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Reaction of Aluminum Hydride with Diethylmagnesium in Tetrahydrofuran. Characterization of New Ethyl-Substituted Hydridomagnesium Aluminum Hydrides

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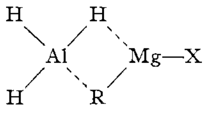
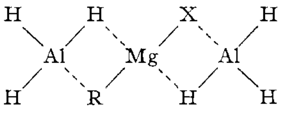
A detailed study of the reaction of aluminum hydride with diethylmagnesium in tetrahydrofuran has been carried out. The reaction was followed in a stepwise fashion by observing changes in the Mg–C and Al–H frequencies in the infrared spectra as well as by complete elemental analysis at different stoichiometries of the reactants. When diethylmagnesium is present in excess, a precipitate of MgH_2 is formed. At a ratio of 0.4:1.0 of aluminum hydride to diethylmagnesium, the predominant product is $C_2H_5MgAl(C_2H_5)_4$. At higher ratios, successive replacement of the ethyl groups with hydrogen takes place and soluble species with a composition $HMgAl(C_2H_5)_nH_{4-n}$ (n = 1–4) are formed. Several of these species have been isolated as solids and characterized by elemental analysis and infrared spectra. $Mg(AlH_4)_2$ precipitates at aluminum hydride: diethylmagnesium ratios of 2 or more.

Introduction

Wiberg and Strebel[1,2] have studied the reactions of Grignard compounds, RMgX (R = C_2H_5; X = Cl, Br, I), with aluminum hydride and diborane. According to these workers, AlH_3 was found to combine with RMgX in diethyl ether to form the successive adducts


(a) $RMgX \cdot AlH_3$


(b) $RMgX \cdot 2AlH_3$

It was also pointed out that AlH_3 does not show any inclination in its reaction with Grignard compounds for exchange of hydrogen atoms with alkyl groups according to eq 1 even at high temperatures.

$$RMgX \cdot AlH_3 \longrightarrow HMgX \cdot AlH_2R \qquad (1)$$

In the reaction of borane with Grignard compounds, however, hydrogen–alkyl exchange was reported to take place as

$$RMgX + BH_3 \cdot THF \longrightarrow RMgX \cdot BH_3 \longrightarrow HMgX \cdot BH_2R \longrightarrow HMgX + BH_2R \qquad (2)$$

This apparent difference between the reactions of Grignard compounds with BH_3 and AlH_3 was explained on the basis of the tendency of alkyl groups bound to aluminum, in contrast with those bound to boron, to form resonance–bridge linkages.

Bauer published a series of articles in 1961 and 1962 on the reaction behavior of diethylmagnesium with diborane[3-5] and with silane[6,7] in diethyl ether. The reaction of diethylmagnesium with diborane was shown to proceed forming a series of complex intermediates (R = C_2H_5)

$$R_2Mg + B_2H_6 \longrightarrow MgH_2(BRH_2)_2 \qquad (3)$$

$$2R_2Mg + B_2H_6 \longrightarrow 2RMgH_2BRH \qquad (4)$$

$$3R_2Mg + B_2H_6 \longrightarrow 3MgH_2 + 2BR_3 \qquad (5)$$

These reports are unusually sketchy and do not provide detailed experimental data. In addition, the postulated intermediates were not characterized in a convincing manner.

It would appear that the reactions of diethylmagnesium with diborane and aluminum hydride merit a more careful and detailed study. We decided to carry out a detailed, systematic study of these reactions in an attempt to define the exact nature of encounters of C–Mg with H–Al and H–B. Such information concerning these reactions should prove helpful in the interpretation of AlH_3 and BH_3 reactions with the more complex Grignard compounds as well as in providing fundamental information concerning interaction of C–Mg with H–M in other systems of interest.

It was decided to study first the reaction of diethylmagnesium with aluminum hydride in tetrahydrofuran, a solvent in which both the reactants exist as unassociated species. It is our intention to describe this reaction with changes in stoichiometry by detailed infrared analysis at each step in the reaction and to isolate and characterize the intermediate and final products formed when possible.

Experimental Section

Apparatus.—All operations were carried out in an atmosphere of nitrogen by using either a nitrogen-filled glove box equipped with a special recirculating system to remove oxygen (manganese oxide) and moisture (Drierite and Dry Ice–acetone traps) or on the bench using Schlenk-type techniques.[8] All glassware was flash flamed and flushed with dry nitrogen prior to use. Infrared spectra were obtained using a Perkin-Elmer 621 grating spectrophotometer. Cesium iodide cells were used for obtaining the liquid spectra. Solid spectra were obtained in Nujol which had

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[4] R. Bauer, *ibid.*, *B*, **16**, 839 (1961).

[5] R. Bauer, *ibid.*, *B*, **17**, 277 (1962).

[6] R. Bauer, *ibid.*, *B*, **17**, 201 (1962).

[7] R. Bauer, *ibid.*, *B*, **17**, 626 (1962).

[8] D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, pp 27–162.

been dried over sodium wire and stored in a nitrogen-filled dry-box. The cells were filled either on the bench top under a strong nitrogen flush or inside the nitrogen-filled glove box. There was no change in the observed spectra even after letting the samples stand inside the cells for a period of 6 hr. No evidence of any interaction of the samples with the cell windows was found.

Materials.—All solvents were distilled immediately prior to use. Tetrahydrofuran (Fisher Certified reagent) was distilled under nitrogen over sodium aluminum hydride, and diethyl ether and dioxane (Fisher reagent) were distilled over lithium aluminum hydride.

