

possible that k_3 is $\leq 10^6$ l./mol sec but then it becomes difficult to explain why the monoalkoxyborane has not been observed.¹⁶ In addition, with ethylborane, where we did observe the dimer and diadduct, we found that the partial pressure of the diadduct did not go to zero as the probe closely approached the sampling orifice. The nonzero intensity at zero time was attributed to the fact that, in the vicinity of the probe where mixing is incomplete, there are high local con-

centrations of the added reagent gas and thus enhanced diadduct formation. Thus the limits on k_3 and k_9 should be lower. We feel then that the observation of no dialkoxyborane at all suggests that $\text{BC}_3\text{H}_9\text{O}$ is $(\text{CH}_3)_2\text{COBH}_3$. If this conclusion is correct, the reaction we are observing is of the same type as reaction 1.

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The Reaction of Diborane with Trimethylamine-Alane and Dimethylaminoalane

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Diborane adds to trimethylamine-alane in toluene or diethyl ether to produce $(\text{CH}_3)_3\text{N}\cdot\text{Al}(\text{BH}_4)_3$. The action of excess diborane in toluene establishes an equilibrium competition between aluminum borohydride and diborane for trimethylamine. Reaction of trimethylamine-borane with aluminum borohydride in toluene produces the same equilibrium mixture. In diethyl ether diborane and $(\text{CH}_3)_3\text{N}\cdot\text{Al}(\text{BH}_4)_3$ form trimethylamine-borane and $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{Al}(\text{BH}_4)_3$. Diborane adds to solutions of dimethylaminoalane in diethyl ether or toluene to form $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$. Excess diborane slowly causes formation of μ -dimethylaminodiborane and aluminum borohydride. In tetrahydrofuran dimethylaminoalane and borane form $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ which reacts with excess borane to produce μ -dimethylaminodiborane and $n\text{-C}_4\text{H}_9\text{OAl}(\text{BH}_4)_2$.

Introduction

A number of workers have shown that diborane adds to aluminum-hydrogen bonds to produce aluminum borohydride derivatives.¹⁻³ Neither the utility of this reaction for the synthesis of aluminum borohydride derivatives nor the behavior of these products in the presence of excess diborane has been explored. This paper describes the preparation of the known compounds $(\text{CH}_3)_3\text{NAl}(\text{BH}_4)_3$ and $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ ⁴ by the addition of diborane to trimethylamine-alane and dimethylaminoalane, respectively, and details the reactions of these materials with excess diborane.

Experimental Section

General Data.—All manipulations involving air- or moisture-sensitive materials were carried out using standard inert-atmosphere and high-vacuum techniques. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer equipped with a 32.1-MHz probe; boron chemical shifts are in ppm relative to diethyl ether-boron trifluoride. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers.

Nmr studies were performed using reaction vessels of the type shown in Figure 1. The overall dimensions of the vessel are such that it may be inserted in and removed from the nmr instrument without disturbing the probe.

Trimethylamine-alane and dimethylaminoalane were prepared by the method of Ruff and Hawthorne.⁵ Aluminum borohydride was generated by the reaction of aluminum chloride with

sodium borohydride.⁶ Trimethylamine-borane was prepared by the method of Schaeffer and Anderson.⁷ Diborane was formed by treating sodium borohydride with warm polyphosphoric acid. The pure solvents diethyl ether, toluene, and tetrahydrofuran (THF) were stored in evacuated bulbs over lithium aluminum hydride and were vacuum transferred directly into reaction vessels when used.

