Volume 11
Number 5
May 1972

Inorganic Chemistry

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
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Concerning the Reactions of Lithium and Sodium Aluminum Hydride with Grignard Reagents in Ether Solvents

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Received July 6, 1971

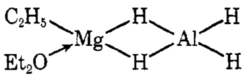
The reaction of lithium aluminum hydride with *n*-butylmagnesium bromide was found to proceed according to the sequence of reactions

$$LiAlH_4 + 6n\text{-}C_4H_9MgBr \longrightarrow 2n\text{-}C_4H_9MgBr + 2MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$
$$LiAlH_4 + 4n\text{-}C_4H_9MgBr \longrightarrow 2MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$
$$LiAlH_4 + 3n\text{-}C_4H_9MgBr \longrightarrow MgH_2 + LiBr + {}^1/_2MgBr_2 + BrMgAlH(n\text{-}C_4H_9)_3$$
$$LiAlH_4 + 2n\text{-}C_4H_9MgBr \longrightarrow MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 + LiBr$$
$$MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 \longrightarrow BrMg_2AlH_4(n\text{-}C_4H_9)_2$$
$$LiAlH_4 + n\text{-}C_4H_9MgBr \longrightarrow n\text{-}C_4H_9MgAlH_4 + LiBr$$
$$n\text{-}C_4H_9MgAlH_4 \longrightarrow HMgAlH_3(n\text{-}C_4H_9)$$

An earlier report that $C_2H_5MgAlH_4$ is prepared from $LiAlH_4$ and ethylmagnesium bromide was shown to be incorrect. The product of this reaction has been shown to be $HMgAlH_3(C_2H_5)$. The stability of $HMgAlH_3R$ compounds was found to be dependent on the alkyl group. When R = C_2H_5 or *n*-C_4H_9, the $HMgAlH_3R$ compounds are stable; however, when R = CH_3, C_6H_5, or *sec*-C_4H_9, the $HMgAlH_3R$ compounds disproportionate to MgH_2 and $Mg(AlH_3R)_2$. The reaction in THF is very similar to that in diethyl ether.

Introduction

Wiberg and Strebel[1] have reported that addition of lithium aluminum hydride to ethylmagnesium chloride in diethyl ether yields a soluble compound of empirical formula $C_2H_5MgAlH_4$. The structure assigned to this compound is shown by I; however, no spectral data were reported to verify this structure.



I

The formation of $C_2H_5MgAlH_4$ can be looked upon as resulting from a simple metathetical exchange reaction involving the formation of stable LiCl as a by-product.

$$C_2H_5MgCl + LiAlH_4 \longrightarrow C_2H_5MgAlH_4 + LiCl \qquad (1)$$

If the product of this reaction has the structure shown in I, then this class of compounds represents a good starting point for the preparation of $HMgAlH_4$ by hydrogenolysis (eq 2), since we have already demonstrated the ease of hydrogenolysis of R–Mg to H–Mg compounds especially when R = *i*-C_3H_7 or *sec*-C_4H_9.[2]

$$RMgAlH_4 \xrightarrow{H_2} HMgAlH_4 + RH \qquad (2)$$

In 1956 Rice[3] reported that when phenylmagnesium bromide was allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 6:1, the resulting product exhibited the empirical formula $(C_6H_5)_2Mg \cdot C_6H_5MgH \cdot 3(C_2H_5)_2O$. When the ratio of Grignard reagent to lithium aluminum hydride was 10:1, a product of empirical formula $C_6H_5MgBr \cdot C_6H_5MgH \cdot 3(C_2H_5)_2O$ was isolated. These compounds were reported to be soluble in benzene and insoluble in diethyl ether. Rice envisioned the reactions as proceeding according to eq 3. At the higher Grignard to lithium aluminum hydride ratios, C_6H_5MgH could complex with the excess $(C_6H_5)_2Mg$ or C_6H_5MgBr in solution to give the products reported.

$$4C_6H_5MgBr + LiAlH_4 \longrightarrow 4C_6H_5MgH + LiBr + AlBr \qquad (3)$$

Because of our desire to prepare $HMgAlH_4$, attempts were made to prepare $RMgAlH_4$ compounds according to the method of Wiberg and Strebel. However, hydrogenolysis of the so-called $RMgAlH_4$ compounds did not produce $HMgAlH_4$. Further inspection of the infrared spectra of the $RMgAlH_4$ compounds showed the absence of absorption in the Mg–C stretching

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[1] P. Strebel, Ph.D. Dissertation, University of Munich, 1958.

[2] W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964); E. C. Ashby, R. A. Kovar, and K. Kawakami, *Inorg. Chem.*, **9**, 317 (1970); E. C. Ashby, R. A. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

[3] H. J. Rice and P. J. Andrellos, Technical Report to the Office of Naval Research, Contract ONR-494(04), 1956.

region (500–550 cm^{-1}) which would be expected if $RMgAlH_4$ had the structure shown in I. Furthermore, in the reaction reported by Wilberg and Strebel all of the reactive magnesium species in solution should be considered (R_2Mg and RMgX). Since R_2Mg is the more reactive of the R–Mg species in solution, it is not clear that all of the reaction with $LiAlH_4$ should proceed through the RMgX species. In addition, it would appear that the hydrogen and R groups could exchange readily in a system such as $RMgAlH_4$ such that rearrangement of $RMgAlH_4$ to $HMgAlH_3R$ might take place readily. Of the two compounds, $HMgAlH_3R$ would be expected to be the more stable since hydrogen would tend to reside on the more electropositive metal (magnesium).