Diethylmagnesium [$(C_2H_5)_2Mg$] was prepared by the dioxane precipitation of $MgBr_2$ from ethylmagnesium bromide.[9] Triply sublimed magnesium (Dow Chemical Co.) was used. Ethyl bromide (Fisher Scientific Co.) was dried over $MgSO_4$ and distilled immediately before use. Ethylmagnesium bromide was prepared in diethyl ether according to standard techniques. A 10% excess of dioxane was used to precipitate the $MgBr_2\cdot$dioxane complex. Diethyl ether was removed from the diethylmagnesium solution by evaporation under partial vacuum. The solid obtained was dissolved in a small portion (~100 ml) of tetrahydrofuran which was also removed under vacuum. The resulting solid was heated under vacuum at 110° for 2 hr. These above steps were carried out to remove any dioxane present in the final product. The dry pure solid thus obtained was redissolved in tetrahydrofuran and the solution was standardized by magnesium analysis. The solution was found to be free of bromide or any other impurities and the ratio of ethane liberated on hydrolysis to magnesium was 1.9:1.0.

Aluminum hydride was prepared by the reaction of 100% sulfuric acid on lithium aluminum hydride in tetrahydrofuran at −10°.[10] Analysis for aluminum and hydrogen gave an Al:H ratio of 1:3.0. Flame photometric analysis showed no lithium present. Chloride impurity was also shown to be absent. Periodic checks for the active hydrogen content in AlH_3 revealed that the tetrahydrofuran solution was stable for up to 6 weeks when stored at 0°. After a period of 6 weeks, there was a loss of ~5% of active hydrogen. Up to 10% losses in the active hydrogen content were noted after 2 months.

Elemental Analyses.—Hydridic hydrogen analysis was performed by hydrolyzing the solid or solution samples in a vacuum line and measuring the liberated hydrogen. Magnesium determinations were carried out by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum was masked by complexation with triethanolamine when present together with magnesium. Aluminum analyses were carried out by addition of excess EDTA followed by back-titrating at pH 4 in 50% ethanol with a solution of zinc acetate using dithizone as indicator. Halide was determined by the Volhard titration and lithium by flame photometry.

Infrared Study of the Reaction of $(C_2H_5)_2Mg$ with AlH_3 in Tetrahydrofuran.—Two hundred milliliters of a 0.20 *M* solution of diethylmagnesium in tetrahydrofuran was transferred into a three-necked round-bottom flask equipped with a Dry Ice–acetone condenser, an addition funnel, and a three-way Teflon stopcock to enable aliquots to be withdrawn under nitrogen flushing by a hypodermic syringe for infrared analysis. A 0.654 *M* solution of aluminum hydride was placed in the addition funnel and added dropwise to the $(C_2H_5)_2Mg$ solution in regular increments. The mixture was kept magnetically stirred. After each addition, the mixture was stirred for another 30 min and then the stirring was stopped to allow the precipitate formed, if any, to settle. A small sample of the clear supernatant solution was withdrawn for infrared analysis. The addition of aluminum hydride was continued until it was in large excess. The entire experiment was repeated using 0.10 and 0.30 *M* diethylmagnesium solutions. The mode of addition was reversed in another experiment where increments of a 0.503 *M* diethylmagnesium solution in tetrahydrofuran were added to a 0.21 *M* solution of aluminum hydride. Figure 1 shows the spectra of reference products and starting materials while Figure 2 shows the infrared spectra obtained for the solution produced on reaction of $(C_2H_5)_2Mg$ and AlH_3 at several stoichiometric ratios.

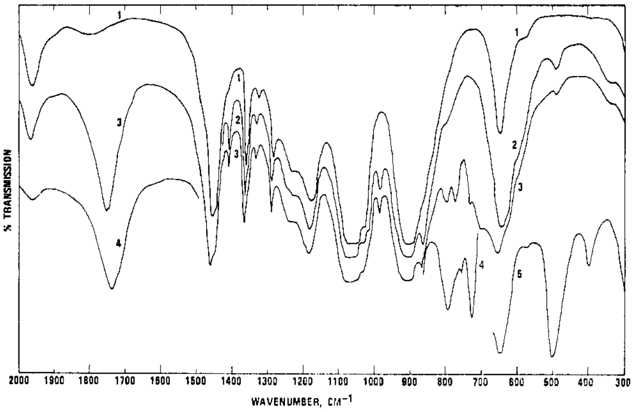

Figure 1.—Infrared spectra (in tetrahydrofuran) of reference products and starting materials: (1) tetrahydrofuran, (2) $(C_2H_5)_3Al$, (3) $(C_2H_5)_2AlH$, (4) AlH_3, (5) $(C_2H_5)_2Mg$.

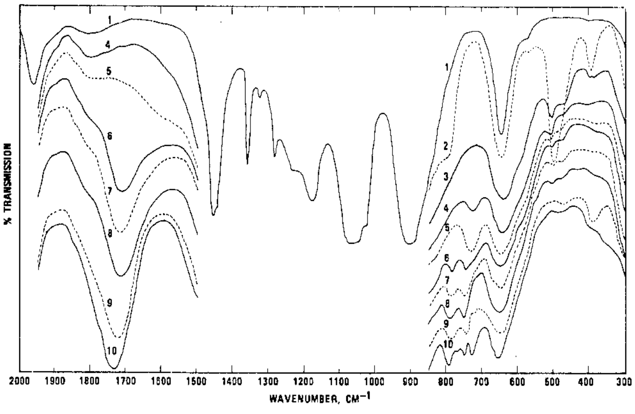

Figure 2.—Infrared spectra of the soluble species formed in the reaction of diethylmagnesium with aluminum hydride in tetrahydrofuran at various stoichiometric ratios: (1) tetrahydrofuran, (2) $(C_2H_5)_2Mg$, (3) 1:0.33, (4) 1:0.50, (5) 1:0.67, (6) 1:1.00, (7) 1:1.50, (8) 1:2.00, (9) 1:3.00, (10) 1:4.00.

