$IF_6^+SbF_6^-$ at 23–25°. Methane and sulfur dioxide react to a slight extent with the complex, producing difluoromethane and sulfuryl fluoride, respectively.

$$CH_4 + IF_6^+SbF_6^- \rightarrow CH_2F_2 + 2HSbF_6 + 2IF_5 \tag{10}$$

$$SO_2 + IF_6^+SbF_6^- \rightarrow SO_2F_2 + IF_4^+SbF_6^- \tag{11}$$

Nitric oxide and nitrogen dioxide form the stable nonvolatile complexes $NO^+SbF_6^-$ and $NO_2^+SbF_6^-$, respectively, and the weak complexes $NO^+IF_6^-$ and $NO_2^+IF_6^-$. The latter decompose under dynamic vacuum.

$$2NO + IF_6^+SbF_6^- \rightarrow NO^+SbF_6^- + NO^+IF_6^- \tag{12}$$

$$NO^+IF_6^- \rightarrow FNO + IF_5 \tag{13}$$

$$2NO_2 + IF_6^+SbF_6^- \rightarrow NO_2^+SbF_6^- + NO_2^+IF_6^- \tag{14}$$

$$NO_2^+IF_6^- \rightarrow FNO_2 + IF_5 \tag{15}$$

Applications. Since $IF_6^+SbF_6^-$ is easily prepared from iodine heptafluoride and antimony pentafluoride, and since it has favorable properties, such as high oxidizing power, low dissociation pressure at ambient temperature, low corrosiveness to glass and fluorinated plastics, and high relative safety, we believe that it will prove useful for applications with radon. These may include (1) analysis of radon in air, (2) purification of contaminated air, and (3) separation of radon from lighter noble gases. Recent tests have shown that ^{222}Rn can be quantitatively collected from 5 to 10 l. of air with very small beds (3 to 10 g) of $O_2^+SbF_6^-$ or $IF_6^+SbF_6^-$. After radioactive equilibrium has been established, it is possible to measure the radon by counting γ-rays of daughters ^{214}Pb and ^{214}Bi. This method of analysis is currently being studied at Argonne. Although $O_2^+SbF_6^-$ and $IF_6^+SbF_6^-$ are decomposed by moisture, they can be used in conjunction with desiccants (calcium sulfate, silica gel, or molecular sieves) in humid atmospheres. Hence they can be used in filter devices ("breather vents") for trapping radon in mines. The high cost of drying humid air, either by chemical or refrigeration methods, is the principal limitation on their use in large continuous-circulation systems. Mixtures of noble gases can be separated by selective oxidation. For example, a mixture of krypton, xenon, and radon can be passed through a bed of $IF_6^+SbF_6^-$ to remove the radon, then through a bed of $O_2^+SbF_6^-$ to remove the xenon; the krypton will pass through unchanged. The radon and xenon can then be recovered by hydrolyzing the beds.

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Registry No. $IF_6^+SbF_6^-$, 55822-77-0; KI, 7681-11-0; ^{222}Rn, 14859-67-7; CO, 630-08-0; NO, 10102-43-9; NO_2, 10102-44-0; SbF_5, 7783-70-2; IF_7, 16921-96-3.

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Aminodifluoroborane

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Aminodifluoroborane is the primary volatile product in the pyrolysis of ammonia–trifluoroborane at 185°. The new compound has an ionization potential of 12.4 ± 0.4 eV, and appearance potentials of principle ions from both aminodifluoroborane and aminoborane permit the calculation of $D(H_2N-BF_2) = 7.6$ eV, $D(H_2N-BH_2) = 8.1$ eV, $\Delta H_f(H_2NBF_2) = -255$ kcal/mol, and $\Delta H_f(H_2NBH_2) = -75$ kcal/mol.

Compounds containing B–N bonds are attractive monomers for the synthesis of thermally stable inorganic polymers. As an extension of previous work carried out in this laboratory on the isolation and characterization of aminoborane,[1] H_2NBH_2, and aminodichloroborane,[2] H_2NBCl_2, we have observed aminodifluoroborane produced from the pyrolysis of ammonia–trifluoroborane, H_3NBF_3.

