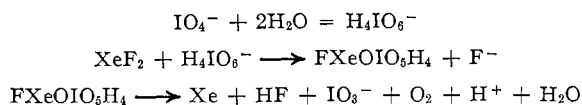


of periodate on XeF_2 . Again ester formation is a possibility, e.g.



The formation of periodate is unaffected by low concentrations of acid but is decreased at high acid concentration. As in the bromine and chlorine systems, we may attribute this to an acid catalysis of reaction 7. Surprisingly, however, the yield of periodate is changed rather little in alkaline solution. This is markedly different from the behavior of the bromine and chlorine systems, and it suggests that in alkaline solution the oxidation of iodate must proceed by a mechanism that is not available to the other halates. The oxidation of water by XeF_2 proceeds very rapidly in alkaline solution, but little is known about the mechanism, and we have no basis for meaningful speculation on the manner of oxidation of iodate in such media.

The reduction of periodate by XeF_2 is inhibited both by acid and by base. The effect of acid may result from protonation of the IO_4^- to H_5IO_6 ,²¹ while the effect of base may result either from the formation of $\text{H}_3\text{IO}_6^{2-}$ ²¹ or from a change in the mechanism of oxidation of water by XeF_2 . We may note that the reduction of XeO_3 by XeF_2 is also markedly inhibited by base.⁹

Schneer-Erdey and Kozmutza²² were able to analyze iodide by oxidizing it to periodate with excess XeF_2 in sulfuric acid solution and then titrating the periodate formed. Our results show that the accuracy of this method must depend on the acidity being kept high enough to suppress the reduction of periodate by XeF_2 .

General Conclusions.—Although the mechanisms we have postulated for the oxidation of the halates by

(21) C. E. Crouthamel, A. M. Hayes, and D. S. Martin, *J. Amer. Chem. Soc.*, **73**, 82 (1951).

(22) A. Schneer-Erdey and K. Kozmutza, *Acta Chim. (Budapest)*, **61**, 325 (1969).

XeF_2 are by no means unique representations of our results, nonetheless they do permit an intercomparison of the three systems. In Table XIII are listed

TABLE XIII

| Halate | E° , V | k_6/k_7 | k_5/k_4 , M^{-1} |
|----------|---------------|-----------|----------------------|
| Chlorate | 1.23 | 29 | 8.9 |
| Bromate | 1.74 | 0.28 | 9.8 |
| Iodate | 1.64 | 25 | 3×10^4 |

values of E° and of k_5/k_4 and k_6/k_7 for each of the systems. The first ratio represents the efficiency with which the halate competes with water for the oxidizing intermediate. The second ratio represents the relative tendency of the oxidized halate intermediate to go on to stable perhalate instead of reverting to halate.

We may see from the table that the efficiency with which the halate is oxidized is a function not of the electrode potential of the halate-perhalate couple but rather of its lability. Thus, for the fairly labile iodine system this ratio is much greater than for the relatively inert chlorine and bromine systems.

The value of k_6/k_7 does not show a clear-cut relationship either to lability or to electrode potential. Only in the bromate-perbromate system is this ratio particularly small. This probably indicates that oxidation of bromate to perbromate requires the formation of an intermediate of unusually high energy, and this energy is dissipated more readily by reversion to bromate than by formation of stable perbromate. The need to form such an energetic intermediate may explain why perbromates have been so difficult to synthesize.

Acknowledgments.—The mass spectrometric measurements were made by Mrs. A. G. Engelkemeir, and the liberation of O_2 from water with KBrF_4 was carried out by Mr. Adolph Venters. Mrs. Alberta Martin provided indispensable technical assistance. The author is grateful to Professor Henry Taube and Dr. Michael Anbar for helpful discussions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332