Our previous study of the reaction of $LiAlH_4$ with magnesium halides[4] indicates that a metathetical exchange reaction involving the formation of lithium halide and Mg–AlH_4 compounds (eq 4) takes place

$$LiAlH_4 + MgBr_2 \longrightarrow BrMgAlH_4 + LiBr \qquad (4)$$

rather than the type reaction reported by Rice (eq 3) in which the AlH_4 group does not maintain its integrity.

Considering these differences in the prior art concerning such a fundamental reaction and our desire to prepare $RMgAlH_4$ compounds, we decided to study the reactions of alkali metal aluminum hydrides with Grignard reagents in ether solvents in detail in order to determine the exact course of this reaction.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water[5] or on the bench using typical Schlenk-tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation.—Infrared spectra were obtained using a Perkin-Elmer Model 621 high-resolution infrared spectrophotometer. Cesium iodide cells were used. X-Ray powder diffraction patterns were run using a Debye–Scherrer camera of 114.6-mm diameter using Cu Kα (1.540 Å) radiation with a nickel filter. Single-walled capillaries of 0.5-mm diameter were used. These were filled in the drybox and sealed with a microburner.

Reagents.—Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use. Triply sublimed magnesium was obtained from Dow Chemical Co. The magnesium was washed with diethyl ether and dried under vacuum prior to use. Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Lithium aluminum hydride solutions in diethyl ether were prepared as described previously.[4] Sodium aluminum hydride was recrystallized from diethyl ether–THF mixtures.

Analytical Procedures.—Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine and titrating the magnesium with EDTA. Hydridic hydrogen was measured by hydrolyzing a weighed sample on a high-vacuum line and transferring the gas to a calibrated bulb *via* a Toepler pump after passing the gas through a liquid nitrogen trap. The experimental procedures used in carrying out several typical reactions are now reported.

Reaction of Lithium Aluminum Hydride with *n*-Butylmagnesium Chloride in Diethyl Ether.—To 45.06 mmol of lithium aluminum hydride was added 150 ml of diethyl ether. To this solution was added 28.71 ml of *n*-butylmagnesium chloride in diethyl ether (0.5642 *M*). The solution was stirred overnight at room temperature. The solution was filtered and 1.6661 g of solid was isolated. *Anal.* Found: Cl, 74.83; Mg, 2.98; Al, 0.99. The clear filtrate gave a Mg:Al:Cl ratio of 1.0:1.02:0.1. The solution contained 95% of the initial amount of magnesium. The infrared spectrum of the filtrate showed bands at 1760 (b), 720, and 680 (sh) cm^{-1}. In a separate experiment the solvent was removed from the filtrate and the resulting solid gave an infrared spectrum with bands at 1760 (b) and 720 cm^{-1}. The X-ray powder pattern of the solid showed no lines for magnesium hydride. When this solid was dissolved in THF, the resulting infrared spectrum gave bands at 1700, 790, and 755 cm^{-1}.

Reaction of Lithium Aluminum Hydride with *sec*-Butylmagnesium Chloride in Diethyl Ether.—To 10 ml of *sec*-butylmagnesium chloride in diethyl ether (2.41 *M*) was added 14.19 ml of lithium aluminum hydride in diethyl ether (1.698 *M*). The solution was stirred overnight. It was then filtered and 1.1582 g of solid was isolated. The solid on analysis gave a Mg:Al:Cl ratio of 1.0:0.02:0.85. The amount of magnesium contained in the solid represented 65% of the initial magnesium. The infrared spectrum of this solid showed it to contain magnesium hydride. Analysis of the solution gave a Mg:Al ratio of approximately 2.0:3.0.

Reaction of Lithium Aluminum Hydride with *n*-Butylmagnesium Bromide at a Mole Ratio of 1:4.—To 100 ml of *n*-butylmagnesium bromide in diethyl ether (0.5786 *M*) was added 6 ml of lithium aluminum hydride in ether (2.424 *M*). The solution was stirred overnight and then filtered. Elemental analysis of the solid gave a Mg:H ratio of 1.0:1.86. The amount of magnesium in the solid corresponded to 46.2% of the initial amount of magnesium. The infrared spectrum and X-ray powder pattern of the solid corresponded to MgH_2. The infrared spectrum of the filtrate showed a band at 670 cm^{-1} and a shoulder at 615 cm^{-1}. No bands were observed in the Al–H stretching region (2000–1600 cm^{-1}). The solvent was then removed from the filtrate under vacuum at room temperature. Benzene was added to the resulting solid and the mixture was stirred overnight. The mixture was then filtered and the analysis of the filtrate gave a Br:Mg:Al:butane ratio of 1.0:0.98:1.03:4.28. No hydrogen or lithium was detected in the filtrate and the amount of aluminum in the benzene solution corresponded to 92.54% of the initial amount of aluminum.

In a separate experiment *n*-butylmagnesium bromide was allowed to react with lithium aluminum hydride in a mole ratio of 4:2.25. At this point all the solid formed initially had redissolved. The infrared spectrum of the solution showed a broad band at 1710 cm^{-1}. The solvent was then removed under vacuum at room temperature and benzene was added. This mixture was then stirred overnight and filtered. The analysis of the filtrate gave a Br:Al:Mg:H ratio of 0.82:1.0:1.71:3.86. This represents 98.4% of the initial amount of aluminum.

