A GENERAL METHOD FOR THE FLUORINATION OF COMPOUNDS CONTAINING BORON-HYDROGEN BONDS

A Thesis Presented to the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

In Partial Fulfillment of the Requirements for the Degree Master of Science

by

John Matthew VanPaasschen

December 1971

ACKNOWLEDGEMENT

This investigation was financially supported by the Research Corporation and the Robert A. Welch Foundation. The author is very grateful for the generous teaching assistantships provided by the Department of Chemistry of the University of Houston which gave not only financial support but also the teaching experience which is so important to this investigator.

Dr. Russell A. Geanangel deserves my sincere thanks for his guidance and support throughout this investigation and in the preparation of this thesis. He always says the right thing at the right time.

Finally, my wife, Kathy, must receive my greatest love and appreciation for remaining her bubbling effervescent self for the duration. Her encouragement and enthusiastic assistance is gratefully acknowledged with love.

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ABSTRACT

A method.for the fluorination of compounds containing boron-hydrogen bonds using anhydrous hydrogen fluoride as the fluorinating agent is described. Trimethylamine-borane and tertiary-butylamine-borane are fluorinated sequentially, forming the heretofore unknown amine-monofluoroborane and the amine-difluoroborane and the known amine-trifluoroborane and ammonium-tetrafluoroborate. Preliminary results are also presented on the methylamine-borane and lithium borohydride systems.

The formation of the new partially fluorinated amineboranes is confirmed. Proton and boron-ll n.m.r. data are presented for all of the trimethylamine-borane and tertiarybutylamine-borane adducts. In addition, fluorine-19 n.m.r. data are presented for the trimethylamine-borane adducts.

This method for the fluorination of hydridic hydrogens on boron requires no special equipment. The reaction can be run in the air (with precautions against excess moisture, in some cases) on a scale greater than 200 millimoles giving yields of better than 80%.

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CHAPTER I

INTRODUCTION

A. Background on trimethylamine-borane, (CH₃)₃NBH₃.

1. Physical properties.

Trimethylamine-borane is a white volatile solid, which sublimes easily at 25° C, and has sufficient vapor pressure to transfer through a -10° C trap using a vacuum system which can attain pressures of 10^{-5} torr. The solid is gummy by nature, stable and nonhygroscopic in air at room temperature. Trimethylamine-borane melts at 92° C (1).

2. Preparations.

Trimethylamine-borane may be purchased but is rather expensive. It may, however, be prepared easily by the reaction (2):

 $(CH_3)_3N + HCl + NaBH_4 \rightarrow (CH_3)_3NBH_3 + NaCl + H_2$ [1] or by the reaction (3):

 $2(CH_3)_3N + B_2H_6 \longrightarrow 2(CH_3)_3NBH_3$ [2]. Reactions [1,2] both give nearly quantitative yields of $(CH_3)_3NBH_3$ of excellent purity. 3. Reactions.

Trimethylamine-borane reacts readily with hydrohalic acids to form the trimethylamine-monohaloborane by the reaction (1):

$$(CH_3)_3NBH_3 + HX \longrightarrow (CH_3)_3NBH_2X + H_2$$
 [3]
(X = Cl, Br, I)

and the dihaloborane and trihaloborane adducts of trimethylamine by the reactions (1,4):

$$(CH_3)_3 NBH_2 X + HX \longrightarrow (CH_3)_3 NBHX_2 + H_2 [4]$$

 $(CH_3)_3 NBHX_2 + HX \longrightarrow (CH_3)_3 NBX_3 + H_2 [5]$
 $(X = Br, I).$

Hydrogen chloride will form the dichloro-trimethylamineborane at an elevated temperature of $150^{\circ}C$ (4) by reaction [4]; however, trimethylamine-trichloroborane has not been prepared by reaction [5].

The mixed hydro-haloboranes of chlorine, bromine and iodine have been prepared by the reaction of trimethylamineborane with a trihaloborane (1,4) in proper stoichiometry as shown below.

$$6(CH_3)_3NBH_3 + 2BX_3 \longrightarrow 6(CH_3)_3NBH_2X + B_2H_6 [6]$$

$$3(CH_3)_3NBH_3 + 2BX_3 \longrightarrow 3(CH_3)_3NBHX_2 + B_2H_6 [7]$$

$$2(CH_3)_3NBH_3 + 2BX_3 \longrightarrow 2(CH_3)_3NBX_3 + B_2H_6 [8]$$

$$(X = Cl, Br, I)$$

Boron trifluoride reacts only by equation [8] to produce trimethylamine-trifluoroborane as the only product, never the mixed hydro-fluoroboranes (1).

Trimethylamine-borane reacts with the hydrides of lithium, sodium and potassium to produce the metal borohydrides and trimethylamine (5):

$$(CH_3)_3NBH_3 + MH \longrightarrow M^+BH_4^- + (CH_3)_3N$$
 [9]
(M = Li, Na, K).

B. Background on anhydrous hydrogen fluoride.

1. Physical properties.

Hydrogen fluoride is a colorless gas at room temperature with a boiling point of 18° C (6). Due to very strong hydrogen bonding, hydrogen fluoride is a very poor ideal gas. The formula is often written (HF)_x where x = 1-4 depending on the pressure and temperature (7). Because of the non-ideal gas behavior of hydrogen fluoride, it is weighed to fix stoichiometries rather than being measured by the ideal gas law.

2. Reactions.

Hydrogen fluoride, unlike the other hydrogen halides, is known to react quite strongly with glass; therefore, reactions involving hydrogen fluoride are generally run in stainless steel or Kel-f apparatus. In 1960 Noth and Beyer reported (1) that they had reacted equimolar amounts of hydrogen fluoride and trimethylamine-borane dissolved in diethyl ether in an attempt to prepare trimethylamine-monofluoro- and difluoroborane by equations [3] and [4], but the only product was trimethylamine-trifluoroborane. These investigators found that only one third of the trimethylamine-borane had been consumed in the reaction and that the yield of trimethylamine-trifluoroborane was virtually 100% based on hydrogen fluoride. Based on this evidence, Noth and Beyer concluded that for kinetic reasons trimethylamine-monofluoro- and difluoroboranes could not be prepared.

CHAPTER II

STATEMENT OF THE PROBLEM

The known compound, diboron tetrafluoride, B_2F_4 , has rather unusual chemistry (8). Certain aspects of the nature of the boron-boron bond are not yet well understood and studies on this subject are hindered by the difficulty in preparing appreciable quantities of diboron compounds such as B_2F_4 . Diboron tetrafluoride is presently synthesized by fluorination of B_2Cl_4 , which is itself prepared by subjecting boron trichloride to an electric or microwave discharge (8). Yields of B_2F_4 seldom exceed 10 millimoles per week. A new, more efficient method for preparing diboron tetrafluoride would greatly assist studies in this area and the research presented in this thesis serves as a basis for such a method.

Diboron tetrafluoride reacts with trimethylamine to form bis(trimethylamine)diboron tetrafluoride (8) by the reaction:

$$2(CH_3)_3N + B_2F_4 \longrightarrow (CH_3)_3NBF_2BF_2N(CH_3)_3$$
 [10].

