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Synthesis and Characterization of Dialkyl(aryl)aminomagnesium Hydrides and Alkoxy(aryloxy)magnesium Hydrides[1]

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Received September 21, 1970

Dialkyl(aryl)aminomagnesium hydrides ($HMgNR_2$ where R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9, C_6H_5) have been synthesized by hydrogenation of dialkyl(aryl)aminomagnesium alkyls, $LiAlH_4$ reduction of dialkyl(aryl)aminomagnesium alkyls, and KH reduction of dialkylaminomagnesium bromides. The hydrides were characterized by elemental analysis, X-ray powder diffraction, and infrared spectroscopy. Infrared absorption bands in the 1500–1600- and 650–700-cm^{-1} regions are assigned to Mg–H stretching and bending modes, respectively, by comparison with the corresponding deuterated compounds. $HMgN(n\text{-}C_4H_9)_2$ and $HMgN(C_6H_5)_2$ are soluble in tetrahydrofuran and have been found to exhibit stereoselectivity in their reduction of ketones. Alkoxy(aryloxy)magnesium hydrides (HMgOR where R = CH_3, *i*-C_3H_7, *tert*-C_4H_9, C_6H_5) were shown to be unstable and to disproportionate readily to MgH_2 and $Mg(OR)_2$.

Introduction

Compounds of the type HMOR and $HMNR_2$ are known[3] where M = Be, Zn, B, or Al. Conspicuous by their absence are such compounds where M = magnesium. Bauer[4] reported the formation of $HMgOC_2H_5$ by C_2H_5MgH cleavage of $(C_2H_5)_2O$ but did not give any evidence that the compound was not a mixture of MgH_2 and $Mg(OC_2H_5)_2$. Coates[3c] has briefly reported the formation of a soluble aminomagnesium hydride when MgH_2 was allowed to react with trimethylethylenediamine in toluene.

Recently we have reported on the preparation of HMgX compounds where X = Cl, Br, or I.[5] Unfortunately we found that these compounds disproportionate in ether solvents to MgH_2 and MgX_2 (eq 1).

$$2HMgX \longrightarrow MgH_2 + MgX_2 \qquad (1)$$

Now we wish to report on the integrity of HMgX compounds where X = OR or NR_2. Shortly we will report on HMgX compounds where X = alkyl or aryl. Thus moving from right to left in the periodic chart, the nature of X will have been studied for HMgX compounds for halogen (group VII), oxygen (group VI), nitrogen (group V), and carbon (group IV). In addition to preparing and characterizing these compounds and studying their structure in solution, we are also interested in evaluating these classes of compounds as stereoselective reducing agents.

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 columns to remove oxygen and Dry Ice–acetone traps to remove solvent.[6]

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 Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. A 300-ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high-pressure hydrogenation. An ebullioscopic apparatus previously described was used for molecular weight determination.[7]

Analyses.—Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[6] Magnesium and aluminum were determined by EDTA titration.

Materials.—Methanol (Fisher Scientific) was distilled after treating with magnesium metal. *tert*-Butyl alcohol (Fisher Scientific) was fractionally crystallized under nitrogen. 2-Propanol (Fisher Scientific) was distilled after drying over Molecular Sieve 4A. Phenol (Mallinckrodt) was distilled at reduced pressure. Diethyl-, diisopropyl-, and di-*n*-butylamine (Eastman Organic Chemicals) were dried over Molecular Sieve 4A and distilled prior to use. Diphenylamine (Eastman Organic Chemicals) was used without further purification.

Diethyl ether was distilled immediately before use from lithium aluminum hydride, and tetrahydrofuran and benzene were distilled from sodium aluminum hydride.

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 Aid (John-Mansville). The solution was standardized by aluminum analysis. In a similar manner a solution of lithium aluminum deuteride (Metal Hydrides Inc.) was prepared. Potassium hydride was obtained from Alfa Inorganics.

Diisopropyl- and diethylmagnesium were prepared by the dioxane precipitation method.[8] Di-*sec*-butylmagnesium was prepared from active $MgCl_2$ and *sec*-butyllithium in benzene.[9] Magnesium hydride was prepared from $LiAlH_4$ and diethylmagnesium in diethyl ether.[10] *Anal.* Calcd for MgH_2: Mg, 92.3; H, 7.65. Found: Mg, 72.9; H, 6.26; Al, 0; $(C_2H_5)_2O$, 20.8 by difference. The ratio of Mg:H is 1.00:2.07.

Alkyl(aryl)oxymagnesium alkyls[11] and dialkyl(aryl)aminomagnesium alkyls[12] were prepared according to the methods described by Coates which involve adding an equivalent amount of alcohol or secondary amine to the appropriate dialkylmagnesium compound in diethyl ether at room temperature. After 1 hr the diethyl ether solvent was removed at reduced pressure and benzene was added in order to prepare a standardized solution in a nonpolar solvent.

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[1] We are indebted to the Office of Naval Research under Contract No. N00014-67-A-0159-0005 and ONR Contract Authority No. NR-92-050/12-5-67-429 for support of this work.