Reaction of Lithium Aluminum Hydride with *n*-Butylmagnesium Bromide in Tetrahydrofuran.—To 43.4 mmol of *n*-butylmagnesium bromide was added 75 ml of THF. To the resulting clear solution was added in a dropwise fashion 40.54 ml of $LiAlH_4$ in THF (1.070 *M*). No solid was formed during the addition and the solution was allowed to stir overnight. The infrared spectrum of the resulting clear solution corresponded to $HMgAlH_3(n\text{-}C_4H_9)$.

Infrared Study of the Reaction of Lithium Aluminum Hydride with *n*-Butylmagnesium Bromide in Diethyl Ether.—A 0.4 *M* solution of *n*-butylmagnesium bromide in diethyl ether was placed in a one-neck round-bottom flask equipped with a side arm with stopcock. A 2.424 *M* solution of $LiAlH_4$ was added to this solution in increments *via* syringe. After each addition the solution was stirred for 0.5 hr and then any solid formed was allowed to settle. A sample of the supernatant solution was then withdrawn *via* syringe for infrared analysis. At a Grignard to hydride ratio of 1.0:0.0 the following bands were observed: 895, 780, and 540 cm^{-1}. At a Grignard to hydride ratio of 6:1 the 895- and 780-cm^{-1} bands remain the same, but the 540-cm^{-1} band has decreased in intensity and new bands at 670 cm^{-1} with a shoulder at 620 cm^{-1} appear. A solid formed at this ratio. At a Grignard to hydride ratio of 4:1 the 895- and 780-cm^{-1} bands are unchanged but the 540-cm^{-1} band has disappeared and the 670- and 620-cm^{-1} bands have increased in intensity and more solid has formed. At a Grignard to hydride ratio of 3:1 the 895- and 780-cm^{-1} bands are the same, the 670- and 620-cm^{-1} bands have decreased somewhat in intensity, but a new band has appeared at 1620 cm^{-1}. The amount of solid does not seem to have changed. At a Grignard to hydride ratio of 2:1, the 895- and 780-cm^{-1} bands are unchanged; however, the 670- and 620-cm^{-1} bands have disappeared and a band at 705 cm^{-1} has appeared. The

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[4] E. C. Ashby, R. D. Schwartz, and B. D. James, *Inorg. Chem.*, **9**, 325 (1970).

[5] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).

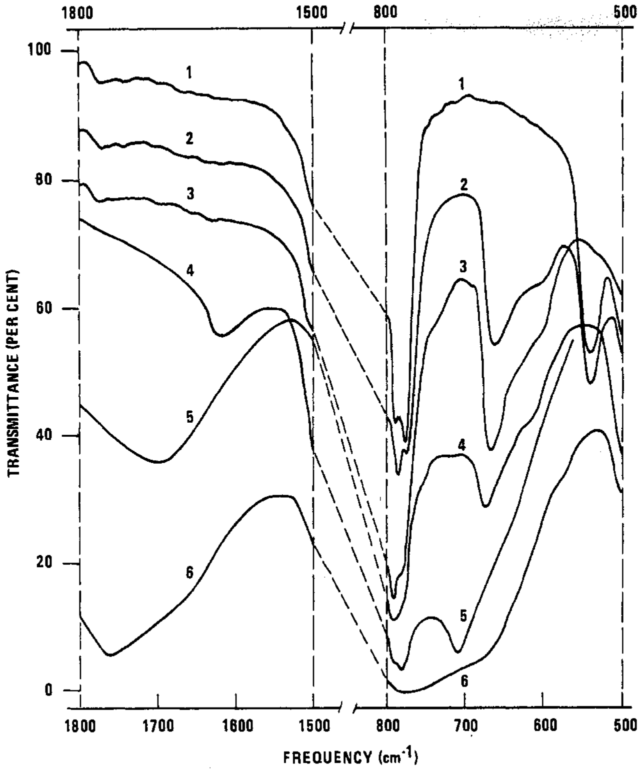

Figure 1.—Infrared examination of the soluble reaction product in the reaction of $LiAlH_4$ with *n*-butylmagnesium bromide in diethyl ether. Mole ratio of $LiAlH_4$:*n*-C_4H_9MgBr: (1) 0:1.0, (2) 0.16:1.0, (3) 0.25:1.0, (4) 0.33:1.0, (5) 0.5:1.0, (6) 1.0:1.0.

band at 1620 cm^{-1} has disappeared; however, an intense band at 1710 cm^{-1} has appeared. At this ratio all the solid has redissolved. At a Grignard reagent:hydride ratio of 1:1, all the solid is still in solution and the solution spectrum shows bands at 1760, 895, 780, snd 680 cm^{-1}.

Preparation of Isopropoxymagnesium Bromide.—To 25 ml of ethylmagnesium bromide in ether (3.016 *M*) was added 200 ml of ether. The solution was then cooled to 0° and 5.77 ml of neat isopropyl alcohol was added slowly. A gas was given off and the solution was stirred overnight. The analysis of the solution gave a Mg:Br ratio of 1.0:1.1.