Reaction of $(C_2H_5)_2Mg$ with AlH_3 at Various Stoichiometric Ratios.—Reactions of diethylmagnesium with aluminum hydride in tetrahydrofuran at room temperature were performed individually at the following ratios: 1:0.50, 1:0.67, 1:1.00, 1:1.50, 1:4.00. The final concentration of diethylmagnesium was kept at 0.20 *M* in each case. The additions were performed at a very slow rate due to the slightly exothermic nature of the reaction such that the reaction temperature was kept at ~25°. The solutions were stirred, each of them, for varying intervals of time from 1 hr to 7 days. In some cases, where there was no initial precipitate up to 24 hr, a very small amount of MgH_2 precipitated after stirring for several days. The precipitates, where formed, were filtered, washed with tetrahydrofuran, and dried *in vacuo* at 80° for 4 hr. Solvent removal from the clear filtrates was accomplished by evaporation under partial vacuum and the resulting solids were dried at room temperature under high vacuum. Some typical infrared spectra of the products obtained are shown in Figures 3 and 4. Elemental analyses of the precipitates as well as of the products obtained upon removal of solvent from the filtrates are summarized in Table I.

Preparation of Magnesium Aluminates by Independent Routes.—Diethylmagnesium was allowed to react separately with triethylaluminum, diethylaluminum hydride, ethylaluminum dihydride, and aluminum hydride in appropriate stoichiometric

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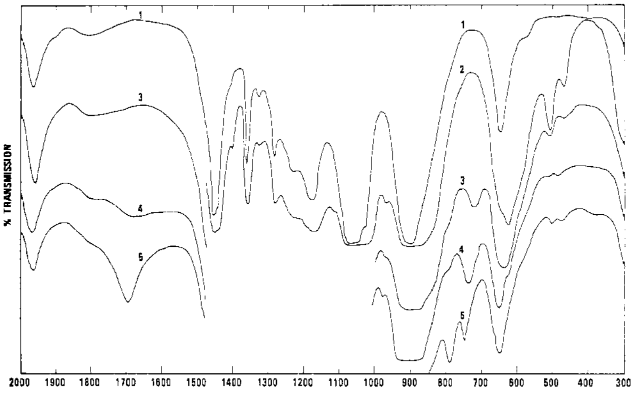

Figure 3.—Infrared spectra (in tetrahydrofuran) of some typical hydridomagnesium ethylaluminate compounds prepared by independent routes: (1) tetrahydrofuran, (2) $(C_2H_5)MgAl(C_2H_5)_4$, (3) $HMgAl(C_2H_5)_4$, (4) $HMgAl(C_2H_5)_3H$, (5) $HMgAl(C_2H_5)_2H_2$.

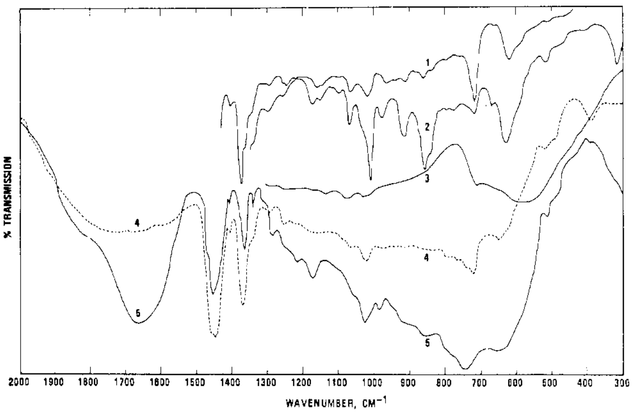

Figure 4.—Solid-state spectra (in Nujol) of some typical products isolated from the reaction of diethylmagnesium with aluminum hydride in tetrahydrofuran. Ratios are for $(C_2H_5)_2Mg:AlH_3$: (1) product obtained from filtrate in 1:0.5 reaction; (2) $HMgAl(C_2H_5)_4$ prepared by another route; (3) precipitate from 1:0.5 reaction; (4) solid obtained from filtrate in 1:1.0 reaction; (5) solid obtained from filtrate in 1:1.5 reaction.

Table I

Elemental Analyses of the Reaction Products at Several $(C_2H_5)_2Mg:AlH_3$ Ratios

Reaction ratio $(C_2H_5)_2Mg:AlH_3$	Precipitate Mg:Al:H:THF[c]	Solid obtained from the filtrate Mg:Al:H:C_2H_5:THF[c]
1:0.50[a]	1.00:0:1.92:0	1.00:1.00:1.07:4.00:2.92
1:0.67[b]	1.00:0:2.10:0	1.00:1.11:1.80:3.00:3.11
1:1.00[b,d]	1.00:0:2.04:0	1.00:1.04:2.82:2.00:1.52
1:1.50[b]	...	1.00:1.02:3.75:1.00:2.60
1:4.00[a]	1.00:2.03:7.20:4.08	...

