containing the compound (**8** or **9**) dissolved in ether was attached, and the solution was slowly added with stirring. After the mixture had been stirred from 1 to 1.5 h, NH_4Cl crystals were cautiously added until the blue color disappeared. Ammonia was allowed to evaporate, and the residue was poured into water and extracted by ether. The ether layer was dried ($MgSO_4$), filtered, and concentrated to give an oil, which was analyzed by GC. The data from duplicate runs on **8** and **9** are given in Table I.

Reduction of 8. Sodium (0.7 g) was dissolved in 50 mL of ammonia and a blue color developed immediately. A 1.5-g sample of **8** dissolved in 15 mL of dry ethyl ether was then added via a dropping funnel. No color change occurred in the solution. After stirring 1.5 h, the reaction mixture was worked up to give 1.3 g of oil. Gas chromatography analysis showed **1a:1b** (77:23).[11]

The reduction of 1 g of **8** was repeated using 0.4 g of sodium to give **1a:1b** (79:21).[11]

Reduction of 9. A 1-g sample of **9** and 0.4 g of sodium treated as above gave **1a:1b** (82:18). This was repeated using 1 g of sodium, which resulted in **1a:1b** (84:16).[11]

Equilibration of 1a by $NaNH_2$. The apparatus described in the reduction procedure was used. A 1-g sample of **1a** dissolved in 15 mL of dry ether was slowly added to a solution containing 0.3 g of sodium dissolved in 50 mL of liquid ammonia, which contained a crystal of $FeSO_4$. When GC studies showed no composition change, the solution was worked up as described in the reduction procedure to yield 1 g of an oil. GC analysis showed that this oil contained **1a:1b** (82:18).[11]

Acknowledgment. We thank the Continental Oil Company's Analytical Research Section for analytical determinations and the American Petroleum Institute for some financial support.

Registry No.—**1a,** 14568-75-3; **1b,** 14568-76-4; **2,** 100-42-5; **4,** 7302-01-4; **5,** 606-83-7; **6,** 16618-72-7; **8,** 22360-63-0; **9,** 22360-6-9; **10,** 4593-90-2; **11,** 6072-57-7; cinnamic acid, 621-82-9.

References and Notes

(1) (a) A. R. Taylor, M.S. Thesis, Oklahoma State University, December, 1974; American Petroleum Institute Graduate Research Assistant, 1974; (b) Oklahoma State University; (c) Continental Oil Company; (d) some financial support from Continental Oil Company is gratefully acknowledged.

(2) (a) R. Fittig and H. Erdmann, *Justus Liebigs Ann. Chem.*, **216,** 817 (1883); (b) H. Stobbe and G. Posnjak, *Ibid.*, **371,** 287 (1909); (c) R. Stoermer and H. Kootz, *Ber. B*, **61,** 2330 (1928); (d) J. Risi and D. Guavin, *Can. J. Res., Sect. B*, **14,** 255 (1936); (e) P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **72,** 4918 (1950); (f) M. J. Rosen, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 665; (g) M. J. Rosen, *J. Org. Chem.*, **18,** 1701 (1953).

(3) (a) B. B. Corson, W. J. Heintzelman, H. Moe, and C. R. Rousseau, *J. Org. Chem.*, **27,** 1636 (1962); (b) H. Ambrust, G. Kilpper, W. Koehler, H. J. Quadbeck-Seeger, H. G. Schecker, and H. J. Sturn, German Offen. 2 101 089, Aug 10, 1972; *Chem. Abstr.*, **77,** 164307w (1972); (c) T. Yamaguchi, T. Takaya, and Y. Okuda, Japan Kokai 73 91 045; *Chem. Abstr.*, **80,** 145893e (1974); (d) J. M. Barton and D. C. Pepper, *J. Chem. Soc.*, 1573 (1964).

(4) G. Wunch, D. Lutenback, and V. Kiener, German Offen. 2 064 099, July 20, 1972; *Chem. Abstr.*, **77,** 126313n (1972).

(5) B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kurz, and H. I. Thayer, *J. Org. Chem.*, **19,** 17 (1954).

(6) Yu. S. Tsybin, A. V. Kessenikh, and R. N. Volkov, *Zh. Org. Khim.*, **5,** 806 (1969); *Chem. Abstr.*, **71,** 38146f (1969).

(7) R. N. Volkov, Yu. S. Tsybin, and V. A. Yanchuk, *Zh. Org. Khim.*, **7,** 1040 (1971); *Chem. Abstr.*, **75,** 63459a (1971).

(8) R. N. Volkov and Yu. S. Tsybin, *Zh. Org. Khim.*, **6,** 480 (1970); *Chem. Abstr.*, 72, 132440q (1970).

(9) R. Kunin, E. Meitzner, and N. Bortnick, *J. Am. Chem., Soc.*, **84,** 305 (1962).

(10) A gift from the Rohm and Haas Co.

(11) Wilkens Instrument Research, Inc., Aerograph. Column: 1/4 in. × 10 ft packed with 10% UC W-98 coated on 80–100 mesh, acid-washed Chromosorb W. Thermal conductivity detection. A typical column temperature for 1 was 200 °C.

(12) K. Tatsuoka and T. Shimizu, Japan Kokai 73 85 563; *Chem. Abstr.*, **80,** 82491z (1974).

(13) A gift from the Ethyl Corp., ethylaluminum dichloride lot no. 2071.

(14) R. Wolovsky and N. Maoz, *J. Org. Chem.*, **38,** 4040 (1973).

(15) W. P. Duncan, E. J. Eisenbraun, A. R. Taylor, and G. W. Keen, *Org. Prep. Proced. Int.*, **7,** 225 (1975).

(16) V. Bertoli and P. H. Plesch, *J. Chem. Soc.*, 1500 (1968).

(17) (a) H. Gilman and J. Bailie, *J. Am. Chem. Soc.*, **65,** 267 (1943); (b) R. L. Augustine, "Reduction", Marcel Dekker, New York, N.Y., 1968.

