the second set, which grew to a maximum as the second set diminished. The solution at this time was yellow. As more chlorine was added the third set began to diminish as a fourth set of peaks appeared. The fourth set of peaks consisted of an aliphatic singlet upfield from the aliphatic singlet in set three and two aromatic multiplets downfield from the those in set three. No change was seen with further addition of chlorine after the fourth set of peaks grew to a maximum. These observations are explained on the basis of the stepwise chlorination of 2,6-dimethylpyridine-borane, producing, successively, 2,6-dimethylpyridine-monochloroborane, 2,6-dimethylpyridine-dichloroborane, and finally 2,6-dimethylpyridine-trichloroborane which was not observed but which decomposed as it was formed to give a trigonal boronium cation and Cl^-.

Bromination.-- The reaction of 2,6-dimethylpyridine-borane

(0.20 m) with bromine proceeded much like that of the chlorine reaction except it was slightly slower. The reaction was monitored by ^{1}H nmr as bromine was added in 1/2 mole-equivalent portions. These observations are explained on the basis of the stepwise bromination of 2,6-dimethylpyridine-borane producing, successively, 2,6-dimethylpyridine-monobromoborane, 2,6-dimethylpyridine-dibromoborane and 2,6-dimethylpyridine-tribromoborane which again was not observed but which decomposed as it formed to give a trigonal cation and Br^-.

Iodination.--The reaction of 2,6-dimethylpyridine-borane and iodine was examined by monitoring the changes in the ^{1}H nmr spectrum as solid iodine was added in 1/2 mole equivalent portions to a solution of 2,6-dimethylpyridine-borane (0.20 M) in CH_2Cl_2. The reaction proceeded as the two previous reactions but was much slower. In order to drive the reaction to completion a period of refluxing was necessary after each addition. These observations are explained on the basis of a stepwise iodination of 2,6-dimethylpyridine-borane producing, successively, 2,6-dimethylpyridine-monoiodoborane, 2,6-dimethylpyridine-diiodoborane, and 2,6-dimethylpyridine-triiodoborane which was not observed, but which decomposed as it formed to give a trigonal boronium cation and I^-. The conductivity increased from 21 μmhos/cm for the monoiodoborane adduct to 36 μmhos/cm for the diiodoborane adduct and as the fourth set of peaks grew to a maximum the conductivity increased to 621 μmhos/cm for the final solution.

E. Halogenation Reactions of 2,4,6-Trimethylpyridine-Borane. Chlorination.--The reaction of 2,4,6-trimethylpyridine-borane and chlorine was examined by monitoring the changes in the ^1H nmr spectrum of a solution of 2,4,6-trimethylpyridine-borane (0.19 M) in CH_2Cl_2 as chlorine was added. The ^1H nmr spectrum of 2,4,6-trimethylpyridine-borane consists of two aliphatic singlets and one aromatic singlet (Figure 11). As chlorine was added slowly at room temperature, a set of three singlets appeared slightly downfield from those of the starting material and grew to a maximum as the pattern of starting material was observed to diminish. A large amount of gas evolution accompanied this change. As additional chlorine was added, a third set of three singlets were observed further downfield from the second set of peaks. As the reaction proceeded the third set of peaks was observed to grow to a maximum. The aromatic singlet in that set was observed to be broadened at first, but then it sharpened as the first and second set of peaks disappeared. With the addition of more chlorine, a fourth set of peaks appeared further downfield from the third set and grew to a maximum as a second and third set diminished. As still more chlorine was added a fifth set of peaks (three singlets) were observed. In this fifth set, the aliphatic singlet representing the 2,6-CH_3 protons was observed upfield from that singlet in set four, while the singlets representing the 4-CH_3 protons appeared downfield from that peak in set four, and the aromatic singlet, was observed far downfield from the aromatic singlet in set four. As the reaction proceeded to completion the fifth set was observed to grow to a maximum as all other peaks disappeared. The spectrum was not changed with further addition of chlorine. These observations are explained on the basis of a stepwise chlorination of 2,4,6-trimethylpyridine-borane producing, successively, 2,4,6-trimethylpyridine-monochloroborane, an otherwise unidentified intermediate, 2,4,6-trimethylpyridine-dichloroborane and finally 2,4,6-trimethylpyridine-trichloroborane which was not observed, but which decomposed as it formed to give a trigonal boronium cation and Cl^-. Because 2,4,6-trimethylpyridine-borane was so slow to react, the dichloroborane adduct began forming while monochloroborane adduct and intermediate were still present.

Bromination.--The reaction of 2,4,6-trimethylpyridine-borane and bromine was also examined by monitoring the changes in the ^1H nmr spectrum of a solution of 2,4,6-trimethylpyridine-borane (0.19 M) in CH_2Cl_2 as a function of the amount of bromine added. The bromination of 2,4,6-trimethylpyridine-borane though much slower than the chlorination was very similar as far as the pattern of sets of peaks observed. The observations are explained on the basis of the stepwise bromination of 2,4,6-trimethylpyridine-borane producing, successively 2,4,6-trimethylpyridine-monobromoborane, an otherwise unidentified intermediate, 2,4,6-trimethylpyridine-dibromoborane and finally 2,4,6-trimethylpyridine-tribromoborane which was not observed but which decomposed as it formed to give a trigonal boronium cation and Br^-.

Iodination.--The reaction of 2,4,6-trimethylpyridine-borane and iodine was examined by monitoring the changes in the ^1H nmr spectrum of a solution of 2,4,6-trimethylpyridine-borane (0.19 M) in CH_2Cl_2 as iodine was added. The iodination reaction was very slow and required extensive refluxing after each addition in order to drive the reaction to completion. The peak sets though different in chemical shift were very similar in pattern to those of the two previous reactions. The observations are explained on the basis of the stepwise iodination of 2,4,6-trimethylpyridine-borane producing, successively, 2,4,6-trimethylpyridine-monoiodoborane, an otherwise unidentified intermediate, 2,4,6-trimethylpyridine-diiodoborane and 2,4,6-trimethylpyridine-triiodoborane which was not observed but which decomposed as it formed to give a trigonal boronium cation and I^-.

V. Synthesis of Methylpyridine-Haloboranes

A. General Procedure.--A three neck, 100 mL Schlenk tube was fitted with a nitrogen blanket, vented into a hood. To a stirred amine-borane solution was added a halogenating agent in small increments. Agents were added as a solid

(I_2) or as a liquid (Br_2), while gaseous halogenating agents (HCl, HBr, Cl_2) were bubbled into the solution through a long pasteur pipette. A 0.75mL aliquot was removed for ^1H nmr after each addition in order to trace the progress of the reaction. Special care was taken to remove all unreacted halogen and hydrogen halide from the reaction mixture by bubbling nitrogen through the solution for 10 to 15 minutes before any aliquot was removed for ^1H nmr analysis. Spectra were taken of starting material as well as final isolated product. Molar quantities involved in the isolation of the mono-, di-, and trihalogenated products were calculated on the basis of equations (6), (7), (8) and (9). Once the reaction had proceeded to a given desired product, that solution was evaporated to dryness and the isolated product was characterized. The chemical shifts obtained from ^1H nmr spectra agreed with those observed earlier in the preliminary halogenation reactions. A summary of those spectra is given in Table III (see pages 33-36).

B. Synthesis of 3,5-Dimethylpyridine-Haloboranes.

1. 3,5-Dimethylpyridine-Monochloroborane.--A solution of 3,5-dimethylpyridine-borane (0.500 g, 4.14 mmol) in methylene chloride (20 mL) was prepared to which small amounts of HCl were added at room temperature. Fizzing and bubbling occurred immediately upon each addition. The solution was filtered and the filtrate evaporated yielding a white solid

powder ($3,5\text{-}(CH_3)_2C_5H_3NBH_2Cl$, 0.506 g, 3.20 mmol, 78.7% yield, mp 145.0-157.6°C, ir: 3150,3100(m),3040,3020,2940(s),2800-2400(vb),2050(m),1970(w),1900(w)1570,1380,1330(s),860,800,720(s)cm^{-1}). Spectral evidence indicated the product was contaminated with a small amount of 3,5-dimethylpyridine-dichloroborane.

2. 3,5-Dimethylpyridine-Dichloroborane.-- A solution of 3,5-dimethylpyridine-borane (0.500 g, 4.14 mmol) in CH_2Cl_2 (20 mL) was prepared and allowed to stand at -55°C for one hour before bubbling in Cl_2. A little chlorine was bubbled very slowly into the solution, and immediately followed by a nitrogen purge until the liquid was colorless. A ^1H nmr scan was then taken to trace the progress of the reaction. As more chlorine was added in this way, two sets of peaks (three singlets each) appeared downfield from the starting material and the reaction continued until the second of the new sets of peaks (three singlets) grew to a maximum and all other peaks disappeared. At this time nitrogen was bubbled into the solution (still at -55°C) for 10 minutes. During the nitrogen purge, the pale yellow solution turned colorless. The solution was then filtered and the filtrate evaporated to dryness, leaving a pale yellow solid ($3,5\text{-}(CH_3)_2C_5H_3NBHCl_2$, 0.292 g, 4.17 mmol, 100.7% yield, mp 95.0-96.9°C, ir: 3040(m),2970,2940(s),2650-2500(vb),2050(w),1960(w),1570,1390,1295,1090(s),880,770(m)cm^{-1}). Three small peaks

were present in the ^1H nmr further downfield from the peaks representing the desired product which were attributed to the formation of a small amount of 3,5-dimethylpyridine-trichloroborane.

3. 3,5-Dimethylpyridine-Trichloroborane.--A solution of 3,5-dimethylpyridine-borane (0.275 g, 2.27 mmol) in methylene chloride (20 mL) was prepared and allowed to stand at -55°C for 1/2 hour. A ^1H nmr spectrum was taken for identification. Chlorine was bubbled through the solution until the solution turned pale yellow. Another ^1H nmr spectrum was taken after a nitrogen purge. Four sets of peaks (three singlets each) were observed including the starting material. As more chlorine was added in this way, the first three sets of peaks were observed to disappear until only the fourth set of peaks (three singlets) remained. Nitrogen was bubbled through the solution to remove chlorine and HCl, and the pale yellow solution was filtered. The filtrate was evaporated under vacuum leaving a yellow powder ($3,5-(CH_3)_2C_5H_3NBCl_3$, 0.391 g, 1.75 mmol, 77.1% yield, mp 110.3-110.8°C, ir: 3110(s),2980(m), 2940,1460,1390(m),1300,1050(b),880,860(m)cm^{-1}).

4. 3,5-Dimethylpyridine-Monobromoborane.--A solution of 3,5-dimethylpyridine-borane (0.500 g, 4.14 mmol) in methylene chloride (20 mL) was prepared and HBr bubbled in very slowly at room temperature. Fizzing and vigorous gas evolution from the solution accompanied the addition of HBr and continued

until the reaction stopped at the monobromo adduct. The colorless solution was filtered and the filtrate evaporated to dryness yielding very dry, powdery white crystals ($3,5-(CH_3)_2C_5H_3NBH_2Br$, 0.747 g, 3.74 mmol, 90.3% yield, mp 202.1-207.2°C, ir: 3050(m),2940(s),2800-2450(vb),2050(m), 1970(w),1900(w),1570,1370,1270,1200(s),860,650(s)cm^{-1}). Due to the speed of the reaction it was difficult to prevent a small amount of the dibromo adduct from forming.

5. 3,5-Dimethylpyridine-Dibromoborane.--A solution of 3,5-dimethylpyridine-borane (0.500 g, 4.13 mmol) in methylene chloride (20 mL) was cooled to -55°C for one hour after which a solution of Br_2 (0.497 g, 3.11 mmol) in methylene chloride (5 mL) was added dropwise to the borane solution and then a ^1H nmr spectrum taken without a nitrogen purge. After additional bromine (0.490 g.,3.06 mmol) had been added, the solution was purged with nitrogen for 20 minutes after which a ^1H nmr spectrum was taken. The spectrum showed a set of three singlets consistent with the presence of the $BHBr_2$ adduct. The orange solution was filtered and the filtrate evaporated to dryness leaving orange crystals ($3,5-(CH_3)_2C_5H_3NBHBr_2$, 1.10 g, 3.96 mmol, 96.8% yield, mp 195.3-200.0°C decomposed, ir: 3040(s),2930(s),2700-2450(vb), 2050(m),1970(w),1900(w),1570,1350,1270,860(s),680(s)cm^{-1}).

6. 3,5-Dimethylpyridine-Tribromoborane.--To a solution of 3,5-dimethylpyridine-borane (0.500 g, 4.14 mmol) in methylene

chloride (20 mL) at room temperature was added dropwise a concentrated solution of bromine (1.68 g, 10.52 mmol) in CH_2Cl_2 (10 mL). A ^1H nmr spectrum was taken after a total of 2.54 mole equivalents of bromine was added. A nitrogen purge was used to remove unreacted bromine and HBr, and then the yellow solution was filtered. The filtrate was evaporated, yielding powdery orange crystals ($3,5-(CH_3)_2C_5H_3NBBr_3$, 1.07 g, 3.02 mmol, 72.9% yield, mp 175.0°C decomposed, ir: 3030(m),2940(m),2800-2450(vb),2050(vw), 1960(vw),1900(vw),1570,1350,860(s),750(s),680(s)cm^{-1}). The reaction was repeated using a more concentrated solution of bromine (0.98 g/mL) and an 85% yield was observed. The latter reaction was quick and the crystals more easily isolated.

