the (0001), (10$\bar{1}$0), and (11$\bar{2}$0) planes were spark cut from the 0.5 in. × 2.0 in., 99.999+% pure crystal. All spark-cut crystal samples were chemically polished by lowering them with tweezers into a vigorously stirred 5% aqueous solution of nitric acid at 0 °C under argon. The samples were not allowed to contact the magnetic stirring bar. The samples were washed as described above.

Magnesium alloys were cut into rectangular solids of ca. 10 × 12 × 2 mm weighing 0.7–0.9 g. Chemical polishing of alloy samples in aqueous, methanolic, or ethanolic nitric acid at 0 or −20 °C or at ambient temperature was unsuccessful. Under all these conditions, the more electropositive metal in the alloy sample (usually magnesium) was preferentially leached from the sample, thereby changing the surface composition. Consequently all alloy samples were metallographically prepared by mechanical polishing. The alloy samples were ground with medium and very fine sandpaper and polished with "0", "00", and "0000" emery paper.

Annealing of magnesium (alloy) samples was carried out by placing the samples in Carius combustion tubes, flushing the tubes with argon, sealing them, and heating the sealed tubes to 500 °C for 26 h.

General Procedure for Grignard Reaction of Metallographically Prepared Magnesium Samples and Microscopic Analysis of the Resulting Corrosion. The magnesium (alloy) sample (0.5–0.7 g, depending on the experiment) was placed in either a 40-mL centrifuge tube or a three-necked, 50-mL, round-bottomed flask immediately after metallographic preparation, and the flask was flame dried again under argon. Reaction vessels were not equipped with magnetic stirring bars—stirring of the reactant solutions was done by swirling gently by hand to minimize abrasion of the metallic sample. Anhydrous solvent (10 mL) was added to the reaction vessel by syringe followed by 0.01 mol (ca. 1 mL) of alkyl halide. The reaction vessel was swirled until a faint cloudiness indicated the start of reaction. The vessel was immediately placed in the appropriate temperature bath (usually ice–water, 0 °C). Gentle manual stirring was continued for several minutes or until reaction was proceeding vigorously. A large percentage of the reactions failed to proceed due to insufficient initiation. Reaction was terminated by removing the magnesium (alloy) sample from solution with tweezers and immediately and thoroughly washing the sample with water and with acetone.

Corrosion of Single-Crystal Spheres. The corrosion of magnesium spheres with alkyl halides was carried out by using the metallographical preparation procedure, the Grignard reaction procedure, and the workup procedure for SEM observation described above. Two spheres 0.125 in. in diameter were spark cut from a magnesium single crystal of 99.95% maximum purity and metallographically prepared for reaction. One sphere was allowed to corrode in 0.05 M ethyl bromide in diethyl ether at 0 °C for 1 h. The reaction vessel was swirled occasionally. The second sphere was corroded under the same conditions by using THF in place of diethyl ether. Both corroded spheres were examined on nearly all surfaces at several magnifications by SEM.

Corrosion Initiation at Dislocations. Disks of single-crystal 99.999+% pure magnesium displaying (0001) and (10$\bar{1}$0) planes were prepared metallographically. Four to six indentations were made in the chemically polished surfaces with a Knoop hardness testing device equipped with 900-g load. The indented disks were allowed to react in 1 N ethereal 1,4-dichlorobutane for 1–2 min, worked up, and prepared for observation under an optical microscope as described above.

Acknowledgment. We are indebted to Dr. Mary Woodville (Dow Chemical Co.), Professor Morris Fine (Northwestern University), and Professors Merton Flemings and Edwin Backman (MIT) for samples of magnesium alloys.

Registry No. Mg, 7439-95-4; Mg(98.5),Li(1.5), 72428-31-0; Mg(95.25),Li(4.75), 72428-30-9; Mg(94.7),Cu(5.3), 72428-29-6; Mg(95),Cu(5), 72428-32-1; Mg(93),Zn(3),Fe(4), 72428-33-2; Mg(95),Ag(5), 72428-34-3; 1-bromopentane, 110-53-2; ethyl bromide, 74-96-4; 1,4-dibromobutane, 110-52-1; 1,4-dichlorobutane, 110-56-5; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; C_6H_5Br, 108-86-1.

Reactions of Magnesium Hydride. 4. Stereoselective Reduction of Cyclic and Bicyclic Ketones by Lithium Alkoxymagnesium Hydrides

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A series of lithium alkoxymagnesium hydrides [$LiMgH_2(OR)$] were prepared and allowed to reduce 4-*tert*-butylcyclohexanone (I), 3,3,5-trimethylcyclohexanone (II), 2-methylcyclohexanone (III), and camphor (IV). It was found that very bulky secondary cyclic alkoxy groups such as 2,2,6,6-tetramethyl- and 2,2,6,6-tetrabenzylcyclohexoxy were very stereoselective in the reduction of these ketones. For example, $LiMgH_2$(2,2,6,6-Me_4-c-HxO) reduced ketone I to provide 89% of the axial alcohol compared to 83% for HMg(2,6-*i*-Pr_2PhO) which previously had provided the greatest degree of selectivity among the new hydrides of magnesium. The dialkoxyhydrides, $LiMgH(OR)_2$ [where RO = 2,2,6,6-Me_4-c-HxO or 2,6-*t*-Bu_2PhO], were also found to reduce ketones I, II, III, and IV stereoselectively but to a lesser extent than the monoalkoxyhydrides, $LiMgH_2(OR)$. These reactions were also accompanied by more enolization than observed for the monoalkoxy reagents.

The use of metal hydrides as stereoselective reducing agents in organic chemistry has received considerable attention.[1-3] Although numerous reports have appeared in the literature concerning the reduction of cyclohexanones by hydrides of boron and aluminum, little is known about reductions with MgH_2 or its derivatives. The reason for this is presumably due to the reported lack of reactivity of MgH_2 and its insolubility in all solvents studied and also because derivatives of magnesium hydride have been unknown until recently.[4] We have prepared some THF-soluble magnesium–hydrogen compounds of the types $HMgOR$[5] and $HMgNR_2$[6] which have been shown to exhibit considerable stereoselectivity toward cyclic and bicyclic ketones.[7] Since HMgOR compounds are such good ste-

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reoselective reducing agents by virtue of their bulky alkoxy group, it is reasonable to assume that the corresponding "ate" complexes (e.g., alkali metal alkoxymagnesium hydrides) might produce an even greater effect.