Reaction of Trimethylamine-Alane with Diborane in Toluene. A solution of 0.175 g (1.96 mmol) of trimethylamine-alane in 5 ml of toluene was stirred magnetically in the presence of 4.20 mmol of diborane in a 250-ml bulb for 1 hr at room temperature. Fractionating the volatile products through -126° resulted in the recovery of 1.14 mmol of diborane, implying a consumption of 3.06 mmol (calcd for $(\text{CH}_3)_3\text{NAl}(\text{BH}_4)_3$, 2.94 mmol). The colorless solid residue in the reaction bulb was sublimed to a -78° cold finger by gentle warming with an infrared heat lamp. The sublimate was identified as $(\text{CH}_3)_3\text{NAl}(\text{BH}_4)_3$ by its melting point of $79-81^\circ$ (lit.⁸ mp 79°) and its known infrared spectrum (Nujol).⁴ This experiment produced 0.133 g (1.02 mmol, 52%) of sublimed product.

In experiments with longer reaction times, more diborane was consumed and work-up of volatile products produced some trimethylamine-borane (identified by ir spectrum). Further attempts at separation resulted in the appearance of more diborane and an easily sublimed colorless solid, identified as $(\text{CH}_3)_3\text{N}\cdot\text{Al}(\text{BH}_4)_3$, strongly suggesting a reversible reaction.

Boron-11 Nmr Study of the Diborane-Trimethylamine-Alane-Toluene System.—A solution of 0.123 g (1.38 mmol) of trimethylamine-alane in 1 ml of toluene was prepared in an nmr reaction vessel. Diborane was added in approximately 0.7-mmol increments and the boron-11 nmr spectrum of the solution was recorded after each addition. The first two spectra consisted only of a single quintet at 37.4 ppm with $J = 85$ Hz. No signal characteristic of diborane was detected. After the third

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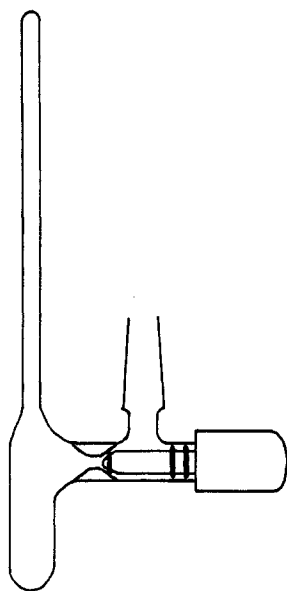
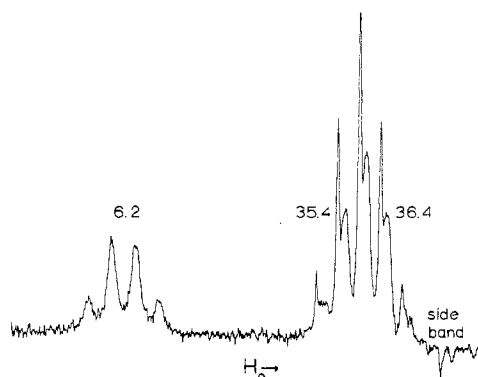


Figure 1.—Reaction vessel for boron-11 nmr studies.

Figure 2.—Boron-11 nmr spectrum of final $(\text{CH}_3)_3\text{NAlH}_2\text{-B}_2\text{H}_6$ products in toluene: quartet 6.2 ppm, $(\text{CH}_3)_3\text{NBH}_3$; quintet 35.4 ppm, $\text{Al}(\text{BH}_4)_3$; quintet 36.4 ppm, $(\text{CH}_3)_3\text{NAl}(\text{BH}_4)_2$; side band, B_2H_6 .

addition the diborane to trimethylamine-alane in the system was slightly greater than 1.5; the nmr spectrum showed, in addition to a very weak quartet at 7 ± 1 ppm, a second very weak but sharper quintet at 35.1 ppm, $J = 85$ Hz, superimposed on a strong quintet at 36.4 ppm, $J = 85$ Hz. Addition of a final 0.7 mmol of diborane caused an increase in the intensity of the quartet and the sharp quintet and resulted in the appearance of a weak diborane signal. The intensity of the quartet and the sharp quintet increased over a period of 2 hr. The final spectrum after 4 hr (Figure 2) clearly shows the quartet (6.2 ppm, $J = 95$ Hz), the two quintets (sharp 35.4 ppm, $J = 86$ Hz; broad 36.4 ppm, $J = 86$ Hz), and the high-field side band of the diborane resonance.

