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

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

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

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

NCO and R = methyl or isopropyl.[3,4]

The previous routes to the title compounds involve low overall yield; theoretically, only 50% of the borate starting material is converted to the dialkylaminohydridophenoxyborane. The synthetic techniques are involved requiring a high-temperature, high-pressure process in eq 1 or the use of highly reactive, relatively difficult to prepare bis(amino)alanes in eq 2. An improved, more convenient synthesis of these compounds was developed in order to facilitate a detailed study of their physical and chemical properties. This paper will report preparative aspects of the title compounds as well as additional studies of intramolecular boron–nitrogen π bonding.

Experimental Section

Handling Procedures. Boron hydrides are known to react with water and oxygen forming hydroxides and oxides, respectively. Precautions were taken in order to prevent contamination by the atmosphere. Boron hydride compounds were handled using Schlenk ware or a drybox under inert nitrogen atmosphere.[5]

General Chemicals. All chemicals were purchased as reagent grade and used without further purification unless otherwise stated.

Spectroscopic Measurements. (A) Infrared. Infrared spectra of neat, liquid samples were recorded using a Perkin-Elmer Model 221 infrared instrument and sodium chloride optics. Solid samples were recorded as a mull in Nujol. All infrared samples were prepared in the drybox.

(B) Proton Magnetic Resonance. Proton NMR spectra were recorded using a Varian A-60A instrument with a Varian variable-temperature accessory. Ambient-temperature spectra were recorded using the neat, liquid sample and trace quantities of methylene dichloride as internal standard. Variable-temperature spectra of selected samples were recorded using sealed NMR tubes containing the neat liquid sample and trace quantities of toluene as internal standard. The chemical shift of all signals was adjusted to make them relative to TMS using literature chemical shift values of τ 4.67 for H_2CCl_2 and τ 7.67 for $C_6H_5CH_3$.[6]

Preparation of Diborane and Secondary Amine–Borane Adducts. An apparatus for the external generation of diborane[7] was employed for the preparation of all secondary amine–borane adducts with the exception of dimethylamine–borane. The external diborane generator consisted of a 250-ml side-arm Schlenk flask fitted with a pressure-equalizing addition funnel. A three-way hose connector was attached to the top of the addition funnel. One arm of the hose connector was fitted with a septum and the other was connected to a nitrogen-vacuum double manifold.[5] The Schlenk flask side arm was connected to a gas dispersion inlet tube which fitted into one of the necks of a 250-ml three-neck flask. One of the other necks was fitted with a water condenser which was connected to a mercury–acetone-filled bubbler and the remaining neck was stoppered. The acetone served to trap unreacted diborane.

Diborane was generated by the reaction between boron trifluoride etherate and sodium borohydride in diglyme

$$3NaBH_4 + 4BF_3\ (\text{etherate}) \xrightarrow{\text{diglyme}} 2B_2H_6(g) + 3NaBF_4 \qquad (3)$$

In a typical reaction, 90 ml of a 1.0 M solution of $NaBH_4$ (0.09 mol) in diglyme (prepared by dissolving $NaBH_4$ in diglyme which was freshly distilled under vacuum from $LiAlH_4$) was added dropwise to 20.0 ml of $BF_3 \cdot O(C_2H_5)_2$ (0.156 mol) in 20.0 ml of dry diglyme. Diborane gas was swept from the generator into a magnetically stirred solution containing 0.10 mol of a secondary amine in 50.0 ml of dry benzene (distilled from $LiAlH_4$ prior to use) by maintaining a slow purge of dry nitrogen through the generator. After completion of the $NaBH_4$ addition the generator was heated for 1 hr at 70–80° to facilitate complete transfer of diborane. The following secondary amines were utilized in this procedure: $HN(C_2H_5)_2$, $HN(n\text{-}C_4H_9)_2$, $HN(i\text{-}C_3H_7)_2$, $HN(CH_2C_6H_5)_2$, HNC_4H_8, and HNC_5H_{10}. The resulting secondary amine–borane adducts were isolated in yields ranging from 80 to 95% by removal of benzene under vacuum. The authenticity of these adducts was established by comparison of appropriate melting points (where possible) and infrared and proton magnetic resonance spectra with appropriate data from the literature.