Bis(trimethylamine)diboron tetrafluoride will react with boron trifluoride to give free diboron tetrafluoride, B_2F_4 , and trimethylamine-trifluoroborane (9) as shown in equation [11]:

$$(CH_3)_3 NBF_2 BF_2 N(CH_3)_3 + 2BF_3 \rightarrow B_2 F_4 + 2(CH_3)_3 NBF_3 [1].$$

Bis(trimethylamine)diborane (4), $(CH_3)_3NBH_2BH_2N(CH_3)_3$, is a known compound (10), related to trimethylamine-borane, but containing a boron-boron single bond. This amine-diboron adduct is not obtained from B_2H_4 (which has not yet been prepared) but is prepared by the reductive coupling of the compound $(CH_3)_3NBH_2Br$. If the hydrogens on boron in $(CH_3)_3NBH_2BH_2N(CH_3)_3$ could be replaced by fluorines without altering the remainder of the molecule, a new route to B_2F_4 might be at hand according to equation [11]. One possible mild fluorination method would involve the use of anhydrous HF as shown in equation [12], giving a direct route to the efficient,

$$(CH_3)_3 NBH_2 BH_2 N (CH_3)_3 + 4HF \longrightarrow (CH_3)_3 NBF_2 BF_2 N (CH_3)_3 [12]$$

large scale preparation of diboron tetrafluoride. Efficient means for the preparation of fluorinated boranes are unknown in the literature (1). The problem, then, was to discover a process by which fluorination reactions could be run efficiently, easily and on a large scale.

Since trimethylamine-borane and bis(trimethylamine)diborane (4) are chemically similar, it was decided that trimethylamine-borane would be a good model system for fluorination. It is known that the other hydrogen halides are effective halogenating agents in such systems, so it seemed that hydrogen fluoride should be a likely fluorinating agent, hopefully lacking in strong oxidative qualities.

It is anticipated that the development of a method for the fluorination of amine-boranes will serve as the foundation for a new method for preparing diboron compounds on a large scale and with less effort than has heretofore been possible.

CHAPTER III

EXPERIMENTAL

A. Apparatus.

1. Vacuum system.

Since many of the compounds used in this investigation have been determined to be moisture sensitive, many reactants, products and solvents were handled in a standard glass vacuum system similar to the one described by Shiver (11). The system consisted of two main manifolds. three reaction trains (one of which was stainless steel), a Toepler system and a low temperature fractionation train. A vacuum of about 10⁻⁵ torr was achieved by the use of a mercury diffusion pump and a mechanical forepump. A liquid nitrogen trap was placed immediately before the mercury diffusion pump to protect it from condensable gases in the system. A Dry Ice-isopropanol trap was placed between the mercury diffusion pump and the forepump in order to protect the latter from mercury vapor. The manifolds were equipped with reaction sites consisting of 9 mm. O-ring joints separated from the manifold by greaseless Teflon stopcocks. The stainless steel manifold also had reaction sites, but these were $\frac{1}{4}$ inch stainless steel Swagelok fittings separated from the manifold by Whitney stainless steel valves. The Toepler system consisted of an automated mercury piston pump which could pump noncondensable gases into a calibrated part of the vacuum system. The fractionation train consisted

of four U-traps and two expansion sections which were calibrated by expanding a weighed amount of carbon dioxide into the train and plotting the results graphically. The fractionation train was used for low temperature fractionations of volatile mixtures as well as for measuring quantities of condensable gases.

2. Dry box.

Manipulations which could not be carried out on the vacuum line but which required a dry, inert atmosphere were carried out in a Lab Con Co dry box. The dry box was equipped with a window, full length gloves and an entrance port. It was continuously flushed with tank nitrogen which had been passed through Linde 4Å molecular sieves, anhydrous calcium chloride and Drierite. Apparatus and samples were first placed in the entrance port and the nitrogen was allowed to flush out oxygen and moisture. The apparatus was then taken into the dry box from the port where the desired manipulations were accomplished. The entrance procedure was reversed in order to take the apparatus back out of the dry box.

3. Reaction vessels.

Reaction vessels for the vacuum system consisted of either a round bottomed flask or a tubular vessel equipped with a large O-ring joint (15 mm.). The reaction vessel was attached to a greaseless Teflon stopcock via the large O-ring joint and attached to the vacuum system via a small O-ring

joint (9 mm.) as seen in Figure 1. With these reaction vessels it was possible to add the nonvolatile reactants in the dry box, then put the apparatus on the vacuum system and add the volatile reactants. When the round bottomed flask was used stirring was accomplished by using a Teflon coated magnetic stir bar (Figure 1b). When the tubular reaction vessel was used stirring was done by a long glass rod with spirals at the stirring end and a piece of iron embedded in the glass at the other (Figure 1a). A solenoid was activated by a four revolution per minute motor. Each time the solenoid was activated the spiralled glass rod would jump or hop. This movement mixed the components of the reaction.

The reaction vessel used for large reactions when the vacuum system was unnecessary consisted of a 300 milliliter three necked flask, each neck having a 24/40 \$ joint as seen in Figure 2. One of the outer necks was equipped with an anhydrous calcium chloride drying tube, the other outer neck was equipped with a rubber septum through which a long hypodermic syringe needle could be passed. The center neck was used for the addition of reactants, either from a pressure compensated dropping funnel or from a lecture bottle of gas. In the cases where hydrogen fluoride was the reactant the center neck was equipped with a cork which fit tightly around a stainless steel tube leading into a lecture bottle of hydrogen fluoride (see Figure 2).



FIGURE 1. REACTION VESSELS



FIGURE 2. SPECIAL REACTION VESSEL FOR HYDROGEN FLUORIDE REACTIONS

4. Nuclear magnetic resonance spectra.

Boron-ll n.m.r. spectra were obtained on a Varian HA-100 high resolution spectrometer using a 32.1 MHz oscillator. Solid samples were run as saturated solutions in a suitable solvent. A capillary containing trimethylborate was placed in the 5 mm. n.m.r. tube and used as an external standard.

Proton n.m.r. spectra were taken on a Varian T-60 high resolution spectrometer at an oscillator frequency of 60 MHz. Solid samples were run as solutions in an appropriate solvent, using tetramethylsilane as an internal standard.

5. Infrared spectra.

Infrared spectra were obtained on a Perkin-Elmer Model 700 infrared spectrometer which produced spectra in the range of 2.5 to 14 microns. Spectra of solid and liquid samples were taken as dilute solutions in an appropriate solvent, usually methylene chloride, using double beam techniques. Gas samples were run at a pressure of about 40 torr in a 5 centimeter gas cell equipped with sodium chloride windows, as seen in Figure 3. Silver chloride windows were used when the spectra of compounds containing fluorine were desired. The 1601 cm⁻¹ absorbance of polystyrene was used to calibrate the spectra.

B. Analytical procedures.

1. Hydrolyzable hydrogen analyses.

In the dry box a small sample (20-40 mg.) was placed in



• • • •

a weighing pig, taken out of the box and weighed on an analytical balance. The pig was then taken back into the dry box where the contents were placed in an hydrolysis vessel. The hydrolysis vessel was a heavy walled flask equipped with a Teflon-to-glass seal which attached to an adapter with a Teflon greaseless stopcock and a 9 mm. O-ring joint. The hydrolysis vessel and weighing pig were taken out of the dry box. The pig was weighed again and the weight of the sample arrived at by difference.

The hydrolysis vessel was placed on the vacuum system at an appropriate reaction site for Toeplerization of any hydrogen given off by the hydrolysis reaction. The vessel was cooled to -196° C, the air pumped away, then about 3-5 ml. of 6 N hydrochloric acid was condensed into the hydrolysis vessel and the stopcock closed. The solution was allowed to warm to room temperature and was stirred magnetically. In some cases it was necessary to heat the hydrolysis vessel to a temperature as high as 100° C in order to achieve complete hydrolysis. After 24 hours the vessel was cooled to liquid nitrogen temperature, the stopcock opened and any noncondensable gases were Toeplerized. The stopcock could then be closed again and the procedure repeated in order to check for complete hydrolysis.