7. <u>3,5-Dimethylpyridine-Monoiodoborane</u>.--A solution of 3,5-dimethylpyridine-borane (0.540 g, 4.47 mmol) in methylene chloride (20 mL) was stirred at room temperature as iodine (0.585 g, 2.36 mmol) was added slowly over a period of 1 hour and 45 minutes. The solution was rapidly stirred. The ^1H nmr spectra taken at intervals during the addition of I_2 indicated that during the later stages of the addition, a small amount of diiodo-adduct was formed. After addition of all of the I_2, a little starting material was still present as well. The orange brown solution was filtered and the filtrate evaporated to dryness, leaving yellow crystals ($3,5-(CH_3)_2C_5H_3NBH_2I$, 0.979 g, 3.97 mmol, 88.8% yield,

153.0-200.0°C decomposed, ir: 3050(m),2940(m),2940-2780(b), 2000(vw),1920(vw),1460,1150(b),880,800(b)cm^{-1}).

8. <u>3,5-Dimethylpyridine-Diiodoboronium Iodide</u>. A solution of 3,5-dimethylpyridine-borane (0.454 g, 3.75 mmol) in methylene chloride (20 mL) was prepared in a 100 mL Schlenk tube. Iodine (2.36 g, 9.29 mmol) was added to the stirred solution over a period of three days. Intervals of refluxing were used to drive the reaction to completion. ^{1}H nmr spectra and conductivity measurements were taken at frequent intervals to determine progress of the reaction. As indicated in the survey discussion above, unusual behavior was observed during the iodination reaction in comparision to the corresponding chlorination and bromination reactions. During the iodination, five sets of peaks (three singlets each) were observed including the starting material in contrast to the four such sets of peaks observed during the other reactions. Diiodo and neutral triiodo products could not be isolated in pure form because some of the neutral triiodinated product converted to the ionic form while the diiodo adduct was still present in solution. The conductivity of the mixture of the diiodo, triiodo, and cation adducts was 138 μmhos/cm while the starting solution was 15 μmhos/cm. As the diiodo adduct disappeared and more cation was produced, the conductivity increased to 177 μmhos/cm. When the reaction was complete, only the three singlets corresponding to the ionic product were observed

and the conductivity of the resulting solution (20 mL) was 927 µmhos/cm. The solvent was evaporated leaving a thick oily residue. Attempts were made to redissolved the oil in methylene chloride and then evaporate the solvent. Once again an oil residue remained.

C. Synthesis of 2-Methylpyridine-Haloboranes 1. 2-Methylpyridine-Monochloroborane.--To a solution of 2-methylpyridine-borane (0.414 g, 3.87 mmol) in CH_2Cl_2 (20 mL) was added gaseous HCl in small increments at room temperature. A duplicate set of peaks appeared downfield from those of the starting material, which grew to a maximum as the peaks due to the starting material disappeared. Evaporation of solvent left white, powdery crystals ($2\text{-}CH_3C_5H_4NBH_2Cl$, 0.468 g, 3.32 mmol, 85.8% yield, mp 70.4-72.9°C, ir: 3050(s),2700-2450(vb), 2000(b,w),1930(b,w)1500-1350(vb),800,750(m)cm^{-1}).

2. 2-Methylpyridine-Trichloroborane.-- A solution of 2-methylpyridine-borane (0.500 g, 4.67 mmol) in CH_2Cl_2 (20 mL) was cooled to -55°C for one hour prior to chlorination. The low temperature served to slow the reaction down and thus prevent the formation of the ionic product. Chlorine was bubbled slowly into the solution until a faint yellow color was visible. Once that color was detected (and still at -55°C), a nitrogen purge was run for 20 minutes to remove all unreacted chlorine and HCl. Evaporation of solvent at room temperature left yellow powdery crystals ($2\text{-}CH_3C_5H_4NBCl_3$,

0.755 g, 3.59 mmol, 76.8% yield, mp 101.3-108.0°C Literature[17] 105-107°C, ir: 3050(s),2850-2640(vb),1540,1440,1310(s), 1090,810(m),710(m),550(s)cm^{-1}).

3. <u>2-Methylpyridine-Dichloroboronium Chloride</u>.--Into a solution of 2-methylpyridine-borane (0.502 g, 4.69 mmol) in CH_2Cl_2 (20 mL) at room temperature was bubbled Cl_2 in large increments at room temperature. A ^1H nmr spectrum taken at the point at which the solution turned yellow indicated that both neutral trichloro adduct and the ionic product were present. The conductivity at that time was 562 mhos/cm. Additional chlorine was added, and the solution was stirred overnight and then heated to reflux for one hour. The ^1H nmr spectra of the resulting solution indicated the presence of only the ionic product with no neutral trichloro product present. The specific conductance of the final solution (20 mL) was 1490 μmhos/cm.* Evaporation of the solvent left yellow crystals ($2\text{-}CH_3C_5H_4NBCl_2{}^+Cl^-$, 0.854 g, 4.06 mmol, 86.6% yield, mp 91.1-94.5°C, ir: 3050(s),2850-2650(vb), 1420-1350(vb),775(m),660(m)cm^{-1}).

4. <u>2-Methylpyridine-Monobromoborane</u>.--Into a solution of 2-methylpyridine-borane (0.470 g, 4.40 mmol) in CH_2Cl_2 (20 mL) was bubbled gaseous HBr at room temperature. The reaction was very sluggish. After ^1H nmr spectra showed

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*This compares favorably to the specific conductance observed for what was proposed to be 4-methylpyridinedichloroboronium heptachloroaluminate in CH_2Cl_2; see reference 16.

complete reaction to monobromo product, a nitrogen purge was run to remove unreacted HBr, and the resulting colorless solution was evaporated to dryness, leaving white crystals ($2\text{-}CH_3C_5H_4NBH_2Br$, 0.755g, 4.07 mmol, 92.5% yield, mp 184.9-189.9°C, ir: 2900(b),2100-1900(vb),1540(s),1290(s),780(b), 470(s)cm^{-1}).

5. <u>2-Methylpyridine-Dibromoborane</u>.-- A solution of 2-methylpyridine-borane (0.515 g, 4.82 mmol) in CH_2Cl_2 (20 mL) was cooled to -55°C for one hour prior to bromine addition. The bromine solution (1.08 g, Br_2, 6.75 mmol) was added dropwise over 2 hours. After all the Br_2 was added, a nitrogen purge (still at -55°C) was run for 15 minutes and a ^1H nmr spectrum taken. A single set of peaks (aliphatic singlet, and three aromatic multiplets) were present downfield from those of the starting material. The conductivity of the solution was 15 μmhos/cm. At this time the colorless solution was evaporated to dryness and the white crystals dried in vacuo ($2\text{-}CH_3C_5H_4NBHBr_2$, 0.940 g, 3.56 mmol, 73.8% yield, mp 144.8-158.7°C, ir: 2900(s),2100-1900(vb),1500-1350(vb), 1100(m),770(s),460(s)cm^{-1}).

6. <u>2-Methylpyridine-Tribromoborane</u>.--To a solution of 2-methylpyridine-borane (0.495 g, 4.63 mmol) in CH_2Cl_2 (20 mL) was added a solution of bromine (2.656 g, 16.0 mmol) at room temperature. A ^1H nmr spectrum of the product solution indicated the tribromo adduct was present alone. Conduc-

tivity measurements were made intermittenly throughout the experiment. The conductivity of the final solution was 49 µmhos/cm. Evaporation of the solvent from the solution left orange crystals ($2\text{-}CH_3C_5H_4NBBr_3$, 1.23 g, 3.58 mmol, 77.3% yield, mp 96.5-101.1°C, ir: 2900(s),2800-2600(b),1560,1200, 1030(b),730(s),680(s)cm^{-1}).

7. Methylpyridine-Dibromoboronium Bromide.--To a solution of 2-methylpyridine-borane (0.503 g, 4.70 mmol) in CH_2Cl_2 was added a concentrated solution of bromine (3.11 g 19.45 mmol) in CH_2Cl_2 at room temperature. Conversion of the tribromo adduct to ionic product was very sluggish, so the reaction was refluxed for several hours and then allowed to stir 48 hours. A ^1H nmr spectrum taken after 48 hours indicated only ionic product was present. The conductivity of the solution was 834 µmhos/cm. The solvent was evaporated leaving orange crystals ($2\text{-}CH_3C_5H_4NBBr_2{}^+Br^-$, 0.643 g, 1.86 mmol, 39.6% yield, mp 95.2-100.0°C, ir: 2950(b), 2840,1540(m),1200(m),750(m),650(s)cm^{-1}).

8. 2-Methylpyridine-Monoiodoborane.--To a solution of 2-methylpyridine-borane (0.557 g, 5.20 mmol) in CH_2Cl_2 (20 ml) iodine (0.66 g, 2.60 mmol) was added very slowly at room temperature. A ^1H nmr spectrum taken after some of the iodine had been added showed a new set of peaks were growing slightly downfield from those of the starting material. After all of the iodine was added (one hour) a second ^1H

nmr scan was taken. A trace of starting material was still present as well as a trace of a third set of peaks downfield from the first two, presumably due to a diiodo product. The orange solution was filtered and the solvent evaporated, leaving an off-white powder (2-$CH_3C_5H_4NBH_2I$, 0.937 g, 4.03 mmol, 77.4% yield, mp 71.5-74.0°C, ir: 2900(b),2050-1900(vw), 1510-1380(vb),1180(m),640(vs)cm^{-1}).

9. <u>2-Methylpyridine-Diiodoborane</u>.--To a solution of 2-methylpyridine-borane (0.504 g, 4.70 mmol) in CH_2Cl_2 (20 mL) iodine (0.330 g, 1.30 mmol) was added slowly at room temperature. Once the fizzing and bubbling became less vigorous, another portion of iodine (0.895 g, 3.53 mmol) was added, and the solution was refluxed for 1-1/2 hours. A ^1H nmr spectrum taken at this time indicated that a mixture of mono and di adducts was present. Another portion of iodine (0.660 g, 2.60 mmol) was added, and after refluxing for an additional 1/2 hour, a ^1H nmr spectrum showed only one set of peaks (singlet, and three multiplets) the position of which was consistent with diiodo product. The solvent was removed by evaporation leaving a dry, yellow powder (2-$CH_3C_5H_4NBHI_2$, 0.663 g, 2.77 mmol, 38.2% yield, ir: 2900(b), 1500-1350(vb),1040(m),650(m)cm^{-1}).

10. <u>2-Methylpyridine-Diiodoboronium Iodide</u>.--A solution of 2-methylpyridine-borane (0.500 g, 4.71 mmol) in CH_2Cl_2 (50 mL) was prepared in a 500 mL, 3 neck flask. A solution

of iodine (3.01 g, 11.8 mmol) in CH_2Cl_2 (75 mL) was added slowly over a period of 90 minutes to the reaction flask. After the first 30 minutes the solution was refluxed, and then after all the iodine was added, the solution was allowed to reflux for 24 hours. After cooling, an aliquot was taken of the reaction mixture for ^1H nmr, which showed only peaks due to the ionic product. Evaporation of solvent resulted in a thick, oily residue, ($2\text{-}CH_3C_5H_4NBI_2{}^+I^-$, 2.01 g, 4.14 mmol, 88.0% yield). Attempts were made to crystallize the product after redissolving the oil in methylene chloride but again crystals did not form.

D. Synthesis of 2,6-Dimethylpyridine-Haloboranes 1. 2,6-Dimethylpyridine-Monochloroborane.--HCl gas was bubbled at room temperature into a solution of 2,6-dimethylpyridine-borane (0.500 g, 4.14 mmol) in CH_2Cl_2 (20 mL). A new set of peaks (singlet, and two aromatic multiplets resembling a doublet and a quartet) appeared in the ^1H nmr downfield from those of the starting material and grew to a maximum as the peaks due to the starting material disappeared. Evaporation of solvent left white crystals ($2,6\text{-}(CH_3)_2C_5H_3NBH_2Cl$, 0.496 g, 3.19 mmol, 77.1% yield, mp 180.1-192.3°C, ir: 3000(s),2000-1900(b),1550-1350(vb),1050,800(s),550(s)cm^{-1}).

2. 2,6-Dimethylpyridine-Dichloroboronium Chloride.--Chlorine gas was bubbled into a solution of 2,6-dimethylpyridine-borane (0.500 g, 4.14 mmol) at room temperature in

methylene chloride (20 mL). The solution turned dark yellow, at which time a ^{1}H nmr spectrum was taken. The spectum indicated the presence of only one product. The solution was purged with nitrogen for 10 minutes and the solvent evaporated from the light yellow solution leaving a yellow solid ($2,6-(CH_3)_2C_5H_3NBCl_2^+Cl^-$, 0.766 g, 3.42 mmol, 82.5% yield, mp 168.8-182.0°C Literature[15] 178°C decomposed, ir: 2500(b), 1500-1300(vb),710(b),410(s)cm^{-1}, Cl analysis[15] observed 47.23% theoretical 47.41%).

3. <u>2,6-Dimethylpyridine-Monobromoborane</u>.--HBr gas was bubbled at room temperature into a solution of 2,6-dimethylpyridine-borane (0.451 g. 3.74 mmol) in CH_2Cl_2 (20 mL). The reaction was monitored by ^{1}H nmr and stopped at a point at which the peaks due to the starting material were nearly gone and peaks due to the product were at a maximum. Peaks indicating a slight impurity of the $BHBr_2$ adduct were also observed. Evaporation of solvent left powdery yellow crystals ($2,6-(CH_3)_2C_5H_3NBHBr_2$, 0.649 g. 3.25 mmol, 86.9% yield, mp 93.5-94.7°C, ir: 2700(m),2300-2100(b),1700-1500(vb),800(b), 700(s)cm^{-1}).

4. <u>2,6-Dimethylpyridine-Dibromoboronium Bromide</u>.--A concentrated solution of bromine (1.93 g, 12.09 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of 2,6-dimethylpyridine-borane (0.486 g, 4.03 mmol) in CH_2Cl_2 (20 mL). Excess Br_2 was removed by warming the solution while purging

with nitrogen. The solution was then evaporated to dryness leaving orange crystals ($2,6\text{-}(CH_3)_2C_5H_3NBBr_2{}^+Br^-$, 1.04 g, 2.93 mmol, 72.7% yield, mp 67.2-70.5°C Literature[15] 171°C decompose, ir: 2880(s),2750(m),1550-1400(b),1280(s),780(s), 560(m)cm^{-1}, Br analysis[15] observed 67.69% theoretical 67.06%).