The Reaction of Lithium Aluminum Hydride with Secondary Amines in Diethyl Ether

By R. G. BEACH AND E. C. ASHBY*¹

Received February 10, 1971

The reaction of LiAlH_4 with secondary amines has been studied in detail. The following compounds are formed at various stages of the reaction: Li_3AlH_6 , $\text{LiAl}_2\text{H}_6\text{NR}_2$, $(\text{R}_2\text{N})_2\text{AlH}$, $\text{LiAlH}(\text{NR}_2)_3$, and $\text{LiAl}(\text{NR}_2)_4$. The compound $\text{LiAl}_2\text{H}_6\text{N}(\text{C}_2\text{H}_5)_2$ was characterized by elemental analysis, infrared spectroscopy, and molecular association studies. A new crystalline modification of Li_3AlH_6 has been observed, and the infrared spectrum of Li_3AlH_6 , prepared by the reaction of *n*-butyllithium with LiAlH_4 , was found to be different from that previously reported.

Introduction

In their characterization of LiAlH_4 , Schlesinger's group reported in 1947 that secondary amines react with LiAlH_4 to produce $\text{LiAl}(\text{NR}_2)_4$.² The reac-

tion products were deduced from gas evolution studies of reaction mixtures. In 1948, in a study using LiAlH_4 for the measurement of active hydrogen from a series

(1) To whom all inquiries should be sent.

(2) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

of compounds, di-*n*-amylamine was found to react extremely slowly to produce 1 mol of active hydrogen.³ The reaction products were not characterized. Recently we have reported a detailed study concerning the reaction of tertiary amines with alkali metal hydrides.⁴ Because of the unusual results uncovered in this study, it seemed of interest to investigate the reaction of secondary amines with LiAlH_4 in diethyl ether in more detail.

Experimental Section

Apparatus.—Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide to remove oxygen and Dry Ice-acetone traps to remove solvent.⁵

Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer. Solution spectra were obtained in a cell with KBr windows and solid spectra were obtained as Nujol mulls between CsI plates. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered $\text{Cu K}\alpha$ radiation. Samples were sealed in 0.5-mm capillaries and exposed for 6 hr. Interplanar spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. An ebullioscopic apparatus previously described was used for molecular association determinations.⁶

Analyses.—Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.⁵ Aluminum was determined by EDTA titration. Nitrogen was determined by separating the amine from a hydrolyzed sample by distillation and titrating with standard acid potentiometrically. Lithium was determined by flame photometry.

Materials.—Piperidine and diethyl- and diisopropylamine (Eastman Organic Chemicals) were dried over Molecular Sieve 4A and distilled prior to use. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared by stirring a diethyl ether slurry overnight followed by filtration of the slurry through dried Celite Analytical Grade Filter Air (Johns-Manville). The resulting clear solution was standardized by aluminum analysis.

Diethylaluminumane⁷ was synthesized by allowing $\text{AlH}_2\text{N}(\text{CH}_3)_2$ and 1 equiv of $(\text{C}_2\text{H}_5)_2\text{NH}$ to react in benzene. After the reaction was complete, the $(\text{CH}_3)_2\text{N}$ and benzene were removed at reduced pressure and diethyl ether was added. The infrared spectrum of the resulting solution in diethyl ether showed an Al-H stretching band at 1832 cm^{-1} .

Reaction of Dialkylamines with LiAlH_4 in Diethyl Ether.

(1) **Diethylamine.**—Diethylamine, diluted in 80 ml of diethyl ether, was added gradually to LiAlH_4 (20.6 mmol) in diethyl ether (100 ml). Vigorous gas evolution resulted on addition of the amine and a white precipitate immediately formed. Infrared spectra were obtained on the supernatant solution at various ratios of reactants. These spectra are shown in Figure 1. The final spectrum was obtained on the clear solution that resulted when the reaction was stirred overnight.

(2) **Piperidine.**—Piperidine diluted in diethyl ether was added in increments to a diethyl ether solution of LiAlH_4 . The observations and infrared spectra were essentially identical with those above except that the final spectrum taken after stirring overnight showed no bands in the Al-H region indicating complete reaction to form $\text{LiAl}(\text{N}(\text{C}_2\text{H}_5)_2)_2$.

