mixture. Workup gave a 55% yield of azobenzene by VPC (based on **1**). *n*-Butylcyclooctatetraene was the only other observed product in the organic layer (by VPC and ^{1}H NMR). Streitwieser and Grant[1] report a 61% yield of azobenzene from nitrobenzene starting with isolated **3**. As Grant and Streitwieser[1] point out, this reaction is unique and is the first example of a synthetic application of uranocenes to organic chemistry. We hope our procedure stimulates the search for new uses of substituted uranocenes.

The procedure described here makes substituted uranocenes readily available from commercial reagents in minimum time. The formation of the substituted dianion in eq 1 also allows for the easy formation of other metal-substituted cyclooctatetraenides.

Experimental Section

General Procedure. All air- and moisture-sensitive compounds were handled with Schlenk techniques or in a Vacuum/Atmospheres Corp. recirculating glovebox under nitrogen. Solvents were distilled or vacuum transferred from $LiAlH_4$ or sodium/benzophenone.

1,1′-Di-*n*-butyluranocene (3). Commercial *n*-butyllithium (2.00 M, 8.9 mL, 17.8 mmol) was added over a period of 10 min to cyclooctatetraene (**1**, 1.00 mL, 8.9 mmol) in 20 mL of diethyl ether with stirring at ambient temperature. Reaction was allowed to continue for 1 h. Completeness of reaction was monitored by VPC of **1**. Excess *n*-butyllithium does not interfere with subsequent reactions. UCl_4 (1.75 g, 4.5 mmol) dissolved in 25 mL of tetrahydrofuran was added dropwise to the solution at 0 °C with stirring. After the solution was stirred for 1 h, solvents were removed on the vacuum line at ambient temperature, and the green solid was transferred to a specially designed Soxhlet extractor.[5] Extraction for 4 days with hexane yielded 1.23 g (2.2 mmol, 50% yield based on **1**) of *n*-butyluranocene, **3**. Identification was made by an identical match of its infrared, NMR, mass, and visible spectra with the literature.[6]

Nitrobenzene. *n*-Butyluranocene, **3**, was prepared in an identical procedure as described above from 1.00 g of cyclooctatetraene (**1**, 8.9 mmol). Nitrobenzene (454 μL, 4.4 mmol) was slowly added to this solution of *n*-butyluranocene and the the solution turned immediately from green to brown. After 5 min, dilute HCl was added to the brown mixture, solids were removed by filtration, and the organic layer was analyzed by VPC for azobenzene (218 mg, 1.2 mmol, 55% yield) with an external standard. Azobenzene was identified by a match of its ^{1}H NMR and VPC retention time with those of authentic material.

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Registry No. **1**, 629-20-9; **3**, 37274-12-7; UCl_4, 10026-10-5; *n*-BuLi, 109-72-8; nitrobenzene, 98-95-3; azobenzene, 103-33-3.

References and Notes

(1) C. B. Grant and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **100**, 2433 (1978).
(2) A. C. Cope and H. O. Van Orden, *J. Am. Chem. Soc.*, **74**, 175 (1952); A. C. Cope and M. R. Kinter, *ibid.*, **73**, 3424 (1951).
(3) (a) J. Gasteigen, G. E. Gream, R. Huisgen, W. E. Konz, and U. Schnegg, *Chem. Ber.*, **104**, 2412 (1971); (b) C. A. Harmon and A. Streitwieser, *J. Org. Chem.*, **38**, 549 (1973).
(4) J. Miller, M. A. Brault, and C. W. DeKock, submitted for publication in *J. Org. Chem.*
(5) C. W. DeKock, R. S. Ely, T. E. Hopkins, and M. A. Brault, *Inorg. Chem.*, **17**, 625 (1978).
(6) A. Streitwieser, Jr., and C. A. Harmon, *Inorg. Chem.*, **12**, 1102 (1973).

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Preparation and Characterization of Alkoxy(aroxy)magnesium Hydrides

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A series of alkoxy- and aroxymagnesium hydrides (HMgOR, where R = Me, *i*-Pr, *t*-Bu, *t*-$BuCH_2$, $PhCH_2CH_2$, c-C_6H_{11}, Ph, Ph_3C, $Ph_2(Me)C$, 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$, and 2,6-*t*-Bu_2-4-MeC_6H_2) has been synthesized by the redistribution of bis(alkoxy or aroxy)magnesium compounds with magnesium hydride in tetrahydrofuran. These compounds were also prepared by the reaction of magnesium hydride with the appropriate alcohol at −78 °C followed by warming the reaction mixture to room temperature. Some of the HMgOR compounds where R = $PhCH_2CH_2$, c-C_6H_{11}, Ph_3C, $Ph_2(Me)C$, 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$, and 2,6-*t*-Bu_2-4-MeC_6H_2 were found to be THF soluble. Interestingly, THF-soluble cyclohexoxymagnesium hydrides could be prepared easily by the reduction of cyclohexanones with magnesium hydride in THF. All hydrides were characterized by elemental analysis, infrared and NMR spectroscopies, ebullioscopic molecular weight studies, X-ray powder diffraction, and vacuum DTA–TGA. Assignments of Mg–H stretching and bending modes have been made by comparison with the corresponding deuterated compounds. The products have been shown to be excellent stereoselective reducing agents toward ketones.