Preparation of Dimethylamine–Borane. The preparation of dimethylamine–borane by the reaction of diborane and dimethylamine was not attempted due to the relatively high volatility of dimethylamine. Dimethylamine–borane was prepared by the reaction of dimethylamine hydrochloride and lithium borohydride

$$LiBH_4 + (CH_3)_2NHCl = LiCl + H_2 + (CH_3)_2NH \cdot BH_3 \qquad (4)$$

Contrary to reports in the literature[8] which indicate predominant formation of dimethylaminoborane $[(CH_3)_2NBH_2]_2$, we were only able to isolate dimethylamine–borane $[(CH_3)_2NH \cdot BH_3]$ in yields of 60–70%. Our preparations involved the conditions specified by Shaeffer and Anderson using diethyl ether as solvent, filtration and removal of solvent from the filtrate, and a preparation which utilized no solvent. In the preparation which was run free of solvent, solid lithium borohydride (5.5 g, 0.25 mol) and dimethylammonium chloride (20.3 g, 0.25 mol) were layered along with a large magnetic stirring bar in a 500-ml flask. The flask was connected to a Schlenk tube cooled to −196° in liquid nitrogen by means of an all-glass connection and the apparatus was continuously evacuated to approximately 1 Torr. The reaction was started by physical mixing of the solid reagents using a large external magnet. A moderate rate of reaction was effected by cooling the reaction flask from time to time with cold tap water. Dimethylamine–borane (10.3 g, 70% yield) had transferred to the Schlenk tube after the reaction had been allowed to proceed for 2 hr. The product distilled under vacuum giving a single fraction at 75–76° and 0.5 Torr. The melting point of the distilled product was 35–36° which compares well with the literature value[9] of 37°. An infrared spectrum of this product exhibited strong NH and BH stretching vibrations at 3035 and 2030 cm^{-1}, respectively.

Preparation of Dialkylaminohydridophenoxyborane Compounds. Pyrolysis of Equimolar Mixtures of Secondary Amine–Borane Adducts and Phenol. Dialkylaminohydridophenoxyborane compounds where the amino moiety is $N(CH_3)_2$, $N(C_2H_5)_2$, $N(i\text{-}C_3H_7)_2$, $N(n\text{-}C_4H_9)_2$, $N(CH_2C_6H_5)_2$, NC_4H_8, and NC_5H_{10} were prepared by heating equimolar mixtures of an appropriate secondary amine–borane and phenol. The reactions were carried out under conditions which were applicable to all of the aminohydridophenoxyborane compounds reported here. The procedure involved charging a 50-ml flask with an equimolar mixture of secondary amine–borane and phenol in the drybox. After sampling a small portion of this mixture for infrared analysis, the flask was connected to a 6-in Vigreaux column which was fitted with distillation head, three-way distillation separator, and collection flasks under nitrogen purge. This apparatus was used to pyrolyze the amine borane–phenol mixture under an atmosphere of dry nitrogen and subsequently to purify the crude aminohydridophenoxyborane products by vacuum distillation.

The exact conditions which were used to prepare diethylaminohydridophenoxyborane are described below. The deviations from this procedure which were used to prepare other secondary aminohydridophenoxyboranes are noted.[10] In a typical preparation diethylamine–borane (4.82 g, 0.041 mol) and phenol (4.05 g, 0.043 mol) were mixed in a 50-ml flask in the drybox. The solid phenol was observed to dissolve in the liquid amine–borane with no apparent reaction.[10] A small portion of this liquid mixture was withdrawn with a syringe for infrared analysis. The flask was attached under nitrogen purge to the 6-in. Vigreux column and distillation assembly. Hydrogen was generated by heating this mixture slowly up to a maximum temperature of 150° over a 1-hr period using a Woods metal bath. Care was exercised during the initial stages of this procedure in order to avoid too rapid gas evolution and loss of liquid material from the flask by occasionally dropping the bath and allowing the mixture to cool slightly. After 1 hr at 150° all gas evolution had ceased. The crude product was allowed to cool to room temperature and a small portion was withdrawn using a syringe for infrared analysis. Pertinent infrared spectra are shown in Figure 1.