(3) **Diisopropylamine.**—Diisopropylamine diluted in diethyl ether was added to a diethyl ether solution of LiAlH_4 . No gas evolution was immediately evident and no precipitate formed. After stirring overnight a bulky precipitate formed which solidified the entire solution. This reaction was not further characterized.

Preparation of $\text{LiAl}[\text{N}(\text{C}_2\text{H}_5)_2]_2$.

(3) J. A. Krynskiy, J. E. Johnson, and H. W. Carhart, *J. Amer. Chem. Soc.*, **70**, 486 (1948).

(4) J. A. Dilts and E. C. Ashby, *Inorg. Chem.*, **9**, 855 (1970).

(5) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(6) F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, **45**, 654 (1968).

(7) W. Marconi, A. Mazzei, F. Bonati, and M. de Malde, *Gazz. Chim. Ital.*, **92**, 1062 (1962).

100 ml of diethyl ether was slowly added to LiAlH_4 (81.6 mmol) in 100 ml of diethyl ether. The precipitate that formed initially disappeared on stirring overnight. An infrared spectrum showed an Al-H stretching band at 1720 cm^{-1} . The reaction was allowed to continue for 2 days under conditions of reflux. The diethyl ether was removed at reduced pressure. A slightly yellow viscous oil resulted. An infrared spectrum of the oil taken as a thin film showed only a very faint Al-H stretching band. *Anal.* Calcd for $\text{LiAl}[\text{N}(\text{C}_2\text{H}_5)_2]_2$: Li, 2.15; H, 0; Al, 8.37; N, 17.37. Found: Li, 2.11; H, 0; Al, 7.60; N, 14.22. Because of the very viscous nature of the compound solvent removal is difficult and not complete.

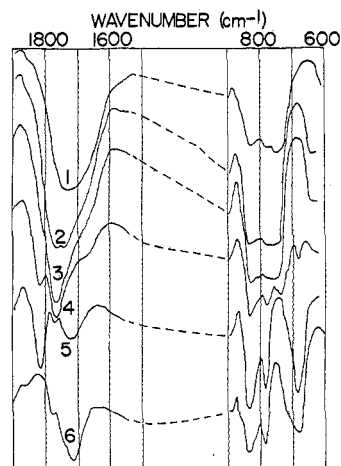


Figure 1.—Infrared spectra of the supernatant solution on adding $(\text{C}_2\text{H}_5)_2\text{NH}$ to LiAlH_4 in diethyl ether at the following $\text{LiAlH}_4:(\text{C}_2\text{H}_5)_2\text{NH}$ ratios: (1) pure LiAlH_4 , (2) 3:1, (3) 2:1, (4) 1:1, (5) 0.5:1, and (6) 0.25:1 after stirring overnight.

Preparation of $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_2$.—Lithium aluminum hydride (25 mmol) in diethyl ether (15 ml) was added slowly to $(\text{C}_2\text{H}_5)_2\text{NH}$ (75 mmol) in diethyl ether. A gas was evolved and a clear solution resulted. Removal of the diethyl ether solvent produced a white solid. *Anal.* Calcd for $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_2$: Li, 2.76; Al, 12.02; H, 0.401. Found: Li, 2.95; Al, 11.15; H, 0.449.

Preparation of $\text{LiAl}_2\text{H}_6\text{N}(\text{C}_2\text{H}_5)_2$. (1) **Reaction of LiAlH_4 and $\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$.**—Lithium aluminum hydride (5.0 mmol) in diethyl ether (8 ml) was added to $\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$ (10.0 mmol) in diethyl ether (10 ml). The infrared spectrum of the resulting solution showed Al-H stretching bands of approximately equal intensity at 1832 and 1770 cm^{-1} . Additional LiAlH_4 (5.0 mmol) was added. The infrared spectrum showed only a single Al-H stretching band at 1770 cm^{-1} . Ebullioscopic association measurement gave association values of 1.09 and 1.22 at 0.071 and 0.144 *m*, respectively. Diethyl ether was removed from a portion of the sample. The desolvated sample was redissolved in diethyl ether. The sample only partially dissolved. After filtration an infrared spectrum (Nujol mull) of the solid showed broad bands characteristic of Li_3AlH_6 .

