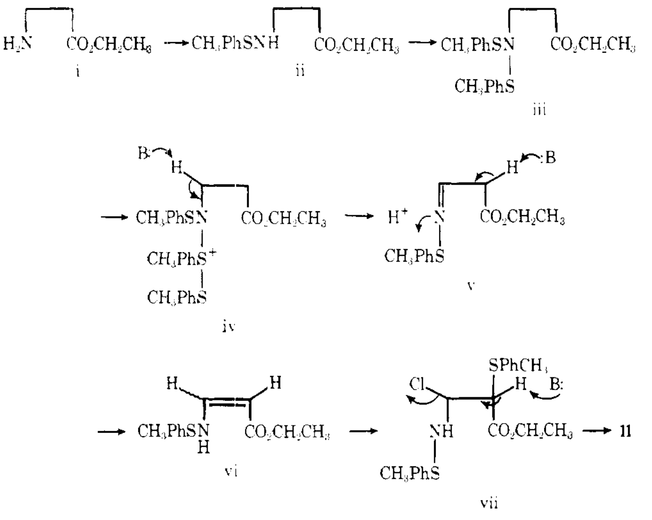

(7) Previously it was noted[1] that 7-(sulfenimino)cephalosporins and 6-(sulfenimino)penicillins underwent a reaction (triphenylphosphine, silica gel, CH_2Cl_2, 26 °C) to give 7(6)-α-*p*-tolylthioamines which we have termed sulfenyl transfer rearrangement. In contrast, amino acid derived sulfenimines **4** and **5** did not lead to isolable α-tolylthioamines under these conditions.

(8) (a) F. A. Davis and E. B. Skibo, *J. Org. Chem.*, **39**, 807 (1974); (b) F. A. Davis, A. J. Friedman, and E. W. Kluger, *J. Am. Chem. Soc.*, **96**, 5000 (1974); (c) F. A. Davis, J. M. Kaminski, E. W. Kluger, and H. S. Freilich, *J. Am. Chem. Soc.*, **97**, 7085 (1975); (d) F. A. Davis and P. A. Mancinelli, *J. Org. Chem.*, **43**, 1797 (1978); (e) F. A. Davis, A. J. Friedman, and U. K. Nadir, *J. Am. Chem. Soc.*, **100**, 2844 (1978); (f) F. A. Davis and P. A. Mancinelli, *J. Org. Chem.*, **42**, 399 (1977).

(9) The little chemistry known concerning sulfenimines (thiooximes) has been summarized in Davis's review on sulfenamides. F. A. Davis, *Int. J. Sulfur Chem.*, **8**, 71 (1973).

(10) Various methods of preparation, see also ref 9: (a) F. A. Davis, W. A. R. Slegeir, S. Evans, A. Schwartz, D. L. Goff, and R. Palmer, *J. Org. Chem.*, **38**, 2809 (1973); (b) F. A. Davis, A. J. Friedman, E. W. Kluger, E. B. Skibo, E. R. Fretz, A. P. Milicia, W. C. LeMasters, M. D. Bentley, J. A. Lacadie, and I. B. Douglass, *ibid.*, **42**, 967 (1977); (c) T. Saito and T. Hiraoka, *Chem. Pharm. Bull. Jpn.*, **25**, 784, 792 (1977); (d) T. Kobayashi, K. Iino, and T. Hiraoka, *J. Am. Chem. Soc.*, **99**, 5505 (1977).

(11) This point was first made by Davis.[9,10a]

(12) M. Brenner and W. Huber, *Helv. Chim. Acta*, **36**, 1109 (1953).

A New, Convenient, and Stereospecific Method for the Dehydration of Alcohols. The Thermal Decomposition of Magnesium, Zinc, and Aluminum Alkoxides. A Mechanistic Study

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Alkoxides of magnesium, zinc, and aluminum thermally decompose at 195–340 °C to give a hydrocarbon, an olefin, and a metal oxide. Kinetic and stereochemical studies indicate that a cyclic, unimolecular six-center transition state is involved. This reaction represents the conversion of an alcohol to an olefin in a stereochemical syn manner and compares favorably as an alternative to the Chugaev and acetate pyrolysis reactions.