Preparation and Properties of RMgH and RMg_2H_3 Compounds

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A series of alkyl- and arylmagnesium hydrides, RMgH (where R = Me, Et, *i*-Pr, Cp, and Ph), has been prepared by the reaction of R_2Mg compounds with an active form of magnesium hydride slurry in THF. These products could also be prepared by the reaction of RLi compounds with hydridomagnesium halide (HMgX, where X = Cl and Br), as demonstrated by the preparation of methylmagnesium hydride by the reaction of CH_3Li with HMgCl in THF. Preparation of compounds of the type RMg_2H_3 (where R = Me and Ph) has also been carried out. Contrary to earlier reports, the RMgH compounds have been found to be soluble and quite stable in THF at room temperature. A band in the region 1250–1300 cm^{-1} in the infrared spectrum of these compounds has been assigned to Mg–H stretching. This band is shifted to 940 cm^{-1} in the deuterio analogues, RMgD. Molecular weight studies of methyl- and ethylmagnesium hydride show these compounds to be dimeric in dilute solution.

The existence of compounds of the type RMgH has been the subject of interest and speculation for many years, as these compounds are analogues of Grignard reagents. Rice and coworkers[1] in 1956 reported the formation of PhMgH by the reaction of PhMgBr with $LiAlH_4$ in 4:1 ratio in ether. Later we showed[2] that the products of this reaction were not the same as reported by Rice. In a communication in 1962, Bauer[3] reported the preparation of C_2H_5MgH by the reaction of silane with $(C_2H_5)_2Mg$ in ether (eq 1).

$$Mg(C_2H_5)_2 + SiH_4 \rightarrow HMgC_2H_5 + H_3SiC_2H_5 \qquad (1)$$

However, he provided no characterization of the product. Sometime later, Coates and Heslop[4] reported evidence for the formation of C_2H_5MgH as an intermediate in the reaction of $(C_2H_5)_2Mg$ and $NaB(C_2H_5)_3H$ (eq 2); however, they reported that the compound was stable only at −78 °C and dissociated at −20 °C to give MgH_2 and $(C_2H_5)_2Mg$ (eq 3).

$$NaEt_3BH + Et_2Mg \rightarrow EtMgH + NaEt_4B \qquad (2)$$

$$2EtMgH \rightarrow Et_2Mg + MgH_2 \qquad (3)$$

Our earlier attempts[5] to prepare C_2H_5MgH by the reaction of $LiAlH_4$ with $(C_2H_5)_2Mg$ in ether in 1:4 ratio and by the reaction of MgH_2 with $(C_2H_5)_2Mg$ in ether were not successful in that MgH_2 was recovered in both cases. In this communication, we wish to report for the first time the successful preparation of pure RMgH compounds.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[6] Filtration and other manipulations were carried out in a glove box equipped with a recirculating system.[7]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solutions were studied in matched 0.10-mm pathlength NaCl or KBr cells. X-ray powder data were obtained on a Phillips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered CuK_α radiation. Samples were sealed in 0.5-mm capillaries and exposed to x-rays for 6 h. The "d" spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer equipped with a standard variable temperature unit. Ebullioscopic molecular-association studies were carried out in THF under vacuum (240 mmHg abs) using the technique developed earlier.[8]

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[6] Methane and ethane in the presence of hydrogen were determined using a previously described tensimeter. Magnesium was analyzed by EDTA titration at pH 10. Phenyl groups present in the complexes were determined as benzene by hydrolysis of the samples with water and analyzing the filtrate by GLC using a SE 30 column at 70 °C. Mesitylene was used as the solvent and hexanol was used as the internal standard.

Materials. Solvents were distilled immediately prior to use over $LiAlH_4$ (ether) or $NaAlH_4$ (THF, benzene, and mesitylene).

Diphenylmagnesium (Ph_2Mg) was prepared by heating a mixture of triply sublimed magnesium (Dow Chemical Co.) and diphenylmercury at 155 °C for 40 h. The crude reaction mixture was extracted with freshly distilled ether or THF and the resulting solution standardized by magnesium analysis. Dimethyl- and diethylmagnesium were prepared by stirring a mixture of dimethyl- or diethylmercury with magnesium metal in 1:2 ratio at room temperature for 24 h followed by extraction of the crude reaction mixture with ether or THF. Diisopropylmagnesium was prepared by the dioxane precipitation method using isopropylmagnesium chloride. Dicyclopentadienylmagnesium was prepared by the reaction of excess cyclopentadiene with $(CH_3)_2Mg$ in diethyl ether.

Lithium aluminum hydride was obtained from Ventron, Metal Hydrides Division. A solution was prepared by refluxing $LiAlH_4$ in ether or THF overnight followed by filtration through a glass-fritted funnel (medium) using predried Celite analytical filter air (Johns-Mansville). The clear solution was standardized by aluminum analysis.

Reaction of $LiAlH_4$ with $(CH_3)_2Mg$ in THF in 1:4 Ratio. When $LiAlH_4$ (4.0 mmol) in THF was added dropwise at room temperature to a well-stirred solution of $(CH_3)_2Mg$ (16.0 mmol) in THF a clear solution resulted. This reaction mixture was stirred for 15 min. The infrared spectrum of the clear solution showed no band due to Al–H stretching in the region 1600–1800 cm^{-1}: IR (THF) 2780 (m), 1410 (m), 1250–1270 (m br), 1140 (m), 695 (vs), 550 (s), 410 (w); NMR: singlet at −1.74 ppm and sextet at −1.32 ppm, ratio singlet:sextet 1:1.

Reaction of $LiAlH_4$ with Ph_2Mg in THF in 1:4 Ratio. Lithium aluminum hydride (3.5 mmol) in THF was allowed to react with a well-stirred THF solution of Ph_2Mg (14.0 mmol) at room temperature. The reaction was exothermic and no precipitate resulted at any stage. The reaction mixture was stirred for 30 min, and the clear colorless solution was analyzed. Anal. Calcd for $4PhMgH + LiAlPh_4$ (Li:Mg:Al:H:Ph): 1.00:4.00:1.00:4.00:8.00. Found: 1.03:4.05:0.98:3.97:8.07. IR: no Al–H stretching in the region 1600–1800 cm^{-1} and bands at 460, 425, and 400 cm^{-1} due to Mg–C, and Al–C stretching modes; NMR: three multiplets were observed by NMR, the internal chemical separation between the upper and the two lower multiplets δ int = 0.60 and 0.69 ppm.