(2) **Reaction of LiAlH_4 and $(\text{C}_2\text{H}_5)_2\text{NH}$.**—Diethylamine (16.9 mmol) in diethyl ether (25 ml) was added slowly to LiAlH_4 (42.3 mmol) in diethyl ether (50 ml). A gas was evolved and a white precipitate formed. After stirring overnight the solution was filtered and the solid was dried *in vacuo*. *Anal.* Calcd for Li_3AlH_6 : Li, 38.66; Al, 50.0; H, 11.23. Found: Li, 36.03; Al, 47.7; H, 9.92. The amount of Li_3AlH_6 recovered was 7.2 mmol of an expected 8.6 mmol. The infrared spectrum (Nujol mull) is shown in Figure 2. The X-ray powder pattern (Table I) indicates a different crystalline modification from that previously reported.⁸ In separate experiments under apparently the same conditions, Li_3AlH_6 containing the reported X-ray powder lines was obtained. An infrared spectrum of the filtrates showed only a single Al-H stretching band at 1770 cm^{-1} . Analysis of the filtrate showed an Li:Al:N:H ratio of 0.54:1.00:0.49:2.83.

Preparation of Li_3AlH_6 from *n*- $\text{C}_4\text{H}_9\text{Li}$ and LiAlH_4 .—Lithium aluminum hexahydride was prepared by a previously reported

(8) R. Ehrlich, A. R. Young, II, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, *J. Amer. Chem. Soc.*, **88**, 858 (1966).

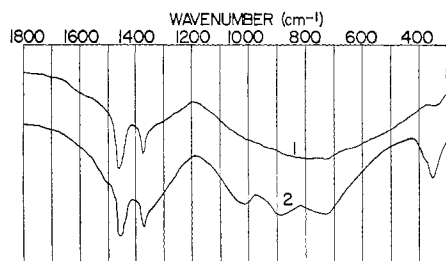


Figure 2.—Infrared spectra (Nujol mull) of Li_3AlH_6 : (A) Li_3AlH_6 prepared from LiAlH_4 and $n\text{-C}_4\text{H}_9\text{Li}$, (B) Li_3AlH_6 prepared from LiAlH_4 and $(\text{C}_2\text{H}_5)_2\text{NH}$.

procedure.⁸ The X-ray powder pattern contained the lines previously reported for Li_3AlH_6 but a few additional lines were observed (Table I). The infrared spectrum (Nujol mull) is shown in Figure 2.

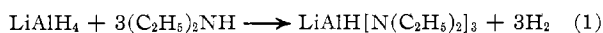
TABLE I
POWDER X-RAY DIFFRACTION PATTERN OF Li_3AlH_6

| $n\text{-C}_4\text{H}_9\text{Li} + \text{LiAlH}_4$ | | | $(\text{C}_2\text{H}_5)_2\text{NH} + \text{LiAlH}_4$ | | | | |
|--|---------|--------------------|--|---------|----|-------|----|
| $d, \text{\AA}$ | I/I_0 | | $d, \text{\AA}$ | I/I_0 | | | |
| 4.94 | w | 1.714 | w | 4.88 | vw | 1.641 | m |
| 4.45 | m | 1.642 ^a | m | 4.45 | m | 1.590 | vw |
| 4.19 | w | 1.592 | vw | 4.22 | m | 1.568 | m |
| 4.04 ^a | vs | 1.569 | vw | 4.07 | w | 1.530 | w |
| 3.93 ^a | vs | 1.528 ^a | m | 3.93 | w | 1.506 | vw |
| 3.81 | m | 1.505 ^a | m | 3.81 | s | 1.483 | vw |
| 3.18 | vw | 1.483 ^a | w | 3.05 | vw | 1.403 | m |
| 2.827 ^a | s | 1.409 ^a | m | 2.823 | w | 1.360 | vw |
| 2.556 ^a | w | 1.348 ^a | w | 2.694 | vw | 1.340 | w |
| 2.498 ^a | vw | 1.334 ^a | w | 2.439 | s | 1.297 | vw |
| 2.426 | m | 1.315 ^a | w | 2.321 | w | 1.266 | w |
| 2.318 ^a | s | 1.276 ^a | w | 2.222 | w | 1.218 | w |
| 2.259 ^a | m | 1.250 ^a | w | 2.137 | m | 1.188 | w |
| 2.139 | m | 1.216 ^a | w | 2.051 | m | 1.160 | w |
| 2.051 | vw | 1.159 ^a | w | 1.973 | vw | 1.087 | w |
| 2.018 ^a | w | 1.131 | w | 1.906 | vw | 1.068 | w |
| 1.971 ^a | w | 1.121 ^a | w | 1.804 | vw | 1.047 | vw |
| 1.799 ^a | m | 1.101 ^a | w | 1.776 | vw | 1.021 | vw |
| 1.774 ^a | m | 1.087 ^a | w | 1.749 | m | | |