Introduction

There has been considerable interest in the preparation of alkoxymetal hydrides (HMOR compounds)[1] and alkali metal alkoxymetal hydrides ($LiM(OR)_3H$, where M = B and Al).[2] Alkoxy derivatives of simple and complex metal hydrides are important as selective reducing agents in organic synthesis. Since selectivity is very much a function of the steric requirement of the reagent, alkoxy derivatives of the metal hydrides find their usefulness in that the steric requirement of the metal hydride can be varied by varying the steric requirement of the alkoxy group. In this respect, alkoxy groups can be varied in size considerably more than other substituent groups. Thus, it is well-known that lithium trimethoxyaluminohydride is a more selective reducing agent toward substituted cyclohexanones than $LiAlH_4$ itself.

Because of the interest in alkoxyaluminohydrides as selective reducing agents, we have prepared a series of sterically hindered alkoxy- and aroxymagnesium hydrides which might also function as selective reducing agents. In this connection, we have recently reported the preparation of a number of THF-soluble alkylmagnesium hydrides[3] and halogenomagnesium hydrides;[4] however, these compounds were found not to be very selective in their reduction of cyclohexanones. We have recently prepared some (dialkylamino)magnesium hydrides[5] and found that these compounds were not only soluble and stable in THF but also functioned very well as selective reducing agents toward a series cyclic ketones.[6] In view of these latter findings, we have decided to prepare a series of alkoxy- and aroxymagnesium hydrides in which the nature of the alkoxy group is varied from small (methoxy) to very large (2,6-di-*tert*-butyl-4-methylphenoxy). There is no prior art in this area except a report by Bauer[7] concerning the formation of HMgOEt which was obtained by EtMgH cleavage of Et_2O. Unfortunately, no evidence was provided

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Table I. Preparation of Alkoxymagnesium Hydrides by the Reaction of MgH_2 with $Mg(OR)_2$ in THF

	reactants						
expt no.	mmol of MgH_2	$Mg(OR)_2$ (mmol)	reacn time, h	solubility in THF	anal. (ratio) Mg:H:ROH	product	molecular assocn in THF
1	5.5	$Mg(OCH_3)_2$ (5.5)	40	insol solid	1.00:0.94:–	$HMgOCH_3$	
2	5.4	$Mg(O\text{-}i\text{-}Pr)_2$ (5.35)	34	insol solid	1.00:0.95:0.99	HMgO-*i*-Pr	
3	5.1	$Mg(O\text{-}t\text{-}Bu)_2$ (5.0)	30	insol, gelatinous ppt	1.00:0.95:1.05	HMgO-*t*-Bu	
4	4.2	$Mg(OCH_2CH_2Ph)_2$	30	less soluble, crystallized from THF	1.00:0.98:1.04	$HMgOCH_2CH_2Ph$	
5	3.95	$Mg(O\text{-}c\text{-}C_6H_{11})_2$ (3.9)	26	less soluble, crystallized from THF	1.00:0.97:1.02	$HMgO\text{-}c\text{-}C_6H_{11}$	
6	5.0	$Mg(OPh)_2$ (4.95)	48	sparingly soluble	1.00:0.96:1.03	HMgOPh	
7	4.5	$Mg(O\text{-}2,6\text{-}Me_2C_6H_4)_2$ (4.5)	2	highly soluble	1.00:0.98:1.03	$HMgO\text{-}2,6\text{-}Me_2C_6H_3$	dimer
8	4.0	$Mg(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_4)_2$ (4.0)	3	highly soluble, crystallized from THF	1.00:0.97:1.02	$HMgO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$	dimer
9	4.2	$Mg(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2$	2	highly soluble, crystallized from THF	1.00:0.98:1.03	$HMgO\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2$	dimer
10	3.8	$Mg(OCPh_2Me)_2$ (3.8)	2	fairly soluble, crystallized from THF	1.00:1.01:0.99	$HMg(OCPh_2Me)$	dimer
11	4.5	$Mg(OCPh_3)_2$ (4.45)	2	highly soluble, crystallized from THF	1.00:0.97:1.04	$HMg(OCPh_3)$	dimer
12	MgH_2			insol	1.00:2.02:–	highly associated	

to show that the isolated product was not a mixture of MgH_2 and $Mg(OEt)_2$. Some time ago during early attempts to prepare alkoxymagnesium hydrides,[5] we reported that these compounds dissociate to MgH_2 and $Mg(OR)_2$ since all attempts to prepare them resulted only in the isolation of physical mixtures of MgH_2 and $Mg(OR)_2$ as determined by X-ray powder diffraction studies. Now we report our successful results on the synthesis and characterization of alkoxy- and aroxymagnesium hydrides and explain why earlier results to prepare these compounds failed.

Experimental Section

Apparatus. All reactions were carried out in an atmosphere of nitrogen either in a nitrogen-filled glovebox equipped with a special recirculating system to remove oxygen (manganese oxide) and moisture (dry ice–acetone traps)[8] or on a bench top by using Schlenk-tube techniques.[9] Infrared spectra were obtained in a cell with KBr windows, and CsI plates were used in obtaining solid spectra as Nujol mulls. NMR spectra were recorded on a 60-MHz Varian A-60 spectrometer. X-powder diffraction 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 h. *d* spacings were evaluated by using a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually. An ebullioscopic molecular weight apparatus, previously described, was used for molecular weight determination at reduced pressure (240 mm).[10] DTA–TGA data were obtained under vacuum with a modified Mettler Thermoanalyzer II.[11]

Analyses. Gas analyses were performed by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[9] Magnesium was determined by EDTA titration at pH 10 with Eriochrome Black T as an indicator. Alkoxy groups were analyzed as alcohols by GLC.