In an attempt to isolate PhMgH from the mixture containing $4PhMgH + LiAlPh_4$ in THF, benzene was added slowly until precipitation began. The mixture was kept overnight and the insoluble solid filtered and dried under vacuum. Anal. Calcd for PhMgH (Li:Mg:Al:H:Ph): 0.00:1.00:0.00:1.00:1.00. Found: 0.07:1.00:0.05:1.03:1.11. X-ray powder pattern PhMgH·THF 8.05 (s), 6.60 (m), 5.40 (w), 4.80 (m), 4.60 (m), 4.21 (vs), 3 85 (w), 3.60 (w), 3.40 (w), 3.30 (w), 3.05 (v), 2.80 (w), 2.40 (w); x-ray of $Ph_2Mg·2THF$ same as above.

Preparation of MgH_2 Slurry in THF. When $LiAlH_4$ in diethyl ether was added dropwise to an equimolar amount of a well-stirred solution of diethyl- or diphenylmagnesium in diethyl ether at room temperature, an exothermic reaction took place and an insoluble white solid appeared immediately. The reaction mixture was stirred for 30 min, and the insoluble solid was separated from the supernatant solution by centrifugation and by removing the supernatant solution using a syringe. This solid was washed with diethyl ether several times and finally made into a slurry in THF. Anal. Calcd for MgH_2 (Mg:H): 1.00:2.00. Found: 1.00:1.98.

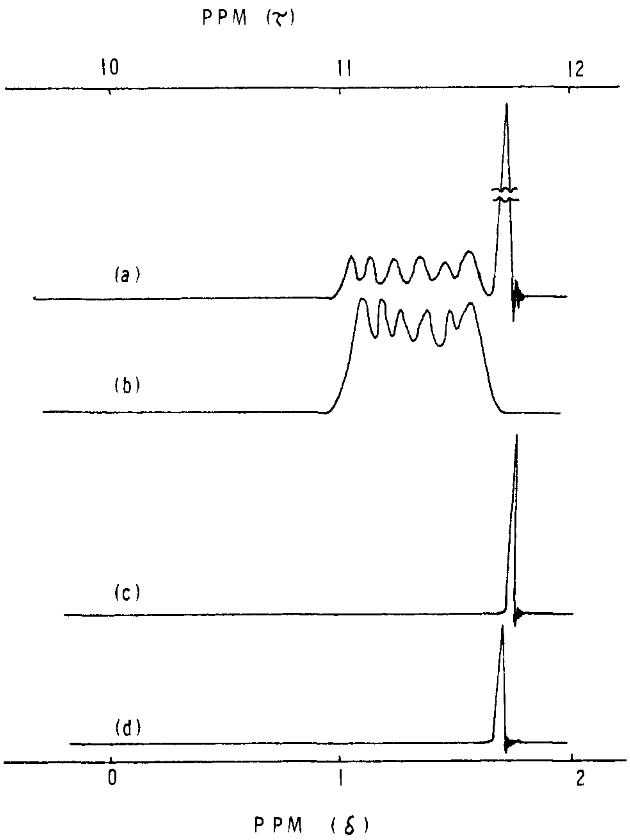

Figure 1. 60-MHz NMR of:

$$\text{(a) } 4(CH_3)_2Mg + LiAlH_4 \xrightarrow{THF} 4CH_3MgH + LiAl(CH_3)_4 \text{ (1.05 M in } CH_3MgH\text{)},$$

(b) $LiAl(CH_3)_4$ in THF (0.95 M),

(c) $(CH_3)_2Mg$ in THF (0.65 M),

$$\text{(d) } (CH_3)_2Mg + MgH_2 \xrightarrow{THF} 2CH_3MgH \text{ (0.70 M in } CH_3MgH\text{)}.$$

Preparation of CH_3MgH. To a well-stirred slurry of MgH_2 (4.40 mmol) in THF was added dropwise a THF solution of $(CH_3)_2Mg$ (4.40 mmol) at room temperature. The reaction mixture was stirred for 30 min during which time all the magnesium hydride dissolved. The resulting clear solution was analyzed, and infrared and NMR spectra were recorded. Anal. Calcd for CH_3MgH ($Mg:H:CH_4$): 1.00:1.00:1.00. Found: 1.00:0.97:1.04.

A THF solution of CH_3MgH was kept overnight at room temperature and analyzed the next day. It contained Mg and H in the ratio 1.00:1.93. When the solvent was removed under vacuum, an amorphous solid formed which did not give an x-ray powder pattern.

Preparation of $CH_3Mg_2H_3$. A THF solution of $(CH_3)_2Mg$ (3.15 mmol) was added dropwise to a well-stirred slurry of magnesium hydride (9.40 mmol) in THF at room temperature. The reaction mixture was stirred at room temperature for 1 h and gave a small amount of a white precipitate. The insoluble solid was filtered and both solid and filtrate were analyzed.

Insoluble solid Anal. Calcd for MgH_2 (Mg:H): 1.00:2.00. Found: 1.00:1.94. The solid contained about 10% of the starting magnesium as magnesium hydride.

Filtrate Anal. Calcd for $CH_3Mg_2H_3$ ($Mg:H:CH_4$): 2.00:3.00:1.00. Found: 2.00:2.96:1.11. When the THF was removed under reduced pressure, it resulted in a white solid. The x-ray powder pattern showed diffuse lines at 3.20 (m), 2.51 (m), 2.26 (m), and 1.68 (m) which corresponds to MgH_2.