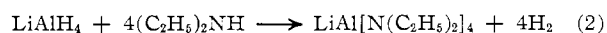
^a Previously reported for Li_3AlH_6 .⁸

Results and Discussion

The addition of $(\text{C}_2\text{H}_5)_2\text{NH}$ to a diethyl ether solution of LiAlH_4 results in hydrogen evolution and the immediate formation of a white precipitate. The precipitate was shown to be Li_3AlH_6 by elemental analysis and comparison of the X-ray powder pattern with that of an authentic sample.⁸ Infrared spectra of the supernatant solution at various ratios of $(\text{C}_2\text{H}_5)_2\text{NH}$ to LiAlH_4 (Figure 1) show sequentially three distinct Al-H stretching bands: 1770, 1720, and 1815 cm^{-1} . Allowing the reaction to proceed overnight at a ratio of $(\text{C}_2\text{H}_5)_2\text{NH}$ to LiAlH_4 of 4:1 resulted in the dissolution of the precipitated Li_3AlH_6 to form a clear solution. An infrared spectrum of the clear solution (Figure 1) showed an Al-H stretching band at 1720 cm^{-1} which is assigned to the compound $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_3$ (eq 1).



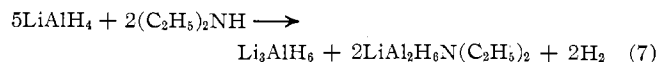
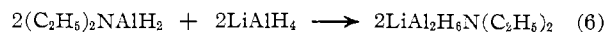
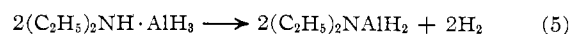
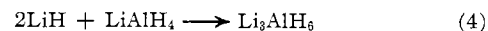
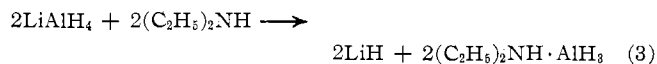
Only by refluxing the reaction mixture for 2 days was the completely aminated compound $\text{LiAl}[\text{N}(\text{C}_2\text{H}_5)_2]_4$ formed (eq 2). The compound $\text{LiAl}[\text{N}(\text{C}_2\text{H}_5)_2]_4$ is a



slightly yellow viscous oil. The difficulty in forming $\text{LiAl}[\text{N}(\text{C}_2\text{H}_5)_2]_4$ can be attributed to steric factors. When piperidine was used, stirring overnight was sufficient to form $\text{LiAl}(\text{NC}_5\text{H}_{11})_4$.

The compound $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_3$ was easily prepared in diethyl ether by inverse addition of reagents. Addition of a solution of LiAlH_4 in diethyl ether to an ether solution of $(\text{C}_2\text{H}_5)_2\text{NH}$ results in gas evolution but no precipitation. An infrared spectrum of the solution shows the Al-H stretching band at 1720 cm^{-1} . Evaporation of the solvent resulted in a white solid which gave the correct elemental analysis for $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_3$.