5. <u>2,6-Dimethylpyridine-Monoiodoborane</u>.--To a solution of 2,6-dimethylpyridine-borane (0.505 g, 4.18 mmol) in CH_2Cl_2 (20 mL) was added iodine (0.531 g, 2.09 mmol) piecewise over a period of one hour. The ^1H nmr spectrum taken after all the iodine was added indicated the reaction had gone to completion. Only traces of starting material and BHI_2 adduct were present. Evaporation of solvent left pale orange crystals ($2,6\text{-}(CH_3)_2C_5H_3NBH_2I$, 0.913 g, 3.70 mmol, 89.6% yield, mp 112.0-114.5°C, ir: 3030(s),2800(s),2050(vw),1950(vw), 1500-1350(vb),1280(s),560(s)cm^{-1}).

6. <u>2,6-Dimethylpyridine-Diiodoboronium Iodide</u>.--A solution of 2,6-dimethylpyridine-borane (0.500 g, 4.13 mmol) in CH_2Cl_2 (20 mL) was prepared and iodine (2.622 g, 10.33 mmol) added slowly at room temperature. After 1/3 of the iodine had been added, the solution was refluxed for 1 hour. Another 1/3 of the iodine was added and the solution refluxed again for one hour. An ^1H nmr spectrum at this point indicated a mixture of BHI_2 and $BI_2{}^+I^-$ adducts were present. The remainder of the iodine was then added, followed by 1/2 hour of reflux. The solution was then stirred at room temperature for 2

days after which a ^{1}H nmr spectum indicated only the ionic product was present. The solvent was evaporated leaving a dark red oil. ($2,6\text{-}(CH_3)_2C_5H_3NBI_2{}^+I^-$, 0.630 g, 2.48 mmol, 60.0% yield, ir: 3060(s),3020,1500-1300(vb),1050(vb),800(s), 640(m)cm^{-1}). Again attempts were made to crystallized the product with no positive results.

E. Synthesis of 2,4,6-Trimethylpyridine-Haloboranes.

1. 2,4,6-Trimethylpyridine-Monochloroborane.--A solution of 2,4,6-trimethylpyridine-borane (0.500 g, 3.70 mmol) in CH_2Cl_2 (20mL) was prepared, into which HCl gas was bubbled at room temperature in small increments. The reaction was monitored by ^{1}H nmr and stopped at a point at which the peaks due to starting material were nearly gone and the peaks due to the product were at a maximum. The solvent was evaporated leaving sticky white crytals ($2,4,6\text{-}(CH_3)_3C_5H_2NBH_2Cl$, 0.537 g, 3.19 mmol, 86.2% yield).

2. 2,4,6-Trimethylpyridine-Dichloroboronium Chloride.---Chlorine gas was bubbled into a solution of 2,4,6-trimethylpyridine-borane (0.505 g, 3.75 mmol) in CH_2Cl_2 (20mL) at room temperature until the solution turned dark yellow, at which time a ^{1}H nmr was taken. In the spectrum, the peaks due to the product were present and all other precursor peaks had disappeared. Unreacted chlorine and HCl were removed with a nitrogen purge and the solvent evaporated leaving sticky yellow crystals ($2,4,6\text{-}(CH_3)_3C_5H_2NBCl_2{}^+Cl^-$, 0.878 g,

3.69 mmol, 98.4% yield, mp 95.5-96.7°C, ir: 3050(s),2590(s), 1550-1350(vb),880(s),650(b)cm^{-1}).

3. 2,4,6-Trimethylpyridine-Monobromoborane.--HBr gas was bubbled into a soluton of 2,4,6-trimethylpyridine-borane (0.498 g, 3.69 mmol) in CH_2Cl_2 (20 mL) at room temperature and the progress of the reaction monitored with ^1H nmr. Addition of HCl was stopped when the ^1H nmr showed the peaks of the product at a maximum and the peaks of the starting material nearly gone. The solvent was evaporated yielding dry powdery white crystals ($2,4,6-(CH_3)_3C_5H_2NBH_2Br$, 0.744 g, 3.78 mmol, 94.1% yield, mp 111.6-115.5°C, ir: 3040(s),2970(s), 1930(b),1550-1350(vb),1200(m),650(m),500(m)cm^{-1}).

4. 2,4,6-Trimethylpyridine-Dibromoboronium Bromide.--A concentrated solution of bromine (2.43 g, 15.16 mmol) was added to a solution of 2,4,6-trimethylpyridine-borane (0.511 g, 3.79 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction was once again monitored by ^1H nmr and stopped at a point at which all peaks other than those of the desired product had disappeared. Unreacted bromine and HBr were removed under a nitrogen purge with gentle heating, and the solvent was then evaporated. Sticky orange crystals remained ($2,4,6-(CH_3)_3C_5H_2NBBr_2{}^+Br^-$, 0.789 g, 2.10 mmol, 55.9% yield, mp 107.1-108.3°C, ir: 3050(s),2600(s),1550-1350(vb),780(vb),520(s)cm^{-1}).

5. 2,4,6-Trimethylpyridine-Monoiodoborane.--Iodine (0.440 g, 1.74 mmol) was added to a solution of 2,4,6-trimethylpyridine-borane (0.503 g, 3.73 mmol) in CH_2Cl_2 (20 mL) piecewise over a period of one hour. The yellow solution was filtered and evaporated leaving light yellow crystals (2,4,6-$(CH_3)_3C_5H_2NBH_2I$, 1.00 g, 3.87 mmol, 104% yield, ir: 3060,2720(b),2580(b),1930(w),1500-1350(vb),1260(b),1070(vb), 860(m),540(m)cm^{-1}). The high yield was a result of unreacted iodine in the product. No attempts were made to recrystallize the product.

6. 2,4,6-Trimethylpyridine-Diiodoboronium Iodide.--Iodine (2.28 g, 8.88 mmol) was added to a solution of 2,4,6-trimethylpyridine-borane (0.400 g, 2.96 mmol) CH_2Cl_2 (20 mL) in small increments at room temperature. After all the iodine was added, and after 4 hours of refluxing, the solution was stirred for several days. At the end of that time a ^1H nmr spectrum showed the peaks of the product at a maximum. The solvent was evaporated yielding sticky dark violet crystals (2,4,6-$(CH_3)_3C_5H_2NBI_2^+I^-$, 1.57g, 6.19 mmol, 103.7% yield). The sticky consistency of the crystals and the high yield were presumably the result of I_3^- formed from unreacted I_2 combining with I^- ion. Due to the poor solubility of the product in methylene chloride, any attempt to recrystallize the product only resulted in loss of product. In each case only an oily residue remained.

RESULTS AND DISCUSSION

Previous work done involving this group of aromatic amine-boranes has shown that, in general, a downfield chemical shift of the ^1H nmr signals is observed as larger or addional halogens replace the protons attached to the boron.[15] This downfield shift has been attributed both to inductive deshielding of the protons and to steric compression between the protons in the amine and the halogens attached to boron. However, the trihalogenated aromatic amine-boranes studied showed anomolous effects, which were interpreted as giving evidence for the formation of trigonal boronium cation by the loss of anionic halide. Because of the complexity of the spectra in the aromatic proton region, it was not possible in that earlier study to determine accurately the chemical shifts of the aromatic protons. Additionally no direct evidence for the existence of ions was obtained. This study then set out first to isolate and characterize as many as possible of the products of the earlier systems (2,6-dimethylpyridine-borane and 2-methylpyridine-borane), then to gather definitive evidence for the existence of ions as the ultimate products of halogenation in those systems, and finally to study two additional systems (3,5-dimethylpyridine-borane and 2,4,6-trimethylpyridine-borane) in which much simpler ^1H nmr spectra were expected to be observed, so as to confirm, especially for the aromatic protons, the tentative conclusions drawn in earlier work.

I. ^{1}H nmr

The four sets of aromatic amine-haloboranes examined in this study offer a variety of steric interactions about the N-B bond. The ^{1}H nmr chemical shifts of the various protons for the four boranes are plotted versus degree of halogenation in Figures 14 to 27 and the results are interpreted as follows:

A. 2,6-Dimethylpyridine-Haloboranes.--All of the protons in the amine (Figures 14, 15, and 16) experienced an increased downfield shift during the first two halogenation steps. This is consistent with both the increase of inductive withdrawal ability of the borane and the increase of steric interaction between borane and amine. The third halogenation step, however, resulted in a further downfield shift only for the aromatic protons (Figures 15 and 16). The aliphatic resonance moved back upfield with a corresponding increase in conductivity. This has been interpreted as the result of reaction to the amine-BX_3 being accompanied by immediate loss of X^- to produce a trigonal boronium cation (amine-BX_2^+). With the third halogen added one would have assumed that the adjacent methyl protons would have been deshielded to an even greater extent due to the increased inductive effect and therefore would have shifted downfield. If a trigonal boronium cation were