Table I. Infrared Data (in THF) of RMgH and RMg_2H_3 Compounds[a]

MeMgH	MeMgD	EtMgH	*i*-PrMgH	CpMgH	PhMgH
2800 (s)	2795 (m)	2760 (m)	2780 (m)	1500 (sh)	1480 (w)
1430 (w)	1425 (w)	1408 (m)	1380 (m)	1450 (s)	1412 (m)
1375 (m)	1350 (w)	1300 (m)	1345 (m)	1005 (s)	1300 (m)
1280–1300 (m br)	1162 (w)	1260 (m br)	1290 (m br)	955–960 (s br)	1250–70 (s br)
1170 (m)	940 (s)	1120 (m br)	1250 (m br)	750 (vs)	1225 (s)
1025 (s)	825 (sh)	970 (m)	1110 (m)	720 (sh)	1120 (m br)
855 (s)	750 (s)	760 (s br)	980 (s)	652 (s)	1000 (s)
650–720 (s br)	500–550 (s br)	700 (s br)	800 (sh)	550 (m br)	820 (sh)
525 (s)	420 (s)	620 (s)	770 (s)		805 (vs)
		505 (vs)	680–700 (s br)		680 (s)
		405 (s)	605 (s)		630 (sh)
			565 (m)		470 (s)
			490 (m)		375 (s)
			420 (m)		

PhMgD	$MeMg_2H_3$	$MeMg_2D_3$	$PhMg_2H_3$	$PhMg_2D_3$	Ph_3Mg_2H
1482 (w)	1480 (m)	1480 (w)	1480 (w)	1480 (w)	1410 (s)
1410 (m)	1410 (s)	1412 (s)	1410 (w)	1408 (w)	1270–1290 (m br)
1300 (w)	1380 (vs)	1380 (s)	1375 (w)	1375 (w)	1220 (m)
1225 (m)	1300 (vs)	1107 (w)	1260–1300 (s br)	1120 (m)	1010 (m)
1120 (m)	1105 (w)	970 (m)	1120 (m)	990 (m)	850 (m)
997 (m)	965 (s)	940 (s)	990 (m)	940 (vs)	700 (vs)
935 (s)	800 (sh)	800 (sh)	800 (sh)	800 (sh)	675 (sh)
820 (sh)	600–720 (vs br)	600–700 (vs br)	730 (s)	730 (s)	635 (sh)
705 (vs)	520 (s)	520 (s)	700 (vs)	700 (vs)	620 (sh)
600–680 (s br)		420 (m br)	670 (s)	670 (s)	465 (m)
470 (s)			620 (vs br)	620 (m)	428 (s)
380 (m br)			460 (vs)	460 (vs)	370 (s)
				420 (m br)	

[a] Registry no.: MeMgH, 63533-51-7; MeMgD, 63533-525 52-8; EtMgH, 63533-53-9; *i*-PrMgH, 63533-54-0; CpMgH, 63533-55-1; PhMgH, 62086-01-5; PhMgD, 63533-56-2; $MeMg_2H_3$, 63588-48-7; $MeMg_2D_3$, 63588-47-6; $PhMg_2H_3$, 62139-40-6; $PhMg_2D_3$, 63588-49-8; Ph_3MgH, 63588-52-3.

Table II. IR and NMR Data for RMgH Compounds

RMgH, where R =	Me	Et	*i*-Pr	Cp	Ph
IR (ν Mg–C) (cm^{-1}) (in THF)	520 (s)	502 (s)	492 (m) 422 (m)	662 (s)	430 (m) 370 (m)
NMR (ppm) (with respect to THF)	3.50	0.58 (t) 2.53 (8)	0.54 (m)	4.07	5.19 (m) 5.89 (m)

Preparation of C_2H_5MgH. When $(C_2H_5)_2Mg$ (5.35 mmol) in 10 mL of THF was added dropwise to a THF slurry of MgH_2 (5.30 mmol) and the reaction mixture stirred magnetically at room temperature, a clear solution resulted within 1 h. An elemental analysis of this solution revealed that it contained Mg, H, and C_2H_6 on hydrolysis in molar ratios 1.00:0.98:1.04. Anal. Calcd for C_2H_5MgH: 1.00:1.00:1.00. The THF solution of C_2H_5MgH was stable at room temperature for at least 1 day as shown by the quantitative evolution of hydrogen produced on hydrolysis. When the solvent was removed under vacuum, a highly viscous liquid resulted.

Preparation of *i*-C_3H_7MgH in THF. To a magnetically stirred slurry of MgH_2 (5.0 mmol) in THF was added dropwise a THF solution of $(i\text{-}C_3H_7)_2Mg$. The reaction mixture was stirred at room temperature for 1 h, forming a clear solution. Elemental analysis of this solution showed that it contained Mg and H in the molar ratio 1.00: 0.96. This solution was stable at room temperature for at least 1 day as determined by gas-evolution analysis. A highly viscous liquid resulted when the THF was removed under vacuum.

Attempted Preparation of *i*-$C_3H_7Mg_2H_3$. Diisopropylmagnesium (4.0 mmol) in THF was added to a 12.0 mmol of a MgH_2 slurry in THF. The mixture was stirred at room temperature overnight and filtered. The filtrate showed a Mg:H ratio of 1.00:1.07. The solid exhibited a Mg:H ratio of 1.00:1.92. The solid contained about 7.8 mmol of unreacted MgH_2.

Preparation of CpMgH in THF. Dicyclopentadienylmagnesium (6.0 mmol) in THF was added to 6.0 mmol of a slurry of MgH_2 in THF, and the mixture was stirred at room temperature for 1 h, resulting in a clear solution. Anal. Calcd for CpMgH (Mg:Cp): 1.00:1.00. Found: 1.00:0.99. The solution was very air sensitive and turned yellowish brown when kept for some time at room temperature. A crystalline solid CpMgH·1.0THF resulted when the solvent was removed under reduced pressure. The x-ray powder diffraction pattern of the solid showed lines at 9.80 (w), 8.65 (w), 6.50 (w), 4.85 (vs), 4.25 (w), and 3.60 (m). X-ray lines due to $Cp_2Mg{\cdot}2THF$ 7.50 (m), 7.05 (s), 6.21 (m), 5.83 (m), 5.00 (m), 4.65 (s), 4.40 (m), 4.20 (w), 3.82 (w), 3.70 (m), 3.25 (m), 3.15, 2.85 (vw), 2.47 (vw).