[a] 24 hr. [b] 7 days. [c] Tetrahydrofuran (THF) determined by difference. [d] Only ~8% of Mg precipitated as MgH_2 after 7 days of reaction.

ratios to give the compounds $C_2H_5MgAl(C_2H_5)_4$, $HMgAl(C_2H_5)_4$, $HMgAl(C_2H_5)_3H$, and $HMgAl(C_2H_5)_2H_2$, respectively. Tetrahydrofuran was used as the solvent in all cases. The mixtures were stirred at room temperature for 3 days. Infrared spectra of the solutions are shown in Figure 3. Solid products obtained upon removal of the solvent were dried at room temperature *in vacuo*. $HMgAl(C_2H_5)_2H_2$ was dried at 50° under high vacuum. Elemental analyses of the products are (tetrahydrofuran (THF) determined by difference). *Anal.* Calcd for $HMgAl(C_2H_5)_4 \cdot 3THF$: Mg, 6.32; Al, 7.01; H, 0.26; C_2H_5, 30.20; THF, 56.20. Found: Mg, 6.41; Al, 7.13; H, 0.28; C_2H_5, 30.66; THF, 55.51. Calcd for $HMgAl(C_2H_5)_3H \cdot 3THF$: Mg, 6.81; Al, 7.56; H, 0.56; C_2H_5, 24.43; THF, 60.63. Found: Mg, 6.62; Al, 8.15; H, 0.49; C_2H_5, 23.72; THF, 61.02. Calcd for $HMgAl(C_2H_5)_2H_2 \cdot 1.5THF$: Mg, 11.02; Al, 12.23; H, 1.37; C_2H_5, 26.35; THF, 49.03. Found: Mg, 10.92; Al, 12.62; H, 1.28; C_2H_5, 26.10; THF, 49.09.

Results and Discussion

The reaction of aluminum hydride with diethylmagnesium in tetrahydrofuran at room temperature has been found to proceed in a stepwise fashion. The course of the reaction is represented by the series of equations

$$5(C_2H_5)_2Mg + 2AlH_3 \longrightarrow 2C_2H_5MgAl(C_2H_5)_4 + 3MgH_2 \quad (6)$$

$$2(C_2H_5)_2Mg + AlH_3 \longrightarrow HMgAl(C_2H_5)_4 + MgH_2 \quad (7)$$

$$3(C_2H_5)_2Mg + 2AlH_3 \longrightarrow 2HMgAl(C_2H_5)_3H + MgH_2 \quad (8)$$

$$(C_2H_5)_2Mg + AlH_3 \longrightarrow HMgAl(C_2H_5)_2H_2 \quad (9)$$

$$2(C_2H_5)_2Mg + 3AlH_3 \longrightarrow 2HMgAl(C_2H_5)H_3 + (C_2H_5)_2AlH \quad (10)$$

$$2(C_2H_5)_2Mg + 4AlH_3 \longrightarrow HMgAl(C_2H_5)H_3 + Mg(AlH_4)_2 + (C_2H_5)_3Al \quad (11)$$

$$3(C_2H_5)_2Mg + 8AlH_3 \longrightarrow 3Mg(AlH_4)_2 + 2(C_2H_5)_3Al \quad (12)$$

$$(C_2H_5)_2Mg + 3AlH_3 \longrightarrow Mg(AlH_4)_2 + (C_2H_5)_2AlH \quad (13)$$

$$(C_2H_5)_2Mg + 4AlH_3 \longrightarrow Mg(AlH_4)_2 + 2(C_2H_5)AlH_2 \quad (14)$$

Upon addition of the first increment of aluminum hydride to diethylmagnesium, MgH_2 precipitates from solution. With further incremental addition of aluminum hydride, the amount of precipitate increases until a ratio of 1:0.4 [$(C_2H_5)_2Mg:AlH_3$] is attained. The predominant species in solution at this ratio is ethylmagnesium tetraethylaluminate (eq 6). Further additions of aluminum hydride cause the successive replacement of ethyl groups by hydrogen (eq 7–10). As aluminum hydride is added, the precipitate of MgH_2 slowly decreases in quantity and finally dissolves completely at a reactant ratio of 1:1. The solutions remain clear upon addition of further increments of aluminum hydride until a reactant ratio of 1:2 [$(C_2H_5)_2Mg:AlH_3$] is reached. At this stage (eq 11), a precipitate of $Mg(AlH_4)_2$ begins to form. Finally, at a ratio of 3:8 (eq 12), the precipitation of $Mg(AlH_4)_2$ is complete and only a trace of magnesium remains in solution at this stage. Further addition of aluminum hydride simply causes redistribution with the triethylaluminum formed to give $(C_2H_5)_{3-n}AlH_n$ species (n = 1–3) (eq 13, 14).

The mode of addition was found to be immaterial in this reaction. Similar results were obtained in the incremental addition of diethylmagnesium to aluminum hydride. The concentrations, however, are somewhat important. It was observed that when the concentration of diethylmagnesium was greater than 0.3 M, the precipitate formed upon initial addition of AlH_3 did not dissolve completely when the ratio of the reactants approached a value of 1:1. Concentrations equal to or less than 0.2 M were found to be completely satisfactory in that the solubility limits of the species being formed in solution were not exceeded except for the highly insoluble MgH_2 and $Mg(AlH_4)_2$.