2. Boron analyses.

In cases in which boron analyses were to be performed on

samples which had undergone hydrolyzable hydrogen analysis the acidic contents of the hydrolysis vessel were washed into a beaker and the pH was adjusted to 6.8 with NaOH. The solution was then saturated with mannitol and back titrated to pH 6.8 with standard .119 N NaOH. The per cent of boron could then be calculated from the volume and normality of NaOH needed for neutralization.

Other boron analyses were carried out using an 8 milliliter, semimicro Parr-bomb (12). In the dry box a small sample (not more than 40 mg.) was placed in a weighing pig, taken out and weighed on an analytical balance, then returned to the dry box where the contents were placed in the bomb. The bomb was charged with about .2 grams of $KClO_{ll}$ (accelerator), 4.0 grams of Na_2O_2 (oxidizer) and 40 milligrams of benzoic acid. Great care was taken in mixing the contents of the charge in order to insure a homogeneous mixture with no lumps. The bomb was sealed and taken out of the dry box. With a pair of tongs the bomb was held in the hottest part of a gas-oxygen flame for 30 seconds to a minute to set off the charge, then cooled in running distilled water. The cooled bomb was opened and placed in a 250 milliliter beaker containing about 75 milliliters of warm water. After about an hour the bomb was removed from the beaker with washing. The solution was made strongly acidic with concentrated HCl (12 N), then the pH was adjusted to 6.8 with NaOH and the analysis carried out as des-

cribed previously.

3. Fluorine analyses.

Fluorine analyses were carried out by the Parr-bomb technique described previously (12). About 10 grams of NH_4 Cl was then added to the warm solution containing the contents of the bomb. This solution was heated until the evolution of ammonia had ceased. The solution was then allowed to cool to room temperature. A 2 N CaCl₂ solution was added dropwise until the precipitation of CaF₂ was completed. The solution was filtered through a weighed crucible containing a sintered glass filter. The crucible was dried at 120° C to constant weight. The weight of CaF₂ could be arrived at by difference.

4. Nitrogen analyses.

Nitrogen analyses were carried out by the standard Kjeldahl method. A sample of not more than 40 milligrams was placed in a digestion tube connected to a reflux bulb and condenser. About 20 milliliters of 12 N NaOH was syringed into the digestion tube through a side arm equipped with a rubber septum. The digestion tube was then heated to 200-250 °C until three-fourths of the solution had condensed into the collection beaker which contained 4% boric acid with a known pH of 4.36. The boric acid-ammonia solution was then back titrated with standard .119 N HCl to a pH of 4.36. The per cent of nitrogen could then be calculated from the volume and concentration of the hydrochloric acid used. It was found that

running a blank was, in general, unnecessary provided that ammonium compounds were kept out of the hood during the analysis and provided that the analysis did not take more than two or three hours.

5. Molecular weight determinations.

Molecular weight determinations were done cryoscopically in an apparatus similar to that described by Jolly (13) (see Figure 4). The apparatus was made up in the inner tube equipped with a rubber stopper through which a Beckman differential thermometer was passed. The stopper was also equipped with a hole plugged with a rubber septum and a hole plugged with a glass tube about 2 feet long sealed at one end. A long glass rod with a spiral on the stirring end and an iron nail embedded in the glass on the other end was placed inside the glass tube which was put in a solenoid. When the solenoid was activated the glass rod "hopped" causing stirring. The inner tube was surrounded by an outer tube which caused an air space between the cooling bath and the sample. The outer tube was placed in a dewar of water kept at $2-4^{\circ}$ C below the freezing point of pure solvent.

Most molecular weight determinations were run using dimethylsulfoxide as the solvent. To determine the cryoscopic constant of dimethylsulfoxide three samples of pure solvent were run to determine the freezing point of pure dimethylsulfoxide. A five milliliter sample was injected with a



FIGURE 4. CRYOSCOPIC MOLECULAR WEIGHT APPARATUS

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hypodermic syringe through the rubber septum as described previously. The temperature of the solution was recorded every 30 seconds for at least 15 minutes after supercooling was observed. The freezing point was then obtained from the cooling curve. Three solutions of trimethylamine-borane were prepared in 50 milliliter erlenmeyer flasks capped with rubber septa. Each solution had an accurately known, but different, concentration. Three samples of each solution were run as described previously. The experimental cryoscopic constant could then be determined from the known molality of the trimethylamineborane solution and the difference in freezing point of the pure solvent and the solution. The cryoscopic constant for dimethylsulfoxide was found to be $3.78^{\circ}/m$ (lit. (14) $3.83^{\circ}/m$).

Samples of an unknown molecular weight were handled as was previously described for trimethylamine-borane. Having found the difference in freezing points between the pure solvent and the solution and knowing the molality of the solution and the cryoscopic constant, the molecular weight could easily be determined using the equation:

Molecular Weight = (K_c)(molality)/△T. C. Starting materials.

Trimethylamine-borane was obtained from the Callery Chemical Company. In most cases it was used without further purification; however, when higher purity was required the

trimethylamine-borane was sublimed from the room temperature portion of the sublimation apparatus to a cold finger kept at -78 °C with Dry Ice.

2. Anhydrous hydrogen halides; HF, HCl, HBr.

Anhydrous hydrogen halides were obtained from the Matheson Gas Company in lecture bottles. The purity of the hydrogen halides was high enough that no further purification was necessary for the purposes of this investigation.

3. Sodium borohydride, NaBH₄.

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Sodium borohydride was obtained from the Matheson Chemical Company and was used without further purification. 4. Tert-butylamine, (CH₃)₃CNH₂.

Tert-butylamine was obtained from the Eastman Chemical Company and was found to be of sufficient purity to require no further purification.

5. Boron trihalides; BF₃, BCl₃, BBr₃.

Lecture bottles of the boron trihalides, BF_3 and BCl_3 , were obtained from the Matheson Gas Company. In most cases they were used without further purification.

When higher purity was required, the boron trifluoride was fractionated through a -160° C trap (isopentane slush) into a -196° C trap (liquid nitrogen). The purer boron trifluoride was found in the -196° C trap and used without further purification.

When high purity boron trichloride was required, it was

fractionated through a -78° C trap (Dry Ice-isopropanol slush), a -lll^oC trap (trichlorofluoromethane slush) and a -196^oC trap. The purer boron trichloride was found in the -lll^oC trap. Hydrogen chloride, found in the -196^oC trap, was found to be the major contaminate in the boron trichloride.

Boron tribromide was obtained from the American Potash and Chemical Corporation and purified by a slow fractionation through a $^{1}-45^{\circ}$ C trap (chlorobenzene slush), a -78° C trap and a -196° C trap. The purer boron tribromide, found in the -78° C trap, was condensed into an all glass storage vessel equipped with a Teflon stopcock and stored under vacuum until needed. 6. Solvents.

a. Ethers. Diethyl ether, $(C_2H_5)_20$; glyme, $CH_3OCH_2CH_2OCH_3$; diglyme, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$; and tetrahydrofuran, C_4H_80 .

Ether solvents were dried by refluxing them first over CaH_2 , then over a mixture of CaH_2 and $LiAlH_4$. The dry solvents were then distilled under vacuum into all glass storage vessels equipped with Teflon stopcocks and stored under vacuum until needed.

Diglyme, because of its low volatility, was distilled off of the CaH_2 , $LiAlH_4$ mixture at $100^{\circ}C$. The middle portion of the distillation was stored in a flask equipped with a rubber septum in the dry box.

b. Methylene chloride, CH₂Cl₂.

Methylene chloride was dried by prolonged stirring over CaH₂, then over a mixture of CaH₂ and NaH. The dry solvent was distilled under vacuum into a storage vessel as previously described and stored under vacuum until needed.

Nanograde benzene was obtained from the Matheson Chemical Company and used as needed without further purification.

