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Concerning the Reaction of Lithium Aluminum Hydride with Diethylmagnesium in Diethyl Ether

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The reaction of lithium aluminum hydride with diethylmagnesium in diethyl ether has been studied in detail. The reaction was found to proceed according to the equations

$$LiAlH_4 + 2(C_2H_5)_2Mg \longrightarrow 2MgH_2 + LiAl(C_2H_5)_4$$
$$2LiAlH_4 + 3(C_2H_5)_2Mg \longrightarrow 3MgH_2 + 2LiAl(C_2H_5)_3H$$
$$LiAlH_4 + (C_2H_5)_2Mg \longrightarrow MgH_2 + LiAl(C_2H_5)_2H_2$$
$$2LiAlH_4 + (C_2H_5)_2Mg \longrightarrow MgH_2 + 2LiAl(C_2H_5)H_3$$

The identity of the aluminum-containing products was established by spectral comparison with redistributed products of $LiAlH_4$ and $LiAl(C_2H_5)_4$. Attempts to prepare C_2H_5MgH and $HMgAlH_4$ by the reaction of $LiAlH_4$ and $(C_2H_5)_2Mg$ are discussed.

Introduction

In a paper on the preparation of group II hydrides Schlesinger, *et al.*,[2] reported that magnesium hydride could be prepared from lithium aluminum hydride and diethylmagnesium in diethyl ether only under very special conditions. It was reported that lithium aluminum hydride in diethyl ether must be added slowly to a 0.5 *M* solution of diethylmagnesium in diethyl ether until the ratio of lithium aluminum hydride to diethylmagnesium is 0.3:1. It was emphasized that unless this procedure was followed exactly, either no magnesium hydride was formed, or if magnesium hydride were formed, it contained excessive aluminum. Under ideal conditions the magnesium hydride product contained 0.1 g-atom of aluminum/g-atom of magnesium. The Schlesinger group uncovered a further interesting aspect concerning this reaction. They found that if diethylmagnesium in diethyl ether was added to a large excess of lithium aluminum hydride solution, a clear solution resulted, from which a compound analyzing for $HMgAlH_4$ precipitated on addition of benzene. The precipitate was not further characterized. These workers further reported that when lithium aluminum hydride in diethyl ether was added to diethylmagnesium solution, a precipitate occurred, but on continued addition of lithium aluminum hydride solution, the precipitate redissolved. On long standing a gelatinous precipitate formed which contained a higher percentage of aluminum than that of the material precipitated by benzene. In view of these interesting features, the report of the possible preparation of $HMgAlH_4$, and the fundamental nature of this reaction, a more detailed study seemed appropriate.

Experimental Section

Apparatus.—Reactions were performed under dry nitrogen at the bench. Filtrations and other manipulations were performed in a glove box equipped with a recirculating system using manganese oxide to remove oxygen. Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer using either KBr or CsI liquid or mull cells. Infrared spectra of the solids were obtained as Nujol mulls.

Analyses.—Gas analysis was accomplished by hydrolysis of samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[3] Magnesium was determined by titration with EDTA at pH 11 using Eriochrome Black T as an indicator. When aluminum was present, it was masked by complexation with triethanolamine. Aluminum was determined by adding excess EDTA and back-titrating with standard zinc acetate at pH 4 in 50% ethanol with dithizone as an indicator. Halide was determined by the Volhard procedure.

Materials.—All solvents were distilled immediately before use from lithium aluminum hydride or sodium aluminum hydride depending on the boiling point of the solvent.

Diethylmagnesium ($(C_2H_5)_2Mg$) was prepared by the dioxane precipitation of $MgBr_2 \cdot 2C_4H_8O_2$ from a diethyl ether solution of ethylmagnesium bromide.[4] Ethylmagnesium bromide was prepared in the usual manner from triply sublimed magnesium obtained from Dow Chemical Corp. and ethyl bromide obtained from Fisher Scientific Co. Ethyl bromide was dried over anhydrous $MgSO_4$ and distilled prior to use. The $(C_2H_5)_2Mg$ was desolvated *in vacuo* at 130° overnight to remove excess dioxane. The desolvated $(C_2H_5)_2Mg$ was dissolved in diethyl ether and the solution was standardized by magnesium analysis. Analysis of the solution for ethane gave a ratio of ethane to magnesium of *2.03:1.00*. Bromide analysis was negative.