Rapid vacuum-line separation of diborane from the less volatile materials showed that 3.35 g-atoms of boron was consumed per g-atom of aluminum. Attempts at further separation again resulted in the appearance of more diborane and $(\text{CH}_3)_3\text{N}\cdot\text{Al}(\text{BH}_4)_3$.

To confirm the reversibility implied by these results (eq 1), a

$$(\text{CH}_3)_3\text{NAl}(\text{BH}_4)_3 + 0.5\text{B}_2\text{H}_6 \rightleftharpoons (\text{CH}_3)_3\text{NBH}_3 + \text{Al}(\text{BH}_4)_3 \quad (1)$$

solution of 0.98 mmol of trimethylamine-borane in 1 ml of toluene was treated with 0.98 mmol of aluminum borohydride in an nmr reaction vessel. Initially, the boron-11 nmr spectrum showed only the quartet and sharp quintet characteristic of the reactants. After 2 hr at room temperature, the spectrum was identical with Figure 2. A rapid fractionation of the volatile products through -126° resulted in the isolation of 0.24 mmol of diborane.

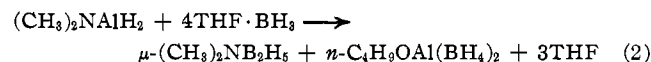
Reaction of Trimethylamine-Alane with Diborane in Diethyl Ether.—A 0.121-g (1.36-mmol) sample of trimethylamine-alane and 3.08 mmol of diborane were allowed to react in 10 ml of diethyl ether. After 48 hr at room temperature, fractionation of the volatile products through -126° produced 0.47 mmol of diborane implying a consumption of 2.61 mmol (calcd for complete reaction, 2.72 mmol). The solvent fraction was distilled through a -45° trap several times to separate trimethylamine-borane, yielding 0.079 g (1.08 mmol), 80% based on reactants. The reaction vessel contained a clear, colorless, involatile liquid which was identified by its infrared spectrum (liquid film) as $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{Al}(\text{BH}_4)_3$ contaminated with a small quantity of trimethylamine-borane.

Reaction of Dimethylaminoalane with Diborane in Toluene.—A solution of 0.188 g (2.57 mmol) of dimethylaminoalane in 10 ml of toluene was stirred magnetically for 4 hr in the presence of 3.34 mmol of diborane in a 250-ml vessel at room temperature. Removal and fractionation of volatile products through -126° resulted in the recovery of 0.69 mmol of diborane, implying a consumption of 2.65 mmol (calcd for $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$, 2.57 mmol). The white solid residue was sublimed to a -78° cold finger by warming with an infrared heat lamp. The sublimed product, 0.173 g (1.71 mmol, 67%), was identified as $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ by its melting point of 156° (lit.⁴ mp 156°) and its known infrared spectrum (Nujol).⁴

In experiments of several days' to 2 weeks' duration the diborane consumption increased. After recovery of diborane, fractionation of volatiles through -63° produced μ -dimethylaminodiborane, identified by its infrared spectrum. No dimethylaminoborane was isolated or detected. Treatment of the toluene fraction with diethyl ether and evaporation produced an involatile liquid identified as $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{Al}(\text{BH}_4)_3$ by its infrared spectrum (liquid film).⁹

Reaction of Dimethylaminoalane with Diborane in Diethyl Ether.—A set of reactions in diethyl ether was carried out in a fashion similar to the above experiments. The same initial production of $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ and subsequent very slow formation of μ -dimethylaminodiborane and aluminum borohydride (diethyl ether complex) was observed.