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TABLE I

ANALYTICAL, INFRARED, AND X-RAY POWDER DATA FOR DIALKYL(ARYL)AMINOMAGNESIUM HYDRIDES

Compound	Analyses, %		Infrared bands, 2000–400 cm^{-1}	X-Ray powder data
	Calcd	Found		
$HMgN(i\text{-}C_3H_7)_2$[a]	H, 0.803 Mg, 19.37	H, 0.619 Mg, 17.76	1500 sh, 1335 w, 1315 w, 1170 w, 1150 s, 1120 m, 975 s, 935 w, 900 m, 825 w, 810 w, 780 w, 725 s, 690 s, 650 s, 570 m, 535 w, 430 w	9.5 s, 5.25 s, 4.20 vvw
$HMgN(i\text{-}C_3H_7)_2$[h]		H, 0.819 Mg, 19.56	1500 sh, 1330 w, 1315 w, 1255 w, 1170 w, 1150 s, 1120 m, 975 s, 935 w, 900 m, 825 w, 810 w, 775 m, 725 s, 690 s, 650 s, 570 s, 545 w, 420 w	9.5 s, 5.20 s, 4.00 vw
$DMgN(i\text{-}C_3H_7)_2$[i]	D, 1.587 Mg, 19.22	D, 1.432 Mg, 20.17	1330 w, 1315 w, 1255 w, 1170 w, 1150 s, 1120 m, 1050 s, b, 975 s, 935 w, 900 m, 825 w, 810 w, 775 w, 715 w, 570 s, 525 s, 465 s	. . .
$HMgN(i\text{-}C_3H_7)_2$[b]		H, 1.45 Mg, 26.90	1590 s, 1345 w, 1320 w, 1170 w, 1150 s, 1110 s, 1090 w, 1025 w, 975 s, 945 m, 890 s, 720 w, 655 s, 580 s, 425 s	11.5 s, 5.50 s, 4.00 m, 3.55 w, 2.80 vw, 2.15 vvw
$HMgN(n\text{-}C_4H_9)_2$[c]	H, 0.656 Mg, 15.83	H, 0.947 Mg, 18.42	1600 s, b, 1260 w, 1230 w, 1215 w, 1155 m, 1130 m, 1105 s, 1075 s, 1055 m, 1010 m, 995 w, 945 m, 915 m, 885 m, 715 s, 675 s, 565 s, 400 s	12.5 s, 4.65 s, 4.30 m, 2.85 w
$HMgN(n\text{-}C_4H_9)_2$[d]		H, 0.727 Mg, 16.91	1550 s, b, 1300 w, 1255 w, 1150 w, 1130 m, 1105 m, 1075 s, 1010 m, 955 w, 855 m, 790 m, 715 s, 650 m, 570 s, 400 w	15.0 vs, 4.40 m
$HMgN(C_2H_5)_2$[e]	H, 1.034 Mg, 24.98	H, 0.752 Mg, 20.74	1520 s, b, 1295 w, 1165 m, 1130 s, 1095 m, 1030 w, 1015 w, 990 m, 845 m, 775 w, 720 s, 670 s, 570 s, 530 s, 440 m	14.0 s, 4.50 vw
$HMgN(C_6H_5)_2$[f]	H, 0.521 Mg, 12.25	H, 0.383 Mg, 10.87	1600 m, b, 1580 s, 1480 s, 1370 m, 1360 sh, 1330 w, 1295 m, 1235 s, 1215 sh, 1170 s, 1070 w, 1020 m, 870 s, 800 m, 740 s, 680 s, 495 s, 435 w	12.0 s, 9.0 w, 7.0 w, 6.10 w, 5.00 m, 3.95 s, 3.5 w, 2.75 w, 2.06 m, 1.80 vw
$HMgN(CH_3)CH_2CH_2N(CH_3)_2$[g]	H, 0.797 Mg, 19.92	H, 1.05 Mg, 21.92	1370 m, 1340 s, 1280 m, 1245 w, 1190 w, 1165 m, 1145 s, 1105 s, 1030 s, 940 s, 845 s, 795 s, 670 w, 575 m, 400 s	9.7 s, 8.0 s, 5.50 m, 4.70 s, 4.00 w, 2.58 vw, 2.40 w

[a] Hydrogenation of $sec\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2$ at 25°. [b] Hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 70°. [c] Hydrogenation of $C_2H_5MgN(n\text{-}C_4H_9)_2$ at 50°. [d] Hydrogenation of $sec\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25°. [e] Hydrogenation of $sec\text{-}C_4H_9MgN(C_2H_5)_2$ at 25°. [f] Hydrogenation of $C_4H_9MgN(C_6H_5)_2$ at 25°. [g] Hydrogenation of $C_2H_5MgN(CH_3)CH_2CH_2N(CH_3)_2$ at 110°. [h] Reaction of $C_2H_5MgN(i\text{-}C_3H_7)_2$ with $LiAlH_4$. [i] Reaction of $i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$ with $LiAlD_4$.