Reaction of Lithium Aluminum Hydride with Isopropoxymagnesium Bromide.—To 75 ml of isopropoxymagnesium bromide in diethyl ether (0.2059 *M*) was added 15.7 ml of lithium aluminum hydride in ether (0.9811 *M*). The solution was then stirred overnight and filtered. The analysis of the filtrate gave a Mg:Al:Br ratio of 1.0:1.77:2.04. The infrared spectrum of the solid obtained from the filtration corresponded to magnesium hydride and showed no bands due to Al–H stretching.

Preparation of Di-*n*-butylaminomagnesium Chloride.—To 30 ml of ethylmagnesium chloride in ether (1.149 m) was added 70 ml of ether. To this solution was then added 5.8 ml of di-*n*-butylamine. The solution was then stirred overnight during which time no precipitate formed.

Results and Discussion

An infrared study of the reaction between *n*-butylmagnesium bromide and lithium aluminum hydride shows that the reaction proceeds by a stepwise exchange of alkyl groups from magnesium to aluminum and an exchange of hydrogen from aluminum to magnesium, as shown in eq 5–11. Although HMgBr would be an initial product, this compound is known to disproportionate rapidly to MgH_2 and $MgBr_2$ in ether solution.

$$LiAlH_4 + 6n\text{-}C_4H_9MgBr \longrightarrow 2MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4 + 2n\text{-}C_4H_9MgBr \quad (5)$$

$$LiAlH_4 + 4n\text{-}C_4H_9MgBr \longrightarrow 2MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4 \quad (6)$$

$$LiAlH_4 + 3n\text{-}C_4H_9MgBr \longrightarrow {}^3/_2MgH_2 + LiBr + {}^1/_2MgBr_2 + BrMgAl(n\text{-}C_4H_9)_3H \quad (7)$$

$$LiAlH_4 + 2n\text{-}C_4H_9MgBr \longrightarrow MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 + LiBr \quad (8)$$

$$MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 \longrightarrow BrMg_2AlH_4(n\text{-}C_4H_9)_2 \quad (9)$$

$$LiAlH_4 + n\text{-}C_4H_9MgBr \longrightarrow LiBr + n\text{-}C_4H_9MgAlH_4 \quad (10)$$

$$n\text{-}C_4H_9AlH_4 \longrightarrow HMgAlH_3(n\text{-}C_4H_9) \quad (11)$$

At a $LiAlH_4$:*n*-C_4H_9MgBr ratio of 1.0:6 (eq 5) the infrared band at 540 cm^{-1} characteristic of *n*-C_4H_9MgBr[6] has decreased in intensity indicating that some of the Grignard reagent has reacted. The band at 670 cm^{-1} with a shoulder at 620 cm^{-1} is characteristic of the AlR_4^- group.[7]

At a $LiAlH_4$:*n*-C_4H_9MgBr ratio of 1.0:4.0 (eq 6) the band at 540 cm^{-1} characteristic of *n*-C_4H_9MgBr[6] has disappeared but the bands at 670 and 620 (sh) cm^{-1} have increased in intensity. This indicates that all the Grignard reagent has reacted. The solid which began to form in the 6:1 case has now increased. In a separate experiment the solid was isolated by filtration and shown by elemental analysis, X-ray powder pattern, and infrared analysis to be MgH_2. The amount of MgH_2 isolated corresponded to a 92.4% yield according to eq 6. The solvent was then removed from the filtrate and the solid thus obtained was stirred in benzene overnight. The mixture was then filtered and the solution was analyzed. The analysis indicated the presence of a compound of empirical formula $BrMgAl(n\text{-}C_4H_9)_4$. The amount of aluminum in the solution indicated a yield of $BrMgAl(n\text{-}C_4H_9)_4$ of 92% according to eq 6.

The products of eq 6 can be envisioned as resulting from two reaction paths. The first path involves reaction of $LiAlH_4$ with the C–Mg bond of the Grignard reagent according to eq 12. The $LiAl(n\text{-}C_4H_9)_4$ thus produced can then react with $MgBr_2$ to yield $BrMgAl(n\text{-}C_4H_9)_4$ according to eq 13.

$$\begin{array}{l} LiAlH_4 + 4n\text{-}C_4H_9MgBr \longrightarrow \\ \quad LiAl(n\text{-}C_4H_9)_4 + 4HMgBr \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad 2MgH_2 + 2MgBr_2 \end{array} \quad (12)$$

$$LiAl(n\text{-}C_4H_9)_4 + MgBr_2 \longrightarrow LiBr + BrMgAl(n\text{-}C_4H_9)_4 \quad (13)$$

The second path involves the reaction of $LiAlH_4$ with the Mg–Br bond of the Grignard reagent according to eq 14. The *n*-$C_4H_9MgAlH_4$ formed rearranges to $HMgAlH_3$ (*n*-C_4H_9) (eq 15) which then reacts with the remaining Grignard reagent according to eq 16 to

$$LiAlH_4 + 4n\text{-}C_4H_9MgBr \longrightarrow LiBr + n\text{-}C_4H_9MgAlH_4 + 3n\text{-}C_4H_9MgBr \quad (14)$$

$$n\text{-}C_4H_9MgAlH_4 \longrightarrow HMgAlH_3(n\text{-}C_4H_9) \quad (15)$$

$$HMgAlH_3(n\text{-}C_4H_9) + 3n\text{-}C_4H_9MgBr \longrightarrow HMgAl(n\text{-}C_4H_9)_4 + 1.5MgH_2 + 1.5MgBr_2 \quad (16)$$

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[6] *n*-C_4H_9MgBr is used throughout this paper to represent the Grignard reagent (*n*-butylmagnesium bromide). If reference is made to the distinct RMgX species then the terminology "*n*-C_4H_9MgBr species" is used.