7. Preparations.

a. Tert-butylamine hydrochloride, $C_4H_9NH_3^+Cl^-$.

Tertiary-butylamine hydrochloride was prepared by the direct interaction of tertiary-butylamine and anhydrous hydrogen chloride (15). In a typical preparation, 20 milliliters of tert-butylamine was dissolved in 100 milliliters of anhydrous diethyl ether and placed in a 500 milliliter erlenmeyer flask. Anhydrous hydrogen chloride from a lecture bottle was then bubbled through the ether solution until no more solid formed. When the reaction was completed the flow of hydrogen chloride was stopped and the solution filtered through a buchner funnel. The solid, tertiary-butylamine hydrochloride, was washed with diethyl ether, air dried for a short time and stored until needed.

b. Tert-butylamine-borane, $C_4H_9NH_2BH_3$.

Tertiary-butylamine-borane was prepared from the reaction of tertiary-butylamine hydrochloride, prepared as previously described, and sodium borohydride (15). Equimolar amounts of tertiary-butylamine hydrochloride and sodium borohydride were weighed out and placed into a round bottomed flask. Glyme was added as the solvent and the flask was stoppered. The cork stopper was equipped with a glass tube which was attached to a mineral oil bubbler so that the rate of hydrogen evolution could be monitored. The reaction was stirred magnetically until no further hydrogen was evolved, about 12 In order to recover the product the reaction mixture hours. was filtered through a fritted funnel containing a frit of medium porosity. This filtration removed the sodium chloride and any unreacted sodium borohydride or tertiary-butylamine hydrochloride, all of which are only slightly soluble in glyme. The glyme was distilled from the filtrate under vacuum leaving tert-butylamine-borane, a white crystaline solid, in the bottom of the flask. When higher purity was necessary the solid was recrystalized from benzene with hexane. The purity of the product was checked with proton n.m.r. The tertbutylamine-borane was stored in a desiccator until needed.

- D. Fluorination of boranes.
- 1. Trimethylamine-borane, (CH₃)₃NBH₃.

A measured quantity of $(CH_3)_3NBH_3$ was placed in a 300 ml. three necked glass flask (as shown in Figure 2) containing about 150 ml. of benzene. The flask was then placed in an ice bath and stirred magnetically. Before hydrogen fluoride addition was begun about .4 ml. of the solution was

withdrawn and placed in an n.m.r. tube and the proton spectrum The contents of the n.m.r. tube were then transferred run. back into the reaction vessel. Hydrogen fluoride was slowly added directly from the lecture bottle for some period of time depending on the reaction size. Another sample was withdrawn,* the proton n.m.r. spectrum run, and the sample returned to the reaction vessel. For a one-hundred millimole reaction the first two additions of hydrogen fluoride were ten minutes in duration at a rate of about one observable bubble every two seconds. The third and fourth additions were usually for five minutes each at the same rate and, as the desired end point of the reaction was approached, additions were carried out for shorter and shorter periods of time. Near the end point, the reaction was warmed to laboratory temperature between additions to insure complete consumption of the hydrogen fluoride in solution. This procedure was continued until the methyl resonance of trimethylamine-borane had disappeared and only the methyl resonance of the desired product, (CH₃)₃NBH₂F, (CH₃)₃NBHF₂, or (CH₃)₃NBF₃ was observed.

The proton n.m.r. spectra of the reaction sequence can be seen in Figure 5. The starting material, $(CH_3)_3NBH_3$, has a methyl resonance at 2.58 ppm (Figure 5a). As HF is added, the $(CH_3)_3NBH_3$ peak can be seen to become less intense as the *The n.m.r. tube cap was provided with a small hole to relieve pressure due to small amounts of hydrogen released when the sample warmed to the temperature of the T-60 probe $(35^{\circ}C)$.

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REACTION SEQUENCE

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FIGURE 5.

TRIMETHYLAMINE-BORANE, HYDROGEN FLUORIDE REACTION SEQUENCE

peak due to the methyl resonance of $(CH_3)_3 NBH_2 F$ arises at 2.42 ppm (Figure 5b). Figure 5c shows the point in the addition of hydrogen fluoride at which the reaction would be stopped if the product desired were $(CH_3)_3NBH_2F$ (a slight excess of HF has been added); however, if $(CH_3)_3NBHF_2$ is desired, more hydrogen fluoride is added and the peak due to $(CH_3)_3NBH_2F$ loses intensity and the peak due to the methyl resonance of (CH₃)₃NBHF₂ arises at 2.32 ppm (Figure 5d). Figure 5e shows the reaction at the stopping point if $(CH_3)_3NBHF_2$ is the desired product. And if still more HF is added the peak at 2.32 ppm loses intensity and a peak due to the methyl resonance of (CH₃)₃NBF₃ arises at 2.58 ppm (not shown). If still more hydrogen fluoride is added, the n.m.r. peak due to the methyl resonance of $(CH_3)_3NBF_3$ disappears altogether as $(CH_3)_3NH^+BF_4^$ forms and precipitates out of the benzene solution. The sum of the peak areas in each spectrum shown in Figure 5 should be equal to the sum of the areas of the peaks in each of the other traces since the methyl concentration is constant through the reaction. However, the peak areas decrease slightly in total intensity as the reaction progresses, due to the formation of small amounts of $(CH_3)_3NH^+BF_4^-$ which precipitate from solution.

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The first step in the isolation and purification of $(CH_3)_3NBH_2F$ was the filtration of the reaction mixture followed by addition of petroleum ether $(30-60^{\circ}C \text{ b.p.})$ and

cooling to precipitate the product. In some cases it was necessary to remove solvent in vacuo and then add more petroleum ether to effectively drive the $(CH_3)_3 NBH_2 F$ from solution. Unless precautions were taken, the product at this point commonly contained small quantities of $(CH_3)_3NBH_3$ and no suitable method was found to separate this material from $(CH_3)_3NBH_2F$. For this reason it was made a practice to add a slight excess of HF in this preparation (monitored again by H n.m.r.) to remove all the trimethylamine-borane and cause the formation of a small amount of $(CH_3)_3 NBHF_2$. The monofluoro-derivative is readily separated from the amine-difluoroborane by extraction with diethyl ether, in which the latter has very low solubility, followed by recovery of the solid product upon evaporation of the solvent in vacuo. Finally, the $(CH_3)_3NBH_2F$ was sublimed. At pressures of 1×10^{-4} mm Hg or less the solid transfers slowly from the room temperature portion of the sublimination apparatus (at 25° C) to a 0° C cold finger. The melting point of the purified material was 117-118°C.

In the purification of $(CH_3)_3NBHF_2$ the reaction mixture was filtered and the product precipitated with petroleum ether as previously described. The precipitate was then washed with diethyl ether and sublimed from 90°C to a 0°C cold finger. Difficulties in separating the trimethylaminedifluoro- and trifluoroboranes dictated that the addition of HF in the preparation of the former compound be stopped just
short of a full stoichiometric amount (while some $(CH_3)_3NBH_2F$ was still detectable in the ¹H n.m.r.). The sublimation was then carried out in two steps: first the small amount of $(CH_3)_3NBH_2F$ was removed at 25°C and then, when this had been removed, the sublimer was heated to 90°C to recover the $(CH_3)_3NBHF_2$. The melting point of the product obtained in this manner was 124-125°C. Typical reactions on a hundred millimole scale had yields of 80-90% based on trimethylamineborane. Table I gives the analytical data obtained for the compounds $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$.