Dialkyl(aryl)aminomagnesium bromides were prepared from C_2H_5MgBr and an equivalent amount of secondary amine in tetrahydrofuran at room temperature.

Preparation of $HMgNR_2$ ($R = C_2H_5$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, C_6H_5). (1) Hydrogenation of Dialkyl(aryl)aminomagnesium Compounds.—Dialkyl(aryl)aminomagnesium alkyl solutions (0.2–0.7 *M*) in benzene (100 ml) were hydrogenated overnight at 3000 psig. The temperature of hydrogenation depended on the particular alkyl group, R in $RMgNR_2'$: 50–70° for the ethyl group and 25° for the *sec*-butyl group. Analytical and spectroscopic data of the precipitate are given in Table I. Hydrogenation was complete in the reactions performed at 50–70°. At 25° some starting compound was generally found in the filtrates.

(2) **Reaction of Dialkylaminomagnesium Alkyls with $LiAlH_4$. (a) $C_2H_5MgN(i\text{-}C_3H_7)_2$.**—To a diethyl ether (25 ml) solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ (38 mmol), $LiAlH_4$ (9.5 mmol) in diethyl ether was added slowly from an additional funnel. An immediate precipitate formed. Analysis of the precipitate is given in Table I. The yield of $HMgN(i\text{-}C_3H_7)_2$ is quantitative. In a similar manner $DMgN(i\text{-}C_3H_7)_2$ was prepared from $LiAlD_4$.

(b) **$C_2H_5MgN(n\text{-}C_4H_9)_2$.**—To a diethyl ether (25 ml) solution of $C_2H_5MgN(n\text{-}C_4H_9)_2$ (28 mmol), $LiAlH_4$ (7.0 mmol) in diethyl ether was added. No precipitate formed. Infrared spectral analysis indicated the formation of $HMgN(n\text{-}C_4H_9)_2$; however the addition of benzene or hexane was not effective in the separation of the reaction products.

(3) **Reactions of MgH_2 and Trimethylethylenediamine.**—A slurry of MgH_2 (10 mmol) in benzene (50 ml) was allowed to react with trimethylethylenediamine (10 mmol) for several days under refluxing conditions. The reaction still contained a solid which was isolated by filtration. The solid was identified as MgH_2 by its infrared spectrum. The weight of the solid and the magnesium content indicated an MgH_2 recovery of 4.1 mmol. The filtrate showed no hydridic activity. Evaporation of benzene from the filtrate resulted in a brown oily resin.

(4) **Reaction of $BrMgNR_2$ with KH ($R = n\text{-}C_4H_9$, C_6H_5).**—A tetrahydrofuran solution of $BrMgNR_2$, prepared by reaction of C_2H_5MgBr with R_2NH in tetrahydrofuran, was stirred at room temperature for 3 days with excess KH. After filtration, analysis of the filtrate gave a ratio of Mg:H:Br as 1.00:0.99:0 when $R = n\text{-}C_4H_9$ and 1.00:96:0 when $R = C_6H_5$.

(5) **Reaction of $(i\text{-}C_3H_7)_2NH$ and $(n\text{-}C_4H_9)_2NH$ with MgH_2.**—A slurry of MgH_2 (7 mmol) and $(i\text{-}C_3H_7)_2NH$ (7 mmol) in benzene (40 ml) was allowed to react for 2 days under refluxing conditions. The solid was isolated by filtration. Infrared analysis of this solid (Nujol mull) showed only bands for MgH_2. The filtrate contained no magnesium. In a similar experiment with $(n\text{-}C_4H_9)_2NH$ and MgH_2 similar results were obtained.

A slurry of MgH_2 (10.9 mmol) and $(n\text{-}C_4H_9)_2NH$ (10.9 mmol) in benzene (100 ml) was allowed to react at 200° overnight in the autoclave. The solid product was isolated and subjected to spectroscopic analysis. The infrared spectrum showed MgH_2 bands, and X-ray powder diffraction showed lines corresponding to the lines of MgH_2. The filtrate contained no magnesium. In a similar experiment with $(i\text{-}C_3H_7)_2NH$, similar results were obtained.

Reduction of Ketones with $HMgNR_2$ ($R = n\text{-}C_4H_9$, $i\text{-}C_3H_7$, C_6H_5).—To a 0.213 *M* tetrahydrofuran solution of ketone (2-methylcyclohexanone, norcamphor) (1 mmol) $HMgNR_2$ (1.5 mmol) ($R = C_6H_5$, $n\text{-}C_4H_9$) in tetrahydrofuran (0.80 *M*) was added. After 2 hr at 0° the reaction mixture was quenched by adding aqueous NH_4Cl. A slurry of $HMgN(i\text{-}C_3H_7)_2$ in tetrahydrofuran was used at room temperature. The alcohols were analyzed by vpc.