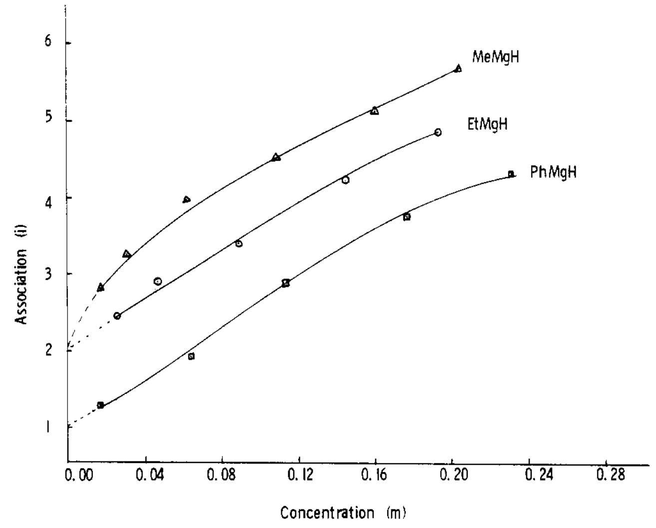

Figure 2. Molecular association of RMgH compounds in THF at reflux temperature (at 260 mmHg).

Preparation of PhMgH in THF.[9] To 8.45 mmol of a MgH_2 slurry in THF was added dropwise 8.5 mmol of Ph_2Mg in THF. A clear so-

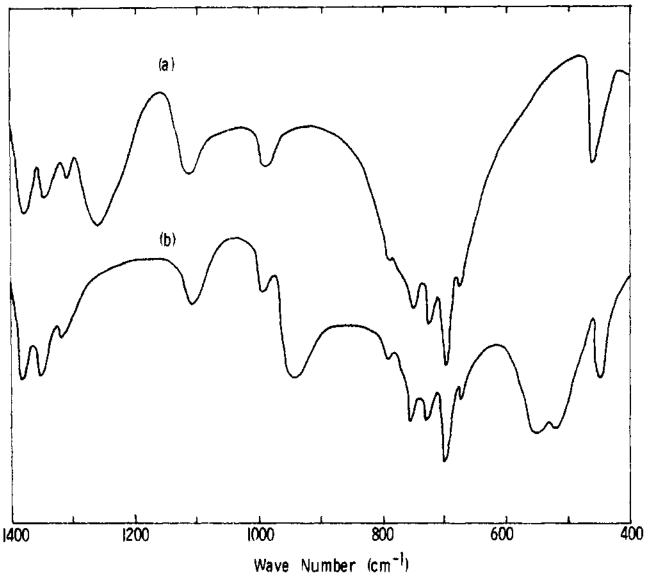

Figure 3. Infrared bands due to Mg–H: (a) $PhMg_2H_3$, and (b) $PhMg_2D_3$.

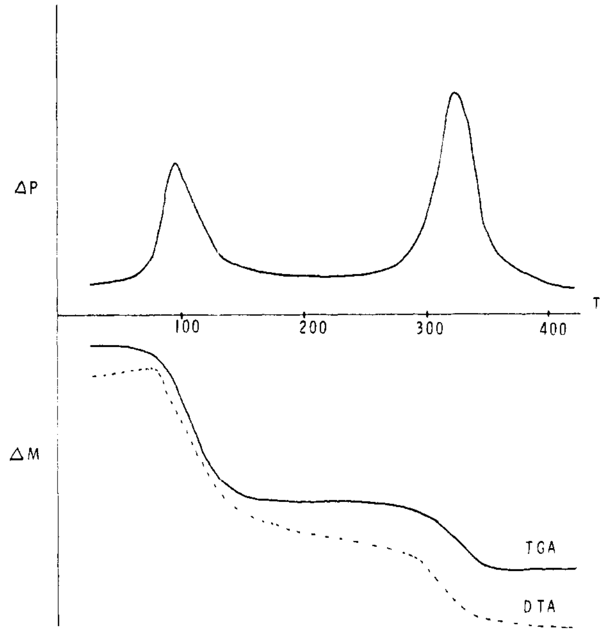

Figure 4. Vacuum DTA–TGA of MeMgH·THF.

lution resulted within a few minutes after stirring at room temperature. Anal. Calcd for PhMgH (Mg:H:Ph): 1.00:1.00:1.00. Found: 1.00:0.97:1.05. This solution was stable for over a 1-month period at 0 °C as determined by gas-evolution analysis. When the solvent was removed under reduced pressure, an amorphous white solid resulted which did not give any x-ray powder pattern. However, when benzene was added to a THF solution an insoluble solid formed which was filtered and analyzed. Anal. Calcd for PhMgH·1THF (Mg:H:Ph:THF): 1.00:1.00:1.00:1.00. Found: 1.00:0.98:1.03:1.05. X-ray powder diffraction pattern 8.05 (s), 6.60 (m), 5.40 (w), 4.80 (m), 4.60 (w), 4.21 (vs), 3.85 (w), 3.60 (w), 3.40 (w), 3.30 (w), 3.05 (vw), 2.80 (vw), 2.43 (vw), 2.40 (w); x-ray pattern of Ph_2Mg·2THF 8.06 (s), 6.61 (m), 5.40 (w), 4.80 (m), 4.60 (w), 4.21 (vs), 3.88 (w), 3.61 (w), 3.40 (w), 3.31 (w), 3.05 (vw), 2.80 (vw), 2.43 (vw), 2.40.

Preparation of $PhMg_2H_3$ in THF.[9] When Ph_2Mg (3.50 mmol) in THF was added dropwise to a stirred slurry of MgH_2 (10.5 mmol) in THF, a clear solution resulted within 30 min. Anal. Calcd for $PhMg_2H_3$ (Mg:H:Ph): 1.00:3.00:1.00. Found: 1.00:2.94:1.07. This solution was dried under vacuum to give a white solid. The solid was placed in diethyl ether, stirred for 1 h, and filtered. The filtrate did not contain magnesium, and analysis of the insoluble solid showed that it contained Mg, H, and benzene on hydrolysis in the ratio 1.00:2.97:1.02. The solid redissolved in THF; however, the THF was cleaved slowly at room temperature and when refluxed in THF an insoluble white solid resulted which on hydrolysis contained Mg, benzene, and n-BuOH in ratios 1.00:1.03:3.02.