TABLE II

INFRARED SPECTRA OF TRIETHYLALUMINUM, DIETHYLALUMINUM HYDRIDE, ALUMINUM HYDRIDE, AND DIETHYLMAGNESIUM (IN TETRAHYDROFURAN) AND MAGNESIUM HYDRIDE (IN NUJOL)[a]

Obsd ir bands, cm^{-1}					
$(C_2H_5)_3Al$	$(C_2H_5)_2AlH$	AlH_3	$(C_2H_5)_2Mg$	MgH_2[b] (Nujol)	Approx assignment[c]
			400 m		δ(Mg–C)
490 m	490 w				Al–C bridge str
			505 vs		ν(Mg–C)
				580[d] br	δ(Mg–H)?
580 sh, s	600 sh, s				CH_2 rock
630 sh, vs					
	700 w				?
	730 sh, m	728 vs			δ(Al–H)
	770 s	755 w			
	800 m	795 s			
800 sh, w			800 sh, w		ν_s(OC)?
862 m	865 m				ν_s(CC)
985 m	985 m				ν(CC) or CH_2 twist?
				850–1300[d] br	ν(Mg–H)
1410 m	1410 m				δ(CH_2–Al)
	1750 vs	1740 vs			ν(Al–H)

[a] Abbreviations: w, weak; m, medium; s, strong; sh, shoulder; v, very; br, broad. [b] See Figure 4, curve 3; assignments from ref 11. [c] Alkyl vibrations assigned according to ref 12–15. [d] Frequencies approximate since bands are very broad.

Infrared spectra of tetrahydrofuran solutions of triethylaluminum, diethylaluminum hydride, aluminum hydride, and diethylmagnesium are shown in Figure 1 and summarized in Table II. Figure 2 provides the infrared spectra of the clear supernatant solutions obtained at various stoichiometric ratios of diethylmagnesium to aluminum hydride. Figures 3 and 4 show the spectra in tetrahydrofuran and in Nujol of the various magnesium aluminate compounds isolated either from the reactions of aluminum hydride with diethylmagnesium at proper stoichiometries or from preparations through independent routes. A summary of these results is shown in Table III. Approximate assignments for the observed frequencies have been made on the basis of assignments made by previous workers[11–22] for analogous compounds.

Elemental analysis at the 1:0.5 ratio (eq 7) showed that 50% of the magnesium was present in solution and the remainder in the precipitate of MgH_2. The product obtained upon removal of solvent from the filtrate analyzed for H:Mg:Al as 1:1.00:1.07 (Table I). These data are consistent with the formation of a compound of empirical formula $HMgAl(C_2H_5)_4$. No bands due to Al–H are observed in the spectra (Figure 2, curve 4; Figure 4, curve 1) indicating the absence of any Al–H containing species. A broad band of weak to medium intensity is observed at 728 cm^{-1}, however, which is close to where δ(Al–H) should appear. Also, a very weak band at 515–518 cm^{-1} is seen and this could be attributed to ν(Mg–C). These two bands would seem to suggest the presence of a compound consistent with a formulation $C_2H_5MgAl(C_2H_5)_3H$ rather than $HMgAl(C_2H_5)_4$. Perhaps an equilibrium such as represented by eq 15 exists in solution and lies predominantly to the right. This equilibrium would explain the appearance

$$(C_2H_5)MgAl(C_2H_5)_3H \rightleftharpoons HMgAl(C_2H_5)_4 \qquad (15)$$

of the 728- and 515-cm^{-1} bands in solution. However, the corresponding ν(Al–H) band is absent in the 1700-cm^{-1} region of the spectrum and this leads one to attribute the 728-cm^{-1} band and the 515-cm^{-1} band to the methyl rocking vibration and $\nu_1(F_2)$ vibration of the tetrahedral anion, respectively.[12] The absence of ν(Al–H) leads to the conclusion that the compound in question exists predominantly as $HMgAl(C_2H_5)_4$ although the infrared data alone are not conclusive on this point.

Absorption bands due to the ethyl group characteristic for most ethylaluminum compounds[13–15, 22] are seen where expected (Table III) though they are somewhat displaced in position. This is not unusual in view of the size, complexity, and the effective electronegativity of the coordinated groups on aluminum. Formation of bridge structures cannot be excluded; this in fact would seem to explain the displacements to some degree. Weak absorptions due to the Al–C bridging bond vibrations are indeed seen (Tables II, III).

An independent synthesis of $HMgAl(C_2H_5)_4$ was carried out according to eq 16. The solution spectra (Figure 3, curve 3) as well as the solid spectra (Figure 4, curve 2) of the compound isolated from this reaction showed the same characteristic bands as in the spectra of the compound obtained from the reaction of diethylmagnesium with aluminum hydride at a 1:0.5 ratio.

$$(C_2H_5)_2Mg + (C_2H_5)_2AlH \longrightarrow HMgAl(C_2H_5)_4 \qquad (16)$$

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TABLE III

INFRARED SPECTRA OF VARIOUS MAGNESIUM ALUMINATE COMPOUNDS[a] OBTAINED FROM THE REACTION OF ALUMINUM HYDRIDE WITH DIETHYLMAGNESIUM IN TETRAHYDROFURAN AS WELL AS THROUGH INDEPENDENT ROUTES (FIGURES 3 AND 4)

