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A Convenient Synthesis of Aminoboranes

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Detailed studies of the synthesis of aminoboranes by the reduction of phenyl borate with aluminum and hydrogen in the presence of secondary amines have been carried out. The amines used were diethylamine, diisopropylamine, and piperidine and the nature of the product formed was found to be a function of the phenyl borate:amine ratio. For example, tris(diethylamino)borane (81%) is prepared in admixture with bis(diethylamino)borane (5%) when diethylamine is used as the solvent whereas bis(diethylamino)borane is prepared exclusively and in high yield (80%) when phenyl borate and diethylamine are employed in a 1:2 molar ratio in benzene solvent. Aluminum–hydrogen reduction of equimolar quantities of phenyl borate and diethylamine in benzene solvent did not afford a high yield of the expected diethylaminoborane. Instead, nearly equimolar quantities of diethylaminohydridophenoxyborane [$HB(OC_6H_5)N(C_2H_5)_2$] and diethylaminobis(phenoxy)borane [$B(OC_6H_5)_2N(C_2H_5)_2$] were isolated. This reaction was found to be insensitive to changes in reaction time or temperature. The reaction sequence proposed to explain formation of the latter products involves (1) intermediate formation of AlH_3 [$Al + {}^3/{}_2H_2 \rightarrow AlH_3$], (2) reaction between AlH_3 and diethylamine forming the more thermodynamically stable bis(diethylamino)alane

$$AlH_3 + R_2NH \longrightarrow AlH_3NR_2H \xrightarrow[-H_2]{} H_2AlNR_2 \xrightarrow[-H_2]{R_2NH} HAl(NR_2)_2$$

and (3) reduction of phenyl borate by bis(diethylamino)alane [$2B(OC_6H_5)_3 + HAl(NR_2)_2 \rightarrow HB(OC_6H_5)NR_2 + B(OC_6H_5)_2NR_2 + Al(OC_6H_5)_3$]. Exchange studies between a number of aminoalanes and borate esters were also carried out.

Introduction

The use of aminoboranes as catalysts,[1] reducing agents,[2] and synthetic intermediates[3] has been reported; however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of these reagents. Until now aminoboranes have been prepared by the reaction of diborane with secondary amines[4] (eq 1) or of an alkali metal borohydride with a dialkylammonium chloride[5] (eq 2).

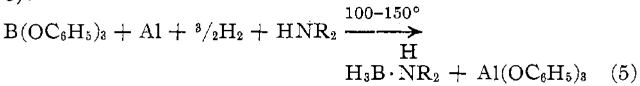
$$B_2H_6 + 2HNR_2 \longrightarrow 2H_3BNR_2H \xrightarrow[-2H_2]{} 2H_2BNR_2 \qquad (1)$$

$$NaBH_4 + R_2NH_2{}^+Cl^- \longrightarrow H_3BNR_2H + NaCl + H_2 \xrightarrow[-H_2]{} H_2BNR_2 \qquad (2)$$

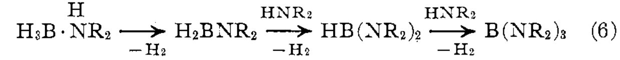
More recently the aluminum–hydrogen system has been used to arrive at a more economic and convenient route to precursors of aminoboranes. In this connection it has been found that aluminum and hydrogen reduces (1) boric oxide in the presence of aluminum chloride to form diborane in 40–50% yield at 750 atm[6] (eq 3), (2) methyl borate (in the presence of an $AlCl_3$–NaCl melt) to form B_2H_6 in ~20–30% yield,[7] and (3) phenyl borate (in the presence of tertiary amines) to form amine–boranes in nearly quantitative yield (eq 4).[8] In the latter case, the soluble amine–boranes were easily separated from the insoluble aluminum phenoxide byproduct by filtration. The reduction of phenyl borate by aluminum and hydrogen in the presence of tertiary amines represents a convenient route to amine–boranes which is probably also the most economic route to this class of compounds. The reaction is thought to proceed through the intermediate formation of AlH_3 followed by reduction of the phenyl borate to diborane which then reacts with the tertiary amine to form the amine–borane. The reduction of phenyl borate with aluminum and hydrogen in the presence of an equimolar amount of a secondary amine was predicted in an analogous way to generate dialkylamine–boranes (eq 5). Unfortunately dialkylamine–boranes are only stable at low temperatures;[9] however when the reaction is carried out in 1:1, 1:2, and 1:3 stoichiometry (phenyl borate:amine) under the conditions of Al–H_2 reduction (120–160°), it should be possible to form dialkylaminoboranes (H_2BNR_2), bis(dialkylamino)boranes ($HB(NR_2)_2$), and tris(dialkylamino)boranes [$B(NR_2)_3$] (eq 6).

$$6(AlH_xCl_{3-x}) + xB_2O_3 \longrightarrow xB_2H_6 + 6AlO_{x/2}Cl_{3-x} \qquad (3)$$

$$B(OC_6H_5)_3 + {}^3/{}_2H_2 + NR_3 + Al \longrightarrow H_3BNR_3 + Al(OC_6H_5)_3 \qquad (4)$$



$$B(OC_6H_5)_3 + Al + {}^3/{}_2H_2 + HNR_2 \xrightarrow{100\text{–}150°} H_3B\cdot\overset{H}{N}R_2 + Al(OC_6H_5)_3 \qquad (5)$$



$$H_3B\cdot\overset{H}{N}R_2 \xrightarrow[-H_2]{} H_2BNR_2 \xrightarrow[-H_2]{HNR_2} HB(NR_2)_2 \xrightarrow[-H_2]{HNR_2} B(NR_2)_3 \qquad (6)$$