We report here reactions of THF soluble lithium alkoxymagnesium hydrides, $LiMgH_2(OR)$[8] (where R = methyl, isopropyl, *tert*-butyl, neopentyl, diphenylmethyl, cyclohexyl, 2-methylcyclohexyl, phenyl, 2,6-diisopropylphenyl, 2,6-di-*tert*-butyl-4-methylphenyl, 2,2,6,6-tetramethylcyclohexyl, and 2,2,6,6-tetrabenzylcyclohexyl), with cyclic and bicyclic ketones such as 2-methylcyclohexanone, 4-*tert*-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and camphor in order to observe any unusual stereoselectivity.

Experimental Section

General Methods. Reactions were performed under nitrogen or argon at the bench by using Schlenk tube techniques[9] or in a glovebox equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone traps to remove solvent vapors.[10] Calibrated syringes equipped with stainless-steel needles were used for transfer of reagents. Glassware and syringes were flamed and cooled under a flow of nitrogen or argon. Ketone, alcohol, and internal standard solutions were prepared by weighing the compound in a tared volumetric flask and diluting with the appropriate solvent.

All melting points are corrected. The proton NMR spectra were determined at 60 MHz by using a Varian Model T-60 NMR spectrometer. The chemical shifts are expressed in parts per million (δ values) relative to Me_4Si as the internal standard. The mass spectra were obtained by using a Hitachi Perkin-Elmer Model RMU-7 or a Varian Model M-66 mass spectrometer. GLC analyses were carried out on a F&M Model 700 or Model 720 gas chromatograph. The IR spectra were obtained by using a Perkin-Elmer Model 621 or Model 257 infrared spectrometer. High-pressure work was conducted by using an autoclave (rated to 15 000 psi) obtained from the Superpressure Division of the American Instrument Co.

Analyses. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[9] Magnesium was determined by titrating hydrolyzed samples with standard EDTA solution at pH 10 with Eriochrome Black T as an indicator. Lithium reagents were analyzed by the standard Gilman double-titration method (titration of total base followed by titration of total base after reaction with benzyl chloride)[11] or by flame photometry. The amount of active C–Mg and C–Li was determined by titrating the active reagent in a drybox with dry 2-butanol in xylene with 2,2′-diquinoline as an indicator. Aluminum was determined by adding excess standard EDTA solution to hydrolyzed samples and then back-titrating with standard zinc acetate solution at pH 4 with dithizone as an indicator. Carbon and hydrogen analyses were carried out by Atlantic Microlab, Inc.

Solvents. Fisher reagent-grade anhydrous diethyl ether was stored over sodium metal and then distilled under nitrogen from $LiAlH_4$ and/or sodium–benzophenone ketyl just prior to use. Fisher reagent-grade THF was dried over $NaAlH_4$ and distilled, with diphenylmethane as an indicator, under nitrogen just prior to use. Fisher reagent-grade benzene and hexane were stirred over concentrated H_2SO_4, washed with Na_2CO_3 and then distilled water, dried over anhydrous $MgSO_4$, and distilled from $NaAlH_4$, under argon, just prior to use.

Preparation of 2,2,6,6-Tetramethylcyclohexanone. This compound was prepared by the method of Borg and co-workers.[12] The crude product was distilled to give a 68% yield of a product: bp 50–53 °C (3 mm),[12] IR (neat, film) 2950 (s), 2920 (m), 2860 (m), 1700 (s), 1470 (s), 1390 (m), 1370 (m), 1040 (m) cm^{-1}; NMR ($CDCl_3$, Me_4Si) δ 1.10 (s, 12 H), 1.55–1.86 (m, 6 H); mass spectrum, *m/e* (relative intensity) 154 (M^+, 74), 140 (7), 111 (7), 83 (53), 82 (76), 78 (18), 72 (32), 70 (13), 69 (65), 57 (23), 56 (100), 55 (62), 41 (86). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.81; H, 11.70.

Preparation of 2,2,6,6-Tetrabenzylcyclohexanone. This compound was prepared according to the procedure of Granger and co-workers.[13] The reaction mixture was worked up, yielding white crystals which upon recrystallization from diethyl ether gave a 33% yield of 2,2,6,6-tetrabenzylcyclohexanone: mp 155–156 °C; IR ($CDCl_3$, cavity cell) 3060 (w), 3040 (w), 3000 (m), 2930 (s), 2860 (w), 1685 (s), 1600 (m), 1490 (s), 1450 (s), 1250 (s), 860 (s) cm^{-1}; NMR ($CDCl_3$, Me_4Si) δ 1.60 (s, 8 H), 2.22–2.97 (m, 6 H), 6.90–7.34 (m, 20 H); mass spectrum, *m/e* (relative intensity) metastable 366.5 ($M^+ - 92$, 35), 227 (23), 275 (10), 224 (34), 91 (100). Anal. Calcd for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 88.90; H, 7.45.

Purification of Alcohols. Methanol (Fisher) was distilled after being treated with magnesium metal. 2-Propanol (Fisher) was distilled over $Al(O\text{-}i\text{-}Pr)_3$, and *tert*-butyl alcohol (Fisher) was fractionally crystallized under nitrogen. Cyclohexanol, 2-methylcyclohexanol, phenol, and 2,6-diisopropylphenol (Ethyl Corp.) were distilled prior to use. Benzhydrol (Aldrich), neopentyl alcohol (Aldrich), and 2,6-di-*tert*-butylcresol (Eastman) were used without further purification.

Preparation of 2,2,6,6-Tetramethylcyclohexanol. This compound was prepared according to the method of Boyer and co-workers.[14] The crude product was distilled to give a 98% yield of 2,2,6,6-tetramethylcyclohexanol: bp 54–55 °C (3.6 mm); NMR ($CDCl_3$, Me_4Si) δ 0.92 (s, 6 H), 0.96 (s, 6 H), 1.12–1.76 (m, 6 H), 1.92 (s, 1 H), 3.00 (s, 1 H); mass spectrum, *m/e* (relative intensity) 156 (M^+, 7), 138 (13), 123 (18), 109 (83), 95 (15), 82 (100), 69 (89), 55 (44), 43 (56), 41 (88); IR ($CDCl_3$, cavity cell) 3500 (br, m), 2945 (s), 2920 (m), 2855 (m), 1460 (s), 1385 (m), 1370 (m), 1030 (m), 850 (m). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.78; H, 12.83.

Preparation of 2,2,6,6-Tetrabenzylcyclohexanol. This compound was prepared according to the method of Boyer and co-workers.[15] The yield of 2,2,6,6-tetrabenzylcyclohexanol after being recrystallized twice from diethyl ether [mp 159–160 °C (lit.[15] mp 161 °C)] was 66%: IR ($CDCl_3$, cavity cell) 3560 (br, m), 3060 (m), 3040 (m), 3010 (s), 2910 (s), 2850 (m), 1610 (m), 1490 (s), 1450 (s), 1070 (m), 1030 (m), 560 (m) cm^{-1}; NMR ($CDCl_3$, Me_4Si) δ 0.72–3.48 (m, 16 H), 6.70–7.40 (m, 20 H); mass spectrum, *m/e* (relative intensity) metastable 368.3 ($M^+ - 92$, 6), 211 (8), 129 (8), 117 (7), 115 (7), 91 (100), 65 (10). Anal. Calcd for $C_{34}H_{36}O$: C, 88.65; H, 7.88. Found: C, 88.55; H, 7.80.