Earlier studies of the pyrolysis of the ammonia–trifluoroborane adduct[3] reported the compound to be appreciably decomposed at 125° and the decomposition to be rapid at 150° according to $4NH_3 \cdot BF_3 \rightarrow 3NH_4^+BF_4^- + BN$. There was no mention of intermediates. More recent work[4] contends that the decomposition is much slower, requires higher temperatures, and produces several H–N–B–F containing species, $NH_3 \cdot BF_3 \rightarrow NH_4^+BF_4^- + [HNBF]_x$, but no boron nitride was reported. These reactions were complete in 36 hr at 252°.

In a similar case,[5] when diethylamine–trifluoroborane was heated at 250° the product was diethylaminodifluoroborane, $2(C_2H_5)_2NH \cdot BF_3 \rightarrow (C_2H_5)_2NH_2^+BF_4^- + (C_2H_5)_2NBF_2$. In this case the reaction is limited to the "extraction" of a molecule of hydrogen fluoride by a second molecule of the adduct. This appears to be the favored mode of reaction of most trifluoroborane adducts since there is no change in the number of strong B–F bonds and the activation energy is thereby diminished.[6]

Experimental Section

Ammonia–trifluoroborane was made from trifluoroborane etherate and ammonia in diethyl ether solution.[7] Small amounts of ammonium tetrafluoroborate remained in the finished product, but it did not

Table I. Mass Spectrum of Aminodifluoroborane

m/e	Intensity	Assignment	*m/e*	Intensity	Assignment
10	0.9	^{10}B	45	55.4	$HN^{11}BF$, $H_2N^{10}BF$
11	3.6	^{11}B	46	100.0	$H_2N^{11}BF$
26	2.7	^{11}BNH, $^{10}BNH_2$	48	17.0	$^{10}BF_2$
27	2.7	$^{11}BNH_2$	49	68.8	$^{11}BF_2$
29	8.0	^{10}BF	63	1.8	$HN^{10}BF_2$, $N^{11}BF_2$
30	7.1	^{11}BF	64	17.9	$HN^{11}BF_2$, $H_2N^{10}BF_2$
43	2.7	$N^{10}BF$	65	57.1	$H_2N^{11}BF_2$
44	13.4	$HN^{10}BF$, $N^{11}BF$			

contribute to the mass spectra at up to 210° as was verified in a blank experiment. Samples of the adduct were placed in a small flask, evacuated, and then heated by means of an oil bath. The evolved vapors were led directly into a Bendix Model 14-107 mass spectrometer. The 90 cm long inlet pathway for the low pressure vapor consisted of glass, copper, and stainless steel tubing at room temperature.

Larger amounts of polymeric aminodifluoroborane, $(H_2NBF_2)_n$, were prepared by the pyrolysis of ammonia–trifluoroborane in an apparatus formed by connecting a 250 ml flask to a cold trap which was in turn connected to vacuum. In a typical experiment, 20 g of the adduct was spread out on the inner walls of the flask, the flask was heated to 185 ± 5° for 2.5 hr by immersion in an oil bath, the system was maintained at 0.2 Torr, and the volatile products were collected in the trap at −196°. It appeared as if two substances were present; one was a clear, glassy substance with a light yellow tint. The other was a fine, white solid, which traveled further before being frozen out. The trap contained a total of 9.0 g of material which was scraped out and placed in a filter apparatus under a nitrogen cover. Methylene chloride was added and the pieces of product were broken up and washed to remove any *B*-trifluoroborazine. The solvent was filtered off and the remaining white material was vacuum dried. Anal. Calcd for H_2BF_2N: H, 3.10; B, 16.68; F, 58.60; N, 21.61; B:N:H:F ratio 1:1:2:2. Found: H, 3.08; B, 16.48; F, 61.48; N, 18.96; ratio 1:0.89:2.00:2.12.