Lithium aluminum hydride ($LiAlH_4$) was obtained from Ventron, Metal Hydride Division. A solution was prepared by stirring a slurry of $LiAlH_4$ in diethyl ether overnight. The solution was filtered through a glass-fritted funnel using dried Celite Analytical Filter-Aid (Johns-Manville). The clear solution was standardized by aluminum analysis.

Lithium tetraethylaluminate ($LiAl(C_2H_5)_4$) was prepared by the procedure of Zakharkin.[5] Lithium was obtained from Foote Minerals and triethylaluminum from Texas Alkyls. The infrared spectrum (Nujol mull) of the $LiAl(C_2H_5)_4$ prepared agreed with that reported for $LiAl(C_2H_5)_4$.[6] A diethyl ether solution

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of $LiAl(C_2H_5)_4$ was prepared and standardized by aluminum analysis.

Infrared Study of the Reaction of $LiAlH_4$ with $(C_2H_5)_2Mg$ in Diethyl Ether.—A 0.10 *M* solution of $(C_2H_5)_2Mg$ in diethyl ether was placed in a three-neck round-bottom flask fitted with a condenser, an addition funnel, and a three-way stopcock. A 1.32 *M* solution of $LiAlH_4$ was placed in the addition funnel. Increments of the $LiAlH_4$ solution were added to the magnetically stirred $(C_2H_5)_2Mg$ solution. After each addition the solution was stirred for 15 min at room temperature before the stirring was stopped to allow the precipitate to settle. Infrared spectra were obtained by withdrawing samples of the supernatant solution by syringe under nitrogen. The additions were continued until $LiAlH_4$ was in large excess. The entire experiment was repeated using a 0.582 *M* $(C_2H_5)_2Mg$ solution. In a like manner a 0.883 *M* solution of $(C_2H_5)_2Mg$ in diethyl ether was added in increments to solutions of $LiAlH_4$ of the following concentrations: 0.100, 0.500, and 1.00 *M*. In Figure 1 a typical set of infrared spectra is shown.

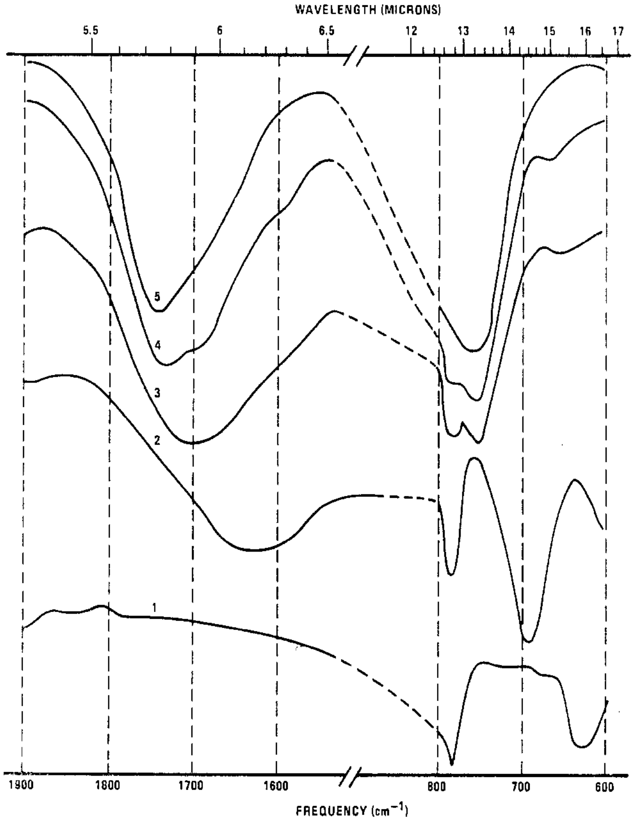

Figure 1.—Infrared spectra of the supernatant solution on addition of $LiAlH_4$ to $(C_2H_5)_2Mg$ in diethyl ether. $LiAlH_4$:$(C_2H_5)_2Mg$ ratio: (1) 0.5:1; (2) 0.67:1; (3) 1.0:1.0; (4) 2:1; (5) pure $LiAlH_4$.

Redistribution of $LiAlH_4$ and $LiAl(C_2H_5)_4$.—Reactions between $LiAlH_4$ and $LiAl(C_2H_5)_4$ were performed by mixing the reagents in appropriate ratio from standard solutions. After stirring for 1 hr at room temperature, infrared spectra were obtained.