Preparation of Reagents. Solutions of $LiAlH_4$ were prepared by refluxing distilled diethyl ether over solid $LiAlH_4$ (Alfa Inorganics) for 20 h followed by filtration in the drybox through a fritted glass funnel with dried Celite as a filter aid. The clear solution was standardized for aluminum content by EDTA titration. Diethylmagnesium was prepared by the reaction of diethylmercury[16] with magnesium metal at 60–80 °C, and a solution in diethyl ether was standardized by magnesium analysis. Lithium hydride was prepared by hydrogenation of *t*-BuLi or *n*-BuLi at 4000 psi of hydrogen for 24 h at room temperature. Sodium hydride was obtained as a 50% mineral oil dispersion from Ventron Hydrides Division. Lithium alkoxides were prepared by the reaction of the appropriate alcohols with a stoichiometric amount of *n*-butyllithium or activated LiH in *n*-hexane. After the mixture was stirred for 1 h at room temperature under an argon atmosphere, the *n*-hexane was removed under vacuum and replaced by a known amount of freshly distilled Et_2O/THF. This procedure was repeated three times.

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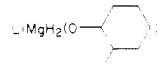
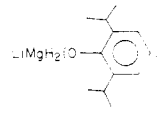
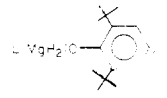
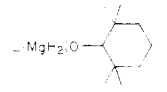
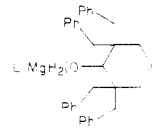
Table I. Preparation of Lithium Alkoxymagnesium Hydrides [$LiMgH_2(OR)$] by the Reaction of Magnesium Hydride with Lithium Alkoxides[a]

expt	reaction time, h	solubility in THF	analysis (ratio) Li:Mg:H:ROH	product
1	10	insoluble	1.05:1.00:1.91:1.02	$LiMgH_2(OCH_3)$
2	7	soluble	1.04:1.00:1.93:1.01	$LiMgH_2$(O-*i*-Pr)
3	7	soluble	1.04:1.00:1.93:1.03	$LiMgH_2$(O-*t*-Bu)
4	6	soluble	1.03:1.00:1.95:1.02	$LiMgH_2(OCH_2$-*t*-Bu)
5	8	soluble	1.04:1.00:1.92:1.02	$LiMgH_2(OCHPh_2)$
6	7	soluble	1.00:1.02:1.95:1.03	$LiMgH_2$(O-c-Hx)
7	8	insoluble	1.03:1.02:1.90:1.04	$LiMgH_2(OPh)$
8	5	soluble	1.02:1.00:1.96:1.00	
9	7	soluble	1.03:1.00:1.92:1.03	
10	6	soluble	1.02:1.02:1.94:1.00	
11	5	soluble	1.01:1.01:1.96:1.00	
12	5	soluble	1.01:1.01:1.97:1.00	

[a] In a 1:1 ratio.

Preparation of MgH_2 Slurry in THF.[17] Lithium aluminum hydride (20 mmol) in ether (32 mL) was allowed to react with a diethyl ether (50 mL) solution of diethylmagnesium [$(C_2H_5)_2Mg$, 20 mmol] at room temperature with constant stirring. The reaction mixture was stirred for about 1 h and the insoluble solid isolated by centrifuging the mixture and then removing the ether solution with a syringe. The resulting solid was washed with freshly distilled THF. Anal. Calcd for MgH_2: Mg/H, 1.00:2.00. Found: 1.00:2.02.

Preparation of Lithium Alkoxymagnesium Hydrides. A known amount of lithium alkoxide in Et_2O/THF was prepared as described above. The lithium alkoxide was allowed to react with a slurry of MgH_2 in THF at room temperature in a 1:1 molar ratio, and the reaction mixture was stirred for 3–5 h, during which time the MgH_2 dissolved. Analyses of the resulting clear solutions are given in Table I.

General Reaction of Hydrides with Ketones. A 10-mL Erlenmeyer flask equipped with a Teflon-coated magnetic stirring bar was dried in an oven and allowed to cool under nitrogen or argon. The flask was then sealed with a rubber serum cap, connected by means of a syringe needle to a nitrogen/argon-filled manifold equipped with a mineral oil filled bubbler. The ketone solutions with internal standard (tetradecane for 4-*tert*-butylcyclohexanone and camphor, hexadecane for 3,3,5-trimethylcyclohexanone, and dodecane for 2-methylcyclohexanone) were syringed into the flask and the known concentration of hydride reagent (solution or slurry) added to the flask at room temperature. After the designated time, the reaction was slowly quenched with H_2O and dried over anhydrous $MgSO_4$. A 10-ft, 5% Carbowax 20M on Chromosorb W column (130 °C column temperature) was used to separate the products of 4-*tert*-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and camphor. A 15-ft, 10% diglycerol on Chromosorb W column (80 °C) was used to separate the products of 2-methylcyclohexanone. The order of elution for each ketone was the same: the ketone first, the axial or exo alcohol second, and the equatorial or endo alcohol last.

Qualitative Rate Studies of the Reactions of Lithium Alkoxymagnesium Hydrides with 4-*tert*-Butylcyclohexanone. The aforementioned conditions for the reduction were set up at the desired temperature. One syringe with the desired amount of ketone and another syringe with a saturated NH_4Cl solution were placed through the serum cap. The ketone was added under an argon atmosphere, and at the desired time the reaction was rapidly quenched. The products were then analyzed in the normal manner.

Results and Discussion

Integrity of the Reagent. The magnesium hydride used in these studies was prepared by the reaction of $(C_2H_5)_2Mg$ with $LiAlH_4$ in diethyl ether (eq 1). A slurry

$$(C_2H_5)_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2\downarrow + LiAl(C_2H_5)_2H_2 \quad (1)$$

of MgH_2 (prepared by this method) in THF was prepared by removing the supernatant solution containing the diethyl ether soluble $LiAl(C_2H_5)_2H_2$ by means of a syringe and then adding freshly distilled THF to the resulting diethyl ether wet MgH_2. This washing operation was carried out several times in order to remove the last traces of $LiAl(C_2H_5)_2H_2$.