Figure 14

^1H nmr Chemical Shifts versus Degree of Halogenation

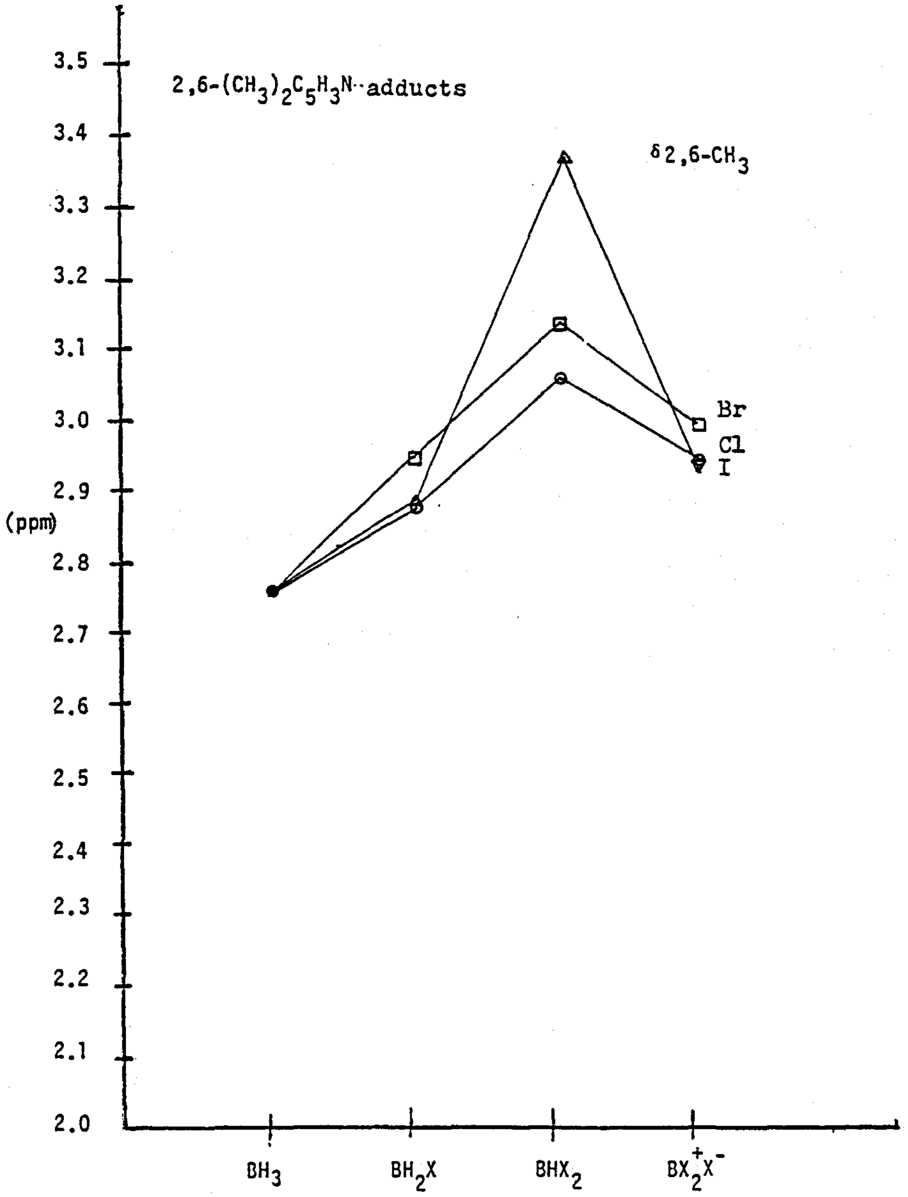


Figure 15

^{1}H nmr Chemical Shifts versus Degree of Halogenation

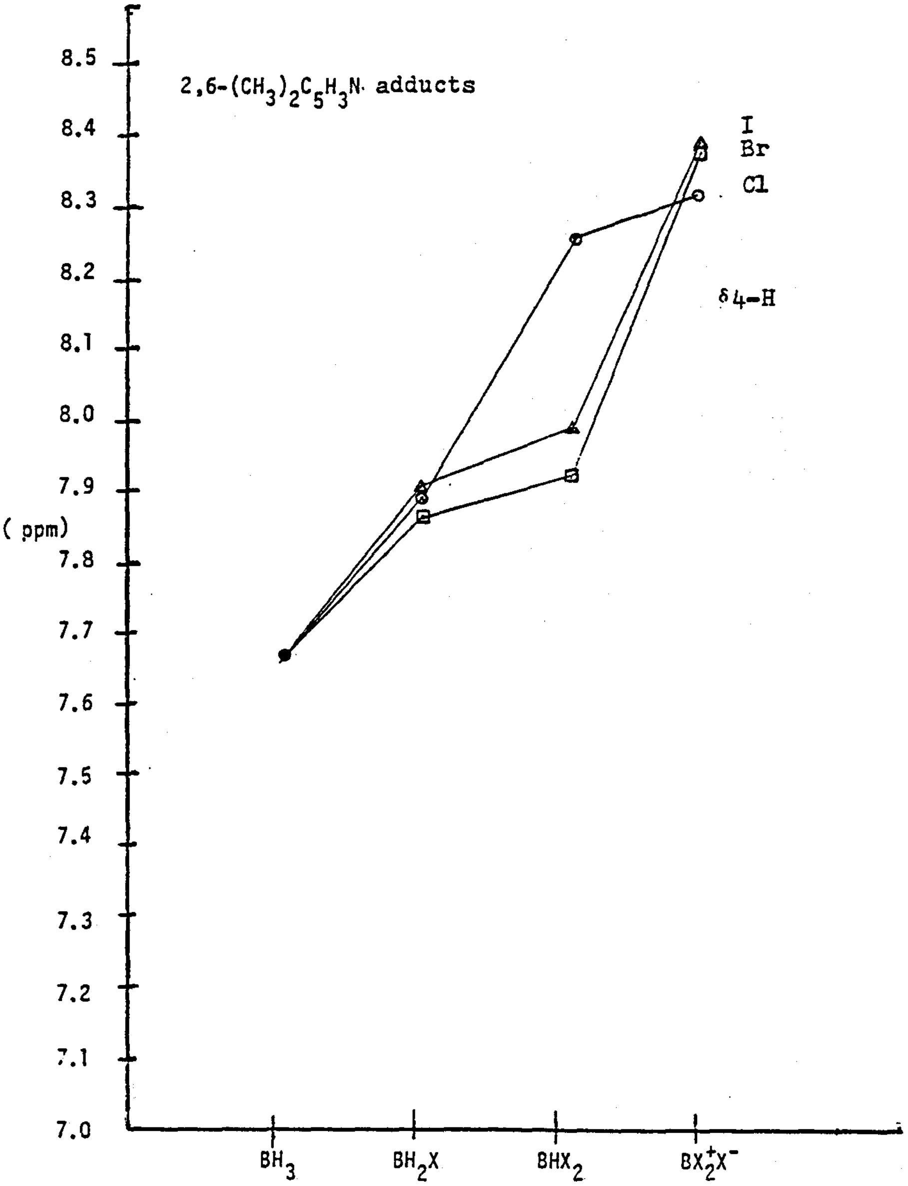
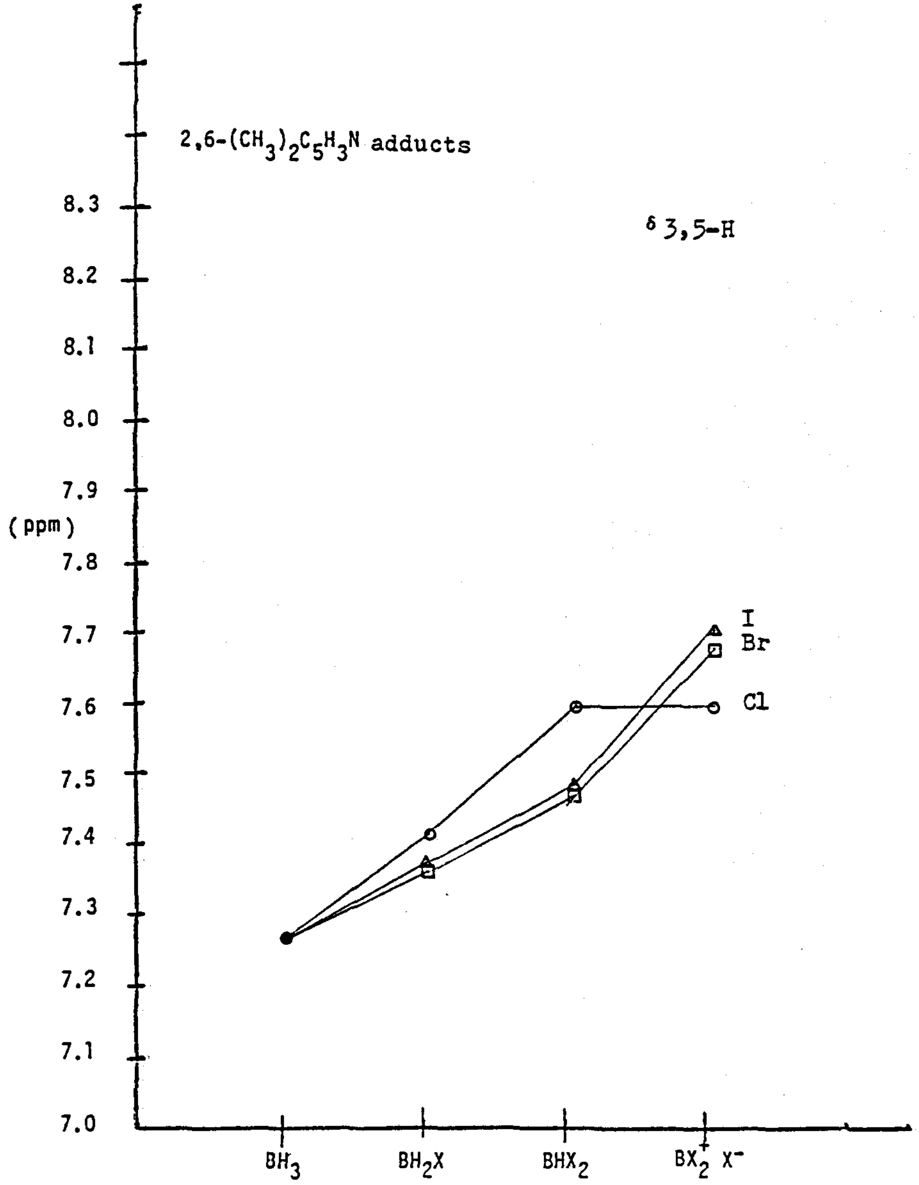


Figure 16

^{1}H nmr Chemcial Shifts versus Degree of Halogenation



to form, this effect should be even more pronounced, due to the introduction of a positive charge at boron. The steric effect resulting from three halogens on boron should also have produced a fairly large downfield shift, but if a trigonal boronium cation were to form, the relief of steric compression as the halide ion came off should cause an upfield shift.* Note that the ring protons which experience no steric compression, shift dramatically downfield as the third step of halogenation occurs. This is consistent with these protons experiencing only inductive effects. The fact that the combination of these two effects resulted in a large upfield shift of the methyl groups at the 2 and 6 position indicated that relief of steric compression was the major influence at those positions as the cation formed.

B. 2-Methylpyridine-Haloboranes.--As in the case of 2,6-dimethylpyridine-haloboranes, all aromatic and aliphatic protons (Figures 17, 18, 19 and 20) experienced an increased downfield shift as the first two halogens were added. This is consistent both with the increased inductive effect and with the increased steric compression expected as larger or additional halogens were added. This trend was still observed even as the third halogen was added, with the 2-CH_3 and 6-H protons moving more dramatically downfield than

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*The assumption of relief of steric strain in this manner requires that the BX_2 group not be coplanar with the ring.