Materials. Methanol (Fisher Scientific) was distilled after treatment with magnesium metal. 2-Propanol (Fisher Scientific) was distilled over $Al(O\text{-}i\text{-}Pr)_3$, and *tert*-butyl alcohol (Fisher) was fractionally crystallized under nitrogen. Neopentyl alcohol (Aldrich), 2-phenylethanol (Fisher), cyclohexanol (Fisher), phenol (Mallinckrodt), and 2,6-diisopropylphenol (Eastman) were distilled after drying over molecular sieves. Triphenylcarbinol (Eastman), diphenyl(methyl)carbinol (Eastman), 2,6-dimethylphenol (Eastman), and 2,6-di-*tert*-butylcresol (Eastman) were used without further purification. Diethyl ether was distilled immediately before use from $LiAlH_4$, and tetrahydrofuran was distilled from $NaAlH_4$. A solution of $LiAlH_4$ in diethyl ether (Ventron, Metal Hydrides Division) was prepared by stirring a slurry overnight followed by filtration. The solution was standardized by aluminum analysis. Dimethyl- and diethylmagnesium in diethyl ether were prepared by the reaction of magnesium metal with dimethyl- and diethylmercury[12] (neat) followed by dissolution in ether.

A slurry of magnesium hydride[13] in THF was prepared by the reaction of diethylmagnesium with $LiAlH_4$ in diethyl ether, followed by filtration and washing of the solid MgH_2 with ether and finally by addition of THF to form a slurry. Anal. Calcd for MgH_2: Mg:H = 1.00:2.00. Found: 1.00:2.01.

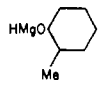
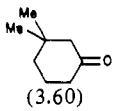
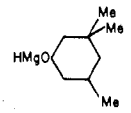
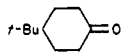
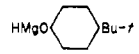
Dialkoxymagnesium or diphenoxymagnesium compounds were prepared by the reaction of 2 equiv of the appropriate alcohol or phenol with dimethylmagnesium in Et_2O/THF solvent and refluxing the reaction mixture for 5 h. Completion of the reaction was determined by checking for the absence of methane evolution on hydrolysis of the sample with HCl.

General Procedure for the Preparation of Alkoxy- and Aroxymagnesium Hydrides. (a) Reaction of MgH_2 with $Mg(OR)_2$ in THF in a 1:1 Molar Ratio. To a known amount of magnesium hydride slurried in THF was added an equivalent amount of a THF slurry or solution of magnesium alkoxide or aroxide, and the reaction mixture was stirred at room temperature for an appropriate period of time (Table I). The resulting insoluble solid or solution was analyzed (Table I), and the infrared spectrum (Table III) and NMR spectrum (Table III) of the products which were soluble in THF were recorded. The solvent was removed under reduced pressure and the resulting solid was characterized by elemental analysis (Table I) and powder diffraction data (Table V).

(b) Reaction of an Alcohol or Phenol with MgH_2 in THF. To a well-stirred slurry of MgH_2 in THF, at −78 °C, was added dropwise a THF solution of alcohol or phenol in an equimolar ratio. The reaction mixture was allowed to warm to room temperature and then stirred for an appropriate amount of time (see Table II). The resulting insoluble solid or clear solution was then analyzed (Table II).

Reaction of MgH_2 with Cyclic Ketones. When a slurry of MgH_2 in THF was allowed to react with a THF solution of ketone in an equimolar ratio and the reactants were stirred at room temperature for 1 h, a clear solution formed. Completion of the reaction was confirmed by the absence of the carbonyl group in the infrared spectrum. A small portion of this solution was analyzed for active

Table II. Preparation of HMgOR Compounds by the Reaction of Alcohols with MgH_2

	reactants					
expt no.	mmol of MgH_2	ROH (mmol)	reacn time, h	solubility and nature of the product after drying	anal. (ratio) Mg:H:ROH	probable product
1	5.62	CH_3OH (5.58)	20	insol white powdery solid	1.00:0.97:–	$HMgOCH_3$
2	4.75	*i*-PrOH (4.70)	18	gelatinous nature, forms amorphous solid	1.00:0.97:–	HMgO-*i*-Pr
3	5.00	*t*-$BuCH_2OH$ (5.00)	10	sparingly soluble, crystallized from THF	1.00:0.99:0.98	$HMgOCH_2$-*t*-Bu
4	5.40	$PhCH_2CH_2OH$ (5.42)	12	fairly soluble, gives crystalline white solid	1.00:0.98:1.01	$HMgOCH_2CH_2Ph$
5	3.85	c-$C_6H_{11}OH$ (3.80)	2	soluble, gives crystalline solid	1.00:0.97:1.02	HMgO-c-C_6H_{11}
6	4.55	2,6-*i*-$Pr_2C_6H_3OH$ (4.50)	1	highly soluble, gives crystalline solid	1.00:0.98:1.00	HMgO-2,6-*i*-$Pr_2C_6H_3$
7	4.25	2,6-*t*-Bu_2-4-MeC_6H_2OH (4.22)	1	highly soluble, gives crystalline solid	1.00:0.99:1.02	HMgO-2,6-*t*-Bu_2-4-MeC_6H_2
8	4.10	$Ph_2(Me)COH$ (4.05)	2	soluble, can be crystallized from THF	1.00:1.01:1.00	$HMgOCPh_2(Me)$
9	3.15	2-Me-c-$C_6H_{10}OH$ (3.12)	1	soluble, gives white powdery solid	1.00:0.97:1.05	HMgO-2-Me-c-C_6H_{10}
10	4.05	 (4.01)	1	soluble, white solid	1.00:0.95:1.03	HMgO-c-C_6H_{11}
11	3.75	 (3.70)	1	soluble, white amorphous solid	1.00:0.96:1.04	
12	3.59	 (3.60)	1	soluble, white amorphous solid	1.00:0.96:1.03	
13	3.50	 (3.45)	1	soluble	1.00:0.97:1.00	

hydrogen and magnesium, and the alkoxy group was determined by GLC analysis of the remaining solution of the product hydrolyzed with a minimum amount of NH_4Cl in water (Table II). A 10-ft column of 5% Carbowax 20M on Chromosorb W (140 °C column temperature) was used to separate the products of 4-*tert*-butylcyclohexanone and 3,3,5-trimethylcyclohexanone from their corresponding alcohols.