Preparation of MgH_2 from $(C_2H_5)_2Mg$ and $LiAlH_4$. (1) **Conditions Reported by Schlesinger, *et al.***[2]—A diethyl ether solution of $LiAlH_4$ (1.66 *M*) was added dropwise from an addition funnel to a 0.50 *M* diethyl ether solution of $(C_2H_5)_2Mg$ until the ratio of reactants was 0.3:1.0 ($LiAlH_4$:$(C_2H_5)_2Mg$). An immediate precipitate formed. After stirring for 1 hr at room temperature, the solution was filtered. The precipitate was washed with diethyl ether and dried for 1 hr *in vacuo* at 70–80°. The infrared spectrum (Nujol mull) of the precipitate showed a very broad band between 950 and 1450 cm^{-1} centering around 1160 cm^{-1} [7] and another broad band at 650 cm^{-1}.[8] *Anal.* Calcd for MgH_2: Mg, 92.34; H, 7.66. Found: Mg, 71.5; H, 6.13; Al, 0; $C_2H_5^-$, 3.99; $(C_2H_5)_2O$, 18.39 by difference. The molar ratio of Mg:H:Al:C_2H_5:$(C_2H_5)_2O$ is 1.00:2.07:0.0:0.05:0.08.

(2) **0.5$LiAlH_4$–1.0$(C_2H_5)_2Mg$.**—This reaction was performed in a manner identical with that above except that the $(C_2H_5)_2Mg$ solution was 0.956 *M*. The precipitate was isolated and dried; 94.7% of the starting magnesium was recovered in the precipitate. *Anal.* Found: Mg, 72.9; H, 6.26; Al, 0.26; C_2H_5, 7.01; $(C_2H_5)_2O$, 13.56 by difference. The molar ratio of Mg:H:Al:C_2H_5:$(C_2H_5)_2O$ is 1.00:2.07:0.01:0.08:0.06. Benzene was added to the filtrate and the diethyl ether was evaporated. A crystalline white solid was isolated and dried. *Anal.* Calcd for $LiAl(C_2H_5)_4$: Al, 17.96; $C_2H_5^-$, 77.41. Found: Al, 17.07; $C_2H_5^-$, 71.95; H, 0. The infrared spectrum agrees with the reported spectrum.[6]

(3) **0.67$LiAlH_4$–1.0$(C_2H_5)_2Mg$.**—In this reaction 94% of the starting magnesium was recovered in the precipitate. *Anal.* Found: Mg, 72.1; H, 6.52; Al, 3.48; $C_2H_5^-$, 6.80; $(C_2H_5)_2O$, 10.78 by difference. The molar ratio of Mg:H:Al:C_2H_5:$(C_2H_5)_2O$ is 1.00:2.18:0.04:0.08:0.05. Addition of benzene to the filtrate and removal of diethyl ether resulted in a precipitate so finely dispersed that it proved impossible to separate for analysis.

(4) **1.0$LiAlH_4$–1.0$(C_2H_5)_2Mg$.**—In this reaction 73% of the starting magnesium was recovered in the precipitate. On standing, additional precipitation occurred in the filtrate. The precipitate was separated and shown by infrared spectrum to be additional magnesium hydride. *Anal.* Found: Mg, 65.8; H, 6.51; Al, 7.29; $C_2H_5^-$, 5.89; $(C_2H_5)_2O$, 14.68 by difference. The molar ratio of Mg:H:Al:$C_2H_5^-$:$(C_2H_5)_2O$ is 1.00:2.36:0.12:0.07:0.10. Adding benzene and evaporating the diethyl ether resulted in a suspension of solids that could not be separated for analysis.

(5) **2.0$LiAlH_4$–1.0$(C_2H_5)_2Mg$.**—In this reaction 88% of the starting magnesium was recovered in the precipitate. A small amount of postprecipitation occurred in the filtrate. *Anal.* Found: Mg, 69.0; H, 7.41; Al, 9.35; $C_2H_5^-$, 2.21; $(C_2H_5)_2O$, 11.97 by difference. The molar ratio of Mg:H:Al:$C_2H_5^-$:$(C_2H_5)_2O$ is 1.00:2.58:12:0.27:0.06. Isolation of the aluminum by-product was unsuccessful.