Figure 17

^{1}H nmr Chemical Shifts versus Degree of Halogenation

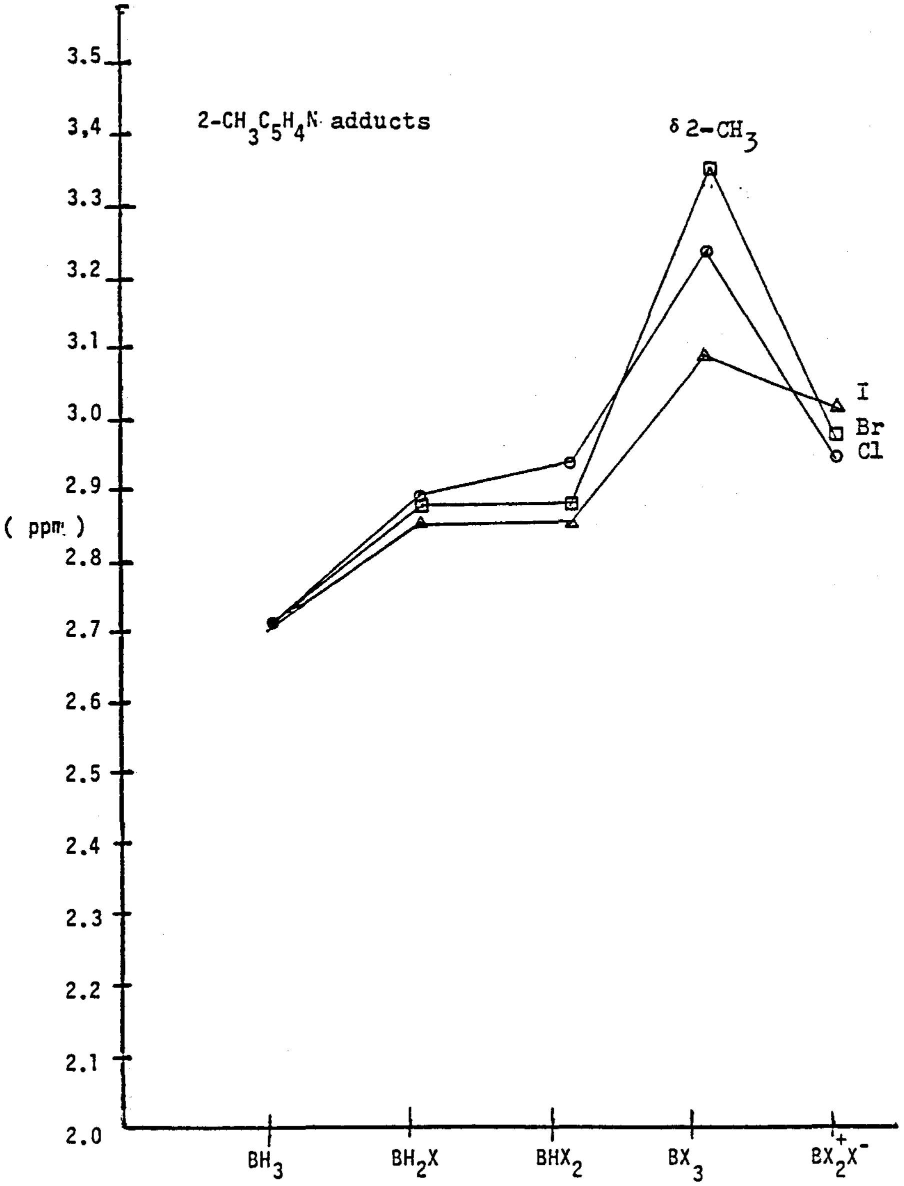


Figure 18

^1H nmr Chemical Shifts versus Degree of Halogenation

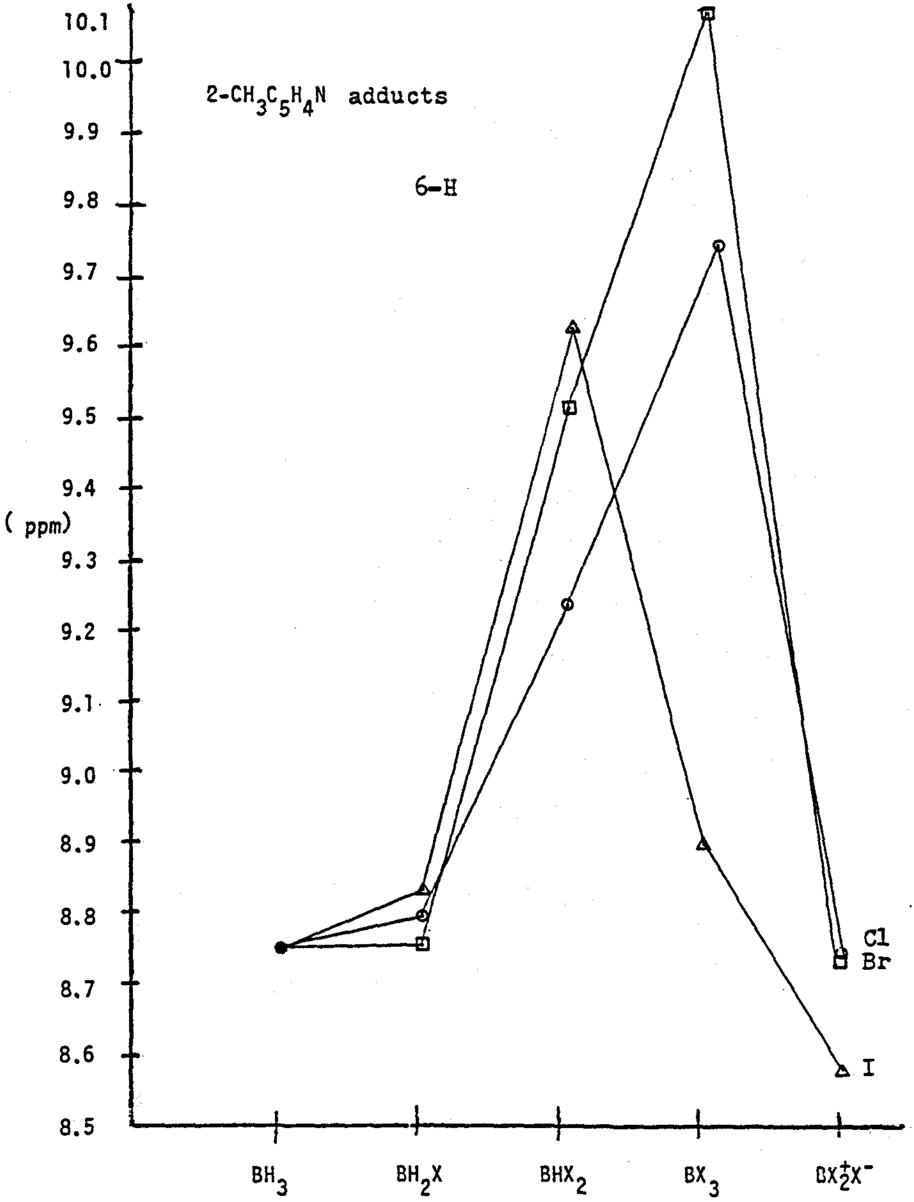


Figure 19

^{1}H nmr Chemical Shifts versus Degree of Halogenation

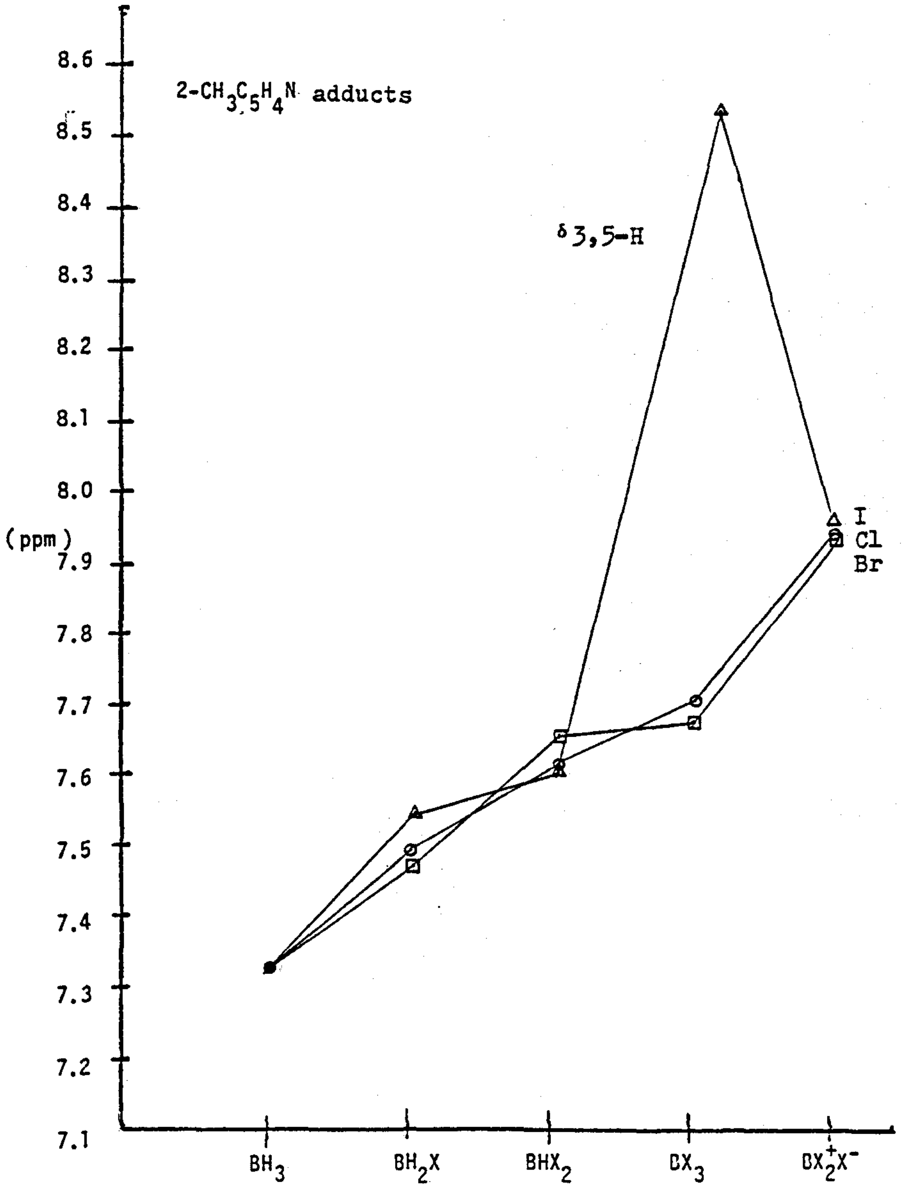
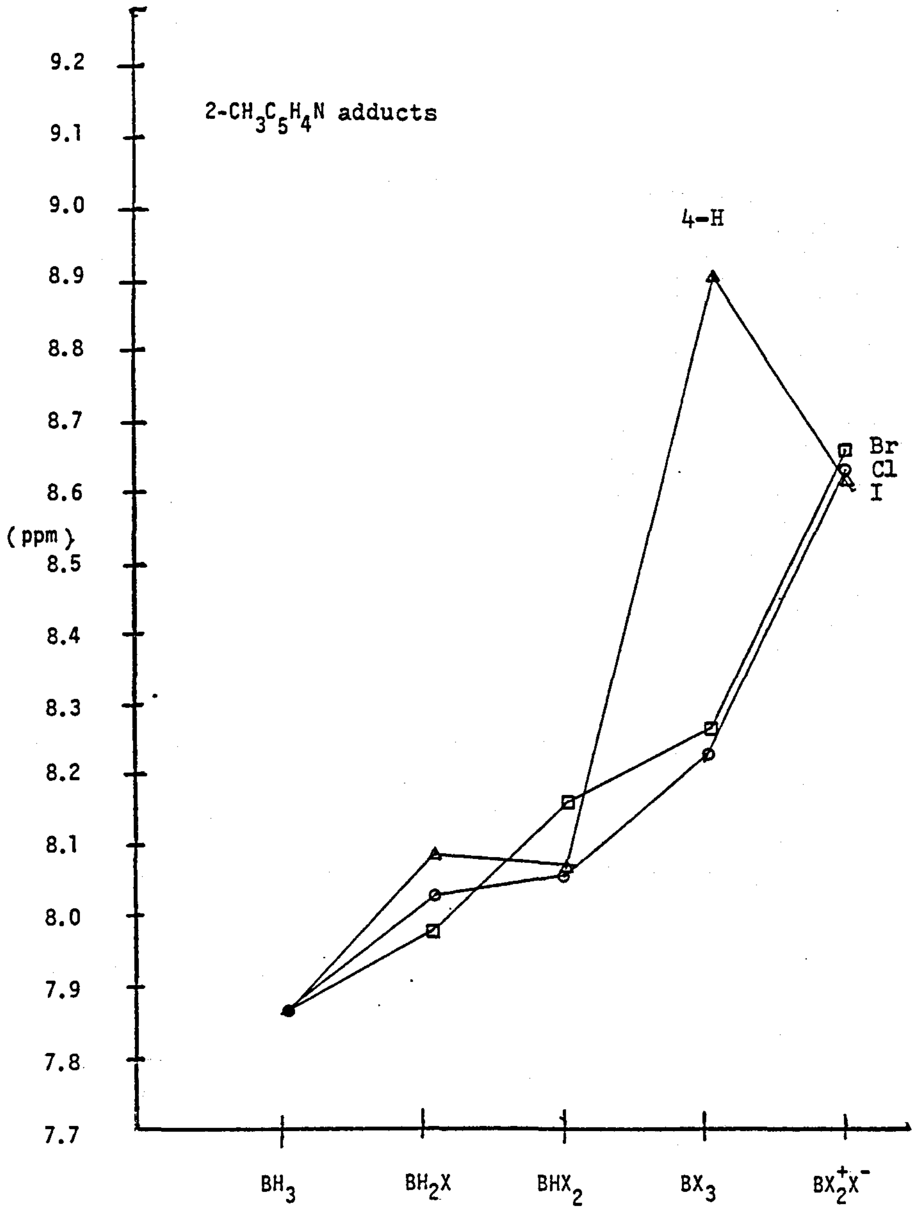


Figure 20

^{1}H nmr Chemical Shifts versus Degree of Halogenation



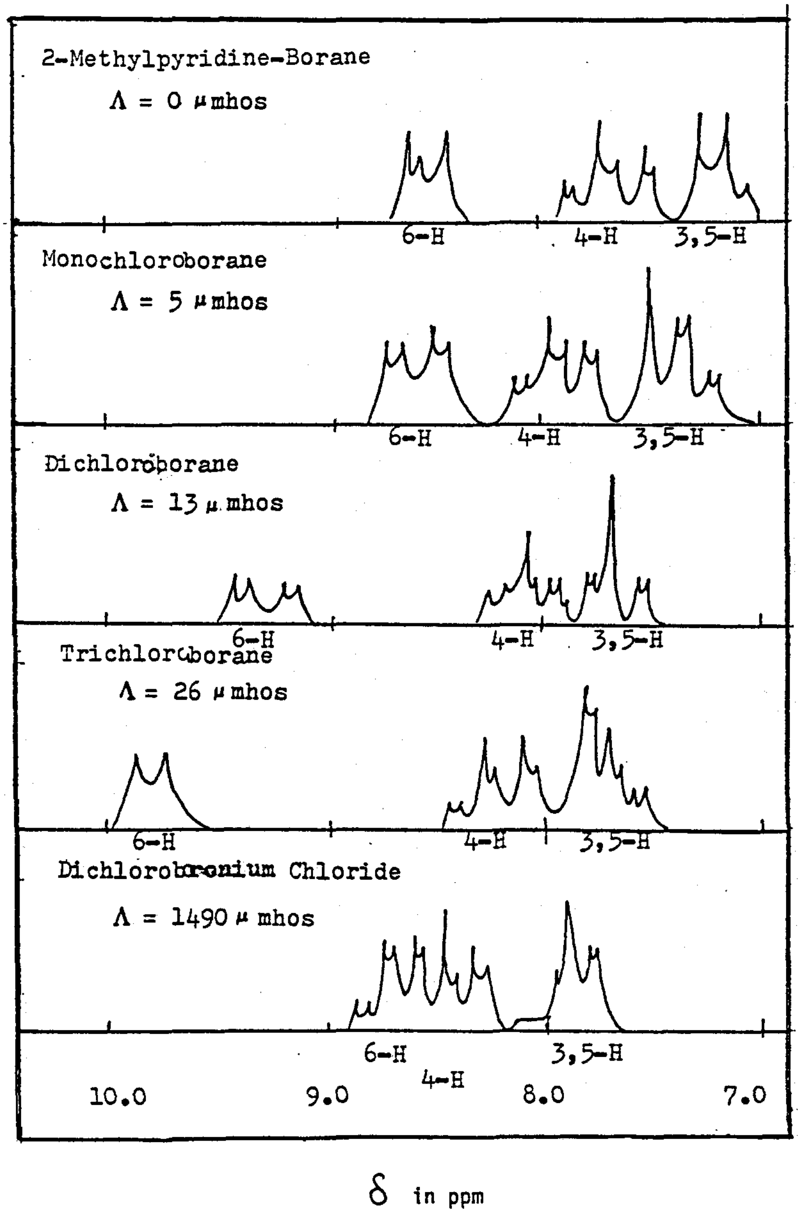
the protons at the 3, 4, and 5 positions. This is consistent with the proposed model in that the 2-CH_3 and 6-H both experienced a combination of steric and inductive effects as the third halogen was added, and thus a larger downfield shift was observed for both. The reaction however did not stop at this point but continued to one more product resulting in some interesting observations in ^1H nmr and conductivity measurements. The peaks representing the aromatic protons at the 3, 4 and 5 positions were observed to shift further downfield whereas the peaks representing the aliphatic 2-CH_3 and the aromatic 6-H (Figures 17 and 18) were observed to shift upfield, all with a corresponding increase in conductivity. This is interpreted as the result of a loss of X^- to produce a trigonal boronium cation with simultaneous relief of steric compression. The introduction of this positive charge should increase the deshielding of all protons by attracting more electron density out of the ring and consequently shifting the signals further downfield. However, along with the formation of positive charge, the 2-CH_3 and 6-H protons experience relief of steric compression and consequently the overall shift for the two sets of protons was an upfield shift, which again implies that relief of steric compression was the dominant effect. The protons at the aromatic 3, 4 and 5 positions, feeling no steric relief would be expected to shift further downfield as the positive charge was formed due to increased inductive effect. Figures 19 and 20 show such behavior. The anomalous behavior of the iodo derivatives may be explained if one assumes that the diiodoborane adduct decomposes to a cation. This would mean that what is in the figures labelled neutral BI_3 adduct is actually a BHI^+ cation adduct. The principal change in the iodo series would then come between the third and fourth species, and the conversion of $2\text{-}(CH_3)C_5H_4NBHI^+I^-$ to $2\text{-}(CH_3)C_5H_4NBI_2^+I^-$ would cause the unusual behavior in the last step.

2-Methylpyridine-borane provided valuable information concerning the combination of steric and inductive effects. This compound was unique of the four compounds studied because only one methyl group was present at the adjacent sites and therefore because of its semi-sterically hindered state the formation of the neutral trihalo-species and of the cation was observed in the same halogenation series. The chemical shifts of the aromatic protons used in plotting were weighted averages of the multiplets observed from actual ^1H nmr data. A representation of that complex coupling (Figure 21) shows the shift of multiplets during chlorination with corresponding increase in conductivity.