Results and Discussion

Some time ago we reported[5] attempts to prepare HMgOR compounds by the hydrogenation of alkylmagnesium alkoxides (eq 1) and by the reaction of alcohols with MgH_2 (eq 2). At

$$R_2Mg + R'OH \xrightarrow[-H_2]{Et_2O} RMgOR' \xrightarrow{H_2} HMgOR' + RH \quad (1)$$

$$MgH_2 + Mg(OR)_2 \xrightarrow{Et_2O} 2HMgOR \quad (2)$$

$$2HMgOR \rightarrow MgH_2 + Mg(OR)_2 \quad (3)$$

that time we reported that the hoped for HMgOR compounds dissociated to MgH_2 and $Mg(OR)_2$ (eq 3) as was suggested by X-ray powder diffraction data. Unfortunately, both attempts (eq 1 and 2) to prepare HMgOR compounds were made by using diethyl ether as a solvent since one has come to expect disproportionation of unsymmetrical main-group metal compounds in THF. Although we failed in our initial attempts to prepare HMgOR compounds, new attractive routes opened up recently when we found that MgX_2,[3] MgR_2,[4] and $Mg(NR_2)_2$[5] compounds react with an unusually active form of MgH_2 in THF to form a clear solution of HMgX, HMgR, and $HMgNR_2$ compounds, respectively. We immediately considered the possibility that HMgOR compounds could be prepared by the reaction of $Mg(OR)_2$ with MgH_2 in THF to form the desired compounds (eq 4). An active form

$$MgH_2 + Mg(OR)_2 \xrightarrow{THF} 2HMgOR \quad (4)$$

of MgH_2 was prepared for these studies by the reaction of Et_2Mg (or Ph_2Mg) with $LiAlH_4$ in diethyl ether (eq 5). A

$$Et_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2Et_2 \quad (5)$$

slurry of the MgH_2 in THF was then prepared by removing the supernatant solution containing the ether-soluble $LiAlH_2Et_2$ (or $LiAlH_2Ph_2$) by means of a syringe and then adding freshly distilled THF to the resulting insoluble ether-wet solid (MgH_2). The dialkoxy- and diaroxymagnesium compounds were prepared by the reaction of the appropriate alcohol with Me_2Mg in Et_2O/THF solvent (eq 6) under refluxing conditions.

$$Me_2Mg + 2ROH \rightarrow Mg(OR)_2 + 2CH_4\uparrow \quad (6)$$

When freshly prepared MgH_2 and $Mg(OR)_2$ (prepared by the above methods) were allowed to react in THF at room temperature, a clear solution resulted in those cases where the magnesium alkoxide or aroxide is soluble in THF [e.g., $Mg(O\text{-}2,6\text{-}Me_2C_6H_3)_2$, $Mg(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2$, $Mg(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2$, $Mg(OCPh_3)_2$, $Mg(OCPh_2Me)_2$] and an insoluble solid always remained in those cases where the magnesium alkoxides are insoluble [e.g., $Mg(OCH_3)_2$, $Mg(O\text{-}i\text{-}Pr)_2$, $Mg(O\text{-}t\text{-}Bu)_2$, and $Mg(O\text{-c-}C_6H_{11})_2$]. The reaction of MgH_2 with soluble magnesium alkoxides and aroxides has been found to be rapid and complete within 1–2 h as determined by the dissolution of insoluble magnesium hydride in the reaction mixture. On the other hand, when both of the reactants (MgH_2 and $Mg(OR)_2$) are insoluble, the reaction was found to be very slow due to the heterogeneous nature of the reactants. In most of the cases involving insoluble

Table III. IR Data (cm^{-1}) of HMgOR Compounds

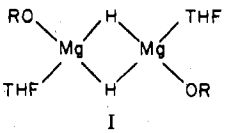
$HMgOCH_3$	HMgO-*i*-Pr	HMgO-*t*-Bu	$HMgOCPh_3$	$HMgOC(CH_3)Ph_2$	HMgO-c-C_6H_{11}	HMgOPh
1618 vs	1600 m, b	1610 m, b	1590 m, b	1590 m, b	1470 vs, b	1590 s
1460 vs	1460 s	1460 vs	1460–40 vs, b	1470 sh	1450 vs	1480 s, b
1378 vs	1378 s	1445 vs	1375 s	1440 vs	1375 s	1455 vs
1250 w	1365 s	1378 vs	1300 m	1375 s	1350 sh	1380 s
1110 s, b	1350 m	1360 vs	1190 sh	1355 sh	1255 m	1280 s, b
1055 s, b	1260 w	1230 s	1180 sh	1302 w	1102 s, b	1160 m
910 s, b	1150 vs, b	1195 vs	1165 s	1290 w	1050 m, b	1065 m
722 m	985 s	1100 w	1150 s	1205 s	980 m	1030 s
610–560 s, b	830 m	1030 w	1114 m	1160 m	890 m	998 m
500 s, b	720 m	942 s	1065 s	1122 m	845 w	880 m
480–505 s, b	575 s, b	880 sh	1025 s	1105 m	790 w	850 m
410 sh	510 m	760 m	937 w	1065 s	722 w	760 s
380 sh	430 s	720 m	910 sh	1025 s	560 s, b	720 w
	330 m	560–535 vs, b	885 ms	940 m	485 m	695 s
		480 vs	775 s	910 m	440 w	610 sh
		400 m	765 s	880 m	360 w	580 s, b
		355 m	750 s	770 m		490 s, b
			700 s	755 m		360 w
			620 m	700 s		
			535 w	615 s		
			505 m	570 s, b		
			410 w	520 m		
			358 m	460 w		
				362 w		
				285 w		