Obsd ir bands, cm^{-1}: $C_2H_5MgAl(C_2H_5)_4$	$HMgAl(C_2H_5)_4$		$HMgAl(C_2H_5)_3H$	$HMgAl(C_2H_5)_2H_2$		$HMgAl(C_2H_5)H_3$		$Mg(AlH_4)_2$		$LiAl(C_2H_5)_4$[c]		Approximate assignment[d]
THF[g]	THF	Nujol	THF	THF	Nujol	THF[b]	Nujol	THF	Nujol	THF	Nujol	
		312 m		290 m								δ(Al–C_2) terminal
					390 m							?
472 m	450 sh		480 w	480 w	485 sh	475 w	480 sh					Al–C bridge str?
	480 w											
510 s												ν(Mg–C)
										508 s	526 s	$\nu_1(F_2)$
	515 w	518 w		510 vw	515 w	507 vw	510 vw					ν(Mg–C) or $\nu_1(F_2)$?
580 sh	640 sh, s	590 sh	620 sh	620 sh	620 sh		640 sh			640 vs, br		
											615 sh	
											640 vs	(CH_2) rock
630 vs, br		630 s			650 w							
		670 w										
	728 m, br	730 sh, w	736 m	752 s	735 w	750 m	745 s, br[e]	750 m	745 s			
		780 sh, w	800 sh, w	795 s	750 sh	790 m	800 sh[e]	800 m	790 s			δ(Al–H)
					790 sh							
		860 s					860 sh[e]					ν_5(CC)?
									875 m			?
		918 m									920[f] sh, w	CH_3 rock
									920 w			?
											960 s	ν(C–C)
975 w	980 vw	975 w	980 sh	980 sh			980 m				985 s	CH_2 twist or ν(C–C)?
		1010 s			1020 m		1020 s					ν_{as}(OC)
									1025 s			?
											1194 m	CH_2 wag
											1277 w	
		1070 m			1070 sh							
		1100 vw										
		1150 vw										
		1175 m			1170 sh		1170 m					ν,τ(CH_2–Al)
		1220 vw					1220 vw					
		1245 m			1250 w		1240 sh					
		1295 vw			1290 vw		1290 vw					ν,τ(CH_2)
1400 sh	1405 sh	1410 w	1410 sh		1400 vw		1405 vw				1426 m[f]	δ(CH_2–Al)
			1700 sh, s[e]	1700 vs	1700 s[e]	1720 vs	1680 vs[e]	1735 vs	1730 s[e]			ν(Al–H)

[a] All compounds exist in solution solvated by THF molecules. In solids the number of solvated THF molecules varies according to the conditions of isolation and desolvation. Composition of solids investigated: $HMgAl(C_2H_5)_4 \cdot 2.92THF$, $HMgAl(C_2H_5)_2H_2 \cdot 1.52THF$, $HMgAl(C_2H_5)H_3 \cdot 2.6THF$, $Mg(AlH_4)_2 \cdot 4THF$. Abbreviations: w, weak; m, medium; s, strong; sh, shoulder; v, very; br, broad. [b] See Figure 2, curve 7. [c] Data from ref 12. [d] Alkyl vibrations assigned following ref 12–15. [e] Frequencies approximate since bands are broad. [f] $NaAl(C_2H_5)_4$. [g] THF is tetrahydrofuran.

Analytical results were in good agreement (*cf.* Experimental Section).

The Al–H bands begin to appear in the infrared spectra at a ratio 1:0.67 of diethylmagnesium to aluminum hydride indicating the formation of an Al–H-containing species at this point. Analyses of the precipitate and the filtrate showed two-thirds of the magnesium to be present in solution and one-third in the precipitate as MgH_2. The Mg:Al:H ratio was found to be 1:1.11:1.80 (Table I) in the solid obtained from the filtrate. Thus, at this ratio, the reaction is best represented by eq 8. Infrared spectra show a broad band at ~1700 cm^{-1} (ν(Al–H)) and a band of medium intensity at 736 cm^{-1}, along with a weak shoulder at 800 cm^{-1} (δ(Al–H)). An independent synthesis of the proposed compound was carried out according to eq 17. The spectrum of

$$(C_2H_5)_2Mg + C_2H_5AlH_2 \longrightarrow HMgAl(C_2H_5)_3H \qquad (17)$$

the product obtained from this reaction (Figure 3, curve 4; Table III) was identical with that of the product at a 1:0.67 ratio of diethylmagnesium to aluminum hydride (Figure 2, curve 5).

At a 1:1 stoichiometry (eq 9) a clear solution results. Spectra show strong bands for ν(Al–H) at 1700 cm^{-1} and δ(Al–H) at 752 and 795 cm^{-1}. A very weak band appears in the Mg–C stretching region (510 cm^{-1}) suggesting again the possible equilibrium shown in eq 18.

$$HMgAl(C_2H_5)_2H_2 \rightleftarrows C_2H_5MgAl(C_2H_5)H_3 \qquad (18)$$

The very weak relative intensity of this 510-cm^{-1} band suggests that if an equilibrium according to eq 18 exists, it lies predominantly to the left.

In a separate experiment, a 1:1 mixture of $(C_2H_5)_2Mg$ and AlH_3 (both 0.2 *M*) was allowed to stir for 24 hr. There was no immediate precipitate and the solution remained clear during the entire period. Infrared spectra of this solution recorded at periodic intervals during the 24-hr stirring period showed no change. After 24 hr, however, a very slight turbidity appeared, and after 7 days of stirring, a very small amount of solid precipitated. Analysis showed that 8% of the total magnesium had precipitated (the precipitate was characterized to be MgH_2) at this stage. The infrared spectrum of the filtrate was essentially unchanged. Equation 19 describes the disproportionation reaction which occurs to the extent of ~8% after several days.