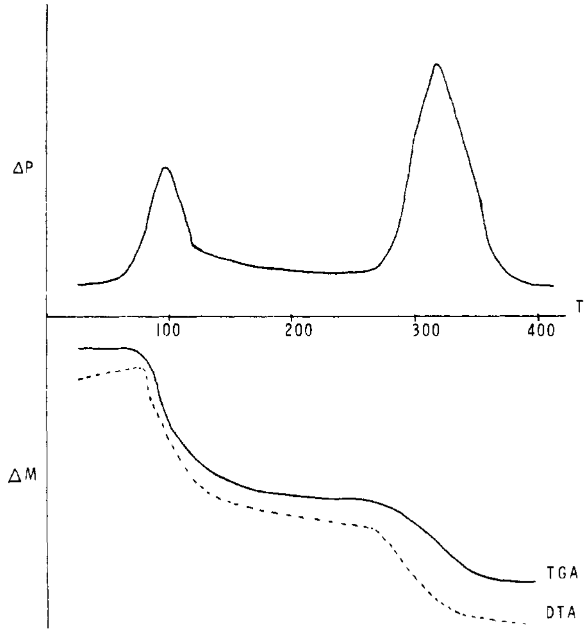

Figure 5. Vacuum DTA–TGA of $MeMg_2H_3$·THF.

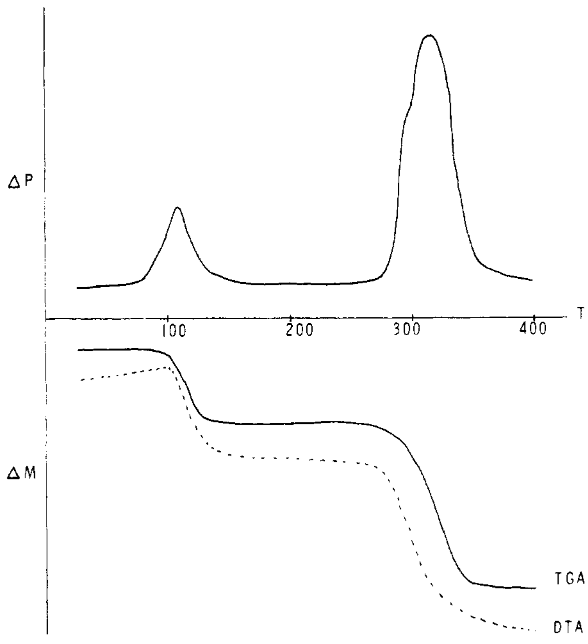

Figure 6. Vacuum DTA–TGA of $PhMg_2H_3$·Et_2O.

Dissociation of PhMgH·1THF in Diethyl Ether. To 4.0 mmol of PhMgH·THF was added 5 mL of diethyl ether, and the resulting mixture was stirred for 1 h at room temperature and filtered. The filtrate on hydrolysis showed that it contained Mg and benzene in the ratio 1.00:1.97. The insoluble solid on hydrolysis exhibited Mg, H, and benzene in the ratio of 1.00:1.47:0.52. Anal. Calcd for $PhMg_2H_3$: 1.00:1.50:0.50. The solid contained about 65% of the total magnesium.

Attempted Preparation of Ph_3Mg_2H in THF. When 10.5 mmol of Ph_2Mg in THF was added dropwise to a stirred slurry of MgH_2 (3.5 mmol) in THF, a clear solution resulted within minutes. When this solution was concentrated by removing THF under vacuum, and kept overnight at room temperature, a white solid crystallized. These crystals were separated, washed with THF, and dried under vacuum. Anal. Calcd for Ph_2Mg (Mg:Ph): 1.00:2.00. Found: 1.00:2.03. The x-ray powder diffraction pattern showed that this solid contained lines due to Ph_2Mg·2THF.

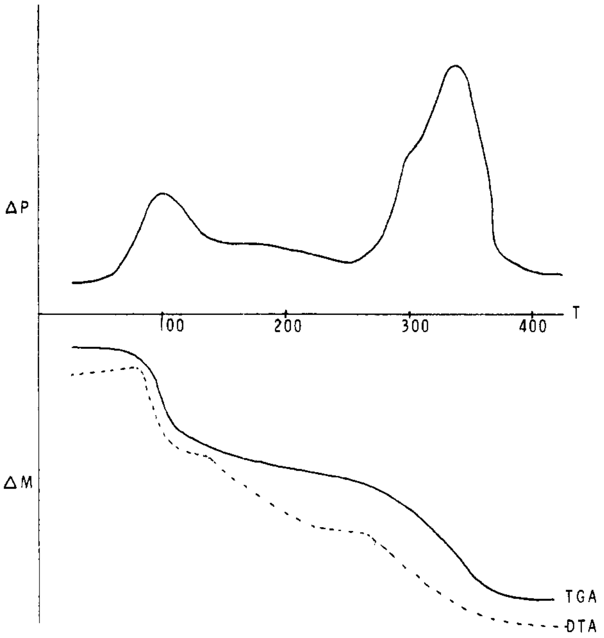

Figure 7. Vacuum DTA-TGA of $PhMg_2H_3{\cdot}THF$.