HMgO-2,6-*i*-$Pr_2C_6H_3$	HMgO-2,6-*t*-Bu_2-4-MeC_6H_2	$DMgOCH_3$	DMgO-2,6-*t*-Bu_2-4-MeC_6H_2	DMgO-2,6-*i*-$Pr_2C_6H_3$	HMgO-2,6-$Me_2C_6H_3$
1590 m	1600 w	1462 vs	1600 w	1595 m	1592 m
1460–1440 vs, b	1480 s, b	1377 vs	1475 s	1458 s	1470–1440 vs, b
1380 s	1422 vs	1250 w	1420 s	1379 s	1380 s
1365 s	1385 s	1115 vs, b	1382 s	1365 m	1270 s
1290 s	1350 m	1056 s, b	1350 m	1290 s	1230 s
1262 s	1300 vs	910 s, b	1300 vs	1262 s	1090 m
1210 m	1260 sh	725 m	1260 sh	1210 m	1030 m
1152 w	1200 w, b	575 m	1200 w	1152 w	910 sh
1110 m	1010 s	500 s	1030–1010 s, b	1110 m	876 sh
1040 s	840 vs	460–205 b	840 vs	1040–1015 s, b	850 m
890 m	785 vs	400 sh	785 vs	840 vs	750 m
860 m, b	670 s, b		665 m	785 vs	690 m
750 s	570 s		570 s	668 s	620 m, b
690 m	535 m		535 m	572 s	570 m, b
580 m, b	430 w		450–400 m, b	535 m	520 m
400 w			400 w	450–420 m, b	340 w
320 w					

reactants, the end product (HMgOR) is also insoluble in THF and thus, in most cases, it was difficult to determine when the reaction was complete. However, the progress of the reaction was followed for the reactions of MgH_2 with $Mg(OR)_2$ (where R = c-C_6H_{11} and $PhCH_2CH_2$). The magnesium alkoxides in these reactions were insoluble in THF; however, when they were allowed to react with a MgH_2 slurry in THF, a clear, colorless solution resulted in both cases within a 24-h reaction time. Thus, the solubility of insoluble magnesium hydride in THF suggests that the reaction with magnesium alkoxides is complete. When magnesium hydride, which is believed to be a highly polymeric material bonded via double-hydrogen-bridge bonds, is allowed to react with a soluble magnesium alkoxide or aroxide [$Mg(O\text{-}2,6\text{-}Me_2C_6H_3)_2$, $Mg(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2$, $Mg(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2$, $Mg(OCPh_3)_2$, $Mg(OCPh_2Me)_2$ which is monomeric in THF],[9] redistribution of hydrogen and alkoxy groups takes place and soluble HMgOR compounds (which are dimeric (Table V) in THF over a wide concentration range) are formed. The infrared spectra of HMgOR compounds (Table III) exhibit the presence of ν(C–O) in the regions 1020–1070 and 1100–1160 cm^{-1} and a band in the region 1400–1480 cm^{-1} which is probably due to the bridging magnesium–hydrogen stretching vibration (MgH_2Mg).[3-5] This assignment is confirmed by comparing the spectra of HMgOR compounds with the spectra of the deuterio analogues, DMgOR, where the band in question is shifted to 1020–1040 cm^{-1}. The broad band at 500–600 cm^{-1} in HMgOR compounds which is shifted to 420 cm^{-1} in DMgOR is probably due to Mg–H deformation. Proton NMR spectra of the THF-soluble HMgOR compounds show the presence of only one type of alkoxy group (Table IV) and the signal due to the hydridic proton attached to magnesium was not observed. These observations are consistent with the dimeric structure I involving double-hydrogen-bridge

Table IV. Proton NMR Data (δ) for HMgOR Compounds in THF

HMgO-2,6-*i*-$Pr_2C_6H_3$	HMgO-2,6-*t*-Bu_2-4-MeC_6H_2	$HMgOCH_2CH_2Ph$	$HMgOCPh_3$
1.19 (d) (2,6-*i*-Pr)	1.39 (s) (2,6-*t*-Bu)	6.92–7.27 (mult) (Ph)	7.19–7.36 (mult) (Ph)
6.79 (protons at 3,5 position)	2.12 (s) (4-Me)	1.26 ($C\text{-}CH_2\text{-}C$)	
6.92 (protons at 4 position)			



I

bonds and equivalent terminal OR groups. Earlier we proposed similar double-hydrogen-bridged structures for HMgX compounds.[4]