Attempt to Prepare C_2H_5MgH.—A 0.121 *M* diethyl ether solution of $LiAlH_4$ (15.3 mmol) was added dropwise to a 0.873 *M* ether solution of $(C_2H_5)_2Mg$ (61.1 mmol). The $LiAlH_4$:$(C_2H_5)_2Mg$ ratio is 0.25:1.0. An infrared spectrum of the supernatant solution showed ν(C–Mg) at 512 cm^{-1},[9] approximately half as intense as the band in the starting $(C_2H_5)_2Mg$ solution. The precipitate was isolated. The infrared spectrum showed typical broad MgH_2 bands. *Anal.* Found: Mg, 73.6; H, 5.73; Al, 0. The molar ratio of Mg:H is 1.00:1.88. The filtrate contained 27.4 mmol of $(C_2H_5)_2Mg$.

In another experiment a slurry of MgH_2 was stirred with a large excess of $(C_2H_5)_2Mg$ in diethyl ether overnight. An infrared spectrum of the supernatant solution using a compensating cell with solvent showed no bands other than those of $(C_2H_5)_2Mg$.

Results and Discussion

Contrary to the Schlesinger[2] report, either mode of addition ($LiAlH_4$ added to $(C_2H_5)_2Mg$ or $(C_2H_5)_2Mg$ added to $LiAlH_4$) results in a precipitate that does not dissolve. Magnesium hydride free of aluminum was obtained, using the conditions, concentration, and ratio of reagents reported. Variation of the concentration of reagents was found to have no effect on the reaction. However, if excess $LiAlH_4$ is used, magnesium hydride containing some aluminum is obtained.

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The infrared study of this reaction shows that the reaction proceeds stepwise exchanging ethyl groups of the magnesium for hydrides of the aluminum as shown in eq 1–4. At a $LiAlH_4:(C_2H_5)_2Mg$ ratio of 0.5:1.0,

$$LiAlH_4 + 2(C_2H_5)_2Mg \longrightarrow 2MgH_2 + LiAl(C_2H_5)_4 \tag{1}$$

$$2LiAlH_4 + 3(C_2H_5)_2Mg \longrightarrow 3MgH_2 + 2LiAl(C_2H_5)_3H \tag{2}$$

$$LiAlH_4 + (C_2H_5)_2Mg \longrightarrow MgH_2 + LiAl(C_2H_5)_2H_2 \tag{3}$$

$$2LiAlH_4 + (C_2H_5)_2Mg \longrightarrow MgH_2 + 2LiAl(C_2H_5)H_3 \tag{4}$$

eq 1, infrared spectrum 1 in Figure 1 shows no Al–H bands in the 1600–1800-cm^{-1} region, but a band appears at 600–630 cm^{-1} characteristic of $LiAl(C_2H_5)_4$. The precipitate was MgH_2 as shown by infrared spectroscopy and elemental analysis and contained essentially all the magnesium in the reaction. In addition the aluminum compound was crystallized from the filtrate and shown to be $LiAl(C_2H_5)_4$ by elemental analysis and infrared spectroscopy. Thus at a $LiAlH_4:(C_2H_5)_2Mg$ ratio of 0.5:1.0, alkyl–hydride exchange is complete and further addition of $LiAlH_4$ only results in a redistribution of $LiAlH_4$ and the product $LiAl(C_2H_5)_4$ as shown in infrared spectra 2, 3, and 4 (Figure 1).

To establish the redistribution of the aluminum compounds further, a separate redistribution study was made. In this connection $LiAl(C_2H_5)_4$ was synthesized from a lithium dispersion and triethylaluminum.

$$3Li + 4(C_2H_5)_3Al \longrightarrow 3LiAl(C_2H_5)_4 + 4Al \tag{5}$$

The resulting $LiAl(C_2H_5)_4$ was allowed to redistribute with $LiAlH_4$ in diethyl ether according to the stoichiometry

$$LiAlH_4 + 3LiAl(C_2H_5)_4 \longrightarrow 4LiAl(C_2H_5)_3H \tag{6}$$

$$LiAlH_4 + LiAl(C_2H_5)_4 \longrightarrow 2LiAl(C_2H_5)_2H_2 \tag{7}$$

$$3LiAlH_4 + LiAl(C_2H_5)_4 \longrightarrow 4LiAl(C_2H_5)H_3 \tag{8}$$

Infrared solution spectra of reactions 6–8 are identical with those obtained from the supernatant solution of reactions 2–4, respectively.