The distillation assembly was connected to a vacuum manifold and the crude product was gradually heated until a steady distillation rate was achieved. A single fraction distilling at 52.5° under 0.20 Torr was obtained. The yield was 4.8 g or 65% the theoretical yield. The analysis of this product is given in Table I.

The remaining dialkylaminohydridophenoxyborane compounds were prepared in an analogous fashion. Conditions under which all products distilled and per cent yield data are summarized in Table II.

Analyses. Freshly distilled samples of aminohydridophenoxyborane compounds were analyzed according to procedures reported previously.[2,11,12] The results of all analyses are summarized in Table I.

Proton Magnetic Resonance Spectra. While the proton magnetic resonance spectra of secondary aminohydridophenoxyboranes did not

Table I. Calculated and Experimental Weight Percent Composition Data for Dialkylaminohydridophenoxyborane Compounds

		% boron		% amine		% hydride hydrogen	
No.	Compd	Calcd	Found	Calcd	Found	Calcd	Found
1	$HBOC_6H_5N(CH_3)_2$	7.26	6.52	29.6	29.4	0.67	0.63
2	$HBOC_6H_5N(C_2H_5)_2$	6.11	6.09	40.7	39.5		
3	$HBOC_6H_5N(i\text{-}C_3H_7)_2$	5.27	5.29	48.8	47.3		
4	$HBOC_6H_5N(n\text{-}C_4H_9)_2$	4.68	4.10	54.9	53.5		
5	$HBOC_6H_5N(CH_2C_6H_5)_2$	3.59	3.58	65.2	64.4		
6	$HBOC_6H_5NC_4H_8$	6.18	5.93	40.0	38.8		
7	$HBOC_6H_5NC_5H_{10}$	5.72	5.38	44.5	42.4		

Table II. Percent Yield and Vacuum Distillation Data for Dialklaminohydridophenoxyborane Compounds from $R_2NH{\cdot}BH_3 + HOC_6H_5 = 2H_2 + HBOC_6H_5NR_2$

		Distillation conditions	
Compd[a]	% yield	Temp, °C	Vacuum Pressure, Torr
1	69	45-48	0.050
2	65	51-53	0.2
3	67	65-67	0.2
4	89	80-83	0.2
5	74	130-132	0.25
6	83	97-98	0.03
7	68	72-74	0.01

[a] Compound numbers are given in Table I.

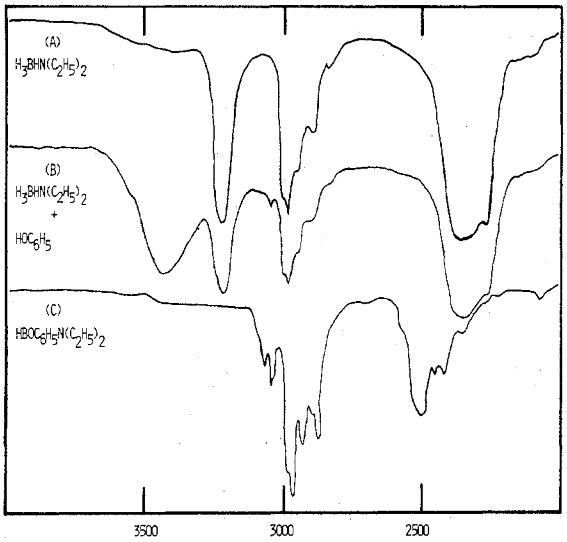


Figure 1. Infrared spectra (4000-2000 cm^{-1}) of diethylamine-borane (A), an equimolar mixture of phenol and diethylamine-borane (B), and diethylaminohydridophenoxyborane (C).

exhibit a signal due to hydridic hydrogen, signals for phenoxy and amino moieties in the expected relative ratio of intensities were observed. The chemical shift, multiplicity, and relative area ratio of all observed signals are summarized in Table III. Doubling or broadening of nitrogen alkyl signals was observed for all of the products at room temperature. This is clearly shown for diisopropylaminohydridophenoxyborane in Figure 2A.