Table V. X-ray Powder Diffraction Data for HMgOR Compounds

$Mg(OCH_3)_2$	$Mg(O\text{-}i\text{-}Pr)_2$	$Mg(O\text{-}t\text{-}Bu)$	$Mg(OPh)_2$	$Mg(O\text{-}c\text{-}C_6H_{11})_2$	$Mg(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2$	$MgO\text{-}2,6\text{-}Me_2C_6H_3$	$HMgOCPh_3$
11.0 vs	8.75 s	9.0 s	10.5 s	10.6 s	10.4 vs	10.6 m	10.5 m
	4.30 m	8.0 s	8.25 s	7.50 m	9.0 s	7.12 m	9.0 m
	3.25 w	4.50 m	6.95 s	5.03 w	8.4 s	3.92 w	8.3 m
	2.50 w	4.30 m	5.95 w	4.80 s	7.50 s	3.30 vw	7.51 m
	2.25 w	4.00 w	5.40 w	4.51 s	5.91 m		5.92 w
	1.66 w	3.50 m	5.15 w	3.65 w	5.20 m		5.31 w
		3.05 w	4.50 s	3.00 w	4.80 s		4.80 m
			4.35 s	2.56 w	4.49 m		4.50 w
			4.15 m		4.30 vs		4.30 m
			3.90 s		4.15 m		4.11 w
			3.80 s		4.00 s		3.95 m
			3.65 w		3.70 m		3.70 w
			3.45 m		3.51 w		3.50 w
			3.30 w		3.34 m		3.30 w
			3.20 w		3.15 m		3.15 w
			3.00 w		2.92 m		2.93 w
			2.90 w		2.75 w		2.75 w
			2.80 w		2.65 w		2.30 w
			2.25 w		2.52 w		2.05 w
					2.38 w		
					2.30 w		
					2.11 w		

$HMgOCH_3$	$HMgO\text{-}i\text{-}Pr$	$HMgO\text{-}t\text{-}Bu$	$HMgOPh$	$HMgO\text{-}c\text{-}C_6H_{11}$	$HMgO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$	$HMgOCPh_2(Me)$
11.0 d	8.70 vs	9.0 s	11.5 s	10.5 vs	10.2 m	11.8 m
8.5 d	8.0 s	8.01 s	10.5 w	7.50 m	8.80 s	6.84 m
2.95 w	4.25 s	4.45 m	5.70 w	4.7 vs	6.90 m	5.35 s
2.75 w	3.45 w	4.20 w	5.60 w	3.80 w	4.91 w	4.55 m
2.35 w	3.25 w	4.02 w	5.02 w	3.30 w	4.45 w	4.38 m
		3.45 m		2.82 vw	4.21 w	4.00 w
		3.03 w			4.10 vs	3.70 m
					3.85 vs	3.62 w
					3.25 vw	3.18 vw
					3.20 vvw	

On the other hand, we had suggested earlier a double-alkoxy-bridge structure for dimeric $MeMgOPh_2(Me)$[14] on the basis of variable-temperature proton NMR data. Methyl groups, however, have less tendency to form bridge bonds when in the presence of alkoxy groups. In the case of alkoxymagnesium hydrides, both hydrogen and alkoxy groups have competitive tendencies to form bridge bonds; however, when the alkoxy group is sterically bulky, then hydrogen bridge bonds are preferentially formed.

The reactions of MgH_2 with $Mg(OR)_2$ compounds in THF (where R = Me, *i*-Pr, *t*-Bu, and Ph) are slow presumably due to the insoluble nature of both reactants. Because of the insoluble nature of the reactants and in some cases products, it was difficult to determine the extent to which the reaction had taken place at any particular time. In any case, when the reaction was allowed to take place for more than 24 h in THF at room temperature, the resulting insoluble products were shown by X-ray powder diffraction to show weak and diffuse lines due to the starting alkoxides. For example, when MgH_2 was allowed to react with $Mg(OCH_3)_2$ for over 24 h and the resulting product was characterized by X-ray powder diffraction, a line due to $Mg(OCH_3)_2$ (Table V) was visible suggesting the presence of unreacted $Mg(OCH_3)_2$. However, when the infrared spectrum of the above solid was recorded in Nujol, it showed a strong band at 1618 cm^{-1} (presumably due to terminal Mg–H stretching) which was not present in the spectrum of the starting material. This observation was confirmed by carrying out a similar reaction of $Mg(OCH_3)_2$ with MgD_2 in THF under similar reaction conditions and comparing the infrared spectrum of the resulting product with that of the earlier one. The band at 1618 cm^{-1}, present in the previous reaction with MgH_2, was absent in the spectrum of the reaction product from MgD_2, and a new band at 1115 cm^{-1} was observed presumably due to the Mg–D stretching vibration. These observations suggest that MgH_2 does react with insoluble $Mg(OCH_3)_2$ at least to some extent, resulting in the formation of $HMgOCH_3$. The formation of HMgOR compounds can also be supported by the behavior of the above reaction products with cyclic ketones[15] and comparing the results with those obtained with MgH_2. MgH_2 reduces 4-*tert*-butylcyclohexanone, 2-methylcyclohexanone, and 3,3,5-trimethylcyclohexanone to give the less stable alcohol (axial alcohol) in yields of 53, 35, and 85%, while the product of the reaction of MgH_2 and $Mg(OCH_3)_2$ gives 76, 98, and 99% and the product of MgH_2 and $Mg(O\text{-}i\text{-}Pr)_2$ gives 9, 68, and 65%, respectively. These data do indicate the different behavior of the reaction products compared to MgH_2 and indirectly indicate the existence of HMgOR compounds. Although one might presume that $Mg(OR)_2$ compounds could affect the reactivity of MgH_2 without forming HMgOR compounds, one would assume that the reaction rate would be rapid as is observed in the case of MgH_2 reduction. On the other hand, the solid obtained after the reaction of MgH_2 with $Mg(OCH_3)_2$ for over 24 h reacted with ketones very slowly and in the case of the product of MgH_2 and $Mg(O\text{-}i\text{-}Pr)_2$, only 50%