Attempted Preparation of HMgOR. (1) Reaction of MgH_2 and ROH ($R = CH_3$, $i\text{-}C_3H_7$, *tert*-C_4H_9, C_6H_5).—In a typical case CH_3OH (6.00 mmol) was added to a slurry of MgH_2 (6.00 mmol) in benzene (50 ml). The mixture was stirred overnight under refluxing conditions. The solid product was isolated by filtration and dried *in vacuo* at room temperature. The reaction was repeated with the other alcohols in benzene and tetrahydrofuran. Analytical and X-ray powder data are given in Table II indicating the solid product to be a physical mixture of MgH_2 and $Mg(OR_2)$. In all cases the filtrates contained no magnesium.

(2) **Hydrogenation of C_2H_5MgO-*tert*-C_4H_9.**—A 0.5 *M* benzene solution of C_2H_5MgO-*tert*-C_4H_9 (50 mmol) (prepared by reaction of $(C_2H_5)_2Mg$ and *tert*-C_4H_9OH) was allowed to react with H_2 at 110° and 3000 psi in a Magne stirrer autoclave overnight. The precipitate was isolated as above. Analytical and X-ray powder data are given in Table II. The filtrate contained 10 mg-atoms of magnesium. The ratio of Mg:H:C_2H_5 in the filtrate was 1.00:0.0:0.88.

TABLE II
ANALYTICAL AND X-RAY POWDER DATA FOR "HMgOR" COMPOUNDS

Compound	Solvent	Mg:H ratio	XR-ay powder data
MgH_2	Diethyl ether	1:2.07	3.19 s, 2.50 s, 2.25 w, 1.67 s
"$HMgOCH_3$"	Benzene	1:1.17	11.0 vs, 3.20 m, 2.50 m, 2.25 w, 1.66 w
"$HMgOCH_3$"	Tetrahydrofuran	1:1.10	11.0 vs, 3.20 m, 2.50 m, 2.25 w, 1.68 w
$(CH_3O)_2Mg$	Benzene	1:0.0	11.0 vs
"HMgO-*i*-C_3H_7"	Benzene	1:1.02	8.75 s, 4.30 m, 3.25 w, 2.50 w, 2.25 vw, 1.66 w
"HMgO-*i*-C_3H_7"	Tetrahydrofuran	1:0.78	8.75 s, 4.30 m, 3.25 w, 2.50 w, 2.25 vw, 1.68 vw
(*i*-$C_3H_7O)_2Mg$	Benzene	1:0.0	8.8 s, 4.30 m
"HMgO-*tert*-C_4H_9"	Benzene	1:0.80	9.0 s, 8.0 m, 4.50 m, 4.30 m, 4.00 vvw, 3.45 w, 3.25 vw, 3.10 vw, 2.50 vw, 1.68 vw
"$HMgOC_4H_9$"	Tetrahydrofuran	1:0.94	9.0 s, 8.0 m, 4.50 m, 4.30 m, 4.00 w, 3.45 w, 3.25 vw, 3.05 w, 2.50 w, 2.25 vw, 1.67 w
"$HMgOC_4H_9$"[a]	Benzene	1:0.80	9.2 s, 8.5 m, 4.53 m, 4.30 m, 3.50 w, 3.20 m, 2.50 m, 2.25 w, 1.67 w
"$HMgOC_4N_9$"[b]	Benzene	1:0.60	8.8 s, 7.9 m, 4.45 m, 4.23 w, 4.00 vw, 3.45 m, 3.25 w, 3.05 w
(*tert*-$C_4H_9O)_2Mg$	Benzene	1:0.0	9.0 s, 8.0 s, 4.50 m, 4.30 m, 4.00 w, 3.50 m, 3.05 w
"$HMgOC_6H_5$"	Benzene	1:0.99	13.5 s, 8.5 m, 5.05 m, 4.60 vw, 4.25 s, 3.25 s, 2.50 w, 2.25 vw, 1.68 w
$(C_6H_5O)_2Mg$	Benzene	1:0.0	10.5 s, 8.5 w, 5.10 m, 4.60 w, 4.25 s, 3.25 m
"$HMgOC_6H_5$"	Tetrahydrofuran	1:1.05	10.5 s, 8.25 m, 6.90 w, 5.90 vvw, 4.85 w, 4.70 w, 4.48 m, 4.35 m, 4.15 m, 3.90 m, 3.75 m, 3.55 w, 3.45 m, 3.30 w, 3.20 w, 3.08 vw, 3.02 vw, 3.00 vw, 2.50 w, 2.40 w, 2.25 vw, 1.87 vw, 1.68 vw
$(C_6H_5O)_2Mg$	Tetrahydrofuran	1:0.0	10.5 s, 8.25 s, 6.95 s, 5.95 w, 5.15 w, 5.40 w, 5.15 w, 4.50 s, 4.35 s, 4.15 m, 3.90 s, 3.80 s, 3.65 w, 3.45 m, 3.30 w, 3.20 w, 3.00 w, 2.90 w, 2.80 w, 2.70 w, 2.40 w, 2.25 w, 1.86 w

[a] Hydrogenation of C_2H_5MgO-*tert*-C_4H_9 at 110° and 3000 psig.
[b] Hydrogenation of *i*-C_3H_7MgO-*tert*-C_4H_9 at 50° and 3000 psig.