Magnesium hydride prepared as describe above was allowed to react with lithium alkoxides (prepared according to eq 2 or 3) in equimolar ratio in THF in order to form

$$n\text{-BuLi} + ROH \rightarrow LiOR + n\text{-BuH}\uparrow \quad (2)$$

$$LiH + ROH \rightarrow LiOR + H_2\uparrow \quad (3)$$

$$LiOR + MgH_2 \rightarrow LiMgH_2(OR) \quad (4)$$

$$LiH + Mg(OR)_2 \rightarrow LiMgH(OR)_2 \quad (5)$$

$$Et_2Mg + 2HOR \rightarrow EtH\uparrow + Mg(OR)_2 \quad (6)$$

the desired lithium alkoxymagnesium hydride (eq 4, Table I). Lithium dialkoxymagnesium hydrides were prepared according to eq 5 by allowing freshly prepared activated LiH or NaH to react with the appropriate magnesium alkoxide. The magnesium alkoxides were prepared by the

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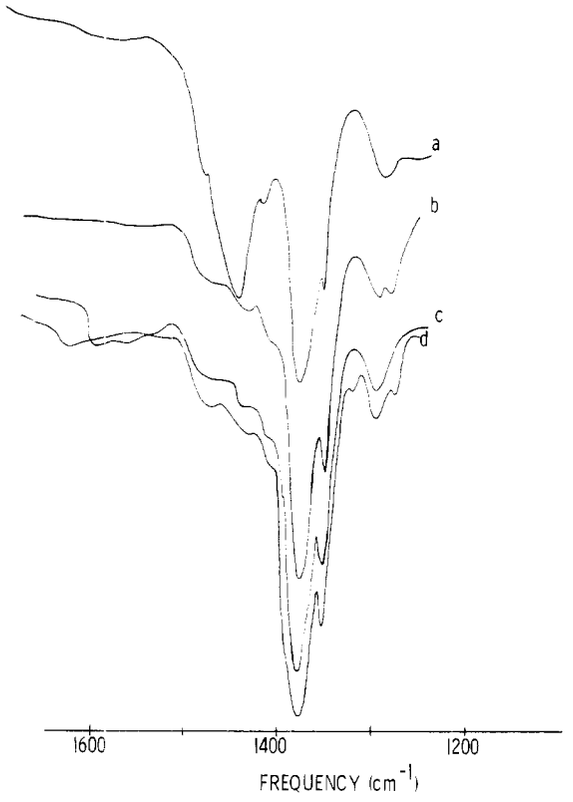


Figure 1. IR spectra of simple and complex metal alkoxides: (a) Li(2,2,6,6-Me_4-c-HxO), (b) HMg(2,2,6,6-Me_4-c-HxO), (c) $LiMgH_2$(2,2,6,6-Me_4-c-HxO), (d) $LiMgH(2,2,6,6\text{-}Me_4\text{-c-HxO})_2$.

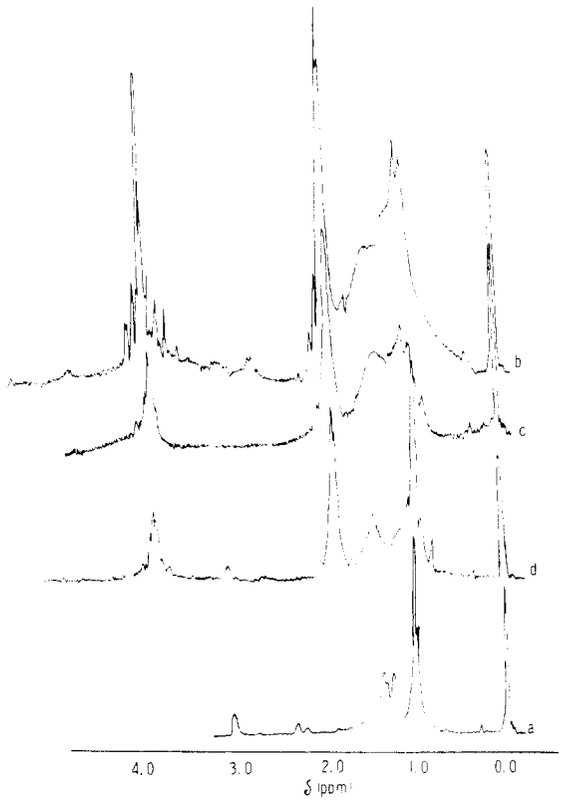


Figure 2. NMR spectra of simple and complex metal alkoxides: (a) Li(2,2,6,6-Me_4-c-HxO), (b) HMg(2,2,6,6-Me_4-c-HxO), (c) $LiMgH_2$(2,2,6,6-Me_4-c-HxO), (d) $LiMgH(2,2,6,6\text{-}Me_4\text{-c-HxO})_2$.

reaction of Et_2Mg with freshly distilled alcohol (eq 6).

Although MgH_2 is insoluble in THF, a clear solution results in most cases when lithium alkoxide is allowed to react with MgH_2 slurry. It is at least theoretically possible that the reaction of lithium alkoxide with MgH_2 proceeds to form a THF solution of alkoxymagnesium hydride (HMgOR)[5] according to eq 7. However, if this was the

$$LiOR + MgH_2 \not\rightarrow LiH\downarrow + HMgOR \quad (7)$$

case, insoluble LiH would be formed, and yet the reaction produces a clear solution. Thus the possibility of forming HMgOR compounds (eq 7) does not seem likely. However, when the THF solvent from the reaction product (eq 4) was removed under vacuum and the resulting solid analyzed by X-ray powder diffraction,[18] lines due to the corresponding magnesium alkoxide were observed, suggesting disproportionation (eq 8) when the solvent is removed. In

$$2LiMgH_2(OR) \rightarrow Li_2MgH_4 + Mg(OR)_2 \quad (8)$$

solution, however, the integrity of $LiMgH_2(OR)$ compounds has been confirmed by infrared (Figure 1) and NMR spectral analysis (Figure 2) as well as molecular association studies.[18] Figure 1 shows that in the 1450-cm^{-1} region, a distinct absorption occurs for $LiMgH_2(OR)$, $LiMgH(OR)_2$, or HMgOR compounds when R = 2,2,6,6-tetramethylcyclohexyl. However, a shoulder appears for HMgOR and $LiMgH(OR)_2$ compounds that does not appear for $LiMgH_2(OR)$ compounds in the 1300-cm^{-1} region. These similarities between HMgOR and $LiMgH(OR)_2$ compounds suggest that disproportionation might be taking place according to eq 9. On the other hand, the

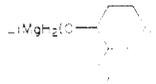
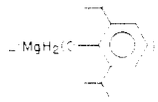
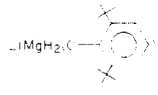
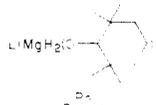
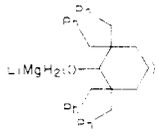
$$LiMgH(OR)_2 \rightarrow HMgOR + LiOR \quad (9)$$