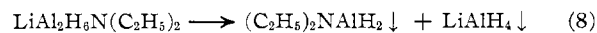
Since Li_3AlH_6 is formed in the initial stages of the reaction, the first step of the reaction must be an alane extraction reaction (eq 3) similar to that reported for tertiary amines.⁴ The very reactive LiH formed then reacts with excess LiAlH_4 to form Li_3AlH_6 (eq 4).⁸ The compound $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{AlH}_3$ would be expected to eliminate hydrogen (eq 5) immediately forming $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$.⁹ The infrared spectrum of a diethyl ether solution of diethylaminoalane, $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$, prepared independently, exhibited an Al-H stretching band at 1832 cm^{-1} which was not observed in the spectrum of this reaction product. Since the formation of $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$ in the reaction seems likely, a further reaction between $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$ and LiAlH_4 is proposed forming a new compound (A) $\text{LiAl}_2\text{H}_6\text{N}(\text{C}_2\text{H}_5)_2$ (eq 6). The complete reaction sequence proposed is shown below



Equation 7 shows the overall stoichiometry of the formation of Li_3AlH_6 and compound A. A reaction carried out at this stoichiometry gave the expected amount of Li_3AlH_6 as the precipitated product and compound A was indicated by both infrared and elemental analyses.

Since the formation of $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$ is proposed as an intermediate in the reaction sequence, a separate experiment was carried out involving $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$ and LiAlH_4 in diethyl ether in order to establish the integrity of eq 6 in the reaction sequence. A diethyl ether solution of diethylaminoalane prepared independently was allowed to react with LiAlH_4 in 1:1 ratio. Infrared analysis of the reaction product showed no Al-H stretching band at 1740 cm^{-1} characteristic of LiAlH_4 but did show a strong Al-H band at 1770 cm^{-1} observed previously in the reaction described by eq 7.

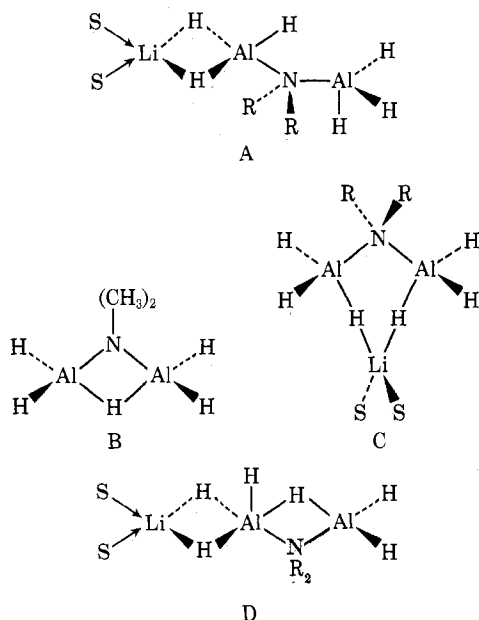
Compound A does not maintain its integrity in the solid state. Evaporation of the diethyl ether solvent gave a white solid. An infrared spectrum of the solid (Nujol mull) showed a sharp band at 1832 cm^{-1} and a broad Al-H band at 1750 cm^{-1} . This spectrum suggests that compound A disproportionates to LiAlH_4 and $(\text{C}_2\text{H}_5)_2\text{NAlH}_2$ in the solid state



When compound A as a solid was redissolved in diethyl ether a small portion did not dissolve. An infrared spectrum (Nujol mull) indicated that the solid was

Li_3AlH_6 . Infrared analysis of the solution showed, in addition to the band at 1770 cm^{-1} , an additional weak band at 1815 cm^{-1} .

An association study indicates that compound A is a monomer at low concentrations. The structure of compound A in solution may be similar to that proposed for $(\text{CH}_3)_2\text{NAl}_2\text{H}_5$ ¹⁰ (structure B); however several structures are possible (A, C, and D).