$$2HMgAl(C_2H_5)_2H_2 \longrightarrow Mg[Al(C_2H_5)_2H_2]_2 + MgH_2 \quad (19)$$

The reaction solution remains clear at a 1:1.5 ratio of $(C_2H_5)_2Mg:AlH_3$. The solution spectrum (Figure 2, curve 7) changed slightly from that observed at the 1:1 ratio; ν(Al–H) was observed at 1720 cm^{-1} and δ(Al–H) at 750 and 790 cm^{-1}. The reaction at this stage is best described by eq 10. The solution spectrum shows some effect due to the $(C_2H_5)_2AlH$ species which is also present in solution at this stage. A shoulder at ~725 cm^{-1} is seen which is due to δ(Al–H) in $(C_2H_5)_2AlH$ (compare Figure 2, curve 7, and Figure 1, curve 3). The band at 1720 cm^{-1} in the solution at this ratio is perhaps a composite of the ν(Al–H) of $(C_2H_5)_2AlH$ (1750 cm^{-1}) and the compound $HMgAl(C_2H_5)H_3$ (1710 cm^{-1}). This is made clearer upon an examination of the spectra of the solid product isolated from the filtrate and uncontaminated by $(C_2H_5)_2AlH$ (removed by extracting with hexane): ν(Al–H) appears at ~1680 cm^{-1} and δ(Al–H) at 745 and 800 cm^{-1}. These frequencies are somewhat approximate since the bands in the solid spectra are quite broad (Figure 4, curve 5). When the solid was redissolved in tetrahydrofuran and the spectra were obtained, ν(Al–H) was observed to be at 1710 cm^{-1} and δ(Al–H) at 750 and 790 cm^{-1}. There was no shoulder at ~725 cm^{-1} due to $(C_2H_5)_2AlH$. Again, a very weak band is observed at 510 cm^{-1} which could be attributed to ν(Mg–C). The intensity of this band is so small that a formulation for the compound as $(C_2H_5)MgAlH_4$ is not justified. Perhaps, here again, the equilibrium represented by eq 20 exists and its position is mainly to

$$(C_2H_5)MgAlH_4 \rightleftharpoons HMgAl(C_2H_5)H_3 \quad (20)$$

the right. The Mg–C and Al–C vibrational frequencies seen at the expected positions in the spectra (Table III) lend further support to the fact that the predominant species being formed is $HMgAl(C_2H_5)H_3$ and not $(C_2H_5)MgAlH_4$.

When the ratio of $(C_2H_5)_2Mg$ to AlH_3 approaches 1:2, a precipitate appears almost immediately. Elemental analysis showed that slightly over 50% of the total magnesium was present in solution and a little less than half precipitated. The precipitate was shown to be $Mg(AlH_4)_2 \cdot 4THF$ by elemental and infrared analyses. The solution spectra (Figure 2, curve 8) are very similar to those of the 1:1.5 reaction mixture (Figure 2, curve 7) except that the effect due to $(C_2H_5)_2AlH$ (which was present in 1:1.5 reaction) is not seen here. The ν(Al–H) is seen at 1710 cm^{-1} and δ(Al–H) at 750 and 790 cm^{-1} (shoulder at ~725 cm^{-1} disappeared; also ν(Al–H) lower than in curve 7, Figure 2). Consequently, the predominant soluble species present at the 1:2 ratio is $HMgAl(C_2H_5)H_3$ and the reaction is described by eq 11.

Further addition of aluminum hydride causes the precipitation of more and more $Mg(AlH_4)_2$. The precipitation is complete at a ratio 3:8 (eq 12). At this stage, no magnesium was detected in solution except for a small trace due to the dissolved $Mg(AlH_4)_2$. Additional increments of aluminum hydride simply redistribute with the triethylaluminum formed to give $(C_2H_5)_{3-n}AlH_n$ species (n = 1–3) (eq 13, 14). The solution spectra at the 1:3 and 1:4 ratios (Figure 2, curves 9 and 10) are a combination of the spectra of $Mg(AlH_4)_2$ (present in small concentration in solution) and the soluble $(C_2H_5)_{3-n}AlH_n$ species. As may be seen from the spectra at the 1:4 ratio (Figure 2, curve 10) ν(Al–H) moves to a higher frequency (1735 cm^{-1}) and a distinct new band appears at 728 cm^{-1} (δ(Al–H) in $(C_2H_5)AlH_2$: 728 cm^{-1}) in addition to the bands at 795 and 750 cm^{-1} (δ(Al–H) for $Mg(AlH_4)_2 \cdot THF$).

The question as to whether the compounds forming in the reaction of aluminum hydride with diethylmagnesium should be formulated as $HMgAl(C_2H_5)_nH_{4-n}$ (I) or as $C_2H_5MgAl(C_2H_5)_{n-1}H_{(4-n)+1}$ (II) (n = 1–4) cannot be answered unequivocally from the infrared data alone. Indeed one observes very weak but real absorption bands in the ν(Mg–C) region which appear not only in the solution spectra but in the solid spectra as well. An explanation can be provided by supposing that the compounds exist as equilibrium mixtures, with I predominating. Taking the case of $HMgAl(C_2H_5)H_3$ as an example, if I was the only existing species, one would not observe any ν(Mg–C), and would observe the Al–ethyl bands. The reverse would be true if the species was predominantly II. The Al–C bands do show up in the solution and solid state spectra of this compound; in addition, a very weak absorption band appears near 510 cm^{-1} (ν(Mg–C)). This band perhaps could be assigned to the $\nu(F_2)$ vibration of the tetrahedral AlX_4^- ion[12] (X = ethyl or H or both), but this assignment would lead to more complicated questions about the steric factors and the geometry of the molecule. The Mg–H frequencies are extremely elusive, especially in solution, and none of the frequencies observed in the compounds investigated could be assigned to this vibration. The most likely explanation for the presence of a weak ν(Mg–C) band would be the presence of an equilibrium (n = 1–4)

$$\underset{\text{II}}{C_2H_5MgAl(C_2H_5)_{n-1}H_{(4-n)+1}} \rightleftharpoons \underset{\text{I}}{HMgAl(C_2H_5)_nH_{4-n}} \quad (21)$$

This equilibrium lies predominantly to the right in solution, and the solids obtained are perhaps mixtures of the two types of species, I being present in a very large excess.