Results and Discussion

The spectrum of the vapor evolving from the adduct at up to 125° was only that of diethyl ether, the reaction solvent, and it appeared and then disappeared as the heating progressed. The spectrum at 185° was that of *B*-trifluoroborazine, but it persisted for only several minutes depending on the amount of sample that was being pyrolyzed. The base peak at *m/e* 135, with isotope peaks at 134 and 133, was in the correct ratio for a B_3 molecule. As this faded away the spectrum in Table I began to appear. The base peak at 70 eV is *m/e* 46 followed by major peaks at 49, 65, and 45. The peaks at *m/e* 65 and 49 are accompanied by their ^{10}B satellites and may be readily assigned as $H_2NBF_2^+$ and BF_2^+, respectively. In the mass spectrum of aminoborane,[1] H_2NBH_2, the base peak occurs at *m/e* 28 which is the ion corresponding to the base peak of *m/e* 46, H_2NBF^+, in this system. The *m/e* 45 peak is larger than predicted for a ^{10}B isotope of H_2NBF^+ due to the presence of $HN^{11}BF^+$. The mass spectrum of this pyrolysis product of H_3NBF_3 at 18 V is much simpler with the base peak now at *m/e* 65 and major peaks at 46, 45, and 49.

Our data support Ryss' contention[4] of a stepwise pyrolysis of ammonia–trifluoroborane since the mass spectra show the presence of both H_2NBF_2 and $(HNBF)_3$. There can be no confusion in assignments, for the mass spectrum of trifluoroborazine contains the monomer, $HNBF^+$, in only 4% relative abundance, and it has no peak at *m/e* 65, $H_2NBF_2^+$, while the spectrum of aminodifluoroborane shows relative abundances of these ions of 55 and 57%, respectively. The changing spectral behavior with sample size is reasonable, for when large solid samples are heated under vacuum, the heating of the solid is nonuniform, and the diffusion of the initial gaseous product, H_2NBF_2, into the vapor space is slow. There is more opportunity for H_2NBF_2 to react further to form the more stable $(HNBF)_3$ which is evolved. At higher temperatures, H_2NBF_2 is formed more rapidly and it escapes. In smaller samples, the solid H_3NBF_3 is more uniformly heated and the initial product can more readily escape.

The optimum temperature for the production of aminodifluoroborane was determined by monitoring the *m/e* 65 peak while raising the temperature of the oil bath around the sample. The ion current began to grow rapidly at about 140° to a maximum at 185° and then began to fall as the temperature was further increased to 220°.

The aminodifluoroborane product was collected by heating several grams of the adduct at 185 ± 5° for 4 hr and quenching the effluent in a trap at liquid N_2 temperature. This trap was connected to the mass spectrometer and warmed stepwise by immersion in a series of slush baths, but no volatile products evolved. Heavier B–N species (to *m/e* 135) began to appear at room temperature, and upon heating the solid material which coated the inside of the trap to temperatures of 100–150°, the spectrum became largely that of trifluoroborazine and aminodifluoroborane. One would expect the H_2NBF_2 to exist as such only at low temperatures, and to react with itself to form higher molecular weight species at more ordinary temperatures. The white solid in the trap was hygroscopic and completely soluble in water at room temperature. A similar polymeric product has been observed from the reaction, $(CH_3)_2BNH_2 + BF_3 \rightarrow (CH_3)_2BF + F_2BNH_2$, wherein the $(F_2BNH_2)_n$ product formed as a white fog that settled out.[8] The similar reaction with $(CH_3)_2BN(CH_3)_2$ permitted the isolation of the less reactive $F_2BN(CH_3)_2$.