C. <u>3,5-Dimethylpyridine-Haloboranes</u>.--Due to the absence of significant coupling between the aromatic protons at the 2, 4, and 6 positions and the $3,5\text{-}CH_3$ protons the ^1H nmr spectrum of 3,5-dimethylpyridine-borane was very simple

Figure 21

^{1}H nmr Pattern for 2-$CH_3C_5H_4NBH_3$ and Derivatives



(three singlets). Of the compounds studied this compound offered the least steric hinderance about the N-B bond, with H occupying both the 2 and 6 positions. Thus it is not surprising that the first, second, and third halogen additions occurred easily. Proton chemical shifts plotted versus degree of halogenation for the 2,6 protons, the 3,5-CH_3 and 4 proton are shown in Figures 22, 23 and 24. A downfield chemical shift was observed for all protons as the first, second and third halogens were introduced. This is consistent with inductive effects expected to be operating in the system. With one exception, roughly equal deshielding of all protons was observed, which is attributed to the fact that little or no steric compression was involved. The exception was in the case of iodine addition, for which the expected downfield shifts were observed as the 1st, 2nd and 3rd halogens were added. Upon standing, the peaks representing the 2 and 6 protons of the triiodinated adduct decreased in intensity as a new peak appeared upfield, and the conductivity of the solution increased dramatically. The observations indicated that an ionic product had formed in this particular case, presumably the amine-diiodoboronium iodide. Because of this exception in the halogenation reactions of 3,5-dimethylpyridine-borane, we can deduce that the steric crowding which occurs between the ring protons at the 2 and 6 positions and the three iodines on boron were small enough to allow

Figure 22

^{1}H nmr Chemical Shifts versus Degree of Halogenation

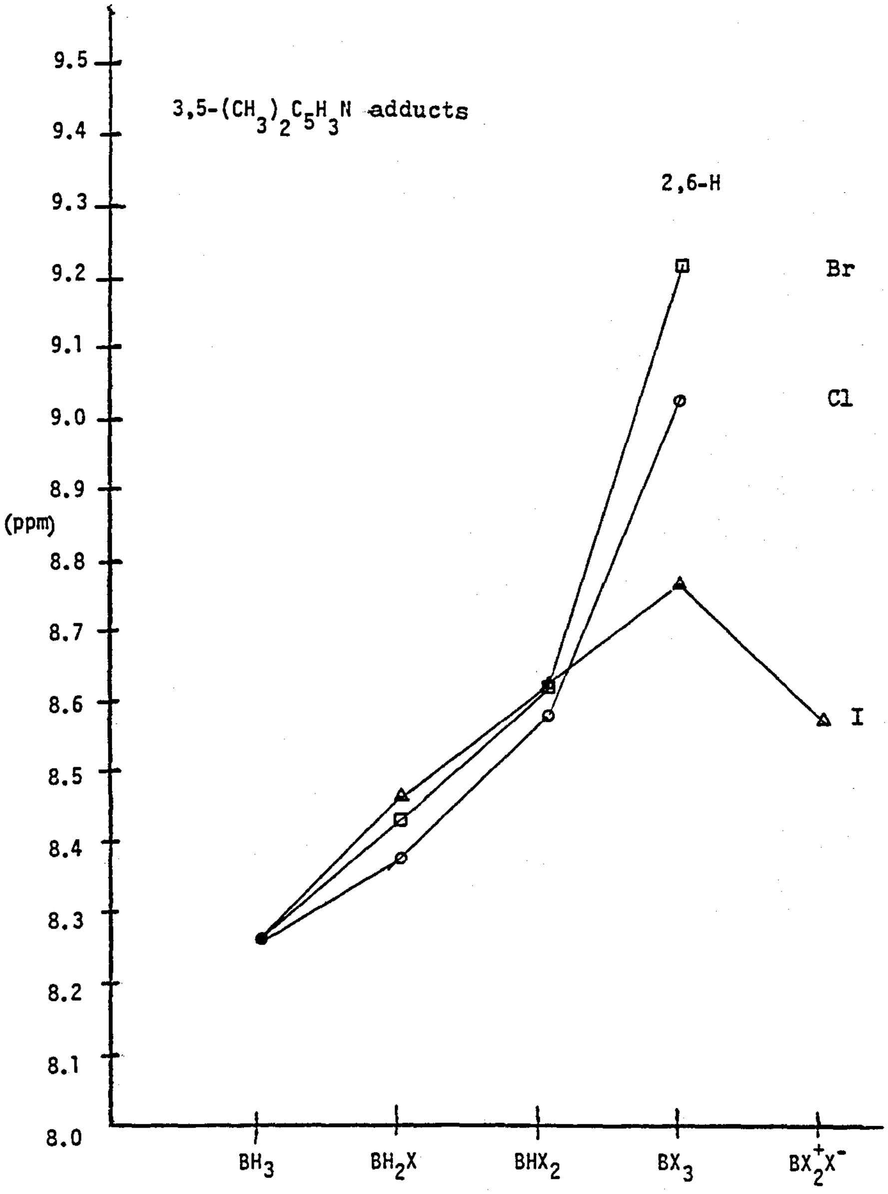


Figure 23

^{1}H nmr Chemical Shifts versus Degree of Halogenation

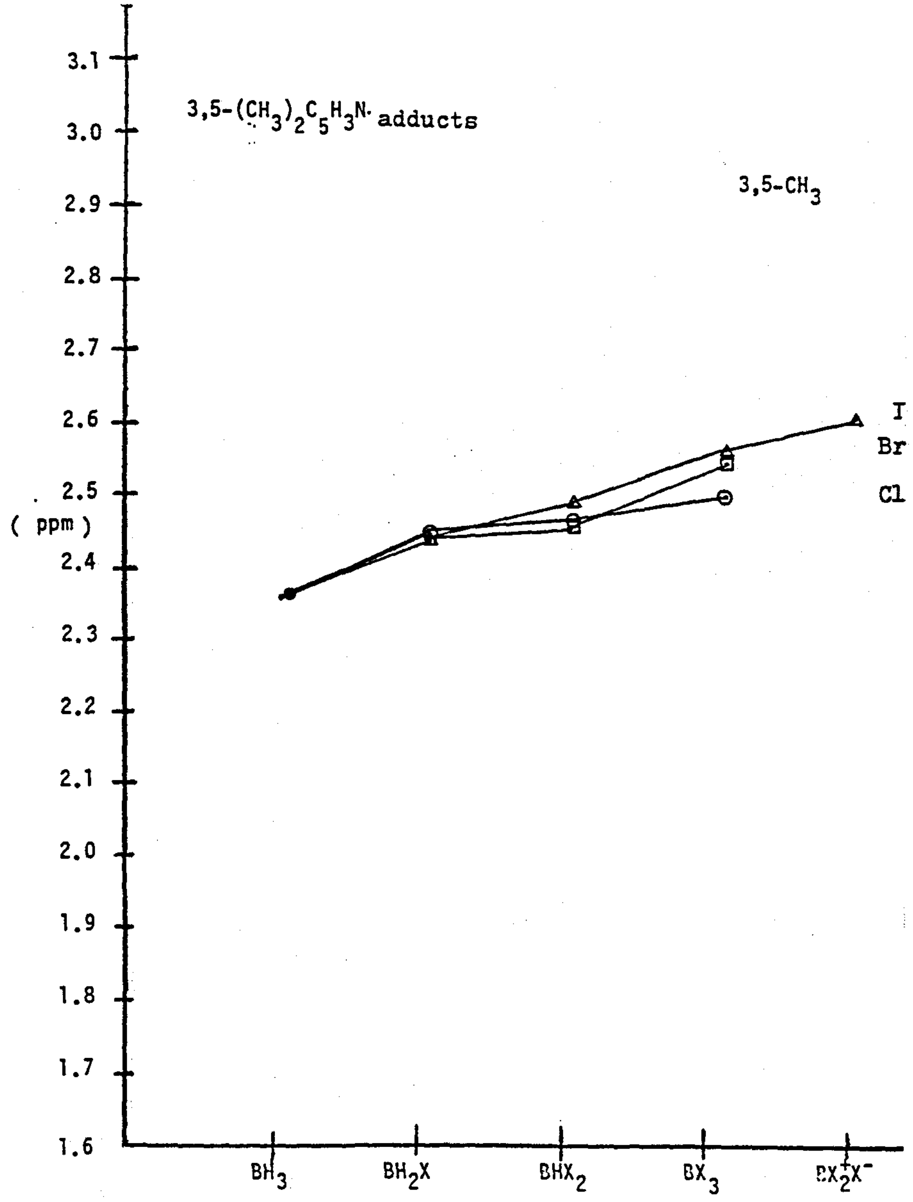
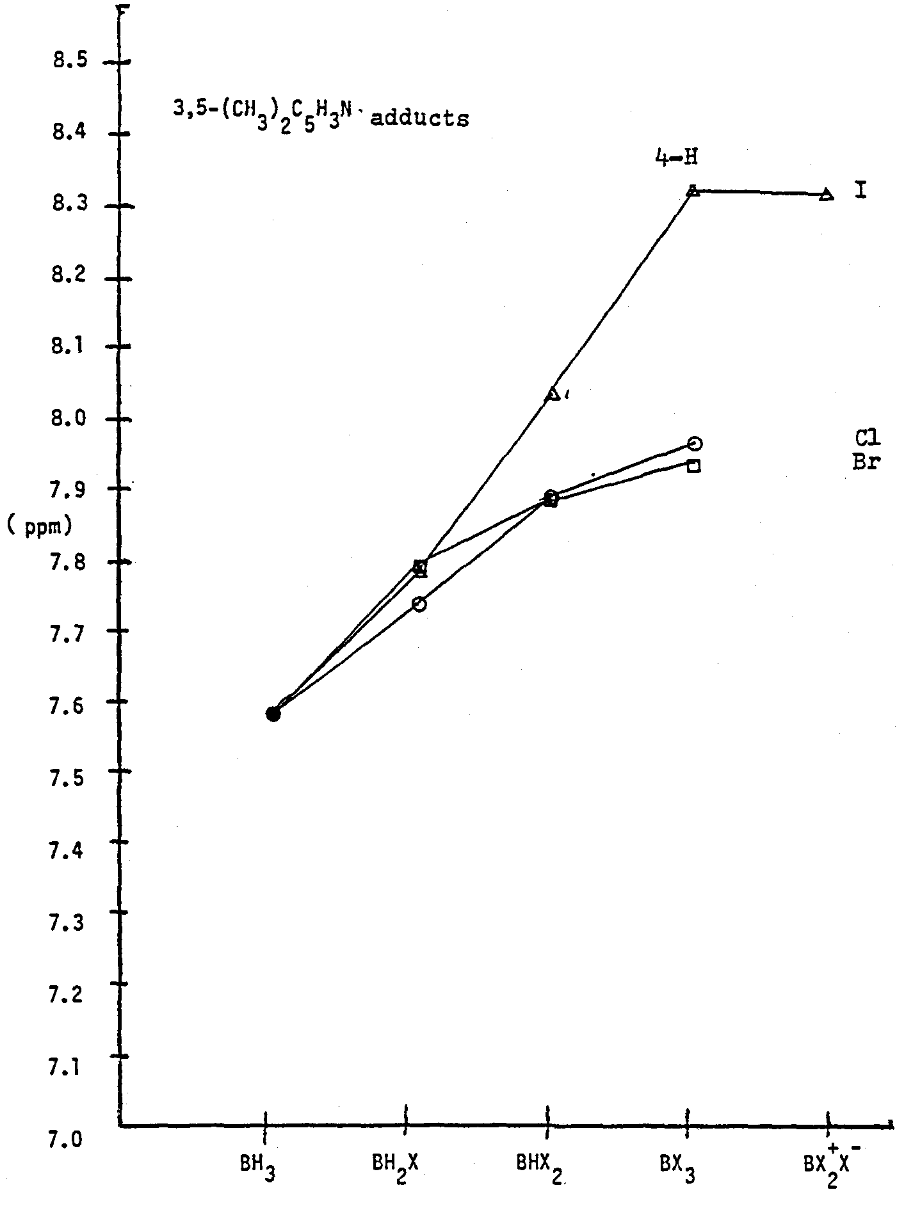


Figure 24

^{1}H nmr Chemical Shifts versus Degree of Halogenation



a neutral triiodo-species to form but were still large enough that over time, conversion did occur to a more stable ionic product. Again the overall shift of the 2,6 protons resulted from a combination of relief of steric compression and increased inductive effects, with the steric effect dominant.

D. 2,4,6-Trimethylpyridine-Haloboranes.--These compounds also showed very simple ^1H nmr spectra, (three singlets), but the shifts of the protons in this amine-borane as halogens were substituted on boron behaved much like those in the 2,6-dimethylpyridine-borane derivatives (See Figures 25, 26, and 27). Downfield shifts were observed for all protons during the addition of the first two halogens. An unidentified intermediate appeared after the first halogen addition, remained during the second addition but disappeared during the third. As the third halogen was added, however an upfield shift was observed for the peaks representing the 2,6-CH_3 protons accompanied by a significant increase in the conductivity of the solution. Once again this is attributed to protons experiencing a combination of steric relief and increased inductive effects accompanying the production of an ionic product. The 4-CH_3 and 3,5-H absorptions were observed to shift dramatically downfield as the conductivity increased. This large downfield shift in position is attributed to increased inductive effects as a result of the introduction of a positive charge into the molecule. On the basis of