Sublimation was also used to separate $(CH_3)_3NBF_3$ from $(CH_3)_3NH^+BF_4^-$. The former will move to a 0°C cold finger in <u>vacuo</u> at 80°C while the latter is essentially nonvolatile at that temperature. The infrared, ¹H, ¹⁹F and ¹¹B n.m.r. spectra of $(CH_3)_3NBF_3$ prepared by this method were the same as those from a sample prepared by the method of Angelici (15). The infrared, ¹H and ¹¹B n.m.r. spectra of $(CH_3)_3NH^+BF_4^-$ were the same as those of a sample prepared by the method of NuHall (16), confirming the prepared by the method of $(CH_3)_3NBF_3$ and $(CH_3)_3NH^+BF_4^-$.

The solvent used in the reaction procedure described previously seems to play an important role in the quality, quantity and ease of preparation of the products described. It has been found that, of the solvents used, the most effective for this reaction are benzene and methylene chloride. In benzene

TABLE I

ANALYTICAL AND PROTON NMR DATA

. FOR TRIMETHYLAMINE DERIVATIVES

| | | | Molec | ular | | Melting |
|--|---------|---------|-------|-------|-------------------|----------------|
| | Anal | ysis % | Weig | ht | ൃ | Point |
| Compound | Calc. | Found | Calc. | Found | 1 _{Hnmr} | ° _C |
| (CH3)3NBH2F ^a | B,11.88 | B,12.0 | 90.9 | 91.0 | 2.42 | 117-118 |
| | F,20.64 | F,20.1 | | | | |
| | N,15.38 | N,15.16 | | | | |
| (CH ₃) ₃ NBHF ₂ ^b | B,10.0 | B, 9.9 | 108.9 | 110.9 | 2.32 | 124-125 |
| | F.34.6 | F,34.3 | | | | |
| | N,12.85 | N,12.71 | | | | |
| (CH ₃) ₃ NBF ₃ ^c | | | | | 2.58 | |
| (CH ₃) ₃ NBH ₃ | | | | | 2.58 | |

- a) For infrared spectrum see Figure 11.
- b) For infrared spectrum see Figure 12.
- c) lit., 2.61 (17)
- a) lit., 2.58 (4)
- e) ¹H nmr run in CH_2Cl_2 and δ is relative to TMS.

or methylene chloride the reaction proceeds at a rapid but safe rate, the starting material and products (except $(CH_3)_3NH^+BF_{4}$ are soluble and the ¹H n.m.r. resonance of the solvents do not interfere with the methyl resonance of the products. Methylene chloride has the added advantage that it has a relatively lower freezing point allowing the reaction to be run at a lower temperature. The reaction seems to give best yields when the reaction is run at -10° C to -20° C. Benzene has the advantage that the chemical shifts of the product methyl resonances are more widely separated than is the case in CH_2Cl_2 , allowing for easier determination of the end point of the reaction. Toluene, diethyl ether, 1,2-dimethoxyethane, bis(2-methoxyethyl)ether and 1,2-bis(2-methoxyethoxy)ethane were also tried, but were found to be less satisfactory for reasons such as overlap of amine-borane methyl resonances with solvent resonances or substantial attack of the glass reaction vessel by the HF. Only very slight etching was observed when C_6H_6 and CH_2Cl_2 were used as solvents for the reaction.

Initially the $HF/(CH_3)_3NBH_3$ system was studied using a metal vacuum line with Kel-F reaction tubes similar to those described by Shriver (II). Quantities of HF were measured by weight difference of a small storage tube before and after vapor transfer of an arbitrary amount into the metal vacuum line. This method was less than satisfactory because the re-

actions were very difficult to control. Typical reactions set up to contain equivalent quantities of HF and $(CH_3)_3NBH_3$ produced complex mixtures of fluorinated products presenting a very difficult separation problem. Therefore this approach was abandoned in favor of the technique previously described. 2. Tert-butylamine-borane, $C_4H_9NH_2BH_3$.

A weighed quantity of tert-butylamine prepared as described previously was placed in a three necked flask as shown in Figure 2. About 50 milliliters of methylene chloride was added as the solvent and the flask was placed in a -10° C bath (ice-salt slush) and stirred magnetically. Before the addition of hydrogen fluoride was begun, about .4 ml. of the solution was withdrawn from the reaction vessel and a 1 H n.m.r. spectrum run. The contents of the n.m.r. tube were then returned to the reaction vessel. Anhydrous hydrogen fluoride was added directly from the lecture bottle as described previously; however, it was found that a much slower rate was necessary in order not to overrun the desired end point of the reaction. The hydrogen fluoride was added at a rate of about one observable bubble every 4-5 seconds. Initial additions were for periods up to 10 minutes for a 20 millimole reaction, but as the desired end point was approached the additions became shorter to ensure against overrunning the end point. As described previously, a ¹H n.m.r. spectrum was run after each addition of hydrogen fluoride in order to monitor

the progress of the reaction.

Figure 6 shows the reaction sequence for the reaction of tert-butylamine-borane with anhydrous hydrogen fluoride. Figure 6a shows the reaction mixture before the addition of hydrogen fluoride. The peak at $\delta = 1.00$ is attributed to the methyl resonance of tertiary-butylamine-borane. As hydrogen fluoride is added this peak at 1.00 ppm can be seen to decrease in intensity as a peak arises at d = 1.07 (see Figure 6b). The peak at 1.07 ppm is attributed to the methyl resonance of tertbutylamine-monofluoroborane. As the reaction progresses. a third peak arises at d = 1.16 (Figure 6c). This peak is attributed to the methyl resonance of tert-butylamine-difluoroborane. If the desired product were tert-butylamine-monofluoroborane the addition of hydrogen fluoride would be stopped when the reaction had progressed to the point shown in Figure If the desired product were tert-butylamine-difluoroborane, 6c. the addition of hydrogen fluoride would be continued until the reaction had progressed to the end point as shown in Figure 6e. If the desired product were tert-butylamine-trifluoroborane the addition of hydrogen fluoride would be continued until a peak arose at $\delta = 1.18$ ppm and the other peaks had diminished substantially. And, finally, if the desired product were tert-butylammonium-tetrafluoroborate the addition of hydrogen fluoride would be continued until the ¹H n.m.r. peak at 1.18 ppm disappeared with no new peaks arising since tert-



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FIGURE 6. TERT-BUTYLAMINE-BORANE, HYDROGEN FLUORIDE REACTION SEQUENCE

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butylammonium-tetrafluoroborate has very low solubility in the solvents used and precipitates from the solution.

The first step in the isolation and purification of $C_{l_1}H_0NH_2BH_2F$ was to filter the reaction mixture to remove any insoluble materials. Some of the methylene chloride solvent was then removed from the filtrate, hexane was added and the mixture cooled to 0°C. The addition of hexane and cooling caused about 90% of the tert-butylamine-difluoroborane to be salted out of the solution. The mixture was filtered and the difluoroborane recovered from the fritted funnel. The solvents, hexane and methylene chloride, were vacuum distilled from the filtrate leaving the white crystalline solid tertbutylamine-monofluoroborane. No suitable method was found for the separation of tert-butylamine-borane from the monofluoroborane adduct, nor was a suitable method found for the separation of tert-butylamine-difluoroborane from the trifluoroborane adduct; therefore, it is very important that the reaction be stopped immediately after the starting material is consumed (as shown in the n.m.r. spectrum in Figure 6c) if the desired product is tert-butylamine-monofluoroborane. However, if the desired product is tert-butylamine-difluoroborane, the reaction may progress to the point shown in Figure 6e, whereupon the product is purified as previously described.

As in the case of the fluorinated trimethylamine adducts, it was found that solvents seem to play an important role in

quality, quantity and ease of preparation of the products described. Methylene chloride and chloroform seemed to give the best results of those solvents used. When benzene was used the major products were t-butylamine-trifluoroborane and t-butylammonium-tetrafluoroborate. The analytical results for the t-butylamine-fluoroborane series are given in Table II.