Several methods are known for the dehydration of alcohols to olefins.[1] These methods include the pyrolysis of esters of carboxylic acids[2,3] and the pyrolysis of xanthates (Chugaev reaction).[4–6] Both reactions involve a syn elimination to produce an olefin. The pyrolysis of esters occurs at 300–600 °C, usually in the vapor phase. The yields are reasonable, but carbon skeleton rearrangements can occur due to the high temperature involved. The Chugaev reaction occurs at 100–250 °C, but preparation of the xanthate may proceed in low yield. The pyrolysis product is often contaminated with sulfur-containing impurities which are usually removed by distillation from sodium metal with an accompanying decrease in yield.

This report concerns a new type of thermal decomposition reaction that compares favorably with the above mentioned reactions and offers an alternative method for the dehydration of alcohols to olefins. The alkoxides of magnesium, zinc, and aluminum have been well characterized[7] and have been evaluated as stereoselective alkylating agents.[8] We now wish to report our study concerning their thermal decomposition.

Results

Magnesium, zinc, and aluminum alkoxides are prepared quantitatively by the reaction of a suitable alkyl or aryl metal compound with an alcohol. This general reaction is

$$(CH_3)_2Mg + Ph_2C(CH_3)OH \rightarrow CH_3MgOC(CH_3)Ph_2 + CH_4 \quad (1)$$

$$Ph_2Zn + i\text{-PrOH} \rightarrow PhZnO\text{-}i\text{-Pr} + PhH \quad (2)$$

$$Ph_3Al + C_6H_{11}OH \rightarrow Ph_2AlOC_6H_{11} + PhH \quad (3)$$

Details of the preparation are given in the Experimental Section and are summarized in Tables I–III. Then, in a second step, the alkoxide is thermally decomposed as illustrated

$$CH_3MgOC(CH_3)Ph_2 \xrightarrow{\Delta} CH_4 + Ph_2C{=}CH_2 + MgO \quad (4)$$

$$PhZnO\text{-}i\text{-Pr} \xrightarrow{\Delta} PhH + CH_3CH{=}CH_2 + ZnO \quad (5)$$

$$Ph_2AlOC_6H_{11} \xrightarrow{\Delta} PhH + \text{cyclohexene} + [PhAlO]_x \quad (6)$$

The products are hydrocarbon, olefin, and metal oxide.

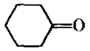
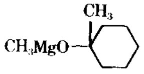
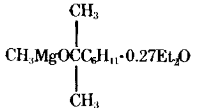
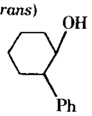
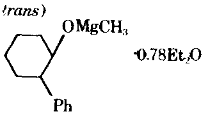
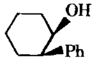
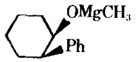
DTA–TGA Data. The decomposition reaction was studied by DTA–TGA (differential thermal analysis–thermogravimetric analysis).[9] These data are summarized in Tables IV–VI. Samples of alkoxides were decomposed under vacuum at 4 °C/min from 25 to 450 °C. Typical DTA–TGA curves are shown in Figures 1–3. The DTA–TGA curves have several common characteristics, i.e., the decomposition is endothermic, coordinated solvent is lost first, and then the main decomposition occurs in one step with no apparent intermediate formed. Both condensable and noncondensable evolved gases are detected and analysis of the product after decomposition indicates that the residue is the corresponding metal oxide.