Two interesting intermediates possible in the reaction of aluminum hydride with diethylmagnesium are C_2H_5MgH and $HMgAlH_4$. It would appear that by simply adjusting the reagent ratio at the appropriate stoichiometry, one could obtain these compounds (see eq 22 and 23). However, at the 3:1 ratio of $(C_2H_5)_2Mg:AlH_3$,

$$3(C_2H_5)_2Mg + AlH_3 \longrightarrow 3C_2H_5MgH + (C_2H_5)_3Al \quad (22$$

$$3(C_2H_5)_2Mg + 5AlH_3 \longrightarrow 3HMgAlH_4 + 2(C_2H_5)_3Al \quad (23)$$

the species in solution was found to be mainly $C_2H_5MgAl(C_2H_5)_4$ and a precipitate of MgH_2 was obtained. Thus, it appears that if C_2H_5MgH is formed as an intermediate, it redistributes rapidly to $(C_2H_5)_2Mg$ and MgH_2.

It was observed that when the ratio of $(C_2H_5)_2Mg$:AlH_3 exceeds 1:1.5, a precipitate of $Mg(AlH_4)_2$ forms immediately. It would appear then that any $HMgAlH_4$ formed at the 3:5 ratio ($(C_2H_5)_2Mg$:AlH_3) quickly redistributes in a way represented by eq 24 or 25.

$$2HMgAlH_4 \longrightarrow MgH_2 + Mg(AlH_4)_2 \qquad (24)$$

$$3HMgAlH_4 + 2(C_2H_5)_3Al \longrightarrow Mg(AlH_4)_2 + HMgAl(C_2H_5)_2H_2 + (C_2H_5)_3Al \qquad (25)$$

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Notes

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Preparation of Cyclo-1,3,5-tri-μ-dimethylamino-2,4-bis(dimethylalumino)-6-dihydridoborane[1]

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The chemistry of $B_3Al_3[N(CH_3)_2]_7H_5$ is under investigation including alkylation by aluminum trimethyl, $[Al(CH_3)_3]_2$.[2,3] In order to understand the results associated with this complicated reaction, it proved necessary to investigate the reaction of $[Al(CH_3)_3]_2$ with dimethylaminoborane, $[(CH_3)_2NBH_2]_2$, and bis (dimethylaminoborane), $[(CH_3)_2N]_2BH$. This latter reaction is reported herein, and the former will be reported in the near future.

Preparation and Characterization of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.—Treatment of $[Al(CH_3)_3]_2$ with excess $HB[N(CH_3)_2]_2$ results in the formation of a white crystalline solid which readily sublimes at 50° *in vacuo*. This material is very soluble in pentane and benzene and inflames upon exposure to the atmosphere. The analytical data, summarized in Table I, are consistent with the formulation $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$, in which the nine total valencies of boron plus aluminum are satisfied by the total sum of H, CH_3, and $N(CH_3)_2$ moieties. The hydrolysis of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ is summarized by

TABLE I
ANALYTICAL DATA FOR $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$

	% Al	% B	% $N(CH_3)_2$	% CH_3 (hydrolyzable)	% hydride	Mol wt
Calcd	20.82	4.17	51.02	23.1	0.77	259.1
Found	20.15	4.11	51.17	23.9	0.75	224

$$Al_2B[N(CH_3)_2]_3(CH_3)_4H_2 + 9H_2O \longrightarrow 2Al(OH)_3 + B(OH)_3 + 3HN(CH_3)_2 + 4CH_4 + 2H_2 \qquad (1)$$

Nuclear Magnetic Resonance Studies.—The ^1H nmr spectrum of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ (500-cps sweep width), Figure 1A, consists of three singlets at +0.79, −2.28, and −2.39 ppm from TMS in the area ratios 2:2:1. The high-field peak, +0.79 ppm, is assigned to terminal methyl groups bonded to aluminum as in $[(CH_3)_2AlN(CH_3)_2]_2$, δ +0.56 ppm.[4] The fact that the +0.79-ppm absorption is sharp and not temperature dependent, in the range +30 to −61°, indicates these methyl groups are equivalent. The field position of the other absorptions, −2.28 and −2.39 ppm, indicate resonances due to $N(CH_3)_2$ groups bonded to boron or aluminum in two slightly different environments in the ratio 2:1. Expansion of this region of the nmr spectrum (250-cps sweep width), Figure 1B, clearly indicates these same two singlets. A proton signal, associated with the BH_2 moiety, is not expected to be observable because of splitting by B, $I = {}^3/_2$, and quadrupole broadening.

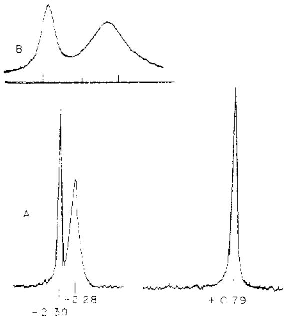

Figure 1.—The ^1H nmr spectrum of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.

The B^{11} nmr spectrum, Figure 2, is a well-defined 1:2:1 triplet, with J_{BH} = 108 ± 3 cps, centered at +17.7 ppm from $B(OCH_3)_3$ (−0.4 ppm from $BF_3 \cdot O(C_2H_5)_2$). The ratio of the absorptions indicates the presence of two equivalent terminal hydrogens bonded to B, while the field position indicates four-coordinate boron, *e.g.*, as in $[H_2BN(CH_3)_2]_2$, δ −4.6 ppm from $BF_3 \cdot O(C_2H_5)_2$, J_{BH} = 116 cps.[5]

Infrared Assignments.—The solid-state infrared spec-

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