(3) **Hydrogenation of *i*-C_3H_7MgO-*tert*-C_4H_9.**—A 0.3 *M* benzene solution of *i*-C_3H_7MgO-*tert*-C_4H_9 (30 mmol) was hydrogenated at room temperature and 3000 psig overnight. No reaction occurred. The hydrogenation was repeated at 50° and 3000 psi overnight. A precipitate formed which was isolated as above. Analytical and X-ray powder data are given in Table II. The filtrate contained 1.0 mg-atom of magnesium and no hydridic hydrogen.

Preparation of $Mg(OR)_2$ ($R = CH_3$, *i*-C_3H_7, *tert*-C_4H_9, C_6H_5).—In a typical case CH_3OH (8.00 mmol) was added to a slurry of MgH_2 (4.00 mmol) in benzene. After refluxing overnight the solid was isolated by filtration. The reaction was repeated with the other alcohols in benzene and tetrahydrofuran. Analytical and X-ray powder data are given in Table II. In all cases the filtrates contained no magnesium.

Results and Discussion

The results of this study show that heretofore unknown dialkyl- and diarylaminomagnesium hydrides ($HMgNR_2$) can be successfully prepared by three different methods. The first method involves the hydrogenation of dialkyl- or diarylaminomagnesium alkyls ($RMgNR'_2$). This method was suggested by the recent report that the formation of an Mg–H bond takes place readily by hydrogenation of a magnesium alkyl compound especially when the alkyl group is *sec*-butyl.[13] In this manner *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$ was allowed to react with H_2 at 25° and 3000 psi to form the white solid $HMgN(i\text{-}C_3H_7)_2$ (I) (see eq 2 and 3). Compound I had

$$(sec\text{-}C_4H_9)_2Mg + HN(i\text{-}C_3H_7)_2 \longrightarrow sec\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2 + C_4H_{10} \quad (2)$$

$$sec\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2 \xrightarrow{H_2} HMgN(i\text{-}C_3H_7)_2 + C_4H_{10} \quad (3)$$

an Mg:H ratio of 1.00:0.84 and a unique X-ray powder pattern which contained no lines typical of MgH_2. The most interesting feature of the infrared spectrum (Nujol mull) (Figure 1) of I was a strong broad band at 1500 cm^{-1} appearing as a shoulder on the Nujol band at 1455 cm^{-1}. The assignment of this band is discussed below. Compound I is insoluble in benzene and diethyl ether and only slightly soluble in tetrahydrofuran (0.021 *M*). The molar ratio of Mg:H in the tetrahydrofuran solution was 1.00:0.98.

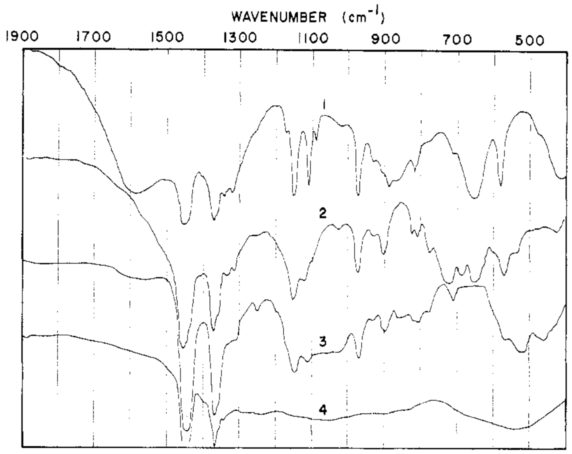

Figure 1.—Infrared spectra (Nujol mulls) of (1) $HMgN(i\text{-}C_3H_7)_2$ prepared by hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ in benzene at 70°, (2) $HMgN(i\text{-}C_3H_7)_2$ prepared by hydrogenation of *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$ in benzene at 25°, (3) $DMgN(i\text{-}C_3H_7)_2$ prepared by $LiAlD_4$ reduction of $C_2H_5MgN(i\text{-}C_3H_7)_2$ in diethyl ether, and (4) MgH_2 prepared from $LiAlH_4$ and $(C_2H_5)_2Mg$ in diethyl ether.

Adding a diethyl ether solution of $LiAlH_4$ to an ether solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ also produces I. This method is suggested by the previously reported observation that $LiAlH_4$ will reduce $(C_2H_5)_2Mg$ quantitatively to MgH_2[10] (see eq 4). On addition of $LiAlH_4$ an imme-

$$LiAlH_4 + 4C_2H_5MgN(i\text{-}C_3H_7)_2 \longrightarrow 4HMgN(i\text{-}C_3H_7)_2 + LiAl(C_2H_5)_4 \quad (4)$$

diate precipitate formed which after filtration could be completely desolvated *in vacuo* at room temperature. The X-ray powder pattern and infrared spectrum (Table I) were the same as for I prepared by hydrogenation of *sec*-$C_4H_9MgN(i\text{-}C_3H_7)_2$.