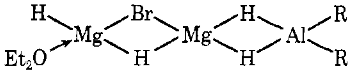
[7] E. C. Ashby and R. G. Beach, *Inorg. Chem.*, **9**, 2300 (1970).

yield $HMgAl(n\text{-}C_4H_9)_4$, MgH_2, and $MgBr_2$. The $HMgAl(n\text{-}C_4H_9)_4$ then reacts with $MgBr_2$ according to eq 17.

$$HMgAl(n\text{-}C_4H_9)_4 + MgBr_2 \longrightarrow BrMgAl(n\text{-}C_4H_9)_4 + 0.5MgH_2 + 0.5MgBr_2 \quad (17)$$

At a $LiAlH_4{:}n\text{-}C_4H_9MgBr$ ratio of 1.0:3.0 (eq 7) the bands at 670 and 620 cm^{-1} decreased in intensity somewhat and a new band at 1620 cm^{-1} appeared. The combination of bands between 600 and 700 cm^{-1} and one at approximately 1600 cm^{-1} was shown earlier[7] to be characteristic of AlR_3H^- compounds.

At a $LiAlH_4{:}n\text{-}C_4H_9MgBr$ ratio of 1.0:2.0 (eq 8) the bands at 670 and 620 cm^{-1} disappeared and a band at 705 cm^{-1} appeared. Also, the band at 1620 cm^{-1} disappeared; however, an intense band at 1710 cm^{-1} appeared. This combination of bands around 1700 and 700 cm^{-1} has been shown[7] to be characteristic of the $AlR_2H_2^-$ group. Also, at this ratio the MgH_2 noted above has all redissolved. In a separate experiment $LiAlH_4$ was added to $n\text{-}C_4H_9MgBr$ in a ratio of 2.25:4.0. The solvent was removed under vacuum and the resulting solid was extracted with benzene. Analysis of the benzene solution after filtration gave a Br:Al:Mg:H ratio of 0.82:1.0:1.71:3.86. This ratio can be rationalized as representing a compound of empirical formula $BrMg_2AlH_4(n\text{-}C_4H_9)_2$. A reasonable structure for this compound is shown by II.



II

At a $LiAlH_4{:}n\text{-}C_4H_9MgBr$ ratio of 1.0:1.0 (eq 10) the solution is clear. The infrared spectrum of the solution shows bands at 1760 and 720 cm^{-1}. This combination of bands has been shown[7] to be characteristic of AlH_3R compounds.

When *n*-butylmagnesium chloride was allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 1:1, a solid was obtained which was shown by elemental analysis and X-ray powder pattern analysis to be lithium chloride. Analysis of the filtrate gave a Mg:Al ratio of 1.0:1.02 and the amount of magnesium in solution represented 95% of the original magnesium. The infrared spectrum of the filtrate showed broad bands at 1760 and 720 cm^{-1} with a shoulder at 680 cm^{-1}. No bands were observed in the Mg–C stretching region (500–535 cm^{-1}). Lithium monoethylaluminate exhibits a broad absorption at 1740 cm^{-1} with a shoulder at 700 cm^{-1}. This band is very similar in shape and position to the Al–H stretching band at 1760 cm^{-1} exhibited by $HMgAlH_3(n\text{-}C_4H_9)$. Thus, we have concluded that the alkyl group is bonded to the aluminum and not magnesium.

In a separate experiment $LiAlH_4$ was allowed to react with $n\text{-}C_4H_9MgBr$ in a 1.0:1.0 ratio. The solution spectrum was identical with that observed earlier in the infrared study when the ratio of $LiAlH_4$ to $n\text{-}C_4H_9MgBr$ was 1:1. The solvent was removed from the reaction mixture and the X-ray powder pattern showed lines corresponding to LiBr plus other lines corresponding to the $HMgAlH_3(n\text{-}C_4H_9)$ isolated from the 1:1 addition of $n\text{-}C_4H_9MgCl$ to $LiAlH_4$ discussed above.

When $HMgAlH_3(n\text{-}C_4H_9)$ was dissolved in THF, the major absorption bands in the infrared spectrum shifted to 1700, 790, and 755 cm^{-1}. Still in THF no bands are observed in the 500–535-cm^{-1} region characteristic of a C–Mg compound, so that the butyl group is also presumed to be attached to aluminum in THF solution.