TABLE II

ANALYTICAL AND PROTON NMR DATA

FOR TERTIARY BUTYLAMINE-BORANE DERIVATIVES

| | | | | - Melting |
|----------------------------|------------------------|-----------------------|-----------|-----------------------------|
| | Analy | ysis % | d | Point |
| Compound | Calc. | Found | L Hnmr | °c |
| t-C4H9NH2BH2F ^a | B, 10.48 | B, 10.21 | 1.07 | 120-122 ^e |
| | н ^с , 1.905 | H [°] , 1.90 | | |
| t-C4H9NH2BHF2b | B, 8.80 | B, 8.60 | 1.16 | 79-81 ^f |
| • • | H ^C , .81 | н ^с , .77 | | |
| t-C4H9NH2BH3 | | | 1.00 | 95 - 96 ^e |
| t-C4H9NH2BF3 | | | 1.18 | |
| | | | | |

- a) For infrared spectrum see Figure 13.
- b) For infrared spectrum see Figure 14.
- c) Only hydrolizable hydrogen.
- d) ¹H nmr run in CH_2Cl_2 and δ is relative to TMS.
- e) Decomposition occurs at the melting point (3).
- f) Decomposition occurs at 83°C.

CHAPTER IV

RESULTS AND DISCUSSION

The fluorination of t-butylamine-borane and trimethylamine-borane with anhydrous hydrogen fluoride under the conditions outlined produce consecutively, the monofluoro-, difluoro- and trifluoroborane-amine adducts and, finally, the ammonium-tetrafluoroborate. The preparative method is simpler and less trying than previous methods which employed metal vacuum lines for handling hydrogen fluoride. The procedure described can also give excellent yields, good purity and large quantities of the B-fluorinated amine-boranes described. The trimethylamine-monofluoro- and difluoro- derivatives are reasonably air and moisture stable compounds, generally intermediate in properties between the amine-trifluoroborane and the amine-borane. On the other hand, the monofluoro- and difluoro-borane adducts of t-butylamine seem to be quite moisture sensitive. T-butylamine-monofluoroborane evolves hydrogen on being exposed to the atmosphere. After the evolution of hydrogen a white unidentified solid remains which is insoluble in the solvents used in this investigation, methylene chloride, benzene, chloroform and toluene. T-butylamine-difluoroborane also evolves hydrogen on being exposed to the atmosphere. After the evolution of hydrogen an unidentified viscous nonvolatile yellow liquid remains which appears to be soluble in the solvents mentioned above. The

known compounds, t-butylamine-borane, t-butylamine-trifluoroborane and t-butylammonium-tetrafluoroborate do not appear to be as moisture sensitive since on exposure to the atmosphere for a week's time only a small amount of hydrogen is evolved.

The melting point data (given in Tables I and II) are of importance in the temperature stability of these partially fluorinated borane adducts. The trimethylamine-borane adducts do not appear to decompose even at 150° C; however, it was found that t-butylamine-monofluoroborane decomposes at its melting point of 122° C and that t-butylamine-difluoroborane decomposes at 83° C, just above its melting point of 81° C. Tbutylamine-borane is known to decompose at its melting point of $95-96^{\circ}$ C (3).

It has been suggested that partially fluorinated amineboranes can not be prepared, because trimethylamine-monofluoroborane, for instance, may spontaneously disproportionate to trimethylamine-borane and trimethylamine-trifluoroborane (1). Such a disproportionation has been of constant concern throughout this investigation; however, there have been no clear indications that such reactions occur in any of the solvents at the temperatures employed in this study. It is possible that disproportionation could occur under other conditions, but it has not detectably hindered the isolation and characterization of the partially fluorinated derivatives.

The ¹¹B and ¹⁹F n.m.r. spectra confirm the stoichiometries

indicated by the analytical results (Table I). The ¹¹B spectrum of (CH3)3NBH2F (Figure 7) consists of a sextet with component peak areas in the ratio of 1:1:2:2:1:1 which can be interpreted as a triplet (J = 113 Hz), each component of which is further split into a doublet (J = 88.5 Hz). The 19 F spectrum of the same sample (Figure 8) consists of a nonet with areas in the ratio of 1:2:2:2:2:2:2:1 most probably arising from a l:l:l:l quartet due to spin coupling of the ^{ll}B nucleus $(I_{11p} = 3/2)$ with the fluorine $(J_{FB} = 87.2 \text{ Hz})$, each member of which is split into a 1:2:1 triplet (J = 43.6 Hz). The near equality of the doublet coupling constant in the ¹¹B spectrum and the quartet splitting in the ¹⁹F spectrum supports the assignment of the former doublet splitting to a single fluorine (i.e. $J_{BF} = 88.5 \text{ Hz}$). Then the triplet splitting in the ¹¹B and ¹⁹F spectra is indicative of two protons, confirming the $(CH_3)_3 NBH_2 F$ stoichiometry.

The ¹¹B n.m.r. spectrum of trimethylamine-difluoroborane (Figure 9) shows a quintet with peak areas in the ratio of 1:2:2:2:1 which is believed to arise from a doublet (J = 146.4 Hz) in which each member shows triplet multiplicity (J = 73.2 Hz). Evidence for the splitting assignments comes from the ¹⁹F spectrum (Figure 10) which also consists of a 1:2:2:2:1 quintet arising in this case from a quartet with equal peak areas (J = 70 Hz) due to coupling with the ¹¹B nucleus, each member of which is split into a doublet



FIGURE 7. BORON-11 NMR SPECTRUM OF TRIMETHYLAMINE-MONOFLUOROBORANE.

FLUORINE 19 NMR T=202 JFB=87.2 $J_{FH} = 43.6$ CH₃)₃NBH₂F

FIGURE 8. FLUORINE-19 NMR SPECTRUM OF TRIMETHYLAMINE-BORANE



FIGURE 9. BORON-11 NMR SPECTRUM OF TRIMETHYLAMINE-DIFLUOROBORANE

FLUORINE 19 NMR

T=164

[J==70

=(

42

FIGURE 10. FLUORINE-19 NMR SPECTRUM OF TRIMETHYLAMINE-DIFLUOROBORANE

 $(CH_3)_3NBHF_2$

(J = 70 Hz). The quartet in the ¹⁹F spectrum is attributed to F-B coupling. The near equality of the ¹⁹F F-B splitting and the ¹¹B triplet splitting $(J_{BF} = 73.2 \text{ Hz} \cong 70 \text{ Hz} = J_{FB})$ supports the assignment of the triplet splitting due to two fluorines. The doublet splitting in the ¹⁹F and ¹¹B spectra is indicative of coupling with a single proton, confirming the stoichiometry, $(CH_3)_3 \text{NBHF}_2$.

The n.m.r. spectral data are contained in Tables III, IV and V. It is of some interest to note that for $(CH_3)_3NBH_2F$, $J_{BF} \cong 2J_{FH}$ and for the difluoro- derivative $J_{BF} \cong J_{FH}$. Such coupling constant relationships are not likely to be purely coincidental since similar cases are fairly common in the literature describing other amine-boranes (17), and it has been observed that, when two or more spin-spin couplings involve the same atom, the coupling constants are frequently integral multiples of one another (17). The reasons for such behavior are not yet clear and further study would seem to be indicated.