Both differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere on the adduct, the salt, and the polymer formed from the product that was volatilized from the adduct at 185° and trapped at −196°. All three materials had comparable volatilities; the adduct totally vaporized at rates more or less linear with temperature between about 230 and 350° while about 8% of the polymer and the salt remained as a black powder upon such heating. Thus BN is not formed in the thermolysis of the adduct. The previously reported[4] endothermic transition of the adduct was observed reproducibly at 167° as was that in the NH_4BF_4 salt at 206°. The formation of NH_4BF_4 in the thermolysis of the adduct was revealed by heating the adduct to 225°, cooling back through the transition (which supercooled from 10 to 35°), and then reheating through the transition. The NH_4BF_4 transition appeared at 200°, somewhat depressed from its value of 206° in the pure salt, as expected thermodynamically. This endotherm at 200° was never present in an initial heat, rather it only appeared upon reheating the adduct, and it grew stronger on repeated thermal cycling. This slow formation also explains the complete volatilization of the adduct notwithstanding the 8% residue upon volatilizing the salt. Discounting the possible exact coincidence of transition temperatures, the formation of NH_4BF_4 in the thermolysis of the polymer is revealed by the characteristic sharp transition which appeared at 206°. Upon beginning to heat the polymer from room temperature and up to 175°, DTA revealed continuous exothermic reaction, TGA revealed continuous weight loss, and MS revealed trifluoroborazine and aminodifluoroborane as volatile products. The competition of exothermic reaction with endothermic vaporization yields the net DTA signal, for the more volatile impurities present in a particular sample, the less pronounced was the exothermic reaction.

Several critical potentials for the appearance of ions from aminodifluoroborane were determined by the linear extrapolation method, and the results are summarized in Table II.

Appearance potentials of ions from aminoborane were determined using the extrapolated voltage difference method,

Table II. Appearance Potentials of Ions from H_2NBF_2

m/e	$11(B^+)$	$45(HN^{11}\text{-}BF^+$	$46(H_2N^{11}\text{-}BF^+$	$49(BF_2^+)$	$65(H_2N^{11}\text{-}BF_2^+)$
App pot., eV	30.0 ± 0.5	14.0 ± 0.2	16.1 ± 0.4	16.1 ± 0.3	12.4 ± 0.4

Table III. Appearance Potentials of Ions from H_2NBH_2[a]

m/e	$10(^{10}B^+)$	$11(^{10}BH^+)$	$13(^{11}BH_2^+)$
App pot., eV	19.2 ± 0.5	18.0 ± 0.1	17.2 ± 0.2

[a] Previously unpublished data determined in this laboratory by C. T. Kwon; see also C. T. K., Ph.D. Thesis, Georgia Institute of Technology, August, 1970.

and the results are summarized in Table III.

Molecular Energetics

It is possible to develop the molecular energetics of aminoborane and aminodifluoroborane. Useful values in this development are $I(B) = 8.26$ eV, $\Delta H_s(B) = 132.6$ kcal/mol, $\Delta H_f(H) = 2.26$ eV, $D(B\text{-}H) = 3.54$ eV,[9] and $I(BH) = 9.77$ eV,[10] which are all either spectroscopic or accurately known calorimetric values. Since $I(BH) + D(B^+\text{-}H) = D(B\text{-}H) + I(B)$, we have rigorously that $D(B^+\text{-}H) = 2.07$ eV, which also agrees with deductions from the electron impact data of Wilson and McGee,[11] and thereby lends more credence to their numbers notwithstanding the inherent inaccuracies in electron impact methods. These authors[11,12] also report $D(BH_3\text{-}BH_3) = 2.56$ eV and $D(BH_3\text{-}CO) = 1.46$ eV, both from their measurements alone and from the combination of their data with those from other investigators. Redundant calculations from multiple perspectives then have verified the accuracy of these values, both of which permit the calculation of the heat of atomization of BH_3 as 11.1 eV or 257 kcal/mol. Since we know $D(B\text{-}H)$ from spectroscopic measurements, then $D(BH_2\text{-}H) + D(BH\text{-}H)$ must equal 7.6 eV.