When lithium aluminum hydride was allowed to react with ethylmagnesium chloride in diethyl ether at a mole ratio of 1:1, a solution was obtained which after filtration was shown by elemental analysis to have a Cl:Mg:Al ratio of 0.1:1.00:1.05. The infrared spectrum of the solution exhibited an absorption band at 1750 cm^{-1} with a shoulder at 1685 cm^{-1}. It is important to note that if the reaction was allowed to become too vigorous, the initially formed $HMgAlH_3(C_2H_5)$ disproportionated to MgH_2 and $Mg[AlH_3(C_2H_5)]_2$. In the case of the formation of $HMgAlH_3(n\text{-}C_4H_9)$, no evidence of disproportionation was observed even under reflux conditions. (See eq 18 and 19).

$$LiAlH_4 + C_2H_5MgCl \xrightarrow[\text{temperature}]{\text{room}} LiCl + HMgAlH_3(C_2H_5) \quad (18)$$

$$LiAlH_4 + C_2H_5MgCl \xrightarrow{\text{ether reflux}} LiCl + {}^1/_2MgH_2 + {}^1/_2Mg[AlH_3(C_2H_5)]_2 \quad (19)$$

We attempted to prepare methylmagnesium aluminum hydride by the reaction of sodium aluminum hydride with methylmagnesium bromide in diethyl ether in order to study the low-temperature nmr spectrum of this compound for structure elucidation purposes. However, a solid was obtained from this reaction which had a Br:Mg:Al ratio of 1.2:1.0:0.80. The infrared spectrum of the solid exhibited bands at 1680 (b) and 710 (b) cm^{-1} and also bands corresponding to magnesium hydride. The analysis of the solution obtained from this reaction by filtration of the solid gave upon elemental analysis a Mg:Al ratio of 1.0:2.12. The conclusion is that $HMgAlH_3(CH_3)$ is unstable and disproportionates to MgH_2 and $Mg[AlH_3(CH_3)]_2$ at room temperature (eq 20 and 21).

$$NaAlH_4 + CH_3MgBr \longrightarrow NaBr + HMgAlH_3(CH_3) \quad (20)$$

$$2HMgAlH_3(CH_3) \longrightarrow MgH_2 + Mg[AlH_3(CH_3)]_2 \quad (21)$$

Sodium aluminum hydride was allowed to react with *sec*-butylmagnesium chloride in diethyl ether in a 1:1 mole ratio. The solution obtained by filtration gave upon elemental analysis a Mg:Al ratio of 1.0:1.67. The infrared spectrum of the filtrate showed broad bands at 1780 and 720 cm^{-1}. The solid resulting from this filtration gave a Mg:Al:Cl ratio of 1.0:0.3:2.0. This solid respresented 50.8% of the initial amount of magnesium. The infrared spectrum of the solid showed bands corresponding to magnesium hydride but no bands were observed characteristic of the Al–H stretching region. Similar results were obtained in the reaction of lithium aluminum hydride with *sec*-butylmagnesium chloride. The conclusion is similar to that arrived at earlier in the reaction of $NaAlH_4$ with methylmagnesium bromide; that is, the initial product $[HMgAlH_3(sec\text{-}C_4H_9)]$ disproportionates to MgH_2 and $Mg[AlH_3\text{-}$

(sec-C_4H_9)]$_2$ under the conditions of the reaction (eq 22 and 23).

$$NaAlH_4 + sec\text{-}C_4H_9MgCl \longrightarrow NaCl + HMgAlH_3(sec\text{-}C_4H_9) \tag{22}$$

$$2HMgAlH_3(sec\text{-}C_4H_9) \longrightarrow MgH_2 + Mg[AlH_3(sec\text{-}C_4H_9)]_2 \tag{23}$$

In an effort to prepare *sec*-butylmagnesium aluminum hydride by an alternate route, *sec*-butyllithium was allowed to react with iodomagnesium aluminum hydride in a 1:1 mole ratio in cyclohexane at 0°. After the reaction was filtered, analysis of the filtrate showed a Mg:Al ratio of 1.0:1.8. The infrared spectrum of the solid corresponded to magnesium hydride and showed no bands due to the Al–H stretching mode. The X-ray powder pattern showed the solid to contain lithium iodide. The conclusion is that a metathetical exchange reaction occurs producing LiI and sec-$C_4H_9MgAlH_4$ which then rearranges to $HMgAlH_3(sec\text{-}C_4H_9)$ which subsequently disproportionates to MgH_2 and $Mg[AlH_3(sec\text{-}C_4H_9)]_2$ (eq 24 and 25).

$$sec\text{-}C_4H_9Li + IMgAlH_4 \longrightarrow LiI + HMgAlH_3(sec\text{-}C_4H_9) \tag{24}$$

$$2HMgAlH_3(sec\text{-}C_4H_9) \longrightarrow MgH_2 + Mg[AlH_3(sec\text{-}C_4H_9)]_2 \tag{25}$$

When $LiAlH_4$ was allowed to react with phenylmagnesium bromide at a mole ratio of 1:6 the physical observations corresponded to those reported by Rice;[2] that is, a solid was formed in the reaction and a brown layer appeared. The solid was dissolved in benzene and recrystallized by addition of diethyl ether. Analysis of this solid gave a Br:Al:Mg:H ratio of 0.41: 0.27:1.79:1.0. The weight per cent values found for Mg (10.24) and H (0.235) are not far from those reported by Rice (Mg, 9.62; H, 0.195). Rice attributes this analysis to the formation of $(C_6H_5)_2Mg\cdot C_6H_5MgH\cdot 3[O(C_2H_5)_2]$ (Mg, 9.62; H, 0.198). The amount of magnesium in the solid corresponded to 16% of the total magnesium. The infrared spectrum of the solid obtained after recrystallization had infrared absorption bands at approximately 700 cm^{-1} characteristic of monosubstituted phenyl groups. There were no bands between 500 and 600 cm^{-1}; however, there was a band at 480 cm^{-1} which could be attributed to Mg–C stretching. No evidence of $LiAlBr_4$ was found; however, analysis of the lower layer produced in the reaction after extraction with benzene did give an Al:Br ratio of 1.0:1.0 with magnesium present in excess indicating the possibility of $BrMgAl(C_6H_5)_4$ as observed in the 1:6 case for the reaction of $LiAlH_4$ with n-C_4H_9MgBr. The $(C_6H_5)_2Mg\cdot C_6H_5MgH\cdot 3[O(C_2H_5)_2]$ reported by Rice could be envisioned as resulting from the sequence of reactions