NMR spectra (Figure 2) show great differences for HMgOR and $LiMgH(OR)_2$ as well as for LiOR and $LiMgH_2(OR)$ compounds in the 1.0-ppm region. A broad absorbance is observed for the HMgOR compounds; however, for $LiMgH(OR)_2$ compounds, a much cleaner spectrum is observed in addition to a change in the chemical shift of the two singlets assigned to the methyl groups on the cyclohexyl ring. HMgOR compounds show two singlets at 0.98 and 0.93 ppm, but the singlets associated with the $LiMgH(OR)_2$ compounds appear at 0.93 and 0.88 ppm. Also, the LiOR compound has only one singlet at 1.00 ppm, but as noted before, the $LiMgH(OR)_2$ and HMgOR compounds both show two singlets. The NMR spectra were all taken at the same concentration of reagent in THF-d_8 with Me_4Si as the internal standard. These observations in addition to the molecular-association studies reported earlier[18] show the separate identity of these compounds. The molecular weight data show that the HMgOR, $LiMgH_2(OR)$, and $LiMgH(OR)$ compounds are dimeric in THF. Also, it is important to note that the molecular weight results do not indicate the presence of a mixture of LiOR and HMgOR (eq 9) when $LiMgH(OR)_2$ is placed in solution.

Stereochemistry of Reduction. The $LiMgH_2(OR)$ compounds prepared by the above method were allowed to react with four representative ketones, i.e., 4-*tert*-butylcyclohexanone (I), 3,3,5-trimethylcyclohexanone (II), 2-methylcyclohexanone (III), and camphor (IV). All yields were determined by GLC as described in the Experimental Section and were based on an internal standard. The purpose of these studies was to evaluate these new hydride reagents as stereoselective reducing agents. We have compared the stereochemical results with that of $LiAlH_4$ which is considered to be the least sterically hindered hydride that reduces cyclic and bicyclic ketones. For example, $LiAlH_4$ results in 10, 80, 24, and 9% equatorial or exo attack, respectively, on ketones I, II, III, and IV. On the other hand, MgH_2 reduces ketones I, II, III, and IV

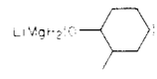
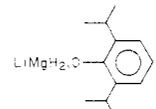
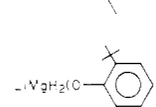
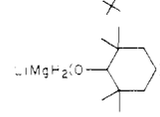
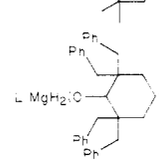
(18) Eugene C. Ashby and A. B. Goel, *Inorg. Chem.*, in press.

Table II. Reactions of 4-*tert*-Butylcyclohexanone with $LiMgH_2(OR)$ Compounds[a]

expt	hydride	rel yield, %[b,d] Ax OH	Eq OH	yield, %[c]
13	MgH_2	23	77	100
14	$LiMgH_2(OCH_3)$	60	40	95
15	$LiMgH_2(O\text{-}i\text{-}Pr)$	70	30	91
16	$LiMgH_2(O\text{-}t\text{-}Bu)$	59	41	98
17	$LiMgH_2(OCH_2\text{-}t\text{-}Bu)$	76	24	95
18	$LiMgH_2(OCHPh_2)$	76	24	90
19	$LiMgH_2(O\text{-}c\text{-}Hx)$	70	30	52
20	$LiMgH_2(OPh)$	28	72	100
21		78	22	83
22		50	50	100
23		59	41	99
24		89	11	86
25		86	14	85

[a] At room temperature in THF. [b] Normalized, % axial alcohol + % equatorial alcohol = 100%. [c] Yield was determined by GLC and was based on an internal standard. [d] Ax = axial and Eq = equatorial.

Table III. Reactions of 3,3,5-Trimethylcyclohexanone with $LiMgH_2(OR)$ Compounds[a]

expt	hydride	rel yield, %[b,d] Ax OH	Eq OH	yield, %[c]
26	MgH_2	85	15	92
27	$LiMgH_2(OCH_3)$	95	5	93
28	$LiMgH_2(O\text{-}i\text{-}Pr)$	98	2	84
29	$LiMgH_2(O\text{-}t\text{-}Bu)$	96	5	100
30	$LiMgH_2(OCH_2\text{-}t\text{-}Bu)$	99	1	88
31	$LiMgH_2(OCHPh_2)$	97	3	80
32	$LiMgH_2(O\text{-}c\text{-}Hx)$	96	4	100
33	$LiMgH_2(OPh)$	90	10	100
34		99	1	100
35		90	10	100
36		93	7	100
37		99	1	100
38		100	0	96

[a] At room temperature in THF in a 1:2 molar ratio. [b] Normalized, % axial alcohol + % equatorial alcohol = 100%. [c] Yield was determined by GLC using an internal standard. [d] Ax = axial and Eq = equatorial.

such that 23, 85, 35, and 8% equatorial or exo attack, respectively, is observed.

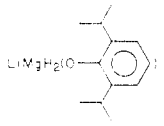
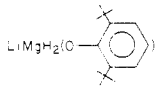
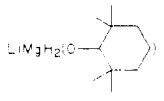
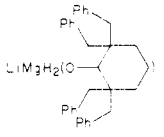
Recently, both alkoxymagnesium hydrides ($HMgOR$)[19] and (dialkylamino)magnesium hydrides ($HMgNR_2$)[20] have been prepared in this laboratory. The most selective reagent among the HMgOR compounds studied was (2,6-diisopropylphenoxy)magnesium hydride which reduced ketones I, II, III, and IV to give 83, 99, 99, and 98% equatorial or endo attack, respectively.[1] On the other hand, [(trimethylsilyl)-*tert*-butylamino]magnesium hydride was the most selective $HMgNR_2$ compound studied. This hydride reduced ketones I, II, III, and IV, giving 73, 99, 98, and 95% equatorial or endo attack, respectively.[21] With these data in hand, the $LiMgH_2(OR)$ compounds were evaluated on a comparative basis. According to Tables II–V, lithium dihydrido(2,2,6,6-tetramethylcyclohexoxy)magnesiate and lithium dihydrido(2,2,6,6-tetrabenzylcyclohexoxy)magnesiate were the most selective in the reduction of ketone I (Table II), providing 89 and 86%, respectively (expt 24 and 25), of the axial alcohol. When allowed to react with ketone II (Table III), the tetrabenzyl derivative (expt 38) produced entirely the axial alcohol. The tetramethyl- and 2-methylcyclohexoxy (expt 34) derivatives as well as the neopentyl derivative (expt 30) produced 99% of the axial alcohol when allowed to react with the ketone under the same conditions.