Thus, it should be possible to synthesize a wide variety of aminoboranes depending on the initial stoichiometry of the reactants and the reaction temperature. The economics of these processes are worthy of note since the raw materials are borax, aluminum, and hydrogen. The final products are aminoboranes and aluminum phenoxide which can easily be separated by filtration of the insoluble aluminum phenoxide. Hydrolysis of the aluminum phenoxide in the presence of sulfuric acid regenerates phenol and forms alum ($Al_2(SO_4)_3$) (a seizing material used in the paper industry). The regenerated phenol can then react with borax and H_2SO_4 to form more phenyl borate.

$$\begin{tikzcd}
B(OC_6H_5)_3 + Al + H_2 \arrow[r, "R_2NH"] & H_3BNR_2H + Al(OC_6H_5)_3 \arrow[d, "H_2SO_4"] \\
C_6H_5OH + Al_2(SO_4)_3 \arrow[u, "borax + H_2SO_4"] & \arrow[l]
\end{tikzcd} \qquad (7)$$

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[2] B. M. Mikhailov and V. A. Dorakhov, *Dokl. Chem.*, **136**, 51 (1961).

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The present study was undertaken to establish procedures for preparing exclusively, in high yield, each of the predicted reaction products. Description of the course of the aluminum–hydrogen–phenyl borate reduction was of additional interest and experiments were conducted to describe the reaction sequence involved.

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by use of either standard bench-top techniques carried out under a dry nitrogen atmosphere or in a drybox equipped with an atmosphere purification system for removal of oxygen and moisture.[10] Infrared spectral measurements were obtained using a Perkin-Elmer 621 automatic grating spectrophotometer. Samples were prepared for analysis in the drybox. Spectra of liquid samples were obtained from the neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer using solvent signals (either benzene or methylene dichloride) as the internal standard.

Hydrogenation reactions were performed using a 300-ml Magnedrive autoclave unit from Autoclave Engineers Inc. The chamber was charged in the drybox, and the contents were heated with stirring under hydrogen for a predetermined time. After sufficient cooling the chamber was vented and soluble products were filtered from excess unreacted aluminum and aluminum phenoxide in the drybox.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from $NaAlH_4$ prior to use. Diethylamine was purchased from Eastman Chemicals and distilled onto active molecular sieve, Type 4-A. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. The aluminum was "activated" prior to use by a modification of the method described by Ziegler.[11] Boric acid and phenol were obtained from Fisher Chemical Co. and used without further purification. Phenyl borate was prepared by the reaction of boric acid and phenol according to the method described by Lappert and coworkers.[12] Ultra Pure hydrogen (99.9995%) was obtained from the Matheson Corp. and used without further purification.

Analyses.—Aminoboranes are relatively stable toward hydrolysis.[13] Complete hydrolysis was effected by boiling in water for extended periods (several hours). Samples for analysis were weighed in 50–100-ml flasks, attached to a distillation column, and 50 ml of distilled water was added. The mixtures were heated to distil the evolved amine into a receiver kept cold with a water–ice slurry. Nitrogen (as secondary amine) in the distillate was determined by titration with standard acid. Boron was determined by standard base titration of the boric acid–mannitol complex.[14] The unsymmetrical dialkylaminohydridophenoxyboranes [$HB(OC_6H_5)NR_2$, R = C_2H_5 and i-C_3H_7] were analyzed by a modification of the above procedure. Boron was separated from phenol (after hydrolysis and removal of the amine by distillation) by distillation of boron as methyl borate.[15] Boron was analyzed in the distillate as described above.

Hydrogen in these compounds was not measured analytically owing to the difficulty of effecting complete hydrolysis on a hydrogen gas liberation manifold. The presence of hydrogen (or absence) was determined qualitatively by infrared spectral techniques.

Reactions: Aluminum–Hydrogen Reductions of Phenyl Borate. A. Preparation of Bis(diethylamino)borane.—In a typical experiment phenyl borate (30 g or 0.1 mol), diethylamine (0.2 mol), aluminum metal (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 180° under 3000 psig of hydrogen for 5 hr (reaction 2, Table I). Vacuum distillation (after filtration of the reaction mixture to remove unreacted aluminum metal and aluminum phenoxide and removal of benzene solvent under vacuum) gave a single fraction which boiled at 62° (15.0 mm). The yield of bis(diethylamino)borane was 13.3 g or 85%. *Anal.* Calcd for $HB(N(C_2H_5)_2)_2$: B, 6.94; N (as amine), 92.5. Found: B, 6.82; N, 91.3. Aluminum phenoxide (~15 g) (determined by comparison of infrared spectral data) was left in the distillation flask.

B. Preparation of Tris(diethylamino)borane.—Phenyl borate (0.1 mol), aluminum metal (2.7 g or 0.1 g-atom), and diethylamine (as solvent, 100 ml) were heated at 180° under 3000 psig of hydrogen for 24 hr (reaction 1, Table I). Vacuum distillation (after filtration and removal of solvent under vacuum) gave two fractions. Bis(diethylamino)borane distilled at 63° (15 mm, yield 5%) and tris(diethylamino)borane distilled at 95° (11 mm, 81% yield). *Anal.* Calcd for $B(N(C_2H_5)_2)_3$: B, 6.94; N (as amine), 92.5. Found: B, 6.82; N, 91.3.