The boron-ll n.m.r. spectra of t-butylamine-monofluoroborane, t-butylamine-difluoroborane, t-butylamine-trifluoroborane and t-butylammonium-tetrafluoroborate all appeared as singlets of varying broadness, showing no resolvable splitting. The reason for the unusually small coupling constants may involve exchange processes in solution. In an attempt to determine if an exchange process was responsible for the lack of coupling seen in the boron-ll n.m.r. spectra of the t-butylamine-hydro-

TABLE III^a

COUPLING CONSTANT AND CHEMICAL SHIFT DATA OF ¹¹B SPECTRA OF TRIMETHYLAMINE ADDUCTS

| | d م م | J _{BF} ° | J _{BH} |
|---|-------------------|-------------------|------------------|
| (CH ₃) ₃ NBH ₃ | 26.6 ^d | - | 101 ^d |
| (CH ₃)3 ^{NBH} 2 ^F | 13.2 | 88.5 | 113 |
| (CH ₃) ₃ NBHF ₂ | 14.2 | 73.2 | 146 |
| (CH ₃) ₃ NBF ₃ | 18.4 ^e | 15.6 ^g | - |
| (CH ₃) ₃ NH ⁺ BF ₄ | 19.4 ^f | _h | |

a) All samples were solutions using CH_2Cl_2 as the solvent except $(CH_3)_3NH^+BF_4^-$ which used CH_3CN as the solvent.

b) $\int - {}^{11}B$ is given in ppm relative to trimethylborate.

- c) J is given in Hz.
- d) lit. (18), $\delta = 26.2$, J = 97 in benzene.
- e) lit. (18), $\delta = 17.5$, in benzene.
- f) lit. (18), $\delta = 19.9$, in water.
- g) lit. (19), J = 15.0.
- h) lit. (19), J = 4.

TABLE IV^a

COUPLING CONSTANT AND CHEMICAL SHIFT DATA OF ¹⁹F SPECTRA OF TRIMETHYLAMINE ADDUCTS

| | Ъ | J _{FB} ° | J _{BH} |
|---|-----|-------------------|-----------------|
| (CH ₃) ₃ NBH ₂ F | 202 | 87.2 | 43.6 |
| (CH ₃) ₃ NBHF ₂ | 164 | 70.0 | 70.0 |
| (CH ₃) 3 ^{NBF} 3 | 158 | 15.6 | - |
| (CH ₃) ₃ NH ⁺ BF ₄ | 154 | - | - |

a) All samples were solutions using CH_2Cl_2 as the solvent except $(CH_3)_3NH^+BF_4^-$ which used CH_3CN as the solvent.

b) ∫ - ¹⁹F is given in ppm relative to trichlorofluoromethane.
c) J is given in Hz.

TABLE Va

CHEMICAL SHIFT DATA OF BORON-11 NMR SPECTRA

FOR T-BUTYLAMINE ADDUCTS

| | م م | |
|---------------|--------|--|
| t-C4H9NH2BH3 | 40.8° | |
| t-C4H9NH2BH2F | 18.1 | |
| t-C4H9NH2BHF2 | 23.3 | |
| t-C4H9NH2BF3 | 18.3 | |
| t-C4H9NH3BF4 | 19.8 | |

- a) All samples were solutions using CH_2Cl_2 as the solvent except $(CH_3)_3NH_3^+BF_4^-$ which used CH_3CN as the solvent.
- b) $d {}^{11}B$ is given in ppm relative to trimethylborate.
- c) $J_{BH} = 94.5 \text{ Hz}.$

fluoroboranes, a low temperature boron-ll n.m.r. study of these compounds was done. It was found that for both t-butylamine-monofluoroborane and t-butylamine-difluoroborane the boron-11 singlet became broader as the temperature was decreased. At -60°C the signals were lost all together as the solid precipitated from solution. T-butylamine-difluoroborane showed a large chemical shift change from 23 ppm to 18 ppm on going from a temperature of $25^{\circ}C$ to $-60^{\circ}C$. This phenomenon is indicative of a system which exhibits some kind of exchange process (17.20). The chemical shift of t-butylamine-monofluoroborane, however, did not appear changed in that temperature range. In spite of these indications of an exchange process, the chemical shifts seem reasonable for each product when they are compared to the chemical shifts of the trimethylamine-borane series (Tables III and V). The stoichiometries of t-butylamine-monofluoroborane and t-butylamine-difluoroborane can, however, be confirmed without the aid of the boron-ll n.m.r. spectra. By analogy with the trimethylamineborane sequence and using the analytical data given in Table II, stoichiometries can be proved. Similar to the trimethylamine-borane sequence, as anhydrous hydrogen fluoride is added to t-butylamine-borane, hydrogen is evolved and the proton n.m.r. signal due to the methyl resonance of the tbutyl group of the amine-borane loses intensity as a new peak arises. This new peak was assumed to be due to the methyl

resonance of t-butylamine-monofluoroborane. This compound was isolated and analyzed for per cent boron and hydrolizable hydrogen and found to have the proper percentages (see Table II) for t-butylamine-monofluoroborane. The compound associated with the second peak to arise in proton n.m.r. was isolated and found to have the proper percentage boron and hydrolizable hydrogen for t-butylamine-difluoroborane, confirming its stoichiometry. The third peak (arising at 1.18J) was attributed to tbutylamine-trifluoroborane. The infrared, proton n.m.r. and boron-11 n.m.r. spectra of this compound were identical with the spectra of an original sample prepared by the reaction of t-butylamine with boron trifluoride. The infrared, proton n.m.r. and boron-ll n.m.r. spectra of the white solid which precipitated from solution on the addition of excess hydrogen fluoride were identical to spectra given by an original sample prepared by the reaction of t-butylamine and fluoboric acid (HBF_{μ}), confirming the presence of t-butylammonium-tetrafluoroborate.

Coyle and Stone observed that, in the amine-boranes they were investigating, there was a reasonably direct relationship between the chemical shift of the methyl protons on the nitrogen and the acid strength. An increase in the δ was observed as stronger acids were coordinated to the nitrogen (20). The The relative strengths of the acids BH_3 and BF_3 in trimethylamine-adducts were found to be nearly equal (17). Based on

Coyle and Stone's method for determining relative acid strengths, the relative acid strength with trimethylamine as the reference base would be $BH_3 \cong BF_3 \rangle BH_2F \rangle BHF_2$. It may be possible to understand this seemingly unusual behavior. If the methyl protons in the trimethylamine-borane molecule are considered, it seems reasonable to expect that any factor which increases the degree to which the electron pair on nitrogen is "donated" to boron will cause a corresponding decrease in the electron density and therefore the shielding and chemical shift of the protons. The two factors which are believed to be of predominant importance here are:

- 1) the effective electronegativity of the BX₃ group, through a straightforward inductive effect, and
- 2) the hybridization of the boron acceptor orbital.

To a first approximation the strength of the donoracceptor interaction will be proportional to the effectiveness of the overlap between the B and N orbitals, other things being equal. In this case the overlap is expected to increase with an increase in the p character of the boron orbital, assuming that the nitrogen hybrid orbital is relatively constant in character throughout the series of compounds presently under discussion. Therefore, knowledge of changes in the boron orbital hybridization would be helpful in accounting for proton chemical shift trends. Williams, Harmon and Spielman (19) have discussed the relationship between the amount of s character in the boron hybrid orbitals and the B-H and B-F coupling constants. By assuming that the B-H bonds in BH_4^- consist of 25% s character, they obtain the following equation.

Applied to $(CH_3)_3NBH_3$, this gives the result that boron orbital used in the BN bond is comprised of approximately 91% p - character.

While they were unable to obtain an analogous relationship for B-F bonds, it was pointed out that more electronegative substituents tend to preempt p character in the orbitals of the atom to which they are bound. This principle suggests that, in the series of compounds from $(CH_3)_3NBH_3$ to $(CH_3)_3NBF_3$, the % p character in the boron orbital in the B-N bond should continuously diminish from its initial value of 91%. As noted before, this is expected to result in a decrease in the BN overlap which, if other things were equal, would cause greater and greater shielding of the methyl protons and a higher chemical shift.