Both the tetramethyl and the tetrabenzyl derivatives (expt 49 and 50) reduced ketone III (Table IV) entirely to the axial alcohol. The neopentyl reagent produced 99% (expt 43) of the axial alcohol. When ketone IV (Table V) was reduced, the tetrabenzyl reagent (expt 63) again was found to be the most selective, providing 99% of the exo alcohol. The next best stereoselective reagent was the tetramethyl reagent (expt 62) which produced 97% of the exo alcohol.

From the data in Table II, it can be seen that the amount of axial alcohol increases as the steric bulk of the R group increases, particularly when one compares the unsubstituted cyclohexyl derivative (70%) to the 2-methyl derivative (78%) and to the tetramethyl derivative (89%). There is also a steady increase in the production of the axial alcohol in proceeding from the primary alkoxy group (OCH_3, 60%) to the secondary alkoxy groups (O-*i*-Pr and cyclohexoxy, 70%). As larger secondary groups are introduced into the system (expt 17, neopentyl; expt 18, benzhydryl), the amount of axial alcohol increased even further to 76%. These results support the theory of steric-approach control that predicts greater approach of the reagent from the least hindered side of the substrate as the steric requirement of the reagent increases.

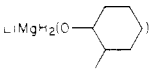
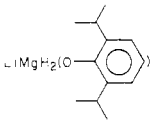
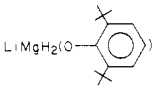
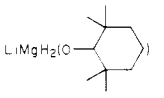
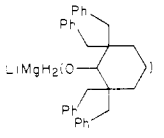
(19) Eugene C. Ashby, J. J. Lin, and A. B. Goel, *Inorg. Chem.*, in press.
(20) Eugene C. Ashby, J. J. Lin, and A. B. Goel, *Inorg. Chem.*, in press.
(21) The reagent bis(dicyclohexylamino)magnesium hydride was prepared and allowed to react under similar conditions with 4-*tert*-butylcyclohexanone, and it was observed that the amount of axial alcohol was increased from 73% for the [(trimethylsilyl)-*tert*-butylamino]magnesium hydride to 90%. This raises the possibility of using more hindered cyclohexyl substituents in order to increase the selectivity of these reagents.
(22) Eugene C. Ashby, J. J. Lin, and A. B. Goel, *J. Org. Chem.*, **43**, 1564 (1978).
(23) Eugene C. Ashby and G. E. Parris, *J. Am. Chem. Soc.*, **93**, 1206 (1971).

Table IV. Reactions of 2-Methylcyclohexanone with $LiMgH_2(OR)$ Compounds[a]

expt	hydride	rel yield, %[b,d] Ax OH	Eq OH	yield, %[c]
39	MgH_2	35	65	100
40	$LiMgH_2(OCH_3)$	71	29	94
41	$LiMgH_2$(O-*i*-Pr)	96	4	92
42	$LiMgH_2$(O-*t*-Bu)	67	33	100
43	$LiMgH_2(OCH_2$-*t*-Bu)	99	1	88
44	$LiMgH_2(OCHPh_2)$	98	2	88
45	$LiMgH_2$(O-c-Hx)	96	4	78
46	$LiMgH_2$(OPh)	38	62	100
47		66	34	100
48		67	33	95
49		100	0	87
50		100	0	85

[a] At room temperature in THF in a 1:2 ratio. [b] Normalized, % axial alcohol + % equatorial alcohol = 100%. [c] Yield was determined by GLC using an internal standard. [d] Ax = axial and Eq = equatorial.

Table V. Reactions of Camphor with $LiMgH_2(OR)$ Compounds[a]

expt	hydride	rel yield, %[b] *endo*-OH	*exo*-OH	yield, %[c]
51	MgH_2	8	92	100
52	$LiMgH_2(OCH_3)$	12	88	88
53	$LiMgH_2$(O-*i*-Pr)	8	92	100
54	$LiMgH_2$(O-*t*-Bu)	10	90	91
55	$LiMgH_2(OCH_2$-*t*-Bu)	9	91	100
56	$LiMgH_2(OCHPh_2)$	4	96	100
57	$LiMgH_2$(O-c-Hx)	15	85	52
58	$LiMgH_2$(OPh)	8	92	100
59		7	93	83
60		8	92	100
61		7	93	100
62		3	97	95
63		1	99	95

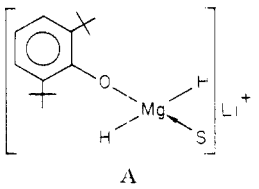
[a] At room temperature in THF in a 1:2 molar ratio. [b] Normalized, % axial alcohol + % equatorial alcohol = 100%. [c] Yield was determined by GLC using an internal standard.

It is interesting to note that the phenoxy reagents produced less axial alcohol compared to the cyclohexoxy derivatives. However, once again, even in the phenoxy series more axial alcohol was produced as the bulk of the reagent increased (expt 20, 22, and 23). The unsubstituted phenoxy reagent reduced ketone I with almost the same stereoselectivity as MgH_2 (expt 13). As diisopropyl and di-*tert*-butyl groups were introduced in the phenoxy system, the amount of axial alcohol increased to only 50 and 59%, respectively. Another observation with respect to the same point shows that the tertiary derivative (expt 16) is not as selective as expected. One might assume from these observations that a small equilibrium amount of MgH_2 is formed by disproportionation (eq 10) and that a

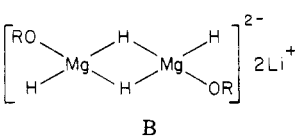
$$LiMgH_2(OR) \rightarrow MgH_2\downarrow + LiOR \qquad (10)$$

significant portion of the reduction takes place with MgH_2. This is not unreasonable since the large steric bulk of the alkoxy or aroxy groups should cause the hydride reagent to react more slowly with the ketones studied, thus allowing sufficient time for a competing side reaction (eq 10) to become significant.

Another explanation of the stereochemical results is that compounds such as $LiMgH_2OPh$ exist as a monomer (A), and $LiMgH_2$(O-*i*-Pr) exists as a dimer (B). This is not



A



B

unreasonable on the basis of past findings[24] that very large alkoxy groups are poor bridging groups compared to smaller alkoxy groups. This suggestion has been confirmed by molecular-association studies. It is clear that attack by monomer A on a ketone is less sterically hindered than attack by dimer B. It is likely that reduction takes place by displacement of the solvent (S) from A. However, since $LiMgH_2OPh$ reduction of ketone I gives practically the same results as MgH_2 reduction, it would appear more likely that disproportionation of $LiMgH_2OPh$ to MgH_2 and LiOPh (eq 10) is the major factor. It is possible that molecular association plays a significant part in the comparison of the results of the reduction of ketone I with $LiMgH_2O$-*t*-Bu and $LiMgH_2O$-*i*-Pr; however, even in these cases, disproportionation to MgH_2 is probably the more important factor.