Results and Discussion

The first evidence obtained concerning the existence of an RMgH compound came from the reaction of $LiAlH_4$ with $(CH_3)_2Mg$ in 1:4 ratio in THF. When $LiAlH_4$ in THF was allowed to react slowly with a THF solution of $(CH_3)_2Mg$ in a 1:4 ratio, no precipitate resulted at any stage and the reaction mixture remained clear. However, if $LiAlH_4$ was added rapidly to the $(CH_3)_2Mg$ solution in THF, a precipitate did appear which redissolved when stirred for a few minutes. Since MgH_2 is very insoluble in THF, the reaction course observed in ether (eq 4) is undoubtedly not involved here.

$$4(CH_3)_2Mg + LiAlH_4 \xrightarrow{Et_2O} 2MgH_2 + 2(CH_3)_2Mg + LiAl(CH_3)_4 \quad (4)$$

An infrared spectrum of the reaction mixture in THF showed bands at 530 and 695 cm^{-1} characteristic of $MgCH_3$[10] and $LiAl(CH_3)_4$, respectively, and also established the absence of any Al-H stretching bands in the region 1600–1800 cm^{-1}. The infrared data favor the reaction pathway (eq 5) in THF.

$$4(CH_3)_2Mg + LiAlH_4 \xrightarrow{THF} 4CH_3MgH + LiAl(CH_3)_4 \quad (5)$$

A proton NMR spectrum of the reaction solution showed a sharp singlet at τ 11.74 (3.53 ppm upfield from the THF multiplet) and a sextet centered at τ 11.32 (Figure 1). The upfield singlet at τ 11.74 was almost at the position of $(CH_3)_2Mg$, and the sextet corresponded to that observed for $LiAl(CH_3)_4$ in THF.[11] The 1:1 ratio of the upfield singlet to the sextet suggested that the number of methyl groups attached to magnesium are the same as those attached to aluminum, which again supports the proposed reaction course (eq 5). Unfortunately, CH_3MgH could not be isolated from the above reaction mixture in a pure state.

Similarly, when lithium aluminum hydride in THF was added to a THF solution of Ph_2Mg in 1:4 molar ratio, a clear solution resulted. The infrared spectrum of the solution showed the absence of any Al-H stretching band in the region 1600–1800 cm^{-1}; instead, a band due to Mg-Ph stretching at 420 cm^{-1} was observed, suggesting the presence of Mg-Ph bands. When the solvent from this reaction mixture was removed under vacuum, the resulting solid showed x-ray powder diffraction lines due to $LiAlPh_4$.[12] These results support the following reaction route:

$$4Ph_2Mg + LiAlH_4 \xrightarrow{THF} 4PhMgH + LiAlPh_4 \quad (6)$$

When benzene was added to the THF solution of this reaction mixture, an insoluble white solid precipitated which corresponded to PhMgH on analysis. However, the x-ray powder diffraction pattern of this solid corresponded to $Ph_2Mg{\cdot}2THF$, indicating disproportionation of the PhMgH to MgH_2 and Ph_2Mg when the solvent is removed.

Table III. Thermal Decomposition of RMgH and RMg_2H_3 Compounds

Compd (wt of sample)	Thermicity	Decomposition range (peak)	% wt loss
$MeMgH{\cdot}0.85THF$ (57.16)	endo	70–110 (85)	56.11
	endo	296–340 (320)	16.35
$PhMgH{\cdot}1.06THF$ (78.54)	endo	75–120 (90)	40.07
	endo	290–369 (348)	44.27
$MeMg_2H_3{\cdot}0.38THF$ (65.85)	endo	70–118 (90)	23.79
	endo	295–340 (318)	12.17
$PhMg_2H_3{\cdot}0.89THF$ (71.72)	endo	75–116 (96)	30.11
	endo	150–280	12.21
	endo	290–365 (336)	32.32
$PhMg_2H_3{\cdot}0.37Et_2O$ (64.35)	endo	90–130 (110)	22.43
	endo	290–339 (315)	50.17

Interestingly, alkyl- or arylmagnesium hydrides, RMgH (where R = Me, Et, *i*-Pr, Cp, and Ph), have been prepared in a pure state simply by the reaction of a dialkyl- or diarylmagnesium compound with an active form of MgH_2 in THF at room temperature (eq 7).

$$MgH_2 + R_2Mg \xrightarrow{THF} 2RMgH \quad (7)$$

The MgH_2 reacts exothermically with the R_2Mg compound producing a clear solution within minutes. The R:Mg:H ratio of the reaction product is 1:1:1 within experimental error. Solutons of the alkyl- or arylmagnesium hydrides are quite stable at room temperature with no apparent THF cleavage. The active form of magnesium hydride was prepared by the reaction of $LiAlH_4$ with $(C_2H_5)_2Mg$ in 1:1 ratio in ether (eq 8).

$$(C_2H_5)_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2Et_2 \quad (8)$$

The infrared spectra of RMgH compounds in THF solution showed bands due to Mg-R groups (Table I) and broad bands in the region 1250–1300 cm^{-1} due to Mg-H stretching. The band in the region 1250–1300 cm^{-1} is assigned to the bridging Mg-H stretching[13] on the basis of the fact that it shifts to 940 cm^{-1} in the deuterio analogues, RMgD. Coates[14] has shown by infrared studies of RBeH compounds that the strong band at 1330 cm^{-1} is the bridging beryllium-hydrogen stretching (BeH_2Be) vibration, since the band shifted to 970 cm^{-1} in the RBeD compound. We have prepared RMgD compounds in THF by the reaction of R_2Mg with MgD_2. By analogy to the RBeH compound, it is suggested that the broad band present in the region 1250–1300 $\mathrm{cm^{-1}}$ in RMgH is due to bridging magnesium–hydrogen ($\mathrm{MgH_2Mg}$) stretching.

The NMR spectra of RMgH compounds in THF showed signals due to alkyl groups attached to magnesium (Table II). Unfortunately, the Mg–H signal was not observed, probably due to its masking by the THF solvent. Molecular-association studies in THF showed $\mathrm{CH_3MgH}$ and $\mathrm{C_2H_5MgH}$ to be dimeric at low concentration and increasing in association with an increase in concentration. However, molecular weight data of PhMgH showed it to be monomeric in infinitely dilute solution (Figure 2).

