

Contribution from the Departments of Chemistry, The University of Florida, Gainesville, Florida 32611, and The University of Richmond, Richmond, Virginia 23173

Exchange of Deuterium for Hydrogen during the Reaction of Dimethylamine-*N-d*-Borane with Halogenating Agents

W. H. MYERS*¹ and G. E. RYSCHKEWITSCH

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During the reaction of dimethylamine-*N-d*-borane with chlorine considerable exchange of hydrogen for deuterium on nitrogen occurred. An extensive investigation of the halogenation reactions of dimethylamine-*N-d*-borane indicated that the exchange process occurred via the loss of deuterium chloride from a molecule activated as a result of halogenation. The extent of substitution of hydrogen for deuterium in the products of these reactions was estimated by comparing NMR and IR spectra.

Introduction

In the course of an NMR investigation,² an *N*-deuterated secondary amine-borane was used as a starting material to prepare several haloborane adducts. An examination of the resulting adducts, however, showed that during the course of the halogenation reactions, some of the deuterium had been replaced by hydrogen, and a few qualitative experiments indicated that the exchange phenomenon was not a simple process. In order that both infrared and NMR data could be used to elucidate the nature of this reaction, a thorough study of the analogous dimethylamine system was undertaken. In previous work,² NMR and infrared data had been collected on authentic dimethylamine-haloboranes; thus, the identification of products was straightforward. (The NMR data are summarized in Table I.) The determination of relative proportions of ND and NH in the products was accomplished in two ways. First, in the infrared spectra of these haloborane adducts, a peak is observed at ca. 3200 cm^{-1} for ν_{NH} and one at ca. 2400 cm^{-1} for ν_{ND} . The ratio of the intensity of these two peaks is a measure of the ratio of NH to ND in the isolated product. When B-H bonds are present, ν_{ND} is overlapped by ν_{BH} so that this comparison cannot be made. Second, in the NMR spectra of these haloborane adducts, a doublet is observed for those undeuterated adducts which have at least one BH bond intact. The fully halogenated adducts show an eight-line pattern (a doublet of quartets), which in the chlorinated case appears as a six-line equally spaced pattern of intensity ratio 1:1:2:2:1:1 because of accidental overlap of two sets of two lines.^{3,4} Since no coupling occurs between the deuterium on nitrogen and the methyl groups, the analogous *N*-deuterated haloborane adducts show a singlet in the cases in which at least one BH bond is intact and a 1:1:1:1 quartet in the cases in which the borane is fully halogenated. Thus, in the partially halogenated products, the ratio of the intensities of the overlapping doublet (NH) and singlet (ND) is a measure of the ratio of NH to ND in the isolated product. In a similar way, for the fully halogenated products, the ratio of the intensities of the outside two lines ($1/4$ of the NH compound intensity) and the center portion (four to six lines) of the spectrum ($3/4$ of the NH compound intensity plus all of the ND compound intensity) may be used as a measure of the ratio of NH to ND in the isolated product.

Experimental Section

Dimethylamine-borane was obtained from Callery Chemical Co. and was used without further purification. Other chemicals and solvents were reagent grade and were used without further purification but were dried over Molecular Sieve 3A where appropriate. Infrared spectra were obtained using either a Beckman IR-10 or a Perkin-Elmer 137 spectrophotometer on samples prepared either as KBr pellets or as CH_2Cl_2 solutions in matched KBr or NaCl cells. Melting points were recorded on a Thomas-Hoover apparatus and are not corrected. Proton NMR spectra were recorded at ambient temperature in CH_2Cl_2 solution with tetramethylsilane (Me_4Si) as an internal standard. The spectra were obtained using either a Varian Model A60-A or a Perkin-Elmer R24-A spectrometer, operating at 60 MHz. The

Table I. NMR Data for Dimethylamine-Haloboranes^a

Amine-borane	$\delta_{\text{CH}_3}^b$	J_{HNCH}^c	$J_{\text{BNCH}}^{c,d}$
$(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$	2.53	5.5	
$(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{Cl}$	2.60	5.5	
$(\text{CH}_3)_2\text{NH}\cdot\text{BHCl}_2$	2.70	5.5	
$(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$	2.92	5.8	2.9
$(\text{CH}_3)_2\text{NH}\cdot\text{BBr}_3$	3.03	5.4	3.4
$(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{I}$	2.76	5.5	
$(\text{CH}_3)_2\text{NH}\cdot\text{BHI}_2$	2.89	5.5	

^a Data from ref 2. ^b In ppm downfield from internal Me_4Si , in CH_2Cl_2 solution. ^c In Hz. ^d Coupling of boron to the methyl protons does not occur when one or more hydrogens are present on boron.⁴

chemical shifts are reported in ppm, downfield from Me_4Si .