In order to assign the infrared bands for the Mg–H stretching and bending modes, $DMgN(i\text{-}C_3H_7)_2$ (II) was prepared by reaction of $C_2H_5Mg(i\text{-}C_3H_7)_2$ with $LiAlD_4$. The infrared spectrum of II (Figure 1) revealed that the bands present in I at 1500, 690, and 650 cm^{-1} were absent in II and that broad bands were present in the spectrum of II at 1050 and 465 cm^{-1} approximately as predicted for the isotopic shift of Mg–H to Mg–D. The bands at 690 and 650 cm^{-1} are in the region expected for metal–hydrogen bending modes. The band at 1500 cm^{-1} is probably a terminal Mg–H stretching band;

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(13) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

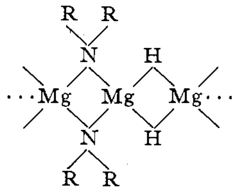
however, in a mixture of MgH_2 and $HMgN(i\text{-}C_3H_7)_2$ as discussed below, the absorption occurs at 1590 cm^{-1} and thus in I there may be some slight bridging interaction of the Mg–H bonds with adjacent molecules. This is the first time that distinct infrared absorption bands have been reported for an Mg–H compound. Reference to Figure 1 shows the characteristic Mg–H bands observed for $HMgN(i\text{-}C_3H_7)_2$ as compared to MgH_2. An Mg–H stretching frequency of 1497 and 1598 cm^{-1} for the $^2\Sigma$ and $^2\Pi$ states, respectively, has been calculated from the vapor-phase electronic emission spectra of Mg–H.[14] In a similar type of compound $HZnN(CH_3)CH_2CH_2N(CH_3)_2$, an infrared band at 1825 cm^{-1} has been reported.[3c]

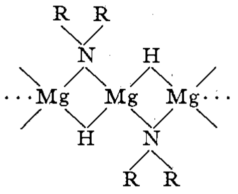
Because of the low solubility of I no molecular weight determination or nmr studies were possible.

An attempt to prepare I by hydrogenation of a benzene solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 70° resulted in the formation of a compound with a different X-ray powder pattern (Table I). The Mg–H infrared bands were very broad and strong at 1590 and 655 cm^{-1} (Figure 1). The Mg:H molar ratio was 1.00:1.30 which could be due to some hydrogenation of the Mg–N bond to form MgH_2, although no MgH_2 lines were visible in the X-ray powder pattern. In this connection, the hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 110° resulted in complete hydrogenation of the Mg–N bond as well as the Mg–C bond to form MgH_2 exclusively (eq 5). The fate of the amine was not determined though diisopropylamine was expected.

$$C_2H_5MgN(i\text{-}C_3H_7)_2 \xrightarrow[110^\circ]{H_2} MgH_2 + C_2H_6 + HN(i\text{-}C_3H_7)_2 \quad (5)$$

Di-*n*-butylaminomagnesium hydride, $HMgN(n\text{-}C_4H_9)_2$ (III), was synthesized by hydrogenation of *sec*-$C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25° and 3000 psig. The infrared spectrum of III (Nujol mull) shows strong bands at 1550 and 650 cm^{-1}, and the X-ray powder pattern contains no lines for MgH_2. Compound III is slightly soluble in benzene (0.09 *M*) and very soluble in tetrahydrofuran. When III is dissolved in tetrahydrofuran, the solution infrared spectrum shows no Mg–H stretching band at 1550 cm^{-1}. The disappearance of the band at 1550 cm^{-1} is probably due to the association of III by metal–hydrogen bridge bonds, which cause the absorption to be broadened and shifted to lower energy and thus not observable. Molecular weight data for III in tetrahydrofuran indicate that III is highly associated. The association is concentration dependent: i = 4.7 and 10 at 0.07 and 0.33 *m* concentrations, respectively. In tetrahydrofuran solution III must be associating by both the hydrido and the amino groups as would be expected by the well-known bridging tendencies of both groups. It is proposed that the association takes place *via* a double-nitrogen and double-hydrogen bridged representation (A); however mixed nitrogen–hydrogen bridge species are also possible (B) (R = $n\text{-}C_4H_9$). The association values were obtained ebullioscopically and are thought to be fairly reliable even though some solvent cleavage occurs during the determination. Over a 24-hr period in refluxing tetrahydrofuran, III decreases in hydridic hydrogen content by 50%. However, since the association measurement was done in less than 3 hr the cleavage should not be too significant.


A


B

Hydrogenation of $C_2H_5MgN(n\text{-}C_4H_9)_2$ at 50° in benzene also produced $HMgN(n\text{-}C_4H_9)_2$, which however was of a different crystalline form (Table I). The Mg:H ratio of the product was 1.00:1.24 indicating that some hydrogenation of the Mg–N occurred. The Mg–H infrared bands occur at 1600 and 675 cm^{-1} (Nujol mull).