Some of the compounds studied were volatile. Sublimation of the alkoxides was especially predominant for the dimethylaluminum alkoxides and some of the alkoxides of magnesium and zinc (mainly the isopropoxides and *tert*-butoxides). An additional problem encountered was the disproportionation of methylzinc alkoxides during preparation and removal of solvent (30% disproportionation for methylzinc cyclohexyl oxide, eq 7).

$$2CH_3ZnOC_6H_{11} \rightarrow CH_3ZnCH_3\uparrow + Zn(OC_6H_{11})_2 \quad (7)$$

0022-3263/79/1944-1221$01.00/0

Table I. Preparation of HMgOR′, CH$_3$MgOR′, PhMgOR′, and PhCH$_2$MgOR′ Compounds

expt. no.	Reactants (mmol)		registry no.	reaction time, h	Anal. %				Anal., ratio				product	registry no.
	MgR$_2$	R′OH			Mg	R	R′O	solvent	Mg	R	R′O	solvent		
1	MgH$_2$[a] (5.00)	*i*-PrOH (4.97)	67-63-0	16	22.8	0.92	56.0	20.3	1.00	0.98	1.01	0.30	HMgO-*i*-Pr·0.30THF	32149-53-4
2	MgH$_2$ (4.52)	*t*-BuOH (4.55)	75-65-0	20	18.3	0.73	56.6	24.4	1.00	0.97	1.03	0.45	HMgO-*t*-Bu·0.45THF	32149-54-5
3	MgH$_2$ (5.45)	C$_6$H$_{11}$OH (5.40)	108-93-0	24	19.1	0.82	77.2	2.84	1.00	1.04	6.95	0.05	HMgOC$_6$H$_{11}$·0.05THF	68986-37-8
4	MgH$_2$ (4.76)	PhCH$_2$CH$_2$OH (4.75)	60-12-8	20	11.0	0.46	54.3	34.3	1.00	1.02	0.99	1.03	HMgOCH$_2$CH$_2$Ph·1.03THF	68986-38-9
5	Mg(CH$_3$)$_2$[b] (5.00)	EtOH (4.95)	64-17-5	1	28.8	17.8	53.4	0.0	1.00	1.11	0.95	0.00	CH$_3$MgOEt	69027-49-2
6	Mg(CH$_3$)$_2$ (5.01)	*i*-PrOH (4.95)		0.5	25.7	14.9	59.4	0.0	1.00	0.94	0.95	0.00	CH$_3$MgO-*i*-Pr[1]	56485-24-6
7	Mg(CH$_3$)$_2$ (5.00)	*t*-BuOH (5.00)		0.5	21.3	13.3	65.3	0.0	1.00	1.01	1.02	0.00	CH$_3$MgO-*t*-Bu	18792-95-5
8	Mg(CH$_3$)$_2$ (5.00)	C$_8$H$_{17}$OH (5.09)	111-87-5	1	13.8	8.5	73.5	4.2	1.00	0.98	1.02	0.10	CH$_3$MgOC$_8$H$_{17}$·0.10Et$_2$O	68986-39-0
9	Mg(CH$_3$)$_2$ (5.02)	C$_6$H$_{11}$OH (4.98)		0.5	18.1	11.2	70.8	0.0	1.00	1.00	0.96	0.00	CH$_3$MgOC$_6$H$_{11}$	68986-40-3
10	Mg(CH$_3$)$_2$ (5.00)	PhCH$_2$CH$_2$OH (5.05)		0.5	15.1	6.95	76.6	0.0	1.00	0.89	1.02	0.00	CH$_3$MgOCH$_2$CH$_2$Ph	68986-41-4
11	Mg(CH$_3$)$_2$ (4.98)	Ph$_2$C=O (5.00)	119-61-9	0.5	7.84	4.89	62.9	24.4	1.00	1.01	0.99	1.02	CH$_3$MgOC(CH$_3$)Ph$_2$·1.0Et$_2$O	56485-23-5
12	Mg(CH$_3$)$_2$ (5.00)	 (4.97)	108-94-1	0.5	16.2	9.73	74.0	0.0	1.00	0.97	0.98	0.00		13132-21-3
13	Mg(CH$_3$)$_2$ (24.5)	*threo*-PhCHCH$_3$CHPhOH (24.6)	7693-85-8	0.5	8.15	4.43	75.0	12.4	1.00	0.88	1.06	0.50	*threo*-PhCHCH$_3$CHPhO-MgCH$_3$·0.50Et$_2$O	68986-42-5
14	Mg(CH$_3$)$_2$ (11.3)	*erythro*-PhCHCH$_3$CHPhOH (11.2)	56844-75-8	0.5	8.48	5.87	72.2	13.4	1.00	1.12	0.98	0.52	*erythro*-PhCHCH$_3$CH-PhOMgCH$_3$·0.52Et$_2$O	68986-43-6
15	Mg(CH$_3$)$_2$ (5.00)	CH$_3$CC$_6$H$_{11}$ (5.02)	823-76-7	0.5	12.1	7.5	70.6	9.8	1.00	0.98	0.99	0.27	 $CH_3MgOC(CH_3)_2C_6H_{11}\cdot 0.27Et_2O$	68986-44-7
16	Mg(CH$_3$)$_2$ (6.79)	(*trans*)  (6.78)	2362-61-0	1	8.9	5.5	64.4	21.2	1.00	0.69	0.95	0.78	(*trans*) 	68986-45-8
17	Mg(CH$_3$)$_2$ (3.00)	(*cis*)  (3.02)	16201-63-1	1	17.8	11.0	71.2	0.0	1.00	0.95	0.99	0.00	(*cis*) 	68986-46-9
18	Mg(CH$_3$)$_2$ (5.07)	C$_6$H$_{11}$OH (10.02)		24(60 °C)	10.9	0.0	89.1	0.0	1.00	0.00	1.95	0.00	Mg(OC$_6$H$_{11}$)$_2$	68986-47-0
19	Mg(CH$_3$)$_2$ (14.92) PhOH (14.90)	C$_6$H$_{11}$OH (14.92)	108-95-2	12(66 °C)	10.2	0.0 41.7	39.1	9.0	1.00	0 1.00	0.99	0.30	C$_6$H$_{11}$OMgOPh·0.30THF	68986-48-1
20	Ph$_2$Mg[c]	EtOH		1	16.1	51.1	29.9	3.9	1.00	0.99	1.02	0.06	PhMgOEt·0.06Et$_2$O	10175-38-9