Synthesis of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$. A sample of $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ (about 5 g) was added to 40 mL of D_2O and stirred for 2 h, during which time most of the borane dissolved. The borane was extracted from the D_2O with two 40 mL portions of CH_2Cl_2 , and the resulting solution was dried over Na_2CO_3 overnight and then filtered and pumped to dryness. A white crystalline solid remained, mp 34.5–35.5 °C (lit.⁵ mp for $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ 36 °C). The NMR spectrum of the material showed a single peak at 2.53 ppm. The infrared spectrum was identical with that of authentic $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$, prepared from $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ and LiBH_4 .⁶

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Cl_2 . A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 20 mL of CH_2Cl_2 , and Cl_2 gas was bubbled in until the solution turned yellow. (The rate of addition was such that the color change occurred within 10 min.) Volatiles were removed by pumping, and a white solid remained. By NMR and IR analysis, the material was shown to be a mixture of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ in a 1:1 ratio.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Br_2 . A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 25 mL of CH_2Cl_2 , and Br_2 was added dropwise with stirring until the solution turned yellow. (The time of addition was about 15 min.) Volatiles were removed by pumping, leaving a white solid. By NMR and IR analysis, the solid was shown to be a mixture of $(\text{CH}_3)_2\text{NH}\cdot\text{BBr}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BBr}_3$ in a 1:9 ratio.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and I_2 . A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (0.026 g, 0.43 mmol) was dissolved in 5 mL of CH_2Cl_2 and I_2 (0.055 g, 0.22 mmol) added piecewise with stirring. By NMR analysis, the product was shown to be $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{I}$ only.

A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (0.110 g, 1.83 mmol) was dissolved in 15 mL of CH_2Cl_2 . I_2 (0.700 g, 2.73 mmol) was added and the solution stirred for 7 h. By NMR analysis, the product was shown to be $(\text{CH}_3)_2\text{ND}\cdot\text{BHI}_2$ only.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and HCl . A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 25 mL of CH_2Cl_2 , and HCl gas was bubbled in for 30 min. The volatiles were removed immediately thereafter by pumping, leaving a gummy solid. By NMR analysis, the material was shown to be $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ in a 1:3 ratio.

In a separate reaction a sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 25 mL of CH_2Cl_2 , and HCl gas was bubbled in for about 10 min, at which time gas evolution from the solution, which had accompanied the addition, ceased. N_2 gas was then bubbled through the solution to purge excess HCl and samples of the remaining solution were taken for spectral analysis. The NMR spectrum was the same as that observed previously. The IR spectrum was taken using matched KBr liquid cells with CH_2Cl_2 as the reference. The

spectrum showed peaks at 3200 cm^{-1} (ν_{NH} , moderate to weak) and at $2300\text{--}2400\text{ cm}^{-1}$ ($\nu_{\text{BH}} + \nu_{\text{ND}}$, strong). Additionally, a new, very low intensity peak was observed at ca. 1800 cm^{-1} , which is the position expected for ν_{BD} .