C. Attempted Preparation of Diethylaminoborane.—Phenyl borate (0.1 mol), diethylamine (0.1 mol), aluminum metal (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 180° under 3000 psi of hydrogen for 2 hr (eq 5, Table I). Vacuum distillation (after filtration and removal of solvent under vacuum) gave two fractions. The first fraction, $HB(OC_6H_5)N(C_2H_5)_2$ (42% yield), distilled at 90° (5 mm) while the second fraction, $B(OC_6H_5)_2N(C_2H_5)_2$ (39% yield), distilled at 120° (0.5 mm). *Anal.* Calcd for $HB(OC_6H_5)N(C_2H_5)_2$: B, 6.11; N (as amine), 40.6. Found: B, 6.12; N, 40.2. Infrared spectral analysis indicated both aromatic, *N*-alkyl, and active hydride environments (B–H at 2498 cm^{-1}). Proton magnetic resonance spectroscopic analysis (in CH_2Cl_2) showed signals at τ 2.87 (aromatic multiplet), 6.76 (ethylmethylene quartet), and 8.80 (ethylmethyl triplet) of relative areas 4.7:4.0:6.2, respectively. *Anal.* Calcd for $B(OC_6H_5)_2N(C_2H_5)_2$: B, 4.02; N (as amine), 26.8. Found: B, 3.82; N, 25.6. Infrared spectral analysis indicated the absence of a B–H stretching band and the presence of both aromatic and *N*-alkyl environments. The proton magnetic resonance spectrum of this compound in CH_2Cl_2 consisted of signals at τ 3.07 (aromatic multiplet), 6.86 (ethylmethylene quartet), and 8.86 (ethylmethyl triplet) of relative areas 10.0:3.7:6.2, respectively.

Essentially the same results were observed when the reaction time was extended to 4 and 24 hr (reactions 6–8, Table I) with the exception that in each case a small quantity (<1% yield) of $H_2B[N(C_2H_5)_2]$ vapor transferred (at 25°, 0.25 mm) into a Schlenk tube cooled in a Dry Ice–acetone slurry prior to vacuum distillation of the major components as described above. The infrared spectrum of this material (Nujol mull) was identical with that of $H_2B[N(C_2H_5)_2]$ prepared by unequivocal synthesis (*vide infra*). The observed melting point of 44° corresponds to the literature value.[16]

D. Synthesis of Bis(piperidino)borane.—Phenyl borate (0.1 mol), piperidine (0.2 mol), aluminum (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 150° under 4000 psig of hydrogen for 12 hr (reaction 3, Table I). The reaction mixture was filtered in the drybox and solvent was removed *in vacuo*. Vacuum distillation of the residue gave one fraction which boiled at 95° at 5 mm. The infrared spectrum of this material (neat between KBr plates) exhibited a B–H stretching frequency at ~2500 cm^{-1}. The proton magnetic resonance spectrum in CH_2Cl_2 indicated the absence of aromatic absorption and the normal resonances characteristic of free piperidine. Analysis of this material revealed an amine:boron ratio of 1.92:1.00 indicating that the compound is bis(piperidino)borane; yield 12 g or 67%. *Anal.* Calcd for bis(piperidino)borane: B, 6.12; amine, 93.4. Found: B, 6.11; amine, 92.1.

E. Attempted Synthesis of Bis(diisopropylamino)borane.—Phenyl borate (0.1 mol), diisopropylamine (0.20 mol), aluminum (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 150° under 4000 psig of hydrogen for 5 hr (reaction 4, Table I). After cooling, the mixture was filtered and the solvent was removed from the filtrate *in vacuo*. Vacuum distillation of the residue gave two fractions. The first fraction boiled at 90° (0.5 mm) and was found to be diisopropylaminohydridophenoxyborane [$HB(OC_6H_5)N(i\text{-}C_3H_7)_2$]. *Anal.* Calcd for diisopropylaminohydridophenoxyborane: B, 5.54; amine, 51.3. Found: B, 5.29; amine, 47.3. The infrared spectrum of this material exhibited a B–H stretching frequency at 2502 cm^{-1}. The proton magnetic resonance spectrum was complex and will be discussed in detail in the Discussion. The spectrum of this material, dis-

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solved in CH_2Cl_2, revealed aromatic and nitrogen isopropyl proton resonances in the expected ratio of 5:14. The 40° spectrum of the nitrogen-alkyl region of the neat material (with trace toluene as internal standard) is shown in Figure 1 while the spectrum obtained at 120° is shown in Figure 2.

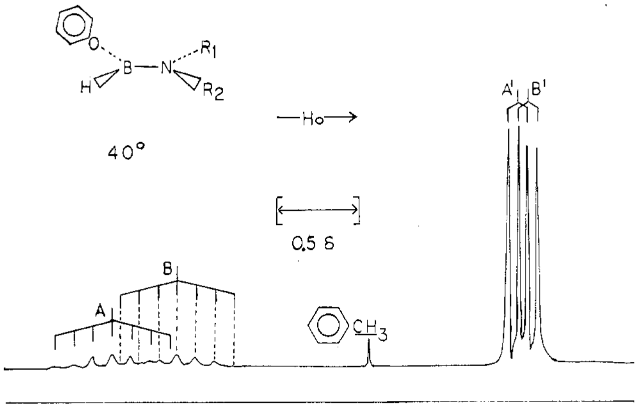

Figure 1.—Nitrogen alkyl proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane at 40°: A, methyne septet at τ 6.20; B, methyne septet at τ 6.62; A', doublet at τ 8.72; B', doublet at τ 8.82. $CH_3C_6H_5$ is the internal standard.