Table VI. Molecular Weight Data[a] for Alkoxy- and Aroxymagnesium Hydrides

compd		concn (molality, *m*) vs. molecular association (*i*)					
$HMgO\text{-}2,6\text{-}Me_2C_6H_3$	*m*	0.024	0.053	0.071	0.102	0.124	0.148
	i	2.13	2.10	2.09	2.25	2.28	2.32
$HMgO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$	*m*	0.027	0.058	0.079	0.115	0.137	0.169
	i	2.05	2.09	2.14	2.25	2.27	2.29
HMgO-	*m*	0.028	0.066	0.095	0.125	0.149	0.169
$2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2$	*i*	1.98	2.05	2.04	2.15	2.14	2.20
$HMgOCPh_3$	*m*	0.024	0.054	0.084	0.109	0.142	0.168
	i	2.10	2.05	2.12	2.18	2.19	2.22
$HMgOCPh_2(Me)$	*m*	0.022	0.048	0.072	0.099	0.132	0.156
	i	2.07	2.14	2.13	2.18	2.25	2.27

[a] Molecular weight studies have been carried out ebullioscopically in refluxing THF at reduced pressure (240 mmHg).

reaction was observed after 24 h.

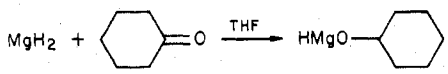
It is true that the product of the reaction of MgH_2 and $Mg(OCH_3)_2$ exhibited an X-ray powder diffraction pattern containing lines due to $Mg(OCH_3)_2$; however, this is to be expected. In the case of HMgX compounds (where X = Cl, Br) we found that these products existed as HMgX entities but dissociated into MgH_2 and MgX_2 when isolated as a solid. A similar dissociation is suggested for alkoxymagnesium hydrides. When insoluble magnesium hydride was allowed to react with insoluble $Mg(O\text{-}c\text{-}C_6H_{11})_2$ in THF, a clear solution with composition $HMgO\text{-}c\text{-}C_6H_{11}$ formed. When the solvent of the above reaction was removed slowly under reduced pressure, a crystalline solid resulted which also analyzed for $HMgO\text{-}c\text{-}C_6H_{11}\cdot THF$, but when the solid material was dried under vacuum and characterized by X-ray diffraction studies, lines due to $Mg(O\text{-}c\text{-}C_6H_{11})_2$ were observed. Thus, these observations show that THF plays an important role in the compound formation, and when it is removed as a solvating ligand, dissociation to MgH_2 and $Mg(OR)_2$ takes place.

Alkoxymagnesium hydrides can also be prepared by the reaction of equimolar amounts of alcohol or phenol and MgH_2 in THF. The reaction is carried out at −78 °C and the reaction mixture is allowed to warm to room temperature (eq 7). This

$$MgH_2 + ROH \xrightarrow{THF} HMgOR + H_2\uparrow \qquad (7)$$

method of preparation has an advantage over the reaction of MgH_2 with $Mg(OR)_2$ (eq 1) in that the present reaction is faster and is usually complete within 1 h. For example, in the preparation of $HMgO\text{-}c\text{-}C_6H_{11}$ and $HMgOCH_2CH_2Ph$ from MgH_2 and $Mg(OR)_2$, 26 and 30 h, respectively, were required for reaction whereas in the reaction of MgH_2 with ROH only 2 and 12 h, respectively, were required (Tables I and II). Alkoxy- and aroxymagnesium hydrides prepared by either method show similar properties. The only disadvantage of the reaction of MgH_2 with ROH compared to the reaction of MgH_2 with $Mg(OR)_2$ is that half of the hydrogen attached to magnesium in MgH_2 is lost as hydrogen.

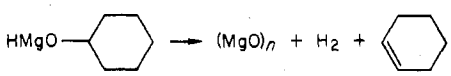
Interestingly, when magnesium hydride was allowed to react with cyclohexanone in a 1:1 ratio in THF (eq 8) in order to



(8)

explore the reactivity and stereoselectivity of MgH_2 toward organic reagents, a clear solution resulted within 1 h. When the solution was analyzed spectroscopically, it was shown to contain $HMgO\text{-}c\text{-}C_6H_{11}$. In this way reactions of magnesium hydride with cyclohexanone and 4-*tert*-butylcyclohexanone have been carried out, and soluble HMgOR compounds have been prepared.

DTA–TGA analyses of several HMgOR compounds have been carried out under vacuum and the decomposition of a representative HMgOR compound was studied (the DTA–TGA of $HMgO\text{-}c\text{-}C_6H_{11}$ is shown in Figure 1). The compound decomposes at 110 and 380 °C with gas evolution due to H_2 and cyclohexene (eq 9). The exotherm at 110 °C is due to desolvation and the one at 380 °C is due to decomposition of $HMgO\text{-}c\text{-}C_6H_{11}$.



(9)

In conclusion, stable, THF-soluble and active alkoxy- and aroxymagnesium hydrides have been prepared by two different methods. The compounds were shown to reduce cyclic ketones to the corresponding alcohols with unusual stereoselectivity. For example $HMgO(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$ (prepared by either of the reaction routes described) is highly soluble and stable in THF. It reduces 2-methylcyclohexanone, 3,3,5-trimethylcyclohexanone, and camphor in quantitative yields and gives the axial alcohols (less stable alcohol) in above 99% yield. It also reduces 4-*tert*-butylcyclohexanone quantitatively to give 82% axial alcohol.