When $\mathrm{(CH_3)_2Mg}$ in THF was added to an active $\mathrm{MgH_2}$ slurry in THF in a 1:3 ratio, about 90% of the initial $\mathrm{MgH_2}$ dissolved. The infrared spectrum of the solution showed a band at 1290 $\mathrm{cm^{-1}}$ which shifted to 940 $\mathrm{cm^{-1}}$ in the deuterio analogue $\mathrm{CH_3Mg_2D_3}$, suggesting that the absorption band is due to the bridging magnesium–hydrogen ($\mathrm{MgH_2Mg}$) band.

$$\mathrm{Me_2Mg + 3MgH_2 \xrightarrow{THF} 2MeMg_2H_3} \tag{9}$$

When the solvent was removed under vacuum, the resulting solid exhibited x-ray lines due to $\mathrm{MgH_2}$, indicating the disproportion of $\mathrm{CH_3Mg_2H_3}$ into $\mathrm{CH_3MgH}$ and $\mathrm{MgH_2}$ (eq 10).

$$\mathrm{CH_3Mg_2H_3 \rightarrow CH_3MgH + MgH_2} \tag{10}$$

When diphenylmagnesium in THF was added to 3 mol equiv of magnesium hydride a clear solution resulted. The elemental analysis of this solution corresponded well to $\mathrm{PhMg_2H_3}$. The infrared spectrum (Figure 3) gave a strong band at 1290 $\mathrm{cm^{-1}}$ which shifted to 935 $\mathrm{cm^{-1}}$ in the deuterio analogue $\mathrm{PhMg_2D_3}$, suggesting that the absorption band is due to the bridging magnesium–hydrogen ($\mathrm{MgH_2Mg}$) bond. The molecular weight of $\mathrm{PhMg_2H_3}$ could not be determined because it cleaved THF under refluxing conditions producing a THF-insoluble product of emperical formula $\mathrm{PhMg_2(OBu^n)_3}$.

The results of vacuum DTA–TGA studies on $\mathrm{CH_3MgH}$, $\mathrm{CH_3Mg_2H_3}$, PhMgH, and $\mathrm{PhMg_2H_3}$ are given in Table III and Figures 4–7. The product RMgH decomposes at 300 °C with gas evolution. The steps involved in the decomposition of RMgH are shown below.

$$1.\ \mathrm{RMgH{\cdot}THF \rightarrow RMgH + THF} \tag{11}$$

$$2.\ \mathrm{RMgH \rightarrow Mg + RH} \tag{12}$$

The $\mathrm{RMg_2H_3}$ compounds decompose over a wide temperature range centered at 300 °C.

$$\mathrm{RMg_2H_3 \rightarrow Mg + RH + H_2} \tag{13}$$

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Registry No.—$\mathrm{(CH_3)_2Mg}$, 2999-74-8; $\mathrm{Ph_2Mg}$, 555-54-4; $\mathrm{MgH_2}$, 7693-27-8; $\mathrm{(C_2H_5)_2Mg}$, 557-18-6; $(i\text{-}\mathrm{C_3H_7})_2\mathrm{Mg}$, 3536-97-8; Dicyclopentadienylmagnesium, 1284-72-6.

References and Notes

(1) H. J. Rice and P. J. Andrellos, Technical Report to the Office of Naval Research, Contract ONR-494(04), 1956.
(2) E. C. Ashby and R. D. Schwartz, *Inorg. Chem.*, **11**, 919 (1972).
(3) R. Bauer, *Z. Naturforschg, B*, **17**, 2.1 (1962).
(4) G. E. Coates and J. A. Heslop, *J. Chem. Soc. A*, 514 (1968).
(5) E. C. Ashby and R. G. Beach, *Inorg Chem.*, **9**, 2300 (1970).
(6) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(7) E. C. Ashby and R. D. Schwartz, *J. Chem. Ed.*, **51**, 65 (1974).
(8) F. W. Walker and E. C. Ashby, *J. Chem. Ed.*, **45**, 654 (1968).
(9) E. C. Ashby and A. B. Goel, *Inorg. Chem.* (in press).
(10) R. M. Salinger and H. S. Mosher, *J. Am. Chem. Soc.*, **86**, 1782 (1964).
(11) J. F. Ross and J. P. Oliver, *J. Organomet. Chem.*, **22**, 503 (1970).
(12) E. C. Ashby and A. B. Goel, unpublished results.
(13) E. C. Ashby and A. B. Goel, *J. Am. Chem. Soc.*, **99**, 310 (1977).
(14) N. A. Bell and G. E. Coates, *J. Chem. Soc.*, 692 (1965).

Oxidative Cyclodehydrogenation of Aromatic Bis(*o*-aminoanils)

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The two bis-Schiff bases, *N,N′*-terephthalidenebis(*o*-aminoaniline) (**1**) and *N,N′*-dibenzylidene-3,3′-diaminobenzidine (**8**), prepared from the respective aldehyde and amine reactants by low-temperature solution condensation, are converted by molecular oxygen in solution to the benzimidazoles **2** and **9**. The oxidative heteroaromatization, especially when catalyzed with ferric chloride, proceeds readily at temperatures as low as 20–60 °C. The unusually mild conditions required for the oxidative ring closure suggest this experimental approach to be well applicable to the polyconversion of analogous polymeric Schiff bases to the corresponding polybenzimidazoles.

A recent note from this laboratory[1] dealt with the copolymerization of aromatic bis(*o*-diamines) with aromatic dialdehydes and the subsequent cyclodehydrogenation of the resultant polyazomethines, to give polybenzimidazoles. Initial observations in that work led us to conclude that the final aromatization step proceeded in the presence of air, as well as in its absence, in the latter case presumably with elimination of molecular hydrogen. Because of the technological implications of this convenient two-step polycondensation process, it was of prime interest to elaborate more favorable experimental conditions by conducting a study of model reactions leading to well-defined nonpolymeric intermediates and products, in which the progress of the aromatization reaction could be monitored by conventional analytical techniques. It was a particular objective to search for experimental conditions that would favor the primary cyclodehydrogenation step and so would lead to highest possible conversion to benzimidazole structures without concurrently promoting degradation of the amine reactants through oxidative and/or thermal change, or outright elimination, of the sensitive amino groups.

In this communication we present the results of a study