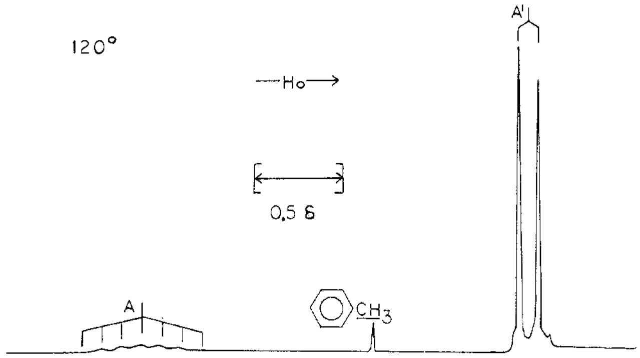

Figure 2.—Proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane at 120°: A, methyne septet at τ 6.42; A', doublet at τ 8.71. $CH_3C_6H_5$ is the internal standard.

The second fraction boiled at 125° (0.5 mm). There was no band in the infrared spectrum of this fraction indicative of a B–H environment. The proton magnetic resonance spectrum of the neat material indicated aromatic and nitrogen isopropyl proton environments in the ratio of 10:14, indicating that the material has the empirical formula $B(OC_6H_5)_2N(i\text{-}C_3H_7)_2$. *Anal.* Calcd for $B(OC_6H_5)_2N(i\text{-}C_3H_7)_2$: B, 3.7. Found: B, 3.9.

F. Aluminum–Hydrogen Reduction of Methyl Borate.—Methyl borate (0.1 mol from Aldrich Chemical Corp. and distilled from sodium metal), diethylamine (0.2 mol), aluminum, (5 g or 0.18 g-atom), and benzene (100 ml) were heated at 140° under 4000 psig of hydrogen for 5 hr. This mixture was cooled, vented, and filtered in the drybox. The proton magnetic resonance spectrum of the filtrate matched exactly that of an equimolar mixture of methyl borate and diethylamine in benzene. No aluminum was found in solution, indicating that no reaction had occurred. Similar results were observed in analogous experiments when the reaction time was extended to 24 hr or at reaction temperatures of 100–180°.

Aminoalane–Borate Ester Exchange Reactions. A. Reaction of Equimolar Quantities of Bis(diethylamino)alane and Phenyl Borate.—Phenyl borate (2.89 g or 0.0100 mol) and bis(diethylamino)alane (1.707 g or 0.00995 mol) prepared by the direct reaction of aluminum, hydrogen, and diethylamine[17] at 180° were weighed and mixed in the drybox (reaction 1, Table II). Immediate evolution of heat was accompanied by solution of the phenyl borate. The infrared spectrum (neat) showed a B–H stretching vibration at 2500 cm^{-1} but no Al–H stretching bands. Benzene (25 ml) was added and the mixture was stirred at 55° for 12 hr. A white precipitate (later identified as aluminum phenoxide by comparison of infrared spectral data) had formed. The mixture was filtered, solvent was removed under vacuum, and the product was separated by vacuum distillation. The product boiled at 63° (15 mm) and was identified as $HB[N(C_2H_5)_2]_2$ by comparison of infrared spectral data. The yield was 1.5 g or 96% recovery of boron. Some 1.8 g of aluminum phenoxide remained in the distillation flask.

B. Reaction of Phenyl Borate and a 0.5 Molar Equiv of Bis(diethylamino)alane.—Phenyl borate (9.2 g or 0.0318 mol) and bis(diethylamino)alane[19] (2.74 g or 0.0159 mol) were mixed in 25 ml of benzene. Evolution of heat was noted. The mixture was stirred for 12 hr at 55°. White solid (later identified as aluminum phenoxide by infrared spectral comparison) formed during this period. The solution was filtered and the solvent was removed under vacuum. Vacuum distillation gave two products, $HB(OC_6H_5)N(C_2H_5)_2$ at 90° (5 mm) (2.87 g or 0.0162 mol) and $B(OC_6H_5)_2N(C_2H_5)_2$ at 120° (0.5 mm) (2.69 g or 0.0101 mol). These products were identified by comparison of appropriate infrared spectral data. Some aluminum phenoxide remained in the distillation flask. Aluminum phenoxide obtained in both the filtration and distillation steps was combined and the yield found to be 5.629 or 0.0184 mol.

C. Reaction of Equimolar Quantities of Diethylaminoalane and Phenyl Borate.—Phenyl borate (10 mmol) and diethylaminoalane (10 mmol from the reaction of equimolar quantities of diethylamine and trimethylamine–alane in benzene solution) were mixed in benzene (25 ml) (reaction 2, Table II). The mixture was stirred at 60° for 12 hr during which time a white solid (later identified as aluminum phenoxide) had formed. The mixture was filtered and the solvent was removed from the filtrate under vacuum, yielding a volatile solid product. This was identified as diethylaminoborane by infrared spectral comparison. Some aluminum phenoxide remained in the distillation flask; yield 0.8 g or 94%.