For comparison purposes a reaction identical with the one described in the previous paragraph was performed using undeuterated $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ instead of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$. The NMR spectrum was consistent with the product being only $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{Cl}$. The IR spectrum, again taken using matched KBr liquid cells with CH_2Cl_2 as the reference, showed peaks at 3200 cm^{-1} (stronger than in the previous reaction) and at $2300\text{--}2400\text{ cm}^{-1}$ (same intensity as before), but no peak at 1800 cm^{-1} was observed.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ with HCl and Cl_2 . A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 20 mL of CH_2Cl_2 . Both HCl gas and Cl_2 gas were bubbled into the solution, the rate of addition being such that the HCl was added in about 10-fold excess over the Cl_2 . After about 7 min of addition, the solution turned yellow, whereupon the addition of gases was stopped and the volatiles were removed by pumping, leaving a white solid. By NMR and IR analysis, the material was shown to be nearly identical with the solid formed by reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ with Cl_2 alone, i.e., $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ in a 1:1 ratio.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ with DCl and Cl_2 . A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 25 mL of CH_2Cl_2 . Both DCl gas and Cl_2 gas were bubbled into the solution, the rate of addition being such that the DCl was added in about 10-fold excess over the Cl_2 .⁷ After about 20 min of addition, the solution turned yellow, whereupon the addition of gases was stopped and the volatiles were removed by pumping, leaving a white solid. By NMR and IR analysis, the solid was shown to be a mixture of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ in 1:3 ratio.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and HCl at Low Temperature and the Syntheses of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$. A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 8 mL of CH_2Cl_2 and the solution cooled to about -78°C by immersion in a dry ice/acetone bath. HCl gas was bubbled into this solution for 10 min, and then N_2 was bubbled in for 30 min to remove excess HCl. After warming to room temperature, the solution was analyzed. By NMR and IR analysis, the product was shown to be $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ only. (The absence of a peak at 3200 cm^{-1} in the IR spectrum showed the absence of NH bonds.)

In another experiment, the solution of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ and HCl at -78°C was allowed to warm up to room temperature without removing HCl beforehand; this then exposed $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ to HCl at room temperature. The NMR spectrum of this solution after 20 min at room temperature showed no fine structure on the singlet due to $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$.

In another experiment, a sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 8 mL of CH_2Cl_2 and cooled to -78°C by immersion in a dry ice/acetone bath. HCl gas was bubbled in at a moderate rate for 50 min. The resulting solution was then allowed to stand (in a dry ice/acetone bath), and the NMR spectrum was monitored. (The NMR samples were purged of HCl prior to warming to room temperature.) After 8.5 h, the NMR spectrum showed $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ in a ratio of 1:3. After 21 h, the ratio was about 1:9, and after 32 hours, the spectrum showed only $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ to be present. An infrared spectrum of the final solution showed no peak at 3200 cm^{-1} , confirming that the product contained no NH bonds.

A portion of the solution of $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ and HCl at -78°C as prepared above was allowed to warm to room temperature without removing excess HCl beforehand. The NMR spectrum of the solution after 20 min at room temperature showed no fine structure on the singlet due to $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ and Cl_2 . A solution of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ was prepared as described above, excess HCl having been purged from the solution by a stream of N_2 bubbled through the solution. Cl_2 was then bubbled in until the solution turned yellow. (The time required was about 15 min.) The volatiles were removed by pumping, leaving a white solid. By NMR and IR analysis, the product was shown to be a mixture of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ in a ratio of about 1:6.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ and Cl_2 . A solution of $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ was prepared as described above, excess HCl having been purged from the solution by a stream of N_2 bubbled through it. Cl_2 was then bubbled in until the solution turned yellow. (The time

required was about 5 min.) The volatiles were removed by pumping, leaving a white solid. By NMR and IR analysis, the product was a mixture of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ in a 1:8 ratio.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Cl_2 at Low Temperature. A sample of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ (about 0.05 g) was dissolved in 10 mL of CH_2Cl_2 and the solution cooled to -78°C by immersion in a dry ice/acetone bath. Cl_2 was bubbled into the solution for 10 min at which time the solution was yellow. The volatiles were removed by pumping, leaving a white solid. The NMR spectrum of the material showed a quartet, centered at 2.93 ppm with intensity ratios of approximately 10:12:12:10. By NMR and IR analysis, the material was shown to be a mixture of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ in a ratio of approximately 1:20.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ and HCl. A sample of nearly pure $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ (about 0.02 g), prepared as described above by the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Cl_2 at -78°C , was dissolved in 3 mL of 0.12 M HCl in CH_2Cl_2 . The ratio of HCl to adduct was thus about 3:1. The NMR spectrum of this solution was then monitored, but there was no observable change in the spectrum, even after 24 days.

Reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ with HCl and Cl_2 . A sample of nearly pure $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ (about 0.02 g), prepared as described above by the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Cl_2 at -78°C , was dissolved in 15 mL of CH_2Cl_2 , and both HCl and Cl_2 were bubbled into the solution for 30 min. The volatiles were then pumped off, leaving a white solid, the NMR and infrared spectra of which were superimposable on the corresponding spectra of the starting material.