When these same lithium alkoxymagnesium hydrides were allowed to react with ketone II, 3,3,5-trimethylcyclohexanone (Table III), the tetrabenzyl derivative (expt 38) produced only the axial alcohol. Again the phenoxy and the diisopropylphenoxy (expt 33 and 35) derivatives produced the axial alcohol in almost the same yield as did MgH_2: 90% vs. 85% (expt 26, 33, and 35). The di-*tert*-butylphenoxy derivative (expt 36) also produced a lesser amount (93%) of the axial alcohol compared to the amounts produced by the cyclohexoxy derivatives. These results can also be explained by assuming disproportion-

(24) (a) E. L. Eliel, R. J. L. Martin, and D. Nasipuri, *Org. Synth.*, **47**, 16 (1967); (b) E. L. Eliel, *Rec. Chem. Prog.*, **22**, 129 (1961); (c) J. C. Richer and E. L. Fliel, *J. Org. Chem.*, **26**, 972 (1961); (d) E. L. Eliel and D. Nasipuri, *ibid.*, **30**, 3809 (1965); (e) J. W. Huffman and J. T. Charles, *J. Am. Chem. Soc.*, **90**, 6786 (1968).

Table VI. Reaction of $LiMgH_2$(O-2,2,6,6-($PhCH_2$)-c-Hx) in THF with 4-*tert*-Butylcyclohexanone[a]

T, °C	t, s	recovered ketone, %	% alcohol[b,c] Ax	Eq
−25	2	75	91	9
	5	70	90	10
	10	67	90	10
	15	67	90	10
	30	66	90	10
	18 000	64	86	14
0	2	75	90	10
	5	67	91	9
	10	56	90	10
	15	47	90	10
	30	37	89	11
	45	37	88	12
	18 000	35	86	14
room temp	2	76	90	10
	5	65	90	10
	10	47	91	9
	15	38	92	8
	30	22	91	9
	45	15	89	11
	60	15	89	11
	18 000	15	86	14

[a] In a 2:1 ratio. [b] Normalized, % axial alcohol + % equatorial alcohol = 100%. [c] Ax = axial and Eq = equatorial.

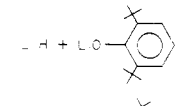
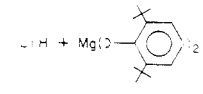
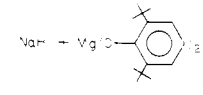
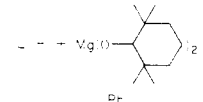
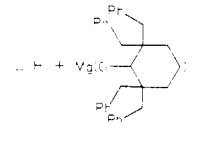
ation of the reagent to MgH_2 as suggested earlier or by assuming differences in molecular aggregation of the reagents, although disproportionation of the reagent seems more likely.

The reduction of 2-methylcyclohexanone (Table IV) with $LiMgH_2(OR)$ compounds produced the same trends described earlier for 4-*tert*-butylcyclohexanone (Table II). Once again the same low yield of axial alcohol was observed for the phenoxy derivative (expt 46, 38%) compared to that for MgH_2 (expt 39, 35%). The other phenoxy derivatives (expt 47, 66%; expt 48, 67%) as well as the *tert*-butyl derivative (expt 42, 67%) produced much less axial alcohol than would normally be expected, which is presumably due to reduction of the ketone by a small equilibrium amount of MgH_2 formed through disproportionation of the reagent (eq 10). Again, there is an increase in selectivity in proceeding from the primary methoxy group (expt 40, 71%) to the secondary isopropoxy (expt 41, 96%) or cyclohexoxy (expt 45, 96%) group of the reagent. As noted before, increasing the steric bulk of the primary alkoxy reagents, i.e., neopentoxy (expt 43), or of the secondary alkoxy reagents, i.e., benzhydryloxy (expt 44), also increased the production of the axial alcohol to 99 and 98%, respectively.

The reactions of the lithium alkoxymagnesium hydrides with camphor (Table V) produced trends similar to those noted for the other ketones except for the differences observed for the methoxy (expt 52, 12%), *tert*-butoxy (expt 54, 10%), neopentoxy (expt 55, 9%), and cyclohexoxy (expt 57, 15%) reagents. These reagents produced amounts of endo alcohol greater than that produced by MgH_2 (expt 51, 8%) alone. This observation implies that the above hydrides have less steric requirement when approaching camphor than MgH_2. This is entirely possible, considering the difference in molecular association; however, the difference in the result involving MgH_2 and the other hydrides just mentioned is not that great, and, therefore, not too much should be made of this point. Other than the observations just mentioned, the trends described earlier seem to be followed for camphor as well. An increase in stereoselectivity is observed as the steric requirement of the reagent increases: cyclohexoxy (expt 57, 15% endo alcohol) < 2-methylcyclohexoxy (expt 59, 7% endo alcohol) < 2,2,6,6-tetramethylcyclohexoxy (expt 62, 3% endo alcohol) < 2,2,6,6-tetrabenzylcyclohexoxy (expt 63, 1% endo alcohol). The phenoxy derivatives (expt 58, 8%, expt 60, 8%, and expt 61, 7% endo alcohol) provide the same selectivity as MgH_2 (8% endo alcohol) for presumably the same reasons described earlier.

Another interesting observation is that the cyclohexoxy reagent shows the lowest yield of alcohols (expt 19, 45, and 57) for the reduction of ketones I, III, and IV but not for the case of ketone II (expt 32). Enolization should be much greater in the cases of ketones I, III, and IV compared to that of II because of the greater steric hindrance in the case

Table VII. Reactions of Cyclic and Bicyclic Ketones with Metal Hydride and Magnesium Alkoxide[a]

expt	reagents (expt no.)	4-*tert*-butylcyclohexanone (I) Ax[b] OH	Eq[b] OH	yield,[c] %	3,3,5-trimethylcyclohexanone (II) Ax[b] OH	Eq[b] OH	yield,[c] %	2-methylcyclohexanone (III) Ax[b] OH	Eq[b] OH	yield,[c] %	camphor (IV) *exo*-OH[b]	*endo*-OH[b]	yield,[c] %
64		74	26	28							91	9	30
65		81	19	80	100	0	90	99	1	85	95	5	100
66		55	45	10							90	10	36
67		89	1	30	100	0	60	99	1	65	97	3	87
68		85	15	37	100	0	55	99	1	60	96	4	81

[a] At room temperature in a 1:2 molar ratio for 24 h. [b] Normalized, % axial alcohol + % equatorial alcohol = 100%. Ax = axial and Eq = equatorial. [c] Yield was determined by GLC using an internal standard.

of ketone II. Why enolization is greater for the cyclohexoxy derivative compared to the other hydrides is not clear, especially in its comparison to $LiMgH_2OPh$. One explanation is that the amount of axial alcohol produced in the reaction of every ketone with $LiMgH_2OPh$ is very nearly the same as that observed for MgH_2. Thus if MgH_2 is the reducing agent for $LiMgH_2OPh$ and MgH_2 gives 100% yield in each case, it is not surprising that those hydride reagents that disproportionate to MgH_2 give no enolization as is observed in the case of MgH_2.