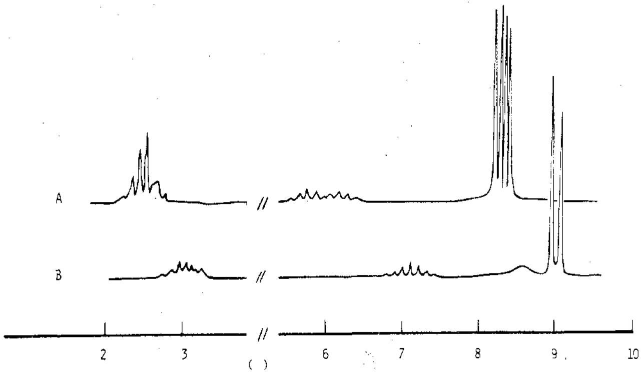


Figure 2. Proton magnetic resonance spectra of diisopropylaminohydridophenoxyborane (A) and the 1:1 ammonia adduct of diisopropylaminohydridophenoxyborane (B).

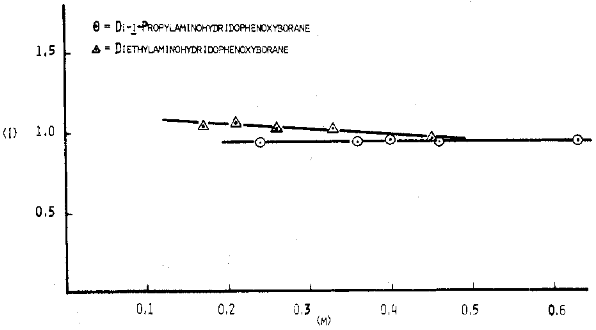


Figure 3. Plot of molecular association number (*I*) against molal concentration for benzene solutions of diethylaminohydridophenoxyborane and diisopropylaminohydridophenoxyborane.

Dibenzylaminohydridophenoxyborane exhibited two sharp benzyl proton singlets at room temperature. Variable-temperature proton magnetic resonance spectra at temperatures above ambient revealed coalesence of these signals near 110°. This signal was observed to split when the sample was allowed to cool to room temperature.

Molecular Weight Measurements. Molecular weights of diethylaminohydridophenoxyborane and diisopropylaminohydro-

Table III. Summary of Proton Magnetic Resonance Data for Dialkylaminohydridoborane Compounds[a]

		Amino alkyl signals	
Compd[b]	Aromatic signals[c]	Protons on the α carbon	Protons on the β and γ carbons
1	2.51 (m) 5.0	6.83 (s, b) 3.0 7.21 (s, b) 3.0	
2	2.85 (m) 4.7	6.78 (m) 4.0	8.80 (t) 6.1
3	2.57 (m) 5.1	5.75 (sep) 6.15 (sep) 2.0	8.25 (d) 8.31 (d) 11.0
4	2.70 (m) 5.0	6.67 (t, b) 4.4	8.27 (m, b) 8.73 (t) 15.0
5	2.17 (s, b) 15.0	5.17 (s) 5.33 (s) 4.1	
6	2.80 (m) 4.8	6.44 (t, b) 6.90 (t, b) 4.0	8.11 (s, b) 4.0

[a] Proton magnetic resonance data for each signal are given in the following order: chemical shift (τ), multiplicity, relative area ratio.
[b] Compound numbers are given in Table I. [c] Key: m, multiplet; t, triplet; d, doublet; sep, septet; b, broad; s, singlet.