Reaction of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ and DCl. A sample of $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ (about 0.04 g) was dissolved in 1 mL of a 0.22 M solution of DCl in CH_2Cl_2 in an NMR tube, and the NMR spectrum was monitored. There was no observable change in the spectrum, even after 11 days.

Discussion

The following points stand out as the principal results of these experiments:

a. During the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$, $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$, or $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ with Cl_2 , exchange of deuterium for hydrogen on nitrogen occurs. In the case of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ exchange occurs even at -78°C , although the extent of exchange at -78°C is much less than at room temperature.

b. Chlorination and exchange of deuterium for hydrogen on nitrogen both result from the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and HCl. Therefore it is not known whether exchange occurs without chlorination also occurring.

c. At -78°C neither $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ nor $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ nor $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ exchanges deuterium for hydrogen on nitrogen in the presence of HCl.

d. Neither $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ nor $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ exchanges deuterium for hydrogen on nitrogen in the presence of HCl at room temperature within 0.5 h.

e. $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ does not exchange deuterium for hydrogen on nitrogen in the presence of both HCl and Cl_2 within 0.5 h.

f. $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$ does not exchange deuterium for hydrogen on nitrogen in the presence of HCl within 24 days. $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$ does not exchange hydrogen for deuterium on nitrogen in the presence of DCl within 11 days.

g. The addition of HCl in large excess during the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Cl_2 has no noticeable effect on the extent of exchange, while the addition of DCl in large excess during the same reaction markedly reduces the extent of exchange.

h. Bromination of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ to the tribromoborane adduct with Br_2 is accompanied by very little exchange. Iodination with I_2 to the mono- or diiodoborane adduct does not induce exchange at all.

Several plausible mechanisms could be proposed for this exchange process; however, one mechanism appears to be consistent with all of the data.

The idea that direct exchange between an ND bond and an HCl molecule might be the principal mechanism is certainly attractive, but if it were, the addition of excess HCl to the system $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3 + \text{Cl}_2$ should have *increased* the extent

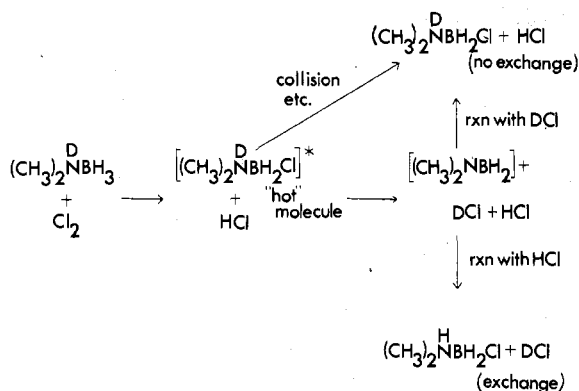


Figure 1. Stepwise mechanism proposed (for the first chlorination step) for the exchange of deuterium for hydrogen on nitrogen in reactions of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$.

of hydrogen incorporation, whereas, in fact, it had no effect at all.

A mechanism requiring that exchange only occur on $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ before *any* reaction takes place to produce halogenated adducts is also attractive, but the fact that significant exchange is observed during the reactions of $(\text{C}-\text{H}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$ with Cl_2 effectively disproves the postulation.

Conversely, any mechanism involving exchange only *after* all halogenation reactions are over is disproved by the fact that HCl does not exchange with $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$, even with Cl_2 present, within the time limits of the reaction.

In reactions which were designed to produce an N-deuterated amine-cyanoborane, Kelly and co-workers noted the presence of peaks at ca. 1800 cm^{-1} in the infrared spectrum of the product which they assigned to BD bonds, implying the scrambling of protons between boron and nitrogen during synthesis.⁸ Evidence on our system cannot completely rule out such scrambling, but the fact that only a very low intensity peak at ca. 1800 cm^{-1} was observed in the products of the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ with HCl implies that if such scrambling does occur, it is only to a negligible extent and that some other process must be the major route for producing NH bonds.