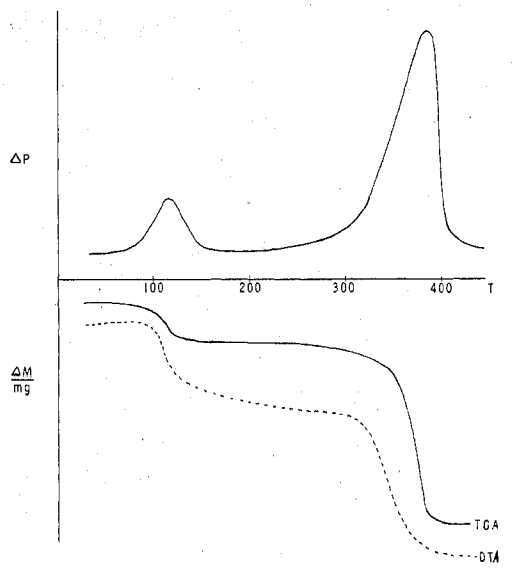


Figure 1. Vacuum DTA–TGA of $HMgO\text{-}c\text{-}C_6H_{11}$.

Acknowledgment. We are indebted to Office of Naval Research (Contract No. N 00014-A-000 5AD) for support of this work.

Registry No. $HMgOCH_3$, 32149-52-3; HMgO-*i*-Pr, 32149-53-4; HMgO-*t*-Bu, 32149-54-5; $HMgOCH_2CH_2Ph$, 68986-38-9; $HMgO\text{-}c\text{-}C_6H_{11}$, 68986-37-8; HMgOPh, 32149-55-6; $[HMgO\text{-}2,6\text{-}Me_2C_6H_3(THF)]_2$, 69531-98-2; $[HMgO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3(THF)]_2$, 69531-99-3; $[HMgO\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2(THF)]_2$, 69532-00-9; $[HMg(OCPh_2Me)(THF)]_2$, 69531-91-5; $[HMg(OCPh_3)(THF)]_2$, 69576-63-2; $Mg(OCH_8)_2$, 109-88-6; $Mg(O\text{-}i\text{-}Pr)_2$, 15571-48-9; $Mg(O\text{-}t\text{-}Bu)_2$, 32149-57-8; $Mg(OCH_2CH_2Ph)_2$, 69517-34-6; $Mg(O\text{-}c\text{-}C_6H_{11})_2$, 68986-47-0; $Mg(OPh)_2$, 7721-07-5; $Mg(O\text{-}2,6\text{-}Me_2C_6H_4)_2$, 65277-19-2; $Mg(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_4)_2$, 65276-35-9; $Mg(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2$, 65277-21-6; $Mg(OCPh_2Me)_2$, 67878-39-1; $Mg(OCPh_3)_2$, 65277-22-7; MgH_2, 7693-27-8; $HMgOCH_2\text{-}t\text{-}Bu$, 69517-35-7; $HMgO\text{-}2\text{-}Me\text{-}c\text{-}C_6H_{10}$, 69517-36-8; CH_3OH, 67-56-1; *i*-PrOH, 67-63-0; *t*-Bu-CH_2OH, 75-84-3; $PhCH_2CH_2OH$, 60-12-8; $c\text{-}C_6H_{11}OH$, 108-93-0; $2,6\text{-}i\text{-}Pr_2C_6H_3OH$, 2078-54-8; $2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2OH$, 128-37-0; $Ph_2(Me)COH$, 599-67-7; $2\text{-}Me\text{-}c\text{-}C_6H_{10}OH$, 583-59-5; $c\text{-}C_6H_{10}O$, 108-94-1; $HMgO\text{-}3,3,5\text{-}Me_3\text{-}c\text{-}C_6H_8$, 69517-37-9; $HMgO\text{-}4\text{-}t\text{-}Bu\text{-}c\text{-}C_6H_{10}$, 69517-38-0; $2\text{-}Me\text{-}c\text{-}C_6H_9O$, 583-60-8; $3,3,5\text{-}Me_3\text{-}c\text{-}C_6H_7O$, 873-94-9; $4\text{-}t\text{-}Bu\text{-}c\text{-}C_6H_9O$, 98-53-3; $DMgOCH_3$, 69517-39-1; $DMgO\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2$, 69517-40-4; $DMgO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$, 69517-41-5.

References and Notes

(1) (a) H. Noth and H. Suchy, *Z. Anorg. Allg. Chem.*, **358**, 66 (1968); (b) N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 823 (1968).
(2) (a) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972, pp 45–130; (b) E. C. Ashby, J. P. Sevenair, and F. R. Dobbs, *J. Org. Chem.*, **36**, 197 (1971), and references therein.
(3) E. C. Ashby and A. B. Goel, *J. Chem. Soc., Chem. Commun.*, 169 (1977).
(4) E. C. Ashby and A. B. Goel, *J. Am. Chem. Soc.*, **99**, 310 (1977).
(5) R. G. Beach and E. C. Ashby, *Inorg. Chem.*, **10**, 906 (1971).
(6) E. C. Ashby, J. J. Lin, and A. B. Goel, *J. Org. Chem.*, **43**, 1564 (1978).
(7) R. Bauer, *Z. Naturforsch., B*, **17**, 201 (1962).
(8) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).
(9) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(10) F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, **45**, 654 (1968).
(11) P. Claudy, J. Bosquet, J. Etienne, and E. C. Ashby, *J. Chem. Educ.*, **52**, 618 (1975).
(12) E. C. Ashby and R. Arnott, *J. Organomet. Chem.*, **14**, 1 (1968).
(13) E. C. Ashby, J. J. Lin, and A. B. Goel, *J. Org. Chem.*, **43**, 1557 (1978).
(14) E. C. Ashby, J. Nackashi, and G. E. Parris, *J. Am. Chem. Soc.*, **97**, 3162 (1975).
(15) E. C. Ashby, J. J. Lin, and A. B. Goel, *J. Org. Chem.*, **43**, 1560 (1978).