Reaction of Dimethylaminoalane with Diborane in THF.—A solution of 0.099 g (1.35 mmol) of dimethylaminoalane in 5 ml of THF was allowed to react with 3.15 mmol of diborane at room temperature for 20 hr. After removal of the volatile products, a colorless, slightly volatile liquid and a very small quantity of solid remained in the reaction vessel. The infrared spectrum (liquid film) of this material correlated exactly with that reported for $n\text{-C}_4\text{H}_9\text{OAl}(\text{BH}_4)_2$.⁸ Repeated fractionation of the volatile products through -126° produced 0.57 mmol of diborane, implying a consumption of 2.58 mmol (calcd for complete reaction (eq 2), 2.70 mmol). A trap at -45°



retained only a minute amount of scarcely volatile unidentified solid; no dimethylaminoborane was found. The THF fraction was condensed into a bulb containing 1 *N* sulfuric acid. Hydrogen of hydrolysis amounted to 6.67 mmol, implying the presence of 1.33 mmol of μ -dimethylaminodiborane (calcd for complete reaction, 1.35 mmol).

In a separate experiment, dimethylaminoalane and diborane (1:1) were allowed to react in THF for 30 min. An infrared spectrum (Nujol) of the solid material remaining after evaporation of the solvent identified the product as $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$, thus confirming the initial formation of this substance in THF.

Boron-11 Nmr Study of the Addition of Diborane to Dimethylaminoalane in THF.—Approximately 0.5-mmol portions of diborane were added to a solution of 0.078 g (1.06 mmol) of dimethylaminoalane in 1 ml of THF in an nmr reaction vessel. The spectra recorded after the first two additions showed only a strong quintet. After the third increment of diborane, the spectrum showed, in addition to a strong broadened quintet, a weak triplet at -5 ppm and a weak sextet at 18 ppm characteristic of μ -dimethylaminodiborane in THF¹⁰ (Figure 3A). A fourth portion of diborane caused the quintet to broaden further and the sextet to increase in intensity (Figure 3B). After addition of a fifth portion of diborane, the spectrum showed a broad strong quintet, a strong μ -dimethylaminodiborane signal,

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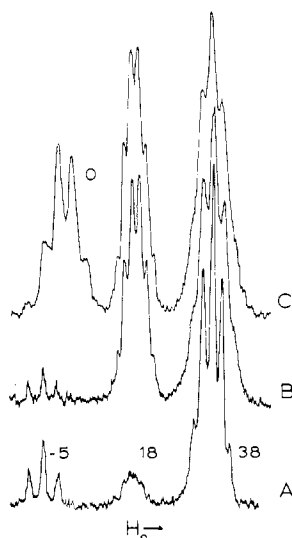
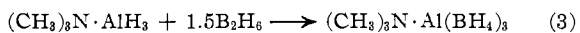


Figure 3.—Boron-11 nmr study of addition of BH_3 to $(\text{CH}_3)_2\text{NAlH}_2$ in THF: spectrum A, $\text{BH}_3:\text{Al} = 3:1$; spectrum B, $\text{BH}_3:\text{Al} = 4:1$; spectrum C, $\text{BH}_3:\text{Al} = 5:1$.

and a quartet of medium intensity at 0 ppm characteristic of tetrahydrofuran-borane (Figure 3C).¹¹

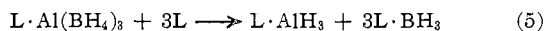
Results and Discussion

The addition of diborane to trimethylamine-alane and dimethylaminoalane occurs readily as summarized in eq 3 and 4. The reactions occur quickly and the

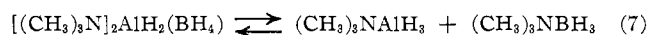
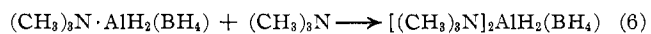


products may be isolated easily and purified by sublimation when toluene is the solvent. Although in all cases an excess of diborane was employed, it is not unlikely that mixed aluminum hydride-borohydride derivatives⁴ could be prepared using appropriate stoichiometry.