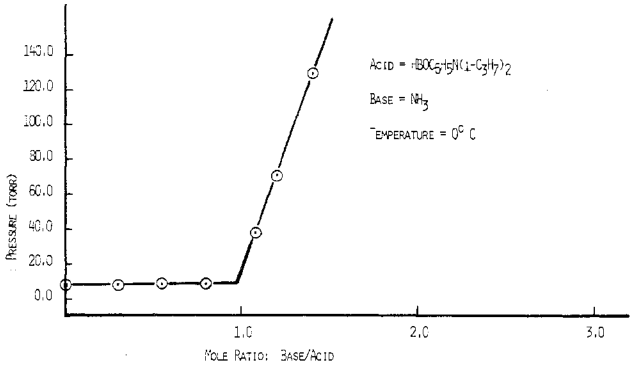


Figure 4. Tensimetric titration of diisopropylaminohydridophenoxyborane with ammonia.

phenoxyborane in benzene solution were determined using a cryoscopic method.[5] A plot of molecular association number (I) against molal concentration for these compounds is shown in Figure 3.

Tensimetric Titrations. The interaction between diisopropylaminohydridophenoxyborane and the Lewis bases trimethylamine and ammonia was determined at 0° using a tensimetric titration procedure. A tensimetric titration apparatus similar to the one described by Shriver using a solenoid stirrer was utilized for this study.[5] Trimethylamine and ammonia (from Matheson) were purified by fractional condensation from traps held at -45.2 and $-83.6°$, respectively. The vapor pressures of these gases were determined at -22.8 and $-45.2°$, respectively, and were found to be 257 and 409 Torr, respectively. Corresponding literature values are 255 and 408 Torr, respectively.[5]

No evidence of interaction was observed between diisopropylaminohydridophenoxyborane and trimethylamine; however, in the case of ammonia a stable 1:1 adduct was formed. A plot of sample pressure in Torr against the experimental molar ratio of ammonia relative to diisopropylaminohydridophenoxyborane is shown in Figure 4. At the end of the titration the excess ammonia was carefully removed under vacuum at 0°. No additional ammonia was released when the sample warmed to room temperature. The liquid adduct was dissolved in a minimum of methylene dichloride and the NMR spectrum of this solution was recorded. The spectrum consisted of a multiplet at τ 3.89, a septet at τ 7.09, a broad singlet at τ 8.55, and a doublet at τ 8.97 of relative intensity 5.2:2.0:3.0:12.0, respectively. This spectrum is shown in Figure 2B.

Results and Discussion

Preparation of Dialkylaminohydridophenoxyborane Compounds. A reasonably convenient preparation of secondary aminohydridophenoxyborane compounds has been developed. The three-step synthesis starting from boron trifluoride–etherate involves intermediate formation of diborane and dialkylamine–boranes (steps 1 and 2, respectively). The dialkylamine–boranes are isolated by removal of benzene solvent under vacuum. Secondary aminohydridophenoxyborane compounds are produced in the third step of the procedure by pyrolysis of equimolar mixtures of phenol and dialkylamine–boranes at 150° for approximately 2 hr. The crude products can be purified easily by vacuum distillation (Table II). Yields based on step 3 were found to vary in the range 70–90%.

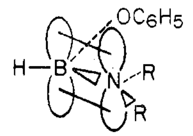
$$BF_3\cdot O(C_2H_5) \xrightarrow[(1)]{NaBH_4} {}^1/_2B_2H_6(g) \xrightarrow[(2)]{HNR_2} H_3B\cdot NR_2H \xrightarrow[(3)]{HOC_6H_5,\ \Delta} 2H_2 + HBOC_6H_5NR_2 \qquad (5)$$

Infrared spectroscopy provides a convenient means of monitoring the pyrolysis reaction (step 3). Pertinent infrared spectra in the region 4000–2000 cm^{-1} are shown in Figure 1. The spectrum of neat diethylaminohydridophenoxyborane is shown in Figure 1A. Nitrogen–hydrogen, aliphatic carbon–hydrogen, and boron–hydrogen stretching frequencies are observed at 3200, 2950, and 2400 cm^{-1}, respectively. The equimolar mixture of diethylamine–borane and phenol exhibits an oxygen–hydrogen stretching frequency at 3450 cm^{-1} in addition to those cited above for diethylamine–borane. The spectrum of the crude product obtained by pyrolysis of the phenol—diethylamine–borane mixture for approximately 2 hr at 150° is shown in Figure 1C. As expected, frequencies for oxygen–hydrogen and nitrogen–hydrogen stretching are no longer present. The spectrum consists of aromatic carbon–hydrogen, aliphatic carbon–hydrogen, and boron–hydrogen stretching frequencies at 3050, 2900, and 2500 cm^{-1}, respectively.