With the reasonable formation of an H atom in the fragmentation of the BH_3 moiety, electron impact data yield $D(BH_2^+\text{-}H) = 0.64$ eV as a consistent value from measurements on B_2H_6, BH_3, and BH_3CO.[12] The calculation of $D(BH^+\text{-}H)$ is more uncertain, however, since in the electron impact process, the hydrogen may appear either as H_2 or as 2H. Rather than guessing, let us see what the value must be to be consistent with the sum $D(BH_2\text{-}H) + D(BH\text{-}H) = 7.6$ eV, in which we have great confidence. From the two identities,

$$D(BH_2\text{-}H) + I(BH_2) = I(BH_3) + D(BH_2^+\text{-}H)$$

and

$$D(BH\text{-}H) + I(BH) = I(BH_2) + D(BH^+\text{-}H)$$

we obtain

$$D(BH_2\text{-}H) + I(BH_2) = 12.96$$

and

$$I(BH_2) - D(BH\text{-}H) = 9.77 - D(BH^+\text{-}H)$$

Substracting these two equations, we find $D(BH^+\text{-}H) = 4.4$ eV, which implies a fragmentation process that produces H_2 rather than 2H and which also involves 0.9 eV of excess energy. Interestingly, this particular process occurs alike in the fragmentation of BH_3, B_2H_6, and BH_3CO, for the apparent values of $D(BH^+\text{-}H)$ are identical from each of these three parent compounds.[12]

The new electron impact data on H_2NBH_2 and H_2NBF_2 of Tables II and III permit further calculations and consistency checks with the above now more or less accurately known values.

But first, we must evaluate $D(BH_2\text{-}H)$, $D(BH\text{-}H)$, and $I(BH_2)$ wherein rigorous interrelations are such that knowledge of any one of these three quantities will permit the internally consistent calculation of the other two. The choices are three: (1) use an experimental value of $I(BH_2) = 9.8$ eV,[13] (2) use a theoretical value of $I(BH_2)$,[14] or (3) estimate the bond dissociation energy relative to that of the corresponding ions using a semiempirical correlation.[15] The values for these quantities then will not involve quite the same level of confidence that has been attached to the related quantities that were just discussed.

We have elected to accept $I(BH_2) = 9.1 \pm 0.2$ eV from recent very accurate ab initio calculations using gaussian basis sets and including valence shell correlation.[14] Confidence is based in part on the results obtained by these authors in their earlier calculations on four related boron hydrides wherein almost chemical accuracies were reported. The semiempirical correlation gave $I(BH_2) = 9.3$ eV.[15] We cannot accept the experimental value since efforts to even detect BH_2 in similar experiments with the pyrolysis of B_2H_6 in this laboratory were unsuccessful.[11] A kinetic analysis also suggests that BH_2 is not a factor in the pyrolysis of B_2H_6.[11] From the identity $I(BH_2) + D(BH^+\text{-}H) = D(BH\text{-}H) + I(BH)$, we then calculate $D(BH\text{-}H) = 3.7$ eV, and since $D(BH\text{-}H) + D(BH_2\text{-}H) = 7.6$ eV, we obtain by difference $D(BH_2\text{-}H) = 3.9$ eV which also implies $\Delta H_f(BH_2) = 3.1$ eV. Interestingly, the ab initio calculations predict $D(BH\text{-}H) = 3.4$ eV,[14] very near the above 3.7 eV.

Using our selected value of $I(BH_2)$, we can now calculate the B–N bond energy in aminoborane,

$$A(BH_2^+) = D(H_2N\text{-}BH_2) + I(BH_2)$$

or

$$D(H_2N\text{-}BH_2) = 17.2 - 9.1 = 8.1 \text{ eV}$$

and since,

$$\Delta H_f(H_2NBH_2) = \Delta H_f(BH_2) + \Delta H_f(NH_2) - D(H_2N\text{-}BH_2)$$

$$\Delta H_f(H_2NBH_2) = 3.1 + 1.75 - 8.1 = -3.25 \text{ eV} = -75 \text{ kcal/mol}$$