$$2C_6H_5MgBr \rightleftharpoons (C_6H_5)_2Mg + MgBr_2 \tag{26}$$

$$4(C_6H_5)_2Mg + LiAlH_4 \longrightarrow 4C_6H_5MgH + LiAl(C_6H_5)_4 \tag{27}$$

$$(C_6H_5)_2Mg + C_6H_5MgH \longrightarrow (C_6H_5)_2Mg\cdot C_6H_5MgH \tag{28}$$

The Schlenk equilibrium for C_6H_5MgBr in ether shows an approximately statistical distribution between the C_6H_5MgBr and $(C_6H_5)_2Mg$ and $MgBr_2$ (eq 26). When $LiAlH_4$ is added to phenylmagnesium bromide, it is reasonable that reaction takes place between $LiAlH_4$ and $(C_6H_5)_2Mg$ to form C_6H_5MgH which is then stabilized by reaction with $(C_6H_5)_2Mg$ to form a complex. We have recently prepared similar complexes ($RMgH\cdot R_2Mg$) where R = CH_3, n-C_4H_9, or C_6H_5 by the hydrogenolysis of unsymmetrical dialkylmagnesium compounds[8]

$$2RMgR' \xrightarrow[\Delta]{H_2} RMgH\cdot RMgR' + R'H \tag{29}$$

The formation of $BrMgAl(C_6H_5)_4$ in the reaction of $LiAlH_4$ with $(C_6H_5)_2Mg$ in a 1:6 ratio can be explained by the sequence of reactions

$$LiAlH_4 + MgBr_2 \longrightarrow BrMgAlH_4 + LiBr \tag{30}$$

$$BrMgAlH_4 + 4(C_6H_5)_2Mg \longrightarrow BrMgAl(C_6H_5)_4 + 4HMgC_6H_5 \tag{31}$$

When $LiAlH_4$ was allowed to react with C_6H_5MgBr in a 1:1 ratio, the lower layer observed initially disappeared and the amount of solid increased relative to the amount observed when the reaction was carried out in a 1:6 ratio. When the solid was filtered, elemental analysis showed a Mg:H ratio of 1.0:1.94. This analysis as well as infrared and X-ray powder pattern analysis shows the solid to be MgH_2. The amount of magnesium in the solid accounts for 48.41% of the original magnesium. Elemental analysis of the filtrate showed a Br:Mg:Al ratio of 2.1:1.0:1.91. The infrared spectrum of the solution showed a broad band at 1750 cm^{-1} and also bands at 1245, 895, 770, and 705 cm^{-1}. These results are analogous to those observed in the reaction of $LiAlH_4$ with *sec*-butylmagnesium bromide indicating that $HMgAlH_3(C_6H_5)$ disproportionates to MgH_2 and $Mg[AlH_3(C_6H_5)]_2$.

Reactions of Grignard Compounds with Excess $LiAlH_4$.—Reactions of $LiAlH_4$ with Grignard reagents in ether at 1.0:1.0 stoichiometry or excess Grignard reagent have just been discussed. The importance of studying reactions in which $LiAlH_4$ is in excess lies in the realization that $HMgAlH_3R$ compounds might be converted to $HMgAlH_4$ according to eq 32. In

$$HMgAlH_3R + LiAlH_4(\text{excess}) \rightleftharpoons HMgAlH_4 + LiAlH_3R \tag{32}$$

this connection $LiAlH_4$ was allowed to react with $HMgAlH_3(n\text{-}C_4H_9)$ in a 3:1 ratio. A trace amount of solid was obtained which gave a Mg:Al:H ratio of 0.0:1.0:2.8. After filtration the solvent was removed from the filtrate and the X-ray powder pattern of the resulting solid showed only lines corresponding to the starting materials, $LiAlH_4$ and $HMgAlH_3(n\text{-}C_4H_9)$.

When n-C_4H_9MgCl was added to $LiAlH_4$ in ether at a ratio of 1:4, a solid was obtained which after filtration was shown by elemental and X-ray powder pattern analysis to be LiCl. The solvent was then removed from the filtrate. The X-ray powder pattern of the resulting solid corresponded to a physical mixture of $LiAlH_4$ and $HMgAlH_3(n\text{-}C_4H_9)$. The results of these experiments indicate that $HMgAlH_3(n\text{-}C_4H_9)$ does not react with $LiAlH_4$ according to eq 32.