In the same series of compounds the increasing inductive effect due to the influence of more and more fluorines is expected to cause a steady reduction in the methyl proton chemical shift. The balance between these two factors will determine the overall value of the methyl proton chemical shift. The observed increase in chemical shift from $(CH_3)_3 NBH_3$ (2.58 δ) to (CH₃)₃NBH₂F (2.42 δ) would appear to indicate that the predominant effect of the initial added fluorine is the reduction of boron p character in the B-N bond, resulting in a lower net $N \rightarrow B$ interaction despite the enhanced inductive effect associated with the fluorine atom. On going to $(CH_3)_3NBHF_2$ (2.32 d), there is another, but smaller, increase in the shift which suggests that the magnitude of the hybridization change in this step is smaller than in the foregoing step and its influence on the ¹H shift is probably tempered by the mounting inductive effect. In the case of $(CH_3)_3 NBF_3$ (2.58 δ), the diminished overlap effectiveness in the B-N bond due to increased appropriation of the boron p character by the fluorines has been entirely neutralized through the strong inductive influence of the three fluorine atoms, resulting in a proton chemical shift nearly unchanged from its value in (CH₃)₃NBH₃.

In the series from t-butylamine-borane to t-butylaminetrifluoroborane, each added fluorine decreases the methyl proton chemical shift. The effect of the added fluorines on the B-N bond, through the influence of the inductive and hybridization effects, is expected to be similar to that described for the fluorinated trimethylamine-boranes. However, these bonding changes are probably not directly reflected in the chemical shift of the t-butyl protons since these protons

are separated by three bonds from the BN group rather than two as was the case for the trimethylamine-adducts. (In fact, framework models suggest that the t-butyl protons may closely approach the boron substituents in space and it is possible that local paramagnetic effects arising from fluorines on boron may markedly influence the proton chemical shift.) Thus no great significance is ascribed to the proton shifts in the series of B-fluorinated t-butylamine-boranes.

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No satisfactory boron-ll chemical shift theory is presently available for determining relative donor-acceptor strengths (17). This is probably due to the fact that factors other than inductive effect may be involved in determining the electron density surrounding the boron. For instance, differences in the strength of the B-N bond and differences in the paramagnetic contribution to the boron-ll chemical shift may be important. To the extent that this is true, it will be difficult to derive bonding information from the boron chemical shifts.

It appears, however, that the trend in the fluorine-19 chemical shifts (decreasing from $(CH_3)_3NBH_2F$ to $(CH_3)_3NBF_3$) is understandable in terms of the inductive effect of the group bound to fluorine. Thus, the effective electronega-tivity of such groups would increase as

 $(CH_3)_3NBH_2 \langle (CH_3)_3NBHF \langle (CH_3)_3NBF_2$ and the diamagnetic shielding of the attached fluorine would

experience corresponding decreases accounting for the decreasing chemical shift trend.

Previous methods for the fluorination of amine-boranes required a metal vacuum line and expensive pumping systems. The new method presented here offers many advantages. The cost of equipment is very low (given the fact that a proton n.m.r. machine is available). The reactions give high yields of highly pure products. And the reactions can be run on a very large scale, safely and with little difficulty. The only disadvantage that was found was that reactions smaller than about 7 mmo. were very difficult to run using this method.

It has been shown that it is possible to isolate partially fluorinated borane adducts, contrary to statements in the literature (1). This new method for the fluorination of hydridic hydrogens on boron could be a general method for the fluorination of hydrides, but more research in this area is very necessary.



FIGURE 11. INFRAPED SPECTRUM OF TRIMETHYLAMINE-MONOFLUOROBORANE

 \mathcal{F}

r.





FIGURE 13. INFRARED SPECTRUM OF T-BUTYLAMINE-MONOFLUOROEORANE



FIGURE 14, INFRARED SPECTRUM OF T-BUTYLAMINE-DIFLUOROBORANE

APPENDIX

In the process of doing the research for this paper, some interesting reactions were run which are tangent to the theme of this paper, but which have the potential of being exciting, meaningful research projects.

At this point in time the relative chemical shifts in the proton. boron-11 and fluorine-19 n.m.r. of the amine adducts of BH_3 , BH_2F , BHF_2 and BF_3 are unexplained. This researcher believes that this is due to our lack of understanding of the nature of the coordinate covalent bond. The n.m.r., it is believed. reflects the hybridization of boron and nitrogen orbitals in the B-N bond and the inductive effect due to electronegative groups attached to the boron. It should be possible to develop a workable relationship between the total % s character and the B-N coupling constant. In order to see this coupling it would be necessary to use adducts enriched in $15_{\rm N}$ since ¹⁴N has a large quadrapole making ¹⁴N coupling unresolvable in most cases. $(^{15}N$ does not have a quadrapole.) By determining the coupling constant for $15_{\rm NH_{ll}}^+$ and BH_{ll}^- , it would be possible to determine the relationship of % s to coupling constant, for the boron and nitrogen cases, by using the equation given by Williams, Harmon and Spielman (19). Consider now the compound $H_3^{15}NBH_3$: by taking a proton n.m.r., J_{HN} can be arrived at, and by running a boron-ll n.m.r. it should be possible to obtain J_{BN} and J_{BH} . From J_{BH} and J_{NH} it is

possible to calculate the amount of s character the boron and nitrogen put into the B-N bond. The sum of the % s character from the boron and nitrogen along with $J_{\rm BN}$ would make it possible to obtain a B-N proportionality constant which would be

$$\texttt{fotal \%s = \%s}_{B} + \%s_{N} = \texttt{K}_{BN}\texttt{J}_{BN}$$

valid regardless of what substituents are present on boron and nitrogen and could be used to determine how the hybridization in the B-N bond changes in various series of amineborane compounds. Such information could be very helpful in accounting for certain aspects of coordinate bond strengths in amine-boranes for which present explanations are less than satisfactory.

In an attempt to prepare the free acids, BH_2F and BHF_2 , from the reaction of BBr_3 and $(CH_3)_3NBH_2F$ or $(CH_3)_3NBHF_2$ it was found that part of the solid product from this reaction was $(CH_3)_3NBBr_3$, indicating that the acids, BH_2F and BHF_2 , had been displaced. A gas phase molecular weight determination of BH_2F indicated that BH_2F exists as a dimer $(BH_2F)_2$. The boron analysis, however, did not come out within acceptable ranges. Other solid and gas products were not analyzed. It is believed by this researcher that under the proper conditions of temperature and solvent that this reaction could be forced to give nearly quantitative yields of the free acid. Comparisons of $(BH_2F)_2$ and BHF_2 could be of great assistance in developing an understanding of the nature of the hydrogen bridge bond. Base strength is a topic which is discussed a great deal (17,20), but what makes a Lewis base strong or weak? It has been suggested that it is more than a polarizability and steric phenomenon, that Lewis base strength may also be related to the strength of the compounded Lewis acid (17). It was found by this researcher that CH_3NH_2 would not displace $(CH_3)_3N$ from either $(CH_3)_3NBH_2F$ or $(CH_3)_3NBHF_2$ indicating that $(CH_3)_3N$ is a stronger base than CH_3NH_2 . This is contrary to published base strength tables (17,21). It is believed that by running substitution reactions as described for methylamine some increased understanding of what base strengths and acid strengths are, can be achieved.

Finally, the method presented here has worked successfully in two cases and has given indications of working in three other cases (the fluorination of $(CH_3)_3PBH_3$, $CH_3NH_2BH_3$ and LiBH₄). It is believed by this investigator that a truly general method has been developed for the fluorination of hydridic hydrogens. More work in this area would add credence to the generality of the method.

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