Intramolecular Boron–Nitrogen π Bonding. Dialkylaminohydridophenoxyborane compounds are formally classified as electron-deficient species, there being only six bonding electrons associated with the boron atom. Three distinct mechanisms for coordinative saturation of the boron atom exist. These are association, intramolecular π bonding, and coordination with a Lewis base. In the pure form or in a non Lewis base type solvent only the first two of these coordinative saturation mechanisms is possible. Steric, mechanistic, and electronic effects are expected to influence the mechanism of coordinative saturation for the neat materials or for solutions of these materials in hydrocarbon solvents. Bulky substituents may prevent association while electronic effects of substituents may affect the state of association by reducing the acceptor properties of the boron.[13]

Both diethyl- and diisopropylaminohydridophenoxyborane were found to be monomeric over the concentration range 0.1–0.6 m in benzene (Figure 3). There is no hint of association at the higher concentrations. These data clearly demonstrate the lack of association of dialkylaminohydridophenoxyboranes in hydrocarbon solvent and may suggest a monomeric environment for the neat materials.

Ambient-temperature proton magnetic resonance spectra of the neat materials and of hydrocarbon solutions of these materials reveal a doubling or a broadening of proton signals for the amino alkyl moieties (see Table III and Figure 2A). The NMR data coupled with the association data discussed above are consistent with a monomeric model with B═N intramolecular π bonding and restricted rotation about this bond

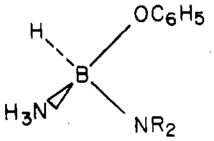


Variable-temperature proton magnetic resonance spectroscopy at temperatures above ambient of diisopropylaminohydridophenoxyborane and dibenzylaminohydridophenoxyborane reveals coalescence of the amino alkyl signals at 90 and 110°, respectively. These spectral changes were found to be reversible. The general appearance of the variable-temperature spectra and comparison with those reported for $XBC_6H_5N(CH_3)_2$ compounds where X = halogen suggests a barrier to rotation on the order of 10–20 kcal/mol.

Dialkylaminohydridophenoxyboranes which have a relatively weak boron–nitrogen π bond are predicted to form stable Lewis adducts with suitable Lewis bases. We have studied the interaction between diisopropylaminohydridophenoxyborane and the bases trimethylamine and ammonia at 0° using a tensimetric titration procedure. While no evidence of interaction was observed with trimethylamine, a stable 1:1 adduct was formed when ammonia was used (see Figure 4 and eq 6).

$$HBOC_6H_5N(i\text{-}C_3H_7)_2 + NH_3 = HBOC_6H_5N(i\text{-}C_3H_7)_2\cdot NH_3 \qquad (6)$$

This adduct was found to be stable at room temperature. The fact that ammonia acts as a stronger base toward diisopropylaminohydridophenoxyborane can be explained on steric grounds. This is supported by the fact that steric crowding is important in the reactions of methylamine bases $[(CH_3)_nNH_{3-n}, n = 1-3]$ and the relatively small acid trimethylboron. The ambient-temperature proton magnetic resonance spectrum of the ammonia adduct of diisopropylaminohydridophenoxyborane (Figure 2B) is entirely consistent with free rotation about the boron–dialkylamino nitrogen bond. This is expected from coordinative saturation of the boron and sp^3 hybridization on boron in the adduct, i.e.