When sodium aluminum hydride was allowed to react with n-C_4H_9MgBr in THF, the products were somewhat different compared to the same reaction using $LiAlH_4$ due to the insolubility of the NaBr byproduct. At a 1:1 ratio, a solid formed which had a Mg:Al ratio of 1.0:1.1. This solid accounts for about 10% of the original magnesium. The infrared spectrum of the solid corresponded to $Mg(AlH_4)_2\cdot 4THF$. The X-ray powder pattern of the solid shows lines

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(8) E. C. Ashby and T. Wall, unpublished results.

corresponding to a physical mixture of NaBr and $Mg(AlH_4)_2 \cdot 4THF$. The elemental analysis of the solution gave a Br:Mg:Al ratio of 0.0:1.04:1.0. The infrared spectrum of the solution corresponds to $HMgAlH_3(n\text{-}C_4H_9)$. The $Mg(AlH_4)_2$ noted above could result from the reaction of $NaAlH_4$ with $MgBr_2$ present in the Schlenk equilibrium.

Lithium aluminum hydride was allowed to react with *n*-butylmagnesium bromide in a 1:1 ratio in THF. No precipitate was produced during the reaction. The infrared spectrum of the solution showed bands at 1700, 790, and 755 cm^{-1}. These bands correspond to those observed previously for $HMgAlH_3(n\text{-}C_4H_9)$ formed in diethyl ether and redissolved in THF.

In addition to studying the reaction of $LiAlH_4$ with RMgX compounds we also studied the reactions of $LiAlH_4$ with YMgX compounds where Y = OR and NR_2. The objective of this work was to prepare $ROMgAlH_4$ and $R_2NMgAlH_4$ compounds which then might be hydrogenolyzed to $HMgAlH_4$. This objective was based on our earlier observation that R_2NMgH compounds can be hydrogenolyzed (eq 33) to R_2NH

$$R_2NMgH \xrightarrow{H_2} R_2NH + MgH_2 \qquad (33)$$

and MgH_2[9], and, therefore, $R_2NMgAlH_4$ might hydrogenolyze to R_2NH and $HMgAlH_4$.

In the reaction of lithium aluminum hydride with isopropoxymagnesium bromide in a 1:1 mole ratio, results similar to those obtained in the Grignard case were observed. Filtration of the reaction mixture yields a solution whose elemental analysis shows a Mg:Al:Br ratio of 1.0:1.77:2.04. The infrared spectrum of the solid obtained by filtration corresponds to magnesium hydride and shows no bands characteristic of the Al–H stretching modes. These results indicate that the $i\text{-}C_3H_7OMgAlH_4$ initially formed rearranges to $HMgAlH_3(O\text{-}i\text{-}C_3H_7)$ and then disproportionates to MgH_2 and $Mg[AlH_3(O\text{-}i\text{-}C_3H_7)]_2$. (See eq 34–37.)

$$C_2H_5MgBr + i\text{-}C_3H_7OH \longrightarrow i\text{-}C_3H_7OMgBr + C_2H_6 \qquad (34)$$

$$i\text{-}C_3H_7OMgBr + LiAlH_4 \longrightarrow i\text{-}C_3H_7OMgAlH_4 + LiBr \qquad (35)$$

$$i\text{-}C_3H_7OMgAlH_4 \longrightarrow HMgAlH_3(O\text{-}i\text{-}C_3H_7) \qquad (36)$$

$$2[HMgAlH_3(O\text{-}i\text{-}C_3H_7)] \longrightarrow MgH_2 + Mg[AlH_3(O\text{-}i\text{-}C_3H_7)]_2 \qquad (37)$$

Dibutylaminomagnesium aluminum hydride was prepared by the reaction of lithium aluminum hydride and di-*n*-butylaminomagnesium chloride in a 1:1 mole ratio. (See eq 38 and 39.) The elemental analysis of the solution obtained from filtration of the reaction mixture gave a Mg:Al:Cl ratio of 1.01:1.00:0.0. The infrared spectrum of the solution showed bands at 1830 (sp) and 870 cm^{-1} with a broad band at 740 cm^{-1}. The compound $(n\text{-}C_4H_9)_2NMgAlH_4$ is also soluble in benzene as the diethyl etherate.

$$(n\text{-}C_4H_9)_2NH + C_2H_5MgCl \longrightarrow (n\text{-}C_4H_9)_2NMgCl + C_2H_6 \qquad (38)$$

$$LiAlH_4 + ClMgN(n\text{-}C_4H_9)_2 \longrightarrow LiCl + (n\text{-}C_4H_9)_2NMgAlH_4 \qquad (39)$$

To summarize, the reaction of $LiAlH_4$ and $NaAlH_4$ with Grignard reagents has been shown to proceed in a stepwise fashion according to eq 5–11. Various intermediates involved in the stepwise process, such as $BrMgAlR_4$ and $BrMg_2AlH_4R_2$, have been isolated and characterized. The stability of the $HMgAlH_3R$ compounds produced by the reaction of $LiAH_4$ with RMgX in a 1:1 ratio was found to be dependent on the nature of the alkyl group. When R = $n\text{-}C_4H_9$, C_2H_5, or C_6H_5, the $HMgAlH_3R$ compounds are stable. When R = CH_3 or *sec*-C_4H_9, the compounds disproportionate to MgH_2 and $Mg(AlH_3R)_2$. The reaction in THF is very similar to that in diethyl ether except when the alkali metal by-product is insoluble in THF. In this case $Mg(AlH_4)_2$ was formed in approximately 10% yield whereas the remainder of the product in solution was found to be $HMgAlH_3R$.

Acknowledgment.—We are indebted to the Office of Naval Research under Contract No. N000 14-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.

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