An independent determination of $\Delta H_f(H_2NBH_2)$ using $A(NH_2^+)$ was impractical due to the low abundance of the ion (less than 2%) and interference from background water and oxygen. Although the precision is good, the accuracy of $A(BH_2^+)$ from H_2NBH_2 is suspicious since the ion is less than 2%, and weak intensities can result in high appearance potentials as has been noted for hydrocarbons.[16]

Using the measured $A(BH^+)$ and assuming formation of NH_2 and H, we note that $A(BH^+)$ must equal $A(BH_2^+) + D(BH^+\text{-}H)$. All three of these quantities are known, and therefore the inaccuracy of this relationship by 3.6 eV implies that the more probable product in forming BH^+ is NH_3,

$$A(BH^+) = A(BH_2^+) + D(BH^+\text{-}H) - D(NH_2\text{-}H)$$

and we see that forcing this equality demands that NH_3 be formed with about 0.9 eV of excess energy. This forced agreement will, of course, yield a consistent calculation of $D(H_2N\text{-}BH_2)$ from our measured $A(BH^+)$ as will forcing $D(B^+\text{-}H) = 2.07$ eV lead to a similarly consistent calculation from our $A(B^+)$. We conclude that our experimental values of $A(BH^+)$ and $A(B^+)$ do not allow really convincing calculations of $D(H_2N\text{-}BH_2)$.

The B–N bond energy in aminodifluoroborane may be calculated from $A(BF_2^+)$ or

$$D(H_2N\text{-}BF_2) = A(BF_2^+) - I(BF_2) = 16.1 - 8.5^{17} = 7.6 \text{ eV}$$

A similar calculation can be developed from $A(B^+)$, but no assumed fragmentation will produce even near consistency with

Table IV. Summary of Molecular Energetic Quantities

$I(BH_2) = 9.1 \pm 0.2$ eV
$D(B\text{–}H) = 3.5$ eV
$D(BH\text{–}H) = 3.7$ eV
$D(BH_2\text{–}H) = 3.9$ eV
$I(H_2NBH_2) = 11.0 \pm 0.1$ eV
$I(H_2NBF_2) = 12.4 \pm 0.4$ eV
$\Delta H_f(H_2NBH_2) = -75$ kcal/mol
$\Delta H_f(H_2NBF_2) = -255$ kcal/mol
$D(H_2N\text{–}BH_2) = 8.1$ eV
$D(H_2N\text{–}BF_2) = 7.6$ eV

the above number. Thus we conclude that our $A(B^+)$ is erroneous, probably due to its low intensity of less than 4%. It is also interesting to compare this bond energy with that of the isoelectronic $D(BF_2\text{–}F)$ at 7.34 eV.[17] $D(H\text{–}NH_2)$ and $D(H\text{–}F)$ at 138 and 134 kcal/mol show this same isoelectronic equivalence. The heat of formation of difluoroaminoborane is $\Delta H_f(H_2NBF_2) = \Delta H_f(NH_2) + \Delta H_f(BF_2) - D(H_2N\text{–}BF_2) = 40.3 + (-120)^{17} - 175$ or, $\Delta H_f(H_2NBF_2) = -255$ kcal/mol, and since we have measured $I(H_2NBF_2)$, then $\Delta H_f(H_2NBF_2^+) = 30$ kcal/mol.

All of these calculations of energetic quantities on BH_3, H_2BNH_2, and F_2BNH_2 are internally self-consistent, and these results may then be safely used in thermochemical calculations.

$A(H_2NBF^+)$ and $A(HNBF^+)$ from Table II permit several additional calculations. From $H_2NBF_2 \rightarrow H_2NBF^+ + F$, we calculate $D(H_2NBF^+\text{–}F) = 16.1 - 12.4 = 3.7$ eV, and from $H_2NBF_2 \rightarrow HNBF^+ + HF$, we calculate $D(HNBF^+\text{–}H) = 3.7$ eV and $D(HNBF^+\text{–}HF) = 1.6$ eV. Separated H and F atoms cannot occur in this fragmentation, for then $D(HNBF\text{–}H)$ would be negative, but this is unreasonable since $HNBF^+$ (m/e 45) is a 30% peak in the mass spectrum of H_2NBF_2 (see Table I). It is also possible to calculate the heats of formation of these ions as $\Delta H_f(H_2NBF^+) = 4.2$ eV and $\Delta H_f(HNBF^+) = 5.7$ eV wherein the usual assumption of no excitation of the products was used.