It was desired to determine if the degree of stereoselectivity was higher in the initial stages of the reaction than after equilibrium had a chance to take place. In this connection, 4-*tert*-butylcyclohexanone was allowed to react with a 100% excess of lithium (2,2,6,6-tetrabenzylcyclohexoxy)dihydridomagnesiate. The results are given in Table VI. As can be seen from the data, the lower the temperature, the greater the observed enolization to reduction ratio. At −25 °C, for example, the major product (64%) after quenching is the starting ketone, 4-*tert*-butylcyclohexanone. It should also be noted that the initial reaction is very fast and that after 30 s little more than 5% change was observed in the yield of product. Also between 30 and 18000 s, less than 5% change was observed in the ratio of alcohols. The thermodynamic product is the equatorial alcohol, and if 4-*tert*-butylcyclohexanone is allowed to react under the equilibrium conditions inherent for Meerwein–Ponndorf–Verley or Birch reductions, the equatorial alcohol is produced in 98–99% yield. For lithium alkoxymagnesium hydride reductions, never less than 86% of the axial alcohol is observed; therefore, if equilibration is taking place, it is taking place very slowly.

Table VII (expt 64–68) lists the results of the reactions of ketones I, II, III, and IV with lithium dialkoxymagnesium hydrides prepared according to eq 5. The most selective reagents were the bis(tetramethylcyclohexoxy) and bis(tetrabenzylcyclohexoxy) hydrides (expt 67 and 68) which reduced ketone I to provide 89 and 85% axial alcohol, respectively. However, a large amount of enolization accompanied the reactions (70 and 63%, respectively). On the other hand, expt 65 shows that the bis di-*tert*-butyl derivative enolized only 20% of the ketone while reducing the ketone to 81% of the axial alcohol. The sodium reagent (expt 66) not only produced a 55:45 axial to equatorial alcohol ratio but also enolized 90% of the ketone. When LiH and LiOR were allowed to react under similar conditions (expt 64), a 74:26 ratio of axial to equatorial alcohol was observed, but 72% of the ketone was enolized.

When ketones II, III, and IV were allowed to react with these reagents, lesser amounts of enolization were observed with very stereoselective results. All the reagents studied produced 99 and 100% axial alcohol when allowed to react with ketones II and III, respectively. The reactions with camphor (ketone IV) produced greater than 90% exo alcohol with little enolization except for expt 64 and 66 which produced 70 and 64%, respectively, of the starting ketone. These reagents represent a method of using lithium and sodium hydride for reduction which has not been previously reported.

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Registry No. $LiMgH_2(OCH_3)$, 72749-25-8; $LiMgH_2$(O-*i*-Pr), 72749-26-9; $LiMgH_2$(O-*t*-Bu), 72749-27-0; $LiMgH_2(OCH_2$-*t*-Bu), 72749-28-1; $LiMgH_2(OCHPh_2)$, 72749-12-3; $LiMgH_2$(O-c-C_6H_{11}), 72749-13-4; $LiMgH_2(OPh)$, 72749-14-5; lithium [(2-methylcyclohexyl)oxy]magnesium hydride, 72749-15-6; lithium (2,6-diisopropylphenoxy)magnesium hydride, 72749-16-7; lithium (2,6-di-*tert*-butylphenoxy)magnesium hydride, 72749-17-8; lithium [(2,2,6,6-tetramethylcyclohexyl)oxy]magnesium hydride, 72749-18-9; lithium [(2,2,6,6-tetrabenzylcyclohexyl)oxy]magnesium hydride, 72749-19-0; lithium methoxide, 865-34-9; lithium isopropoxide, 2388-10-5; lithium *tert*-butoxide, 1907-33-1; lithium 2,2-dimethylpropoxide, 3710-27-8; lithium diphenylmethoxide, 2036-66-0; lithium cyclohexyl oxide, 4111-51-7; lithium phenoxide, 555-24-8; lithium 2-methylcyclohexyl oxide, 72727-48-1; lithium 2,6-diisopropylphenoxide, 72727-49-2; lithium 2,6-di-*tert*-butylphenoxide, 55894-67-2; lithium 2,2,6,6-tetramethylcyclohexyl oxide, 72727-50-5; lithium 2,2,6,6-tetrabenzylcyclohexyl oxide, 72727-51-6; magnesium hydride, 7693-27-8; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *cis*-3,3,5-trimethylcyclohexanol, 933-48-2; *trans*-3,3,5-trimethylcyclohexanol, 767-54-4; 2,2,6,6-tetrabenzylcyclohexanol, 3849-12-5; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; *endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 507-70-0; *exo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 124-76-5; [(2,2,6,6-tetramethylcyclohexyl)oxy]magnesium hydride, 72727-52-7; lithium bis[(2,2,6,6-tetramethylcyclohexyl)oxy]magnesium hydride, 72749-24-7; 2,2,6,6-tetramethylcyclohexanone, 1195-93-3; 2,2,6,6-tetrabenzylcyclohexanone, 7382-13-0; 2,2,6,6-tetramethylcyclohexanol, 6948-41-0.

Hydrometalation. 5. Hydroalumination of Alkenes and Alkynes with Complex Metal Hydrides of Aluminum in the Presence of Cp_2TiCl_2

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Terminal alkenes and internal alkynes are reduced rapidly and in high yield by reaction with $LiAlH_4$, $NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, $LiAlH_2(NR_2)_2$, $NaAlH_2(NR_2)_2$, or Vitride [$NaAlH_2(OCH_2CH_2OCH_3)_2$] in the presence of a catalytic amount of Cp_2TiCl_2 in THF at room temperature. When these reactions were quenched with D_2O or I_2, quantitative yields of the corresponding deuterium or iodine compounds were obtained in most cases. This method provides a convenient and high-yield route to alkyl- and vinylaluminum compounds as intermediates in organic synthesis.

Considerable interest in recent years has been directed toward the development of carbometalation and hydrometalation reactions involving alkenes and alkynes. The reasons for this interest are clear: first, alkenes and alkynes are very fundamental and economic building blocks for more complex organic compounds, and second, carbometalation and hydrometalation provide routes to form carbon–metal bonds which can then be functionalized

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