It would not be incorrect to assume that, during the first step of the reaction of $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ and Cl_2 , direct exchange could occur between HCl and unreacted $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$. As evidenced by the reaction of D_2O and $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$ to produce $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$, exchange may occur at nitrogen in the presence of an acidic group, and HCl would certainly qualify. However, once the borane is at least monochlorinated, HCl alone can no longer cause exchange; yet exchange does occur in the presence of Cl_2 . Since the function of Cl_2 is to chlorinate the amine-borane, it would seem reasonable to conclude that the chlorination process momentarily "activates" molecules for exchange.

One mechanism which appears to be consistent with all of the data involves the loss of DCI from an activated (or "hot") molecule still in an excited vibrational state as the result of halogenation, thus producing an aminoborane as an intermediate. If the aminoborane picks up HCl, present in the solution as a by-product of the halogenation reactions taking place, then exchange occurs. If it picks up DCI again, no net exchange occurs. The stepwise equations for this mechanism for the first step of chlorination are shown in Figure 1.

The mechanism would suggest that if chlorination occurs at room temperature, nearly all of the "activated" molecules produced would have the energy required to undergo loss of DCI but that most of the molecules would quickly dissipate that energy by collision or some other thermal path. Thus, in the presence of a certain minimum amount of HCl, the

extent of exchange would be determined almost entirely by the probability that an excited DCI molecule will dissipate its excess energy through the loss of DCI. In other words, the addition of excess HCl would have little effect on the ratio of hydrogen to deuterium on nitrogen in the product. On the other hand, addition of excess DCI would tend to sweep out the HCl produced by reaction, leaving only DCI for exchange, thus reducing the amount of hydrogen incorporated into the product.

Note that this mechanism requires that the intermediate aminoborane molecule have a lifetime sufficiently long so as to allow escape of DCI from the solvent cage. Otherwise, the aminoborane would simply re-add DCI, and no net exchange would have taken place.

The mechanism would also suggest that the energy imparted to the amine-borane as a result of bromination must be less than that imparted as a result of chlorination, in order that the chances be less that a brominated molecule would have sufficient energy to allow it to undergo loss of DBr. Iodination must impart still less energy so that no exchange at all occurs. These ideas are reasonable when one recalls that Cl_2 is a much more powerful halogenating agent than Br_2 toward amine-boranes and Br_2 is more powerful than I_2 .⁹

Two points concerning this mechanism deserve further comment. The first is that the idea of an "activated" molecule as the key intermediate requires not only a reactive step which is *very* energetic but also one which isolates (or concentrates) the energy of reaction in a BCl bond for a finite period of time. A concerted process (as opposed to a radical process, for which precedence exists in systems of this sort¹⁰) would not concentrate the energy effectively since the energy of reaction would be distributed over at least two bonds. Thus, this mechanism would imply a radical process for the halogenation reactions.

A second and related point is the fact that although on statistical grounds one would predict loss of DCI would be *more* likely when more than one chlorine is coordinated to boron, one actually finds *less* exchange occurring. The rationalization which seems the most reasonable is that the energy isolated in one BCl bond at the moment of reaction is quickly distributed over other BCl bonds *if they exist*. This is reasonable because the BCl motions would be expected to be highly coupled to each other when more than one chlorine is coordinated to boron. Therefore, the first halogenation step gives the most exchange because the energy of reaction remains concentrated in one BCl bond for a longer period of time.

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Registry No. $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_3$, 65761-09-3; Cl_2 , 7782-50-5; Br_2 , 7726-95-6; I_2 , 7553-56-2; HCl, 7647-01-0; DCI, 7698-05-7; $(\text{C}-\text{H}_3)_2\text{NH}\cdot\text{BCl}_3$, 13072-44-1; $(\text{CH}_3)_2\text{ND}\cdot\text{BCl}_3$, 65761-10-6; $(\text{CH}_3)_2\text{NH}\cdot\text{BBR}_3$, 54067-18-4; $(\text{CH}_3)_2\text{ND}\cdot\text{BBR}_3$, 65802-27-9; $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{I}$, 65761-11-7; $(\text{CH}_3)_2\text{ND}\cdot\text{BHI}_2$, 65761-12-8; $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{Cl}$, 52920-74-8; $(\text{CH}_3)_2\text{ND}\cdot\text{BH}_2\text{Cl}$, 65761-13-9; $(\text{CH}_3)_2\text{ND}\cdot\text{BHCl}_2$, 65761-14-0.

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