Figure 25

^{1}H nmr Chemical Shifts versus Degree of Halogenation

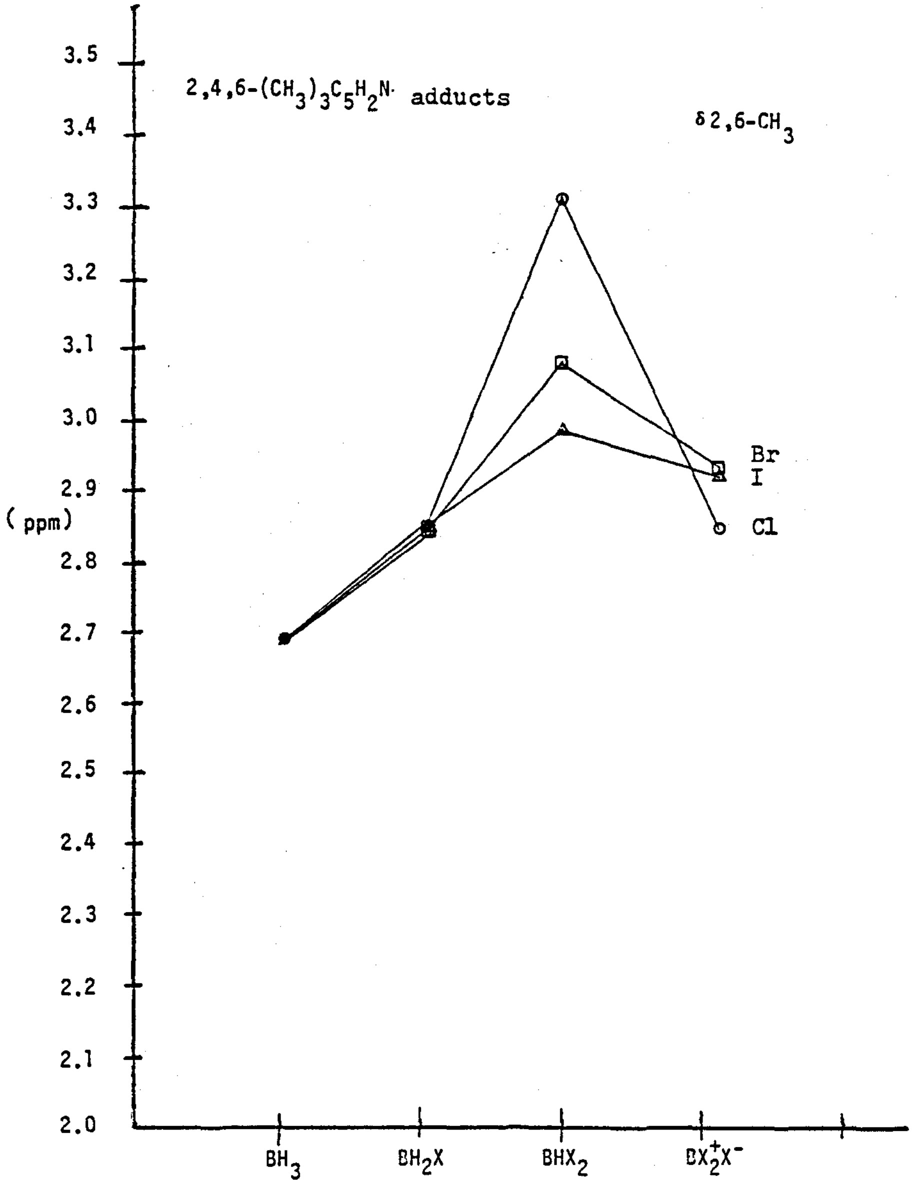


Figure 26

^{1}H nmr Chemical Shifts versus Degree of Halogenation

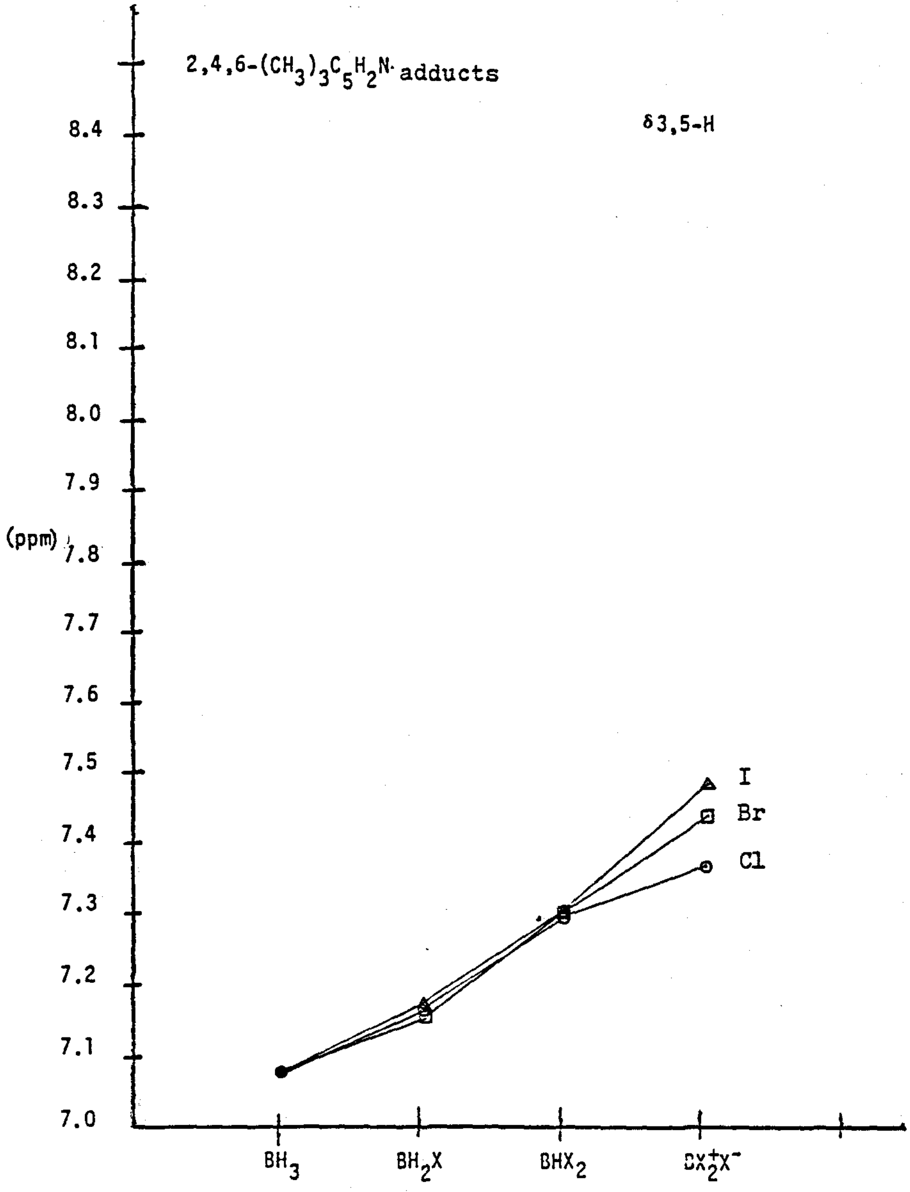
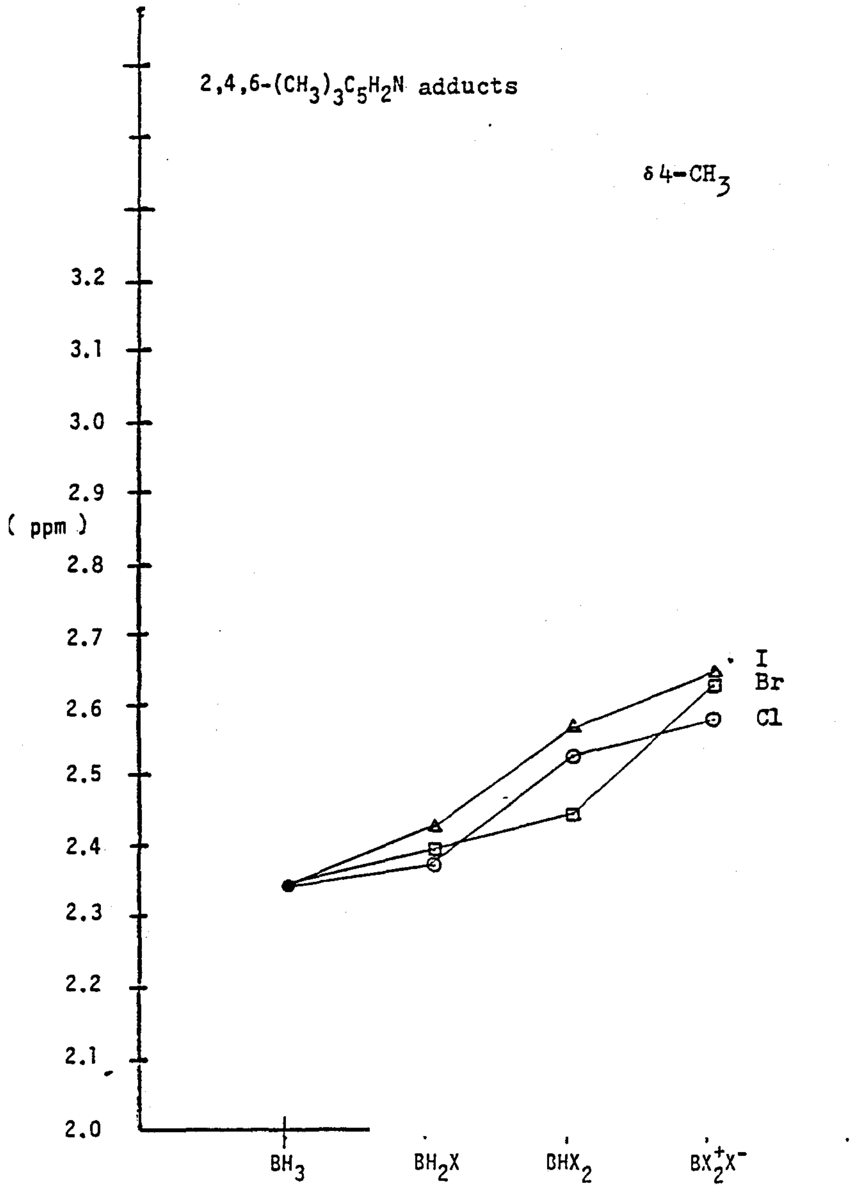


Figure 27

^1H nmr Chemical Shifts versus Degree of Halogenation



induction effects alone, one would have expected the 2,6-CH_3 signal to shift just as dramatically downfield, as those protons would have felt this increase. Because the overall shift observed was upfield we conclude that the effect of relief of steric compression was much larger and therefore was dominant. (Further work could be done in isolation and identification of the intermediate).

II. Product Characterization

A. IR Results.--A characteristic absorption due to B-H stretching was observed between 2500 and 1900 cm^{-1} for all amine-boranes with BH bonds. As hydrogens were replaced by halogens that absorption grew weaker, and absorptions due to B-X (X=halogen) stretching appeared in the region between 800 and 450 cm^{-1}. These changes helped to characterize the isolated products and to confirm the ^1H nmr data.

B. Conductivity.--An extensive conductivity study was done on the halogenation of 2-methylpyridine-borane due to its unique steric characteristics. This compound was the most informative of the four studied, and it was thought that by following this compound closely with frequent conductivity measurements during chlorination, bromination and iodination, many correlations could be made concerning the other compounds. Conductivity measurement were made for each of the three halogenation reactions for 2-methylpyridine-borane beginning with the starting material and continuing through until the final ionic product was isolated. In general, for each of the 2-methylpyridine-borane halogenation reactions, the conductivity was very small as the first, second and third halogens were added. Then over time the conductivity increased as the product began to decompose into ionic species. The ^1H nmr peaks from the 2-CH_3 and 6-H were observed to shift upfield in resonance as all other peaks were observed to shift further downfield. Table IV lists the measured specific conductance of the reaction solution as the trichloroborane adduct of 2-methylpyridine converted to the dichloroboronium cation, along with the measured intensities of the ^1H nmr peaks of the 2-methyl protons in the two species. As the table shows, the conductivity increases with the increase in the intensity of the peak from the cation.

Spotchecks were run on several of the other reactions to confirm observations made, in this experiment. For example, conductivity readings taken during the iodination of 2,6-dimethylpyridine-borane showed only a small conductivity during the first two halogenation steps but as the third halogen was added a dramatic increase was observed. The iodination reaction of 3,5-dimethylpyridine-borane was traced via conductance because of unusual observations made during the ^1H nmr work-up.

C. Mass Spectra.--In addition to ^1H nmr, infrared,

Table IV

2-Methylpyridine-Trihaloboranes
Peak Intensity versus Conductivity

Chlorination	BX_3	$BX_2^+X^-$	
Borane Group	Relative Intensity		Conductivity(μohm^{-1}cm^{-1})
Trichloro	5.5	-	26
Mixture	4.5	1.5	640
Mixture	2.5	2.25	842
Mixture	2.0	5.0	917
Cation + Chloride	-	5.5	1490

Bromination	BX_3	$BX_2^+X^-$	
Borane Group	Relative Intensity		Conductivity(μohm^{-1}cm^{-1})
Tribromo	6.25	-	78
Mixture	5.5	1.25	Σ 209
Mixture	2.75	4.25	591
Cation + Bromide	1.00	5.00	834

and conductivity measurements, mass spectra were run on several 2-methylpyridine-borane derivatives as further proof of structure. The ionic derivatives, 2-methylpyridine-dichloroboronium chloride and 2-methylpyridine-dibromoboronium bromide, were not volatile, as expected for ionic salts. The neutral trihalogenated species, 2-methylpyridine-trichloroborane and 2-methylpyridine-tribromoborane were volatile, and mass spectra of these were obtained. The compounds did not have a molecular ion as such, but they did fragment into identifiable components (Figures 28 and 29).

Both of the trihaloborane adducts of 2-methylpyridine fragmented into two major components, 2-methylpyridine$^+$ and BCl_3^+ or BBr_3^+, and the trichloroborane adduct also showed a fragment at 174 presumably 2-methylpyridine-BCl_2^+ formed by loss of Cl. Fragmentation patterns for each major component were observed. For example, BCl_2^+ and BBr_2^+ were observed, and expected fragments for the 2-methylpyridine were observed. The isotope patterns observed agreed with the theoretical patterns predicted taking into account the natural abundance* of ^{79}Br, ^{81}Br, ^{35}Cl, ^{37}Cl, ^{11}B, ^{10}B, ^{12}C and ^{13}C though the agreement was better for the Br derivative than for the Cl derivative.

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*Approximate isotopic abundances: $^{35}Cl=75\%$, $^{37}Cl=25\%$; $^{79}Br=50\%$, $^{81}Br=50\%$; $^{10}B=20\%$, $^{11}B=80\%$; $^{12}C=99\%$, $^{13}C=1\%$ (for the calculations which follow, ^{12}C is treated as being 100%).