An attempt to prepare III by $LiAlH_4$ reduction of $C_2H_5MgN(n\text{-}C_4H_9)_2$ in diethyl ether (eq 6) was unsuccessful because both of the products of this reaction are soluble and could not be separated. The infrared spectrum of the reaction mixture shows that the expected products were formed. No Al–H bands were observed in the 1600–1700-cm^{-1} region of the spectrum, but an Mg–H band at 1500 cm^{-1} was observed. Compound III prepared in benzene by hydrogenation of *sec*-$C_4H_9MgN(n\text{-}C_4H_9)_2$ has very slight solubility in diethyl ether, but when formed in diethyl ether, it does not precipitate. Presumably III prepared in diethyl ether is an etherate which is soluble, but the stability of the desolvated crystalline lattice is such that resolvation does not occur. Presumably this method of preparing $HMgNR_2$ compounds is successful only when the $HMgNR_2$ compound is insoluble in diethyl ether and thus easily separated from the soluble by-product $LiAlR_4$.

$$4C_2H_5MgN(n\text{-}C_4H_9)_2 + LiAlH_4 \longrightarrow 4HMgN(n\text{-}C_4H_9)_2 + LiAl(C_2H_5)_4 \quad (6)$$

Another route to III involves the reduction of $BrMgN(n\text{-}C_4H_9)_2$ by KH in tetrahydrofuran (eq 7). This reaction is complete in 3 days and represents the most convenient route to solutions of III in tetrahydrofuran.

$$KG + BrMgN(n\text{-}C_4H_9)_2 \longrightarrow HMgN(n\text{-}C_4H_9)_2 \quad (7)$$

Diphenylaminomagnesium hydride (IV) was synthesized by the hydrogenation of *sec*-$C_4H_9MgN(C_6H_5)_2$ in benzene. However, tetrahydrofuran solutions of IV can be most conveniently prepared by the KH reduction of $BrMgN(C_6H_5)_2$ in tetrahydrofuran. The Mg–H infrared stretching band (Nujol mull) occurs at about 1600 cm^{-1} largely hidden by the absorption of the phenyl groups. In a tetrahydrofuran solution spectrum with the phenyl groups and solvent absorptions, no Mg–H band is observable. Compound IV is only slightly soluble in benzene but is soluble in tetrahydrofuran (1 *M*). Colorless needle-shaped crystals are formed from a saturated solution of IV in tetrahydrofuran. Ebullioscopic molecular weight data indicate that IV is a dimer in tetrahydrofuran: i = 1.88 and 1.92 at 0.106 and 0.168 *m* concentrations, respectively. Again, however, because of solvent cleavage these association values must be viewed with caution. The hydridic hydrogen in solution decreased from an Mg:H ratio of 1.00:0.96 to a ratio of 1.00:0.81 during the measurement. In contrast to III when bridging apparently occurs with both hydrido and amino groups, the bridging in IV must be with only one group, although it is

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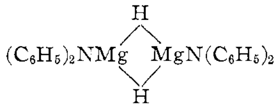
[14] M. A. Khan, *Proc. Phys. Soc., London*, **80**, 523 (1962).

not obvious which group is the bridging group. Although the NR_2 group is normally a stronger bridging group than hydrogen, in the case of IV the opposite may be true because of steric factors or because of the lower basicity of the diphenylamino group. If $HMgN(C_6H_5)_2$ did bridge through the diphenylamino groups, then it is not clear why further bridging through hydrogen bridge bonds does not take place as in the case proposed for $HMgN(n\text{-}C_4H_9)_2$. Thus the representation of IV as dimerizing through hydrogen bridge bonds appears as reasonable in the absence of X-ray structure data as dimerization through diphenylamino groups. For clarity in the representation of IV no solvent molecules are included; however, each magnesium is thought to be coordinated with at least one tetrahydrofuran molecule.



IV

Diethylaminomagnesium hydride, $HMgN(C_2H_5)_2$, was synthesized by hydrogenation of *sec*-$C_4H_9MgN(C_2H_5)_2$ (Table I). The compound $HMgN(C_2H_5)_2$ is insoluble in benzene and only slightly soluble in tetrahydrofuran (0.08 *M*).

Trimethylethylenediaminomagnesium hydride, $HMgN(CH_3)CH_2CH_2N(CH_3)_2$ (V), was synthesized by the hydrogenation of $C_2H_5MgN(CH_3)CH_2CH_2N(CH_3)_2$ in benzene (Table I). Compound V is slightly soluble in benzene (0.13 *M*) and is unstable in refluxing benzene over a period of several days. An attempt to purify a sample by Soxhlet extraction resulted in loss of hydridic activity. An attempt was made to prepare V by the direct reaction of trimethylethylenediamine and MgH_2 reported earlier by Coates.[3c] No reaction occurred at room temperature; however, under conditions of atmospheric reflux for several days approximately half of the MgH_2 reacted. No hydridic activity was found in solution presumably because of the thermal decomposition of the hydride. The thermal decomposition may proceed by a hydride attack on the aminomethyl groups. Evaporation of the solvent gave a brown oily resin.