D. Reaction of Equimolar Quantities of Methyl Borate and Bis(diethylamino)alane.—Methyl borate (1.14 ml or 10.0 mmol) was added to a stirred solution of bis(diethylamino)alane[19] (1.721 g or 10.0 mmol) in benzene (50 ml) (reaction 3, Table II). Solid formation (as a gel suspended in benzene) was rapid after approximately 30 sec. The mixture was filtered after 1 hr yielding a white solid and clear colorless filtrate. The solid was washed with additional benzene. The solvent was removed from the combined filtrates under vacuum yielding a relatively involatile liquid. This was shown to be bis(diethylamino)borane by infrared spectral comparison. The yield was 1.53 g or 9.8 mmol (98%).

E. Reaction of Equimolar Quantities of Methyl Borate and Diethylaminoalane.—Methyl borate (0.54 ml or 4.74 mmol) was added to a stirred solution of diethylaminoalane (0.04779 g or 4.74 mmol) in benzene (50 ml) (reaction 4, Table II). Solid formation was rapid (20 sec). The mixture was filtered after 5 hr yielding a white solid and a clear filtrate. Removal of solvent from the filtrate gave a white, volatile solid which was shown to be diethylaminoborane by infrared analysis. The diethylaminoborane was redissolved in benzene and made up to a known volume, and the yield was determined to be 91%.

F. Reaction of Equimolar Quantities of Methyl Borate and Bis(piperidino)alane.—Methyl borate (0.63 ml or 5.52 mmol) was added to a stirred solution of bis(piperidino)alane[18] (1.078 g or 5.52 mmol) in benzene (50 ml) (reaction 5, Table II). Formation of a solid was apparent after approximately 30 sec. This solid was separated by filtration yielding a clear colorless filtrate. Solvent was removed from the filtrate under vacuum yielding 0.915 g of a clear liquid material. This was found to be bis(piperidino)borane by analysis. *Anal.* Calcd for bis(piperidino)borane: B, 6.12; amine, 93.4. Found: B, 6.15; amine, 93.8 (yield 92%).

Unequivocal Synthesis of $H_3BN(C_2H_5)_2H$.—Diborane, generated by the reaction of $NaAlH_4$ and BF_3 in ether,[18] was passed through a trap cooled in a Dry Ice–acetone slurry and allowed to bubble through diethylamine in benzene. Isolation of liquid $H_3BN(C_2H_5)_2H$ was effected by removal of solvent under vacuum. *Anal.* Calcd for $H_3BN(C_2H_5)_2H$: B, 12.4; N (as amine), 84.0. Found: B, 12.6; N, 85.6. Infrared spectral analysis revealed N–H and B–H stretching frequencies at 3260 and 2330 cm^{-1}, respectively.

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TABLE I

PREPARATION OF AMINOBORANES BY ALUMINUM–HYDROGEN REDUCTION OF PHENYL BORATE (3000 PSI)

$$B(OC_6H_5)_3 + R_2NH + Al \xrightarrow[H_2]{\Delta} H_nB(NR_2)_{3-n} + Al(OC_6H_5)_3$$

Reaction no.	Amine	$B(OC_6H_5)_3$:amine molar ratio	Time, hr	Temp, °C	Products	Yield, %
1	Diethylamine	1:∞ (amine solvent)	24	180	$B[N(C_2H_5)_2]_3$ $HB[N(C_2H_5)_2]_2$	81 5
2[a]	Diethylamine	1:2	5	180	$HB[N(C_2H_5)_2]_2$	85
3	Piperidine	1:2	12	150	$HB(NC_5H_{10})_2$	67
4	Diisopropylamine	1:2	5	150	$HB(OC_6H_5)N(i\text{-}C_3H_7)_2$ $B(OC_6H_5)_2N(i\text{-}C_3H_7)_2$	34 56
5[a]	Diethylamine	1:1	2	180	$HB(OC_6H_5)N(C_2H_5)_2$ $BN(C_2H_5)_2(OC_6H_5)_2$	42 39
6	Diethylamine	1:1	4	180	$H_2BN(C_2H_5)_2$ $HB(OC_6H_5)N(C_2H_5)_2$ $BN(C_2H_5)_2(OC_6H_5)_2$	<1 40 35
7	Diethylamine	1:1	24	180	$H_2BN(C_2H_5)_2$ $HB(OC_6H_5)N(C_2H_5)_2$ $BN(C_2H_5)_2(OC_6H_5)_2$	<1 38 37
8	Diethylamine	1:1	24	100	$HB(OC_6H_5)N(C_2H_5)_2$ $BN(C_2H_5)_2(OC_6H_5)_2$	32 47

[a] These results are each representative of three runs under the specified conditions.

Unequivocal Synthesis of $H_2BN(C_2H_5)_2$.—Diethylaminoborane was prepared by pyrolyzing $H_3BN(C_2H_5)_2H$ at 200° for 4 hr. The crystalline product melted at 44° (lit.[16] value 44°) and showed B–H stretching bands at 2422 and 2358 cm^{-1}. No N–H stretching band was visible.

Results and Discussion

Aluminum–Hydrogen Reduction of Borate Esters.—Reaction conditions and results of aluminum–hydrogen reduction of phenyl borate in the presence of a variety of secondary amines are summarized in Table I.