Aluminum borohydride is a strong Lewis acid which reacts with a stoichiometric quantity of strong base or with an excess of weak base to form complexes of the type $\text{L}\cdot\text{Al}(\text{BH}_4)_3$. With excess strong base borane groups can be displaced as shown in eq 5.⁹ In certain

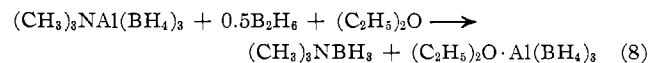


cases reversible reactions have been found to occur (eq 6 and 7).¹² This work has demonstrated that amine-

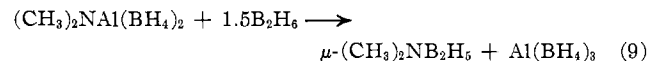


and aminoaluminum borohydrides are susceptible to attack by Lewis acids (diborane) as well as by Lewis bases. In the diborane- $(\text{CH}_3)_3\text{N}\cdot\text{Al}(\text{BH}_4)_3$ -toluene case a reversible system is established in agreement with eq 1, demonstrating that aluminum borohydride is a sufficiently strong Lewis acid to compete effectively with diborane for a limited quantity of base. In Figure 2 the broadened quintet is characteristic of $(\text{CH}_3)_3\text{N}\cdot\text{Al}(\text{BH}_4)_3$;¹⁸ the sharper quintet can be assigned to aluminum borohydride. The labile nature of this system is responsible for the difficulties encountered in

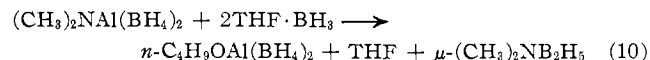
the separation of volatile products. In diethyl ether, diborane and $(\text{CH}_3)_3\text{NAl}(\text{BH}_4)_3$ produce the same products, but the reaction (eq 1) is driven to the right by the formation of the aluminum borohydride complex with the solvent (eq 8).



In the diborane- $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ -toluene or -ether systems, the aluminum-nitrogen bond is also separated (eq 9), but the reaction is much slower. In THF



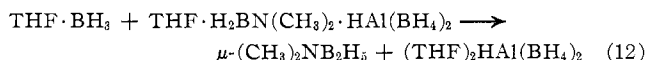
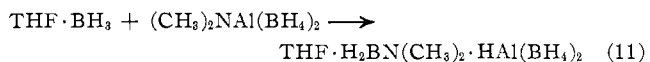
the rate of aluminum-nitrogen bond dissociation is greatly enhanced, but the reaction involves solvent cleavage (eq 10). Ashby and Foster reported a similar



ring opening in their study of the reaction of lithium aluminum hydride with borane in THF.²

The most probable reason for the higher rate of Al-N bond separation by borane in THF is the greater base strength of the solvent. Ruff discovered that $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ is associated in benzene solution;⁴ almost certainly this association occurs through a dative bond between aluminum and nitrogen. The action of THF may help to promote the dissociation of this bond, freeing the lone pair on nitrogen to interact with a molecule of tetrahydrofuran-borane.

The nmr study of the addition of borane to $(\text{CH}_3)_2\text{NAl}(\text{BH}_4)_2$ in THF may offer a clue to the initial course of this reaction. The weak triplet at -5 ppm in Figures 3A and 3B implies the presence of some BH_2 -containing substance. Since dimethylaminoborane has not been found among the products of any reactions in this work, in speculation the Al-N bond separation process may be represented by



With the exception of the coordinated solvent molecule, the product postulated in eq 11 is similar in empirical formula with a substance isolated by Burg and Randolph from the gas-phase reaction of dimethylaminoborane with aluminum borohydride.¹⁴ The substance was formulated as an $\text{H}_3\text{BN}(\text{CH}_3)_2$ -substituted aluminum borohydride, although neither nmr nor infrared evidence exists to establish the structure. It is interesting that the compound reacted with diborane in the absence of solvent at 90–100° to give μ -dimethylaminodiborane and aluminum borohydride.

The second product in eq 12 is suggested as a possible intermediate since it is known to decompose easily to $n\text{-C}_4\text{H}_9\text{OAl}(\text{BH}_4)_2$.¹ The formation of this particular substance is not essential, however, since THF ring opening could occur by an alternate pathway.

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