Figure 28

Electron Impact Mass Spectrum of 2-$CH_3C_5H_4NBCl_3$

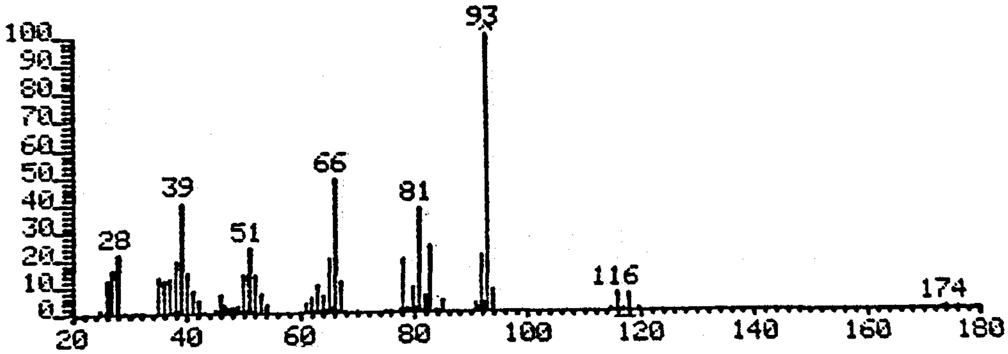
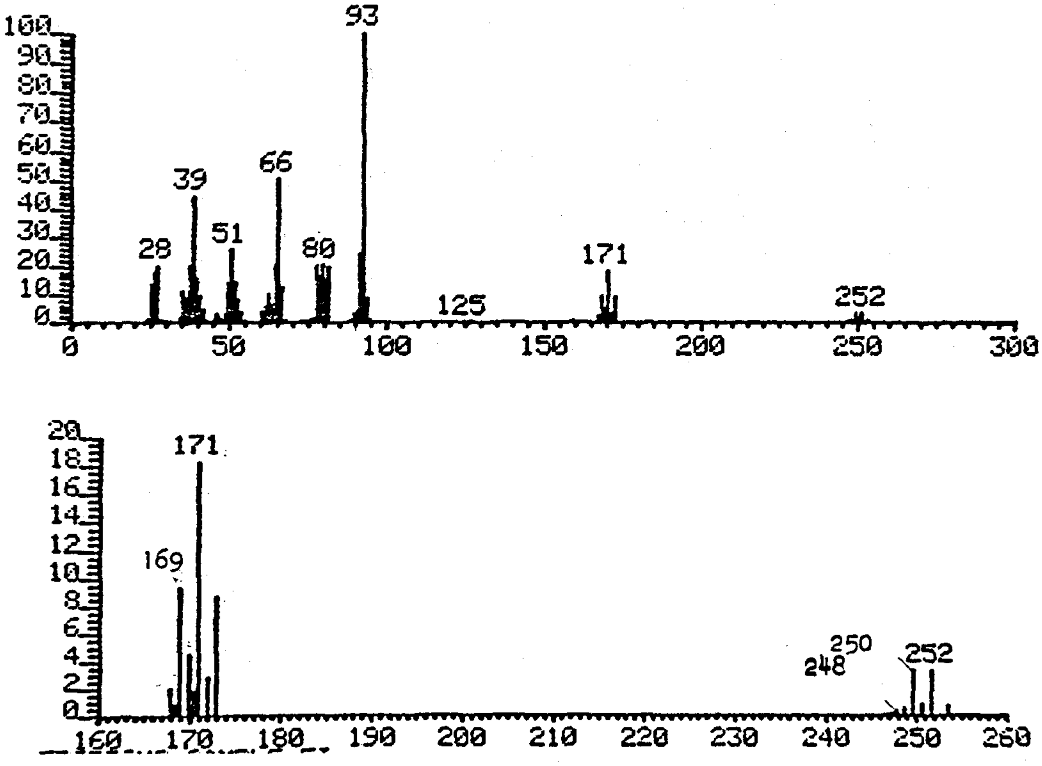


Figure 29

Electron Impact Mass Spectrum of 2-$CH_3C_5H_4NBBr_3$



Tables V and VI show the theoretical pattern expected for the various halogen containing fragments observed and compare the theoretical patterns to the patterns actually observed.

Table V

Mass Spectrum of 2CH$_3$C$_5$H$_4$NBCl$_3$

I. Fragment: 2-CH$_3$C$_5$H$_4$N$^{\cdot +}$ = M.W. = 93 (expect m/e = 93 theor.)
(found = 93 obs.)

II. Fragment: BCl$_3^+$

Isotope Possibilities (m/e)

10	11	10	11	10	11	10	11
35	35	35	35	35	35	37	37
35	35	35	35	37	37	37	37
35	35	37	37	37	37	37	37
115	116	117	118	119	120	121	122

Relative Intensity:	Theoretical	Observed
115 = (1/5)(3/4)(3/4)(3/4)	= 27	14
116 = (4/5)(3/4)(3/4)(3/4)	= 108	108
117 = (1/5)(3/4)(3/4)(1/4)	= 9	14
118 = (4/5)(3/4)(3/4)(1/4)	= 36	108
119 = (1/5)(3/4)(1/4)(1/4)	= 3	-
120 = (4/5)(3/4)(1/4)(1/4)	= 12	14
121 = (1/5)(1/4)(1/4)(1/4)	= 1	-
122 = (4/5)(1/4)(1/4)(1/4)	= 4	-

III. Fragment: BCl$_2^+$

Isotope Possibilities (m/e)

10	11	10	11	10	11
35	35	35	35	37	37
35	35	37	37	37	37
80	81	82	83	84	85

Relative Intensity:	Theoretical	Observed
80 = (1/5)(3/4)(3/4)	= 9	8
81 = (4/5)(3/4)(3/4)	= 36	36
82 = (1/5)(3/4)(1/4)	= 3	4
83 = (4/5)(3/4)(1/4)	= 12	24
84 = (1/5)(1/4)(1/4)	= 1	1
85 = (4/5)(1/4)(1/4)	= 4	4

IV. Fragment: 2-CH$_3$C$_5$H$_4$NBCl$_2^+$

Sum of (2-CH$_3$C$_5$H$_4$N and BCl$_2$)$^+$:

	Theoretical	Observed
173	= 9	10
174	= 36	30–40
175	= 3	--
176	= 12	10–15
177	= 1	--
178	= 4	--

Table VI

Mass Spectrum of $2\text{-}CH_3C_5H_4NBBr_3$

I. Fragment: $2\text{-}CH_3C_5H_4N^+$ = M.W. = 93 (expect m/e = 93 Theor.)
found = 93 Obs.)

II. Fragment: BBr_3

Isotope Possibilities (m/e)

10	11	10	11	10	11	10	11	10	11	10	11	10	11	10	11
79	79	79	79	79	79	81	81	79	79	81	81	81	81	81	81
79	79	79	79	81	81	79	79	81	81	81	81	79	79	81	81
79	79	81	81	79	79	79	79	81	81	79	79	81	81	81	81
247	248	249	250	249	250	249	250	251	252	251	252	251	252	253	254

Relative Intensity: Theoretical	Observed
247 = (1/5)(1/2)(1/2)(1/2) = 1	1
248 = (4/5)(1/2)(1/2)(1/2) = 4	4
249 = (1/5)(1/2)(1/2)(1/2) = 3	3
250 = (4/5)(1/2)(1/2)(1/2) = 12	12
251 = (1/5)(1/2)(1/2)(1/2) = 3	3
252 = (4/5)(1/2)(1/2)(1/2) = 12	12
253 = (1/5)(1/2)(1/2)(1/2) = 1	1
254 = (4/5)(1/2)(1/2)(1/2) = 4	4

III. Fragment: BBr_2^+

Isotope Possibilities (m/e)

10	11	10	11	10	11
79	79	79	79	81	81
79	79	81	81	81	81
168	169	170	171	172	173

Relative Intensity: Theoretical	Observed
168 = (1/5)(1/2)(1/2) = 1	1
169 = (4/5)(1/2)(1/2) = 4	4
170 = (1/5)(1/2)(1/2) = 2	2
171 = (4/5)(1/2)(1/2) = 8	8
172 = (1/5)(1/2)(1/2) = 1	1
173 = (4/5)(1/2)(1/2) = 4	4

CONCLUSIONS AND SUMMARY

The observations presented concerning the halogenation products of 2-methylpyridine-borane and 2,6-dimethylpyridine-borane have confirmed the observations made by Kegley and Tiedemann.[15] Further, the proposed explanations for those observations have been strongly supported, both with the isolation and characterization of many of the products in those systems and with detailed spectral and conductimetric analysis of the reaction systems.

As larger or additional halogens are added in place of hydrogen in these amine-boranes, downfield shifts are observed for the ^1H nmr signals of the 3, 4 and 5 aromatic protons. The same is true for the protons at or in the methyl groups at the 2 and 6 positions of 2,6-dimethylpyridine-borane and 2-methylpyridine-borane for the first two steps of halogenation. However, the third step of halogenation of 2,6-dimethylpyridine-borane is accompanied by an <u>upfield</u> shift of the signals due to the 2 and 6 methyl groups, and although the third step of halogenation of 2-methylpyridine-borane does give an initial downfield shift for the proton at the 6 position and the methyl group at the 2 position, upon standing these signals are replaced by new ones upfield, at the same time as new signals replace those of the 3, 4, and 5 protons at positions much further downfield.* The conductivity changes which accompany these changes clearly indicate the sudden formation of ionic species in the reaction solutions, strongly supporting the proposal that the changes are the result of the loss of halide ion from a trihaloborane adduct giving a three coordinate boronium cation and halide ion.

Mass spectral evidence supported the assignment of structure of the penultimate products in the halogenation of 2-methylpyridine-borane. Identifiable fragments of both 2-methylpyridine-trichloroborane and 2-methylpyridine-tribromoborane were observed, and the isotopic patterens observed confirmed the assignments.

Infrared spectra showed the disappearance of the B-H stretching bands in the 2500-1900 cm^{-1} region as the trihalogenated products formed, and the appearance of bands in the B-X stretching region (800-450 cm^{-1}) confirmed the presence of boron-halogen bonds in all of the halogenation products.

Having confirmed and extended the work on these systems, investigation was made of two new amine-borane systems, chosen to have extremely simple ^{1}H nmr patterns and chosen

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*Fratiello and Schuster[22] in a variable temperature ^{1}H nmr study observed similar behavior for the protons at the 2 and 6 positions in 4-methylpyridine-borane. This shifting was attributed to dipolar solvent interaction, polarization of ligand molecules, electron density effects, and paramagnetic effects.

to provide both more and less steric crowding around the B-N bond. The first, 3,5-dimethylpyridine-borane, having no methyl groups in the 2 or 6 positions, should have little steric interaction between the amine and the borane. Consequently, we predicted that no ionic products should form and that reactions should be fast and clean. This was so, with the exception of the last step of iodination, in which an ionic product was formed. The evidence for this was a large increase in conductivity, accompanying which were the same changes in the ^1H nmr signals as were seen in the earlier cases, namely downfield shifts of the signals of the 3, 4, and 5 protons and an upfield shift of the 2 and 6 protons. As was the case with the formation of the ionic product in the final step of the 2-methylpyridine-borane iodination, there was an apparently neutral product formed which then converted to the ionic product. This implies that there was indeed more room around the B-N bond in the 3,5-dimethylpyridine adducts since only the most crowded adduct, BI_3, showed the decomposition to ionic products, while all three of the 2-methylpyridine adducts decomposed this way. It is possible that prolonged heating or other destructive treatment of the other two 3,5-dimethylpyridine-trihaloborane adducts might have caused their decomposition in a parallel manner, but such behavior was not observed in the isolation procedures to which they were subjected in this work.

The second new amine-borane system studied, 2,4,6-trimethylpyridine-borane, should be at least as crowded as was 2,6-dimethylpyridine-borane, and therefore we predicted that it should behave substantially as did 2,6-dimethylpyridine-borane. With one exception this was the case. The same behavior was observed, including the formation of an ionic product without the neutral trihaloborane adduct being observed. Further, the reactions in this series were more sluggish than any of the corresponding reactions in other systems, consistent with the reactions being the most hindered by crowding around the borane.

The exception was that an unidentified intermediate was observed between the monohaloborane and dihaloborane adducts in all cases. There have been similar intermediates observed from time to time in these systems and in systems like these,[15b] but no determination has yet been made of what they might be. As far as this work is concerned, we note their presence and we leave their isolation and characterization to subsequent workers. The ultimate products and all of the pertinant intermediates were identified.

The evidence obtained in this study justifies the claim that in systems of this sort ^1H nmr shifts are the result of both steric and inductive effects. Further in those cases in which steric and inductive effects oppose, steric effects appear to dominate. The loss of halide ion from one of these trihalogenated amine-borane results both in an increased inductive effect from the introduction of a positive charge in the remaining boronium ion and in a relief of steric compression for those parts of the amine adjacent to the borane group. Since the 3, 4, and 5 protons and methyl goups experience only the inductive effect, they shift downfield at all stages of halogen substitution. The protons and methyl groups at the 2 and 6 positions experience both increased steric compression and increased inductive effects for most of the stages of halogen substitution, but when the halide ion is lost these protons experience a conflicting set of effects. Increasing inductive effects from the introduction of the positive charge and decreased steric compression from the symmetry change as the boron becomes trigonal. Because their overall shift was upfield, we conclude that the relief of steric compression dominated the increased inductive effect.

This report should not be read as an attempt to minimize the importance of inductive forces, but rather we wish to stress the existence of steric effects at work along with inductive effects in systems of this sort. Since the B-N bond is isoelectronic to the C-C bond, we suggest that effects of this sort may be quite general, and that consideration be given to steric effects whenever ^1H nmr spectra are interpreted.

It is interesting in this regard that some of those who have been involved in the pioneering work on inductive effects in amine-haloboranes have recently begun to recognize that other factors may be playing a significant role in determining the nmr spectra of these systems. Recent work by Miller and his group[2] has shown that both ^{15}N and ^{11}B chemical shifts are dominated by "halogen effects" rather than by simple donor acceptor inductive effects. We suggest that these "halogen effects" are actually steric effects, and we suggest that atoms like hydrogen which can be in direct through-space contact with the halogens on boron are more likely to experience these effects than are the nitrogen and boron atoms which are inside the molecule and which would therefore be insulated from such contact.

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BIOGRAPHICAL SKETCH

Debra Hinton Reid was born on February 23, 1955, in Richmond, Virginia, to William and Doris Hinton. She was reared there and graduated from Henrico High School in 1973.

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