The more interesting or potentially useful energetic quantities that were either developed or used in this study are summarized in Table IV.

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Registry No. H_2NBF_2, 50673-31-9; H_3NBF_3, 15433-37-1; H_2NBH_2, 14720-35-5.

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Dialkylaminohydridophenoxyboranes. Convenient Preparation and Studies of Intramolecular Boron–Nitrogen π Bonding

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A convenient preparation of dialkylaminohydridophenoxyborane compounds ($HBOC_6H_5NR'_2$) has been developed according to the following three-step sequence: (1) $4BF_3$ (etherate) + $3NaBH_4 = 3NaBF_4 + 2B_2H_6(g)$; (2) $^1/_2B_2H_6(g) + HNR'_2 = H_3BNHR'_2$; (3) $H_3BHNR'_2 + HOC_6H_5$ + heat $= 2H_2 + HBOC_6H_5NR'_2$; $HNR'_2 = HN(CH_3)_2$, $HN(C_2H_5)_2$, $HN(i\text{-}C_3H_7)_2$, $HN(n\text{-}C_4H_9)_2$, $HN(CH_2C_6H_5)_2$, HNC_4H_8, and HNC_5H_{10}. The final products are isolated in yields ranging from 70 to 90% by vacuum distillation at moderate temperatures. Molecular association and variable-temperature proton magnetic resonance studies of these compounds in benzene solution are consistent with a planar, monomeric configuration with considerable π interaction between boron and nitrogen and hindered rotation about this bond. The Lewis acid behavior of diisopropylaminohydridophenoxyborane toward ammonia and trimethylamine was determined using a tensimetric titration procedure. No evidence of interaction was observed with trimethylamine while a stable 1:1 adduct was formed in the case of the reaction involving ammonia: $HBOC_6H_5N(i\text{-}C_3H_7)_2 + NH_3 = HBOC_6H_5N(i\text{-}C_3H_7)_2{\cdot}NH_3$. The room-temperature proton magnetic resonance spectrum of the ammonia adduct of diisopropylaminohydridophenoxyborane has demonstrated relatively unrestricted rotation about the secondary amino nitrogen–boron bond.

Introduction

A number of trigonal boron compounds containing three different substituents have been reported.[1] Those which have been described contain a dialkylamino group and two other substituents (R_2BNXY) which are either hydrogen, halogen, alkoxy, hydroxy, thio, or phosphine groups. The first reported dialkylaminohydridophenoxyborane compounds (R_2NBXY where X and Y are hydrogen and phenoxy, with R = ethyl or isopropyl) were prepared by hydrogenation of triphenyl borate in the presence of aluminum and a secondary amine (eq 1) or by the exchange reaction of triphenyl borate and bis(dialkylamino)alanes (eq 2).[2] The room-temperature proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane in benzene exhibited two magnetically distinct isopropyl environments. This was tentatively interpreted in terms of a planar, monomeric configuration involving boron–nitrogen π bonding and restricted rotation about this bond.[2] This assignment was made by comparison with similar spectra of $XB(NR_2)C_6H_5$ compounds where X = halogen or

$$2B(OR)_3 + Al + 2HNR'_2 \overset{H_2}{=\!=} HBORNR'_2 + B(OR)_2NR'_2 + Al(OR)_3 + {}^1/_2H_2 \quad (1)$$

$$2B(OR)_3 + HAl(NR'_2)_2 = HBORNR'_2 + B(OR)_2NR'_2 + Al(OR)_3 \quad (2)$$

$$R = C_6H_5;\ R' = C_2H_5,\ i\text{-}C_3H_7$$