Attempts to isolate $LiAl(C_2H_5)_3H$, $LiAl(C_2H_5)_2H_2$, and $LiAl(C_2H_5)H_3$ from the $LiAlH_4:(C_2H_5)_2Mg$ reactions were not successful. On adding benzene and removing ether from the filtrates, precipitates of such small particle size were formed that they could not be separated. However, since the magnesium is essentially removed from the solution as MgH_2, the ratio of $H:C_2H_5$ in solution is known from the starting ratio of $LiAlH_4:(C_2H_5)_2Mg$. Infrared spectra show that $LiAl(C_2H_5)_3H$ (1625, 690 cm^{-1}) and $LiAl(C_2H_5)_2H_2$ (1700, 760 cm^{-1}) are distinct compounds. The infrared spectrum of $LiAl(C_2H_5)H_3$ (1740, 1700, 760 cm^{-1}) may be a composite of $LiAlH_4$ and $LiAl(C_2H_5)_2H_2$ spectra which would indicate disproportionation of $LiAl(C_2H_5)H_3$

$$2LiAl(C_2H_5)H_3 \longrightarrow LiAlH_4 + LiAl(C_2H_5)_2H_2 \tag{9}$$

A phase diagram of the $NaAlH_4$–$NaAl(C_2H_5)_4$ system showed no evidence for $NaAl(C_2H_5)H_3$.[10]

Magnesium hydride contaminated with some aluminum impurity (0.1 g-atom) is obtained if excess $LiAlH_4$ is used. This suggests that some reaction may be occurring between the MgH_2 produced and the aluminum by-products

$$LiAl(C_2H_5)_nH_{4-n} + MgH_2 \rightleftarrows LiH + H\text{–}Mg\text{–}Al(C_2H_5)_nH_{4-n} \tag{10}$$

$$2LiAl(C_2H_5)_nH_{4-n} + MgH_2 \rightleftarrows 2LiH + Mg[Al(C_2H_5)_nH_{4-n}] \tag{11}$$

The equilibrium would be expected to lie almost entirely to the left. A reaction between NaH and $Mg(AlH_4)_2$ has been shown to produce $NaAlH_4$ and MgH_2.[11]

A possible intermediate in this reaction may be C_2H_5MgH. Such a compound could be prepared by simply adjusting the stoichiometry of the reaction of $LiAlH_4$ and $(C_2H_5)_2Mg$ appropriately.

$$LiAlH_4 + 4(C_2H_5)_2Mg \longrightarrow 4C_2H_5MgH + LiAl(C_2H_5)_4 \tag{12}$$

Coates[12] has reported evidence for the intermediate C_2H_5MgH in a study of the reaction of $(C_2H_5)_2Mg$ and $NaB(C_2H_5)_3H$. When an experiment was performed at a $LiAlH_4:(C_2H_5)_2Mg$ ratio to produce C_2H_5MgH, the precipitate proved to be MgH_2 as shown by elemental analysis and infrared spectroscopy. The filtrate still contained $(C_2H_5)_2Mg$ as shown by infrared spectroscopy (ν(C–Mg) 512 cm^{-1}), and magnesium analysis showed that almost half of the starting magnesium was still in solution. The reaction is then described by eq 13 rather than eq 12. If C_2H_5MgH is an intermediate in

$$LiAlH_4 + 4(C_2H_5)_2Mg \longrightarrow 2MgH_2 + LiAl(C_2H_5)_4 + 2(C_2H_5)_2Mg \tag{13}$$

the reaction, it either reacts faster than $(C_2H_5)_2Mg$ with $LiAlH_4$ or disproportionates rapidly to $(C_2H_5)_2Mg$ and MgH_2. No complex formation or redistributed product between MgH_2 and $(C_2H_5)_2Mg$ could be found when MgH_2 was stirred with a large excess of $(C_2H_5)_2Mg$ in diethyl ether.

The MgH_2 prepared by the $LiAlH_4$ reduction contains about 15% diethyl ether after drying *in vacuo* at 70–80°. Studies by simultaneous dta–tga indicate that complete desolvation could be accomplished without decomposition of the MgH_2 at about 150°.[13]

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