MgH_2 and diisopropyl- or di-*n*-butylamine did not react even under forcing conditions to form $HMgNR_2$ compounds (eq 8). In all cases unreacted MgH_2 was recovered.

$$MgH_2 + R_2NH \not\longrightarrow HMgNR_2 + H_2 \qquad (8)$$

No attempt was made to prepare dimethylaminomagnesium hydride because the intermediate required for hydrogenolysis, $RMgN(CH_3)_2$, is unstable and disproportionates to R_2Mg and $(CH_3)_2Mg$.[12]

The reduction of two ketones was studied in order to evaluate $HMgNR_2$ compounds as stereoselective reducing agents. The ketones are norcamphor and 2-methylcyclohexanone. Norcamphor with $HMgN(n\text{-}C_4H_9)_2$ gave 97% endo alcohol and with $HMgN(C_6H_5)_2$ 94% endo alcohol in approximately 80% yield under the conditions used, 0° and 2 hr. The endo alcohol is the expected product if the reducing agent approaches the substrate from the least hindered side of the ketone. $LiAlH_4$ under similar conditions gives 89% of the endo alcohol.[15] 2-Methylcyclohexanone with $HMgN(n\text{-}C_4H_9)_2$ gave 72% cis alcohol and with $HMgN(C_6H_5)_2$ 80% cis alcohol in 55% yield under the conditions used. The cis alcohol is the least stable alcohol. $LiAlH_4$ gives only 24% cis alcohol under similar conditions.[15] A slurry of $HMgN(i\text{-}C_3H_7)_2$ in tetrahydrofuran was used at room temperature. With 2-methylcyclohexanone $HMgN(i\text{-}C_3H_7)_2$ gave 71% cis alcohol. These results indicate that the reducing agents are attacking the substrates from the least hindered side which is consistent with the association data which indicated $HMgN(n\text{-}C_4H_9)_2$ to be highly associated and $HMgN(C_6H_5)_2$ to be at least a dimer.

In contrast to the stable aminomagnesium hydrides, the alkoxymagnesium hydrides are unstable and disproportionate to MgH_2 and magnesium alkoxide (eq 9).

$$2HMgOR \longrightarrow MgH_2 + Mg(OR)_2 \qquad (9)$$

The X-ray powder patterns (Table II) for "HMgOR" ($R = CH_3$, $i\text{-}C_4H_7$, *tert*-C_4H_9, C_6H_5) all show lines of MgH_2, and, in addition, the remaining lines are those of the appropriate $(RO)_2Mg$ also listed in Table II.

The synthesis of HMgOR compounds was attempted by two methods, direct reaction of MgH_2 and ROH and hydrogenation of alkylmagnesium alkoxides (RMgOR). Although the MgH_2 used was an active form prepared by $LiAlH_4$ reduction of $(C_2H_5)_2Mg$ in diethyl ether, the direct reaction with alcohols was slow and proceeded only under refluxing conditions in tetrahydrofuran or benzene. Apparently the reaction formed the intermediate "HMgOR" compound which then disproportionated to MgH_2 and $(RO)_2Mg$ (eq 10). Hydrogenation of C_2H_5MgO-*tert*-C_4H_9 at 110° in benzene resulted in the formation of a mixture of MgH_2 and $Mg(O\text{-}tert\text{-}C_4H_9)_2$ (Table II). Since disproportionation might have occurred at the higher temperature, it was considered desirable to attempt to synthesize the compound at a lower temperature. $i\text{-}C_3H_7MgO$-*tert*-C_4H_9 was synthesized and hydrogenated at room temperature. No reaction occurred at room temperature, and the hydrogenation was repeated at 50°. A product was isolated and shown to be a mixture of MgH_2 and $Mg(O\text{-}tert\text{-}C_4H_9)_2$ by X-ray powder diffraction comparison with an authentic sample.

$$MgH_2 + ROH \longrightarrow HMgOR + H_2 \longrightarrow 0.5MgH_2 + 0.5Mg(OR)_2 \qquad (10)$$

All magnesium alkoxides ($Mg(OR)_2$) were synthesized by the reaction of MgH_2 with 2 equiv of the appropriate alcohol. All of the magnesium alkoxides are insoluble in the solvents used, benzene and tetrahydrofuran. The phenol case is somewhat complicated by the formation of different crystalline forms from different solvents.

The infrared spectra of "HMgOR" and $Mg(OR)_2$ compounds are identical. In the case of "HMgOR," the very broad weak bands of MgH_2 are not evident in the spectra. However, in no case was there any indication of Mg–H bands similar to the Mg–H bands found for the amino compounds.

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[15] H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, **87**, 5620 (1965).