Reference to this table indicates that attempts to prepare tris(diethylamino)borane and bis(diethylamino)borane (reactions 1 and 2, respectively) were quite successful. In this connection bis(diethylamino)borane was prepared exclusively when aluminum and hydrogen were allowed to react with phenyl borate and 2 equiv of diethylamine. On the other hand, when diethylamine was used as solvent, tris(diethylamino)borane (81%) was generated in admixture with bis(diethylamino)borane (5%).

$$B(OC_6H_5)_3 + Al + H_2 + 2N(C_2H_5)_2H \longrightarrow HB[N(C_2H_5)_2]_2 + Al(OC_6H_5)_3 + {}^3/_2H_2 \quad (8)$$

$$B(OC_6H_5)_3 + Al + H_2 + 3N(C_2H_5)_2H \longrightarrow B[N(C_2H_5)_2]_3 + Al(OC_6H_5)_3 + {}^5/_2H_2 \quad (9)$$

The conditions for synthesis of bis(diethylamino)borane were extended to include direct preparation of bis(piperidino)- and bis(diisopropyl)aminoborane. Bis(piperidino)borane was generated in moderate yield (67%) in reaction 3, Table I, while markedly contrasting results were observed in the corresponding reaction with diisopropylamine (reaction 4, Table I). In this reaction none of the expected bis(diisopropylamino)borane could be isolated. Instead the reaction products were found to be diisopropylaminohydridophenoxyborane (yield 34%) and bis(phenoxy)diisopropylaminoborane (yield 56%).

Attempts to prepare diethylaminoborane exclusively and in high yield were not successful. Product analysis of reaction 5 (Table I) revealed formation of two compounds, $HB(OC_6H_5)N(C_2H_5)_2$ in 42% yield and $B(OC_6H_5)_2N(C_2H_5)_2$ in 39% yield.

$$2B(OC_6H_5)_3 + Al + H_2 + 2N(C_2H_5)_2H \longrightarrow HB(OC_6H_5)N(C_2H_5)_2 + B(OC_6H_5)_2N(C_2H_5)_2 + Al(OC_6H_5)_3 \quad (10)$$

Isolation of these products indicates incomplete reduction of the B–OC_6H_5 bonds and suggests that aluminum–hydrogen reduction of phenyl borate in the presence of *equal equivalents* of diethylamine involves a stepwise reduction. The initial results (reaction 5) suggest that additional reaction time is required in order to effect complete reduction necessary for the preparation of diethylaminoborane. In this connection, reaction times were extended to 4 and 24 hr (reactions 6 and 7). A low yield (<1%) of diethylaminoborane was isolated in each of these reactions; in addition, the major products (and respective yields) were found to be identical, within experimental error, to results observed when the reaction time was 2 hr. The same products were isolated even when the reaction temperature was lowered to 100° with a reaction time of 24 hr (reaction 8) indicating that failure to isolate diethylaminoborane is not due to thermodynamic instability of this material at higher temperatures.

Aminoalane Reductions of Borate Esters.—Inability to generate the expected diethylaminoborane by aluminum–hydrogen reductions of 1:1 molar mixtures of phenyl borate and diethylamine (reactions 5–8) and isolation of diethylaminohydridophenoxyborane and bis(phenoxy)diethylaminoborane in equal yields approximating 50% suggest a particular reaction sequence. Incomplete reduction of all phenoxyboron bonds suggests that (1) the active reducing agent is *not* an unlimited quantity of AlH_3 (generated by the reaction of excess Al and hydrogen) since AlH_3 would be expected to reduce phenyl borate to diborane, (2) the active reducing agent ("Al–H species") is present in limited quantity and functions only to reduce some of the phenyl borate, and (3) the quantity of actual reducing agent is limited by the quantity of secondary amine present initially.

The reaction sequence which is consistent with these general requirements and which we propose is the sequence operative in reactions 5–8 (Table I) involves (1) the intermediate formation of AlH_3 (by the reaction of aluminum and hydrogen, (2) reaction of AlH_3 and diethylamine forming the more thermodynamically stable bis(diethylamino)alane, and (3) reduction of phenyl borate by the aminoalane. The exact sequence proposed is described below:

step I

$$2HNR_2 + Al \xrightarrow{H_2} HAl(NR_2)_2 \tag{11}$$

step II

$$2B(OC_6H_5)_3 + HAl(NR_2)_2 \longrightarrow HB(OC_6H_5)NR_2 + B(OC_6H_5)_2NR_2 + Al(OC_6H_5)_3 \quad (R = C_2H_5) \tag{12}$$

Independent verification of this reaction sequence has been obtained. With reference to step I we have found[17] that reaction of aluminum, hydrogen, and diethylamine in benzene solvent results in predominant formation of the corresponding bis(dialkylamino)alane by the reaction sequence shown in eq 13. It was demonstrated by dta–tga studies that bis(dialkylamino)alanes are more thermodynamically stable than the corresponding dialkylaminoalanes (H_2AlNR_2), and, thus, the former compounds are formed preferentially in this reaction. Prior art concerning step II is rather sparse. Some previous studies provide information concerning the reduction of borate esters with alkoxyalanes,[19] alanes, and alkali metal hydrides.[20] The reduction of borate esters with aminoalanes has not been studied in any detail; thus we attempted to study this reaction by characterizing the aminoalane reduction of phenyl borate at two different stoichiometries. In the first reaction, equimolar quantities of bis(diethylamino)alane and phenyl borate were allowed to react. Isolation of bis(diethylamino)boranes was nearly quantitative according to the reaction

$$Al + {}^3/_2H_2 \xrightarrow{HNR_2} H_3AlNR_2H \xrightarrow[-H_2]{} H_2AlNR_2 \xrightarrow[-H_2]{HNR_2} HAl(NR_2)_2 \tag{13}$$

$$B(OC_6H_5)_3 + HAl(NR_2)_2 \longrightarrow HB(NR_2)_2 + Al(OC_6H_5)_3 \quad (R = C_2H_5) \tag{14}$$