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Registry No. $BH_3{\cdot}HN(C_2H_5)_2$, 2670-68-0; $BH_3{\cdot}HN(n\text{-}C_4H_9)_2$, 55124-34-0; $BH_3{\cdot}HN(i\text{-}C_3H_7)_2$, 55124-35-1; $BH_3{\cdot}HN(CH_2C_6H_5)_2$, 55124-36-2; $BH_3{\cdot}HNC_4H_8$, 55124-37-3; $BH_3{\cdot}HNC_5H_{10}$, 4856-94-4; $BH_3{\cdot}HN(CH_3)_2$, 74-94-2; $HBOC_6H_5N(CH_3)_2$, 55124-38-4; $HBOC_6H_5N(C_2H_5)_2$, 32015-64-8; $HBOC_6H_5N(i\text{-}C_3H_7)_2$, 32015-58-0; $HBOC_6H_5N(n\text{-}C_4H_9)_2$, 55124-39-5; $HBOC_6H_5N(CH_2C_6H_5)_2$, 55124-40-8; $HBOC_6H_5NC_4H_8$, 55124-41-9; $HBOC_6H_5NC_5H_{10}$, 55124-42-0; $HBOC_6H_5N(i\text{-}C_3H_7)_2{\cdot}NH_3$, 55124-43-1; C_6H_5OH, 108-95-2.

References and Notes

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Reactions of Pentaborane(11) with Ethers

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Reactions of pentaborane(11) (B_5H_{11}) with ethers were studied at low temperatures by means of ^{11}B NMR spectroscopy. The reactions of B_5H_{11} with dimethyl and diethyl thioethers give the symmetrical cleavage products $R_2S{\cdot}BH_3$ and $R_2S{\cdot}B_4H_8$. Species that are produced in the reaction system of B_5H_{11} and oxoethers are very dependent upon the base strength of the ether. Strongly basic tetrahydrofuran can effect the unsymmetrical cleavage of B_5H_{11} to produce $H_2B(THF)_2{}^+B_4H_9{}^-$. Evidence for the formation of this cleavage product is based on the NMR spectral evidence and on the observed reaction products produced in the reaction of HCl with the B_5H_{11}–THF system. A second species is observable in the THF–B_5H_{11} system which is more predominant at higher temperatures. This species is assigned as the simple adduct $B_5H_{11}{\cdot}THF$. Moderately basic ethers like dimethyl and diethyl ethers produce only one observable species which is considered to be $B_5H_{11}{\cdot}OR_2$. Weakly basic diisopropyl ether does not react with B_5H_{11}. No direct evidence for the symmetrical cleavage of B_5H_{11} by oxoethers has been observed. The similarities and differences between these reactions and analogous B_4H_{10} reactions are discussed.

Introduction

The reactions of pentaborane(11) (B_5H_{11}) with some Lewis bases have been systematized in terms of symmetrical and unsymmetrical cleavage reactions. Symmetrical cleavage takes place with carbon monoxide and phosphines PF_2X (X = H, F, Cl, Br, I, $N(CH_3)_2$)[1]

$$B_5H_{11} + 2L \rightarrow H_3B{\cdot}L + L{\cdot}B_4H_8$$

where L represents the Lewis bases mentioned above. Unsymmetrical cleavage of B_5H_{11} has been found to occur in the reaction of the borane with ammonia[2]

$$B_5H_{11} + 2NH_3 \rightarrow H_2B(NH_3)_2{}^+B_4H_9{}^-$$

Reactions of ethers[3] and many amines[4] with B_5H_{11} are reported to give complex mixtures of borane derivatives and boranes. The boranes isolated from these reactions include diborane(6) (B_2H_6), tetraborane(10) (B_4H_{10}), pentaborane(9) (B_5H_9), hexaborane(10) (B_6H_{10}), and nonaborane(15) (B_9H_{15}). These boranes were speculated to be a result of the decomposition of the unstable ether adduct of tetraborane(8), $B_4H_8{\cdot}OR_2$, which initially would have been formed in the symmetrical cleavage reaction of B_5H_{11}.[4] This speculation was apparently proposed on the basis of the known reactions of B_2H_6 and B_4H_{10} with ethers, which generally give the symmetrical cleavage products of the boranes, e.g.

$$B_4H_{10} + 2THF \rightarrow THF{\cdot}BH_3 + THF{\cdot}B_3H_7{}^5$$

Since none of the etherates of B_4H_8 have been isolated from the reactions of B_5H_{11} with ethers and the mechanism for the formation of the higher boranes from such reactions is not understood, the present investigation of B_5H_{11}–ether systems was undertaken. Observations of the systems were made by