Addition of $(\text{C}_2\text{H}_5)_2\text{NH}$ in excess of the LiAlH_4 : $(\text{C}_2\text{H}_5)_2\text{NH}$ ratio of 2.5:1 results in further gas evolution and the appearance of an infrared band at 1815 cm^{-1} in the supernatant solution (Figure 1). The 1815 cm^{-1} band is observed for $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{AlH}$ prepared independently. Further addition of $(\text{C}_2\text{H}_5)_2\text{NH}$ results in the formation of a mixture of $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_3$, $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{AlH}$, and compound A. The precipitated Li_3AlH_6 slowly reacts with additional amine until at a 1:3 LiAlH_4 : $(\text{C}_2\text{H}_5)_2\text{NH}$ ratio the only product of the reaction is $\text{LiAlH}[\text{N}(\text{C}_2\text{H}_5)_2]_3$.

The Li_3AlH_6 formed in the extraction reaction in some instances gave an X-ray powder pattern similar to that reported for Li_3AlH_6 formed from $n\text{-C}_4\text{H}_9\text{Li}$ and LiAlH_4 .⁸ A few additional lines were observed (Table

I) even for Li_3AlH_6 prepared from $n\text{-C}_4\text{H}_9\text{Li}$ and LiAlH_4 . A new crystalline modification (Table I) was formed in other cases under what was thought to be identical conditions. Possibly there is very little energy difference in the two forms and minor changes in conditions result in formation of the two different forms. For a similar compound, Li_3AlF_6 , three crystalline modifications have been reported.¹¹

The infrared spectrum of Li_3AlH_6 prepared from $n\text{-C}_4\text{H}_9\text{Li}$ and LiAlH_4 (Figure 2) shows two very broad bands centered around 700 and 1400 cm^{-1} . The infrared spectrum of Li_3AlH_6 was previously reported to show only a single absorption at 1720 cm^{-1} .⁸ Since the previously reported spectrum was obtained as a KBr pellet, some hydrolysis of the compound may have occurred during the formation of the pellet. The infrared bands observed here are consistent with the bands observed for Na_3AlH_6 at 1300 and 800 cm^{-1} .¹² The infrared spectrum (Nujol mull) of Li_3AlH_6 from the reaction of LiAlH_4 and $(\text{C}_2\text{H}_5)_2\text{NH}$ shows splitting of the broad band at 700 cm^{-1} into three bands at 725 , 885 , and 1020 cm^{-1} and an additional band at 350 cm^{-1} with a possible shoulder at 370 cm^{-1} . All the Li_3AlH_6 infrared spectra from the $(\text{C}_2\text{H}_5)_2\text{NH}$ and LiAlH_4 reaction show some degree of splitting that is not observed with Li_3AlH_6 from $n\text{-C}_4\text{H}_9\text{Li}$ and LiAlH_4 although the observed bands are very broad. However, there is no correlation between the X-ray powder data and the infrared spectra. In some cases the $(\text{C}_2\text{H}_5)_2\text{NH}$ and LiAlH_4 reaction produces Li_3AlH_6 with the same powder pattern as the Li_3AlH_6 from the $n\text{-C}_4\text{H}_9\text{Li}$ and LiAlH_4 reaction but the infrared spectrum still shows splitting. There should be six vibrational bands for an octahedral AlH_6 ³⁻¹³ with only two infrared active.¹³ If the shoulder on the band at 350 cm^{-1} is real or if the broad band at 1400 cm^{-1} under the Nujol bands is split, there are six bands visible in the X-ray spectrum (Figure 2) indicating that the octahedron is completely distorted allowing the forbidden bands to become active.

Acknowledgment.—We are indebted to the Office of Naval Research under Contract No. N00014-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.

(11) G. Garton and B. M. Wanklyn, *J. Inorg. Nucl. Chem.*, **27**, 2466 (1965).

(12) E. C. Ashby and B. D. James, *Inorg. Chem.*, **8**, 246 (1969).

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(10) A. R. Young, II, and R. Ehrlich, *J. Amer. Chem. Soc.*, **86**, 5399 (1964).