The infrared spectrum of the neat mixture obtained after initial mixing of the reagents exhibited a B–H stretching frequency at 2500 cm^{-1} and no Al–H stretching frequency. These data indicate that the first step of the exchange, transfer of hydrogen from aluminum to boron, occurs rapidly; however, the observation that "aluminum phenoxide" is dissolved in benzene (see Experimental Section) indicates that the intermediates actually present in this reaction are mixed, unsymmetrical $B(OC_6H_5)_n(NR_2)_{3-n}$ compounds (where $n = 1$ or 2). Equilibria among the species present allows isolation of the most volatile component [bis(diethylamino)borane] and forces the reaction to completion. These results indicate that aminoalanes exchange both hydrogen and secondary amino groups with phenyl borate when the aminoalane is present in sufficient quantity. The proposed stepwise reaction is

$$B(OC_6H_5)_3 + HAlNR_2 \longrightarrow HB(OC_6H_5)_2 + Al(NR_2)_2OC_6H_5 \rightleftharpoons HB(OC_6H_5)NR_2 + Al(OC_6H_5)_2NR_2 \rightleftharpoons HB(NR_2)_2 + Al(OC_6H_5)_3 \tag{15}$$

The reaction of phenyl borate and 0.5 molar equiv of bis(diethylamino)alane was studied to determine whether the incompletely exchanged boron species $HB(OC_6H_5)N(C_2H_5)_2$ and $B(OC_6H_5)_2N(C_2H_5)_2$ could be isolated when the aminoalane is present in limiting quantity. Infrared spectral analysis of the mixture obtained after initial mixing of the reagents indicates the absence of an Al–H stretching band and the presence of a B–H stretching band at ~2500 cm^{-1}. Thus, the first step of the exchange, transfer of hydride from aluminum to boron, occurs rapidly. Isolation of $HB(OC_6H_5)N(C_2H_5)_2$, $B(OC_6H_5)_2N(C_2H_5)_2$, and $Al(OC_6H_5)_3$ was nearly quantitative thus establishing the reaction sequence shown in eq 16 as a reasonable path in the proposed exchange reactions. Apparent solubilization of aluminum phenoxide in benzene is indicative of a complex equilibrium involving unsymmetrical, incompletely exchanged species. As before, the most volatile components (in this case $HB(OC_6H_5)N(C_2H_5)_2$ and $B(OC_6H_5)_2N(C_2H_5)_2$) were isolated by vacuum distillation.

$$\begin{tikzcd} 2B(OC_6H_5)_3 + HAl(NR_2)_2 \arrow[r] \arrow[d] & HB(OC_6H_5)NR_2 + B(OC_6H_5)_2(NR_2) + Al(OC_6H_5)_3 \arrow[d, shift right] \\ HB(OC_6H_5)_2 + Al(NR_2)_2OC_6H_5 + B(OC_6H_5)_3 \arrow[r, shift left] & HB(OC_6H_5)NR_2 + Al(OC_6H_5)_2NR_2 + B(OC_6H_5)_3 \arrow[l, shift left] \arrow[u, shift right] \end{tikzcd} \quad (R = C_2H_5) \tag{16}$$

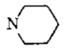
The results of the aminoalane–phenyl borate exchange reactions are in agreement with our observations concerning the reaction of equimolar mixtures of phenyl borate and diethylamine with aluminum and hydrogen. These exchange reactions successfully account for formation of the exact products (with analogous per cent yields) and in addition provide direct explanation of the apparent solubilization of aluminum phenoxide in benzene. These reactions provide convincing evidence that reactions of equimolar quantities of phenyl borate and diethylamine with aluminum and hydrogen proceed through intermediate formation of the bis(diethylamino)alane.

The aminoalane–borate ester reduction study was expanded to include the reaction of a greater variety of aminoalanes with phenyl borate and in addition the reaction of aminoalanes with methyl borate. The reactions studied and the results are summarized in Table II.

TABLE II

REACTION OF EQUIMOLAR QUANTITIES OF AMINOALANES WITH BORATE ESTERS IN BENZENE

$$H_nAl(NR_2)_{3-n} + B(OR')_3 \longrightarrow H_nB(NR_2)_{3-n} + Al(OR')_3$$

Reaction no.	NR_2	R'	n	Yield, %
1	$N(C_2H_5)_2$	C_6H_5	1	96
2	$N(C_2H_5)_2$	C_6H_5	2	94
3	$N(C_2H_5)_2$	CH_3	1	98
4	$N(C_2H_5)_2$	CH_3	2	91
5		CH_3	1	92

Reaction 1 was discussed above. Aminoalane reductions of methyl borate (reactions 3–5) proceed more cleanly than analogous reactions with phenyl borate in that precipitation of by-product aluminum methoxide is complete (presumably due to the higher heat of crystallization of this reagent) and the aminoborane is separated by simple filtration of the benzene solution. Reduction of borate esters by aminoalanes and synthesis of the corresponding aminoboranes appears to be a

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(19) H. Nöth and H. Suchy, *Z. Anorg. Allg. Chem.*, **358**, 49–68 (1968).

(20) H. I. Schlesinger and H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, **75**, 186 (1953).

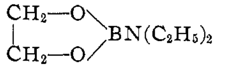
perfectly general reaction as evidenced by the successful synthesis of both diethylamino- and bis(diethylamino)-borane (reactions 1 and 2, respectively, involve phenyl borate while reactions 3 and 4, respectively, involve methyl borate). These reactions can logically be extended to include synthesis of the general series of aminoboranes as evidenced by the successful synthesis of bis(piperidino)borane from bis(piperidino)alane and trimethyl borate (reaction 5).

In view of our observations concerning the successful preparation of aminoboranes by aminoalane reductions of *methyl borate* we decided to substitute methyl borate for phenyl borate in the reaction with aluminum and hydrogen in the presence of a secondary amine. Such a substitution has obvious economic and practical merit since methyl borate is commercially available and phenyl borate is not. Surprisingly, no reaction of methyl borate with aluminum, hydrogen, and diethylamine under a variety of reaction conditions (see Experimental Section) was observed. This is an interesting observation in light of our earlier report that phenyl borate is reduced in high yield with aluminum and hydrogen in the presence of a tertiary amine to the amine–borane ($H_3B \cdot NR_3$) whereas the corresponding reaction using methyl borate does not take place. Since the bis(dialkylamino)alane reduces methyl borate to the bis(dialkylamino)borane, it is clear that the bis(dialkylamino)alane is not formed in the reaction of dialkylamines with aluminum and hydrogen with methyl borate although the reaction does occur with phenyl borate. It has been shown experimentally that no reaction at all takes place between methyl borate, diethylamine, aluminum, and hydrogen although the same reaction mixture minus methyl borate produces bis(diethylamino)alane in high yield. Thus it is clear that methyl borate or something contained in the methyl borate prevents reaction. A possible explanation involves the greater sensitivity of methyl borate to hydrolysis resulting in the formation of methyl alcohol which then deactivates the aluminum powder. The methyl borate used in these reactions was distilled over sodium and the reactions were carried out using precautions against atmospheric exposure; however it is possible that only minute contamination is needed to produce the observed effect.

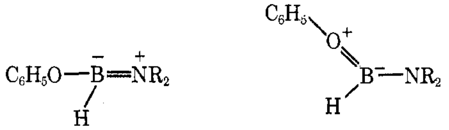
Properties of Dialkylaminohydridophenoxyboranes.—The dialkylaminohydridophenoxyboranes which were isolated have not been described previously. However, they are similar to analogous dialkylaminohydridothioboranes[21,22] which have been described. The dialkylaminohydridophenoxyboranes are liquids at room temperature and can be distilled under vacuum (see Experimental Section for details); they are stable to disproportionation up to their boiling points and are infinitely miscible with common hydrocarbon and ether solvents. They are hydrolyzed by water to hydrogen, boric acid, secondary amine, and phenol.

Ambient-temperature proton magnetic resonance spectra of the aminohydridophenoxyboranes are complex. In addition to normal phenoxy environments (and absence of hydride resonances) these compounds exhibit two nonequivalent nitrogen–alkyl environments of equal intensity. The alkyl region of the proton magnetic resonance spectrum of diisopropylaminohydridophenoxyborane is shown in Figure 1. Two partially overlapping septets (A and B centered at τ 6.62 and 6.20, respectively) and two doublets (A′ and B′ centered at 8.72 and τ 8.82, respectively) are clearly resolved at 40°.

Nonequivalent dialkylamino environments in these derivatives are most likely a result of boron–nitrogen π bonding and hindered rotation about this bond. That nonequivalence is not due to the existence of associated species was demonstrated by a magnetic resonance dilution study (spectra were recorded in benzene solution in the concentration range 1.0–0.05 *m*) which indicated that alkyl nonequivalence was independent of concentration. A variable-temperature study of the neat material (with trace toluene as internal standard) was performed. The resonances present in the 40° spectrum broadened with an increase in temperature. At 90° the resonances for the isopropyl methyl groups coalesced into a broad doublet while the methyne protons appeared as a broad (featureless) absorption at $\tau \sim 6.4$. These signals were observed to sharpen as the temperature was raised. At 120° (Figure 2) the methyne protons appear as a distinct septet centered at τ 6.42 while the isopropyl methyl protons appear as a sharp doublet centered at τ 8.71. These spectra were found to be reversible. These spectral characteristics are very similar to those reported for $XB(NR_2)C_6H_5$ species (X = halogen, NCO; R = methyl, isopropyl) which were also interpreted in terms of nitrogen–boron π bonding and hindered rotation.[23,24] Boron–nitrogen π bonding in the aminohydridophenoxyboranes is interesting in view of possible competition with oxygen–boron π bonding. That boron–nitrogen π bonding is preferred when both are possible has also been suggested by infrared studies[25] in the system



and suggests that the resonance structure of type I is more important than that of type II.



I

II

It is interesting to speculate on possible boron–nitrogen π bonding in the dialkylaminobis(phenoxy)borane derivatives which were isolated. No distinction is possible by nmr since B–N π bonding and coplanarity of the heavy-atom framework results in a plane of symmetry through boron and nitrogen and thus alkyl equivalence. In fact, proton magnetic resonance spectra of these derivatives ($B(OC_6H_5)_2NR_2$, R = C_2H_5 and *i*-C_3H_7) give rise to *single*, well-resolved *N*-alkyl signals at ambient temperature.

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