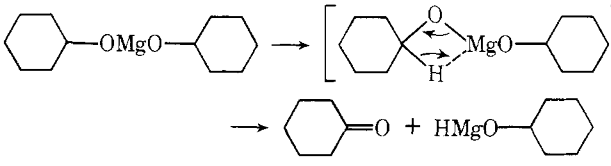
	(5.00)	(5.05)										
21	Ph_2Mg (4.02)	i-PrOH (4.02)		1	14.1	44.7	34.3	6.9	1.00 1.02 1.02	0.16	$PhMgO$-i-$Pr·0.16Et_2O$	25079-50-9
22	Ph_2Mg (9.70)	$PhCH_2CH_2OH$ (9.65)		2	10.9	35.1	54.1	0.0	1.00 1.02 1.00	0.00	$PhMgOCH_2CH_2Ph$	68986-49-2
23	Ph_2Mg (4.64)	$C_6H_{11}OH$ (4.62)		1	6.4	20.4	26.3	46.9	1.00 0.97 1.01	2.39	$PhMgOC_6H_{11}·2.39Et_2O$	68986-50-5
24	Ph_2Mg (3.07)	$Ph_2C(CH_3)OH$ (3.09)	599-67-7	1	6.4	20.1	51.5	22.0	1.00 0.94 0.99	1.14	$PhMgOC(CH_3)Ph_2·$ $1.14Et_2O$	68986-51-6
25	$Mg(CH_2PH)_2$[d] (1.74)	EtOH (1.75)		1	12.4	46.5	23.0	18.1	1.00 0.95 0.97	0.48	$PhCH_2MgOEt·0.48Et_2O$	68986-52-7
26	$Mg(CH_2Ph)_2$ (3.17)	i-PrOH (3.19)		1	11.3	42.2	27.3	19.2	1.00 0.99 1.01	0.56	$PhCH_2MgO$-i-$Pr·0.56Et_2O$	68986-18-5
27	$Mg(CH_2Ph)_2$ (3.30)	$C_6H_{11}OH$ (3.25)		1	8.7	32.6	35.4	23.3	1.00 0.95 0.98	0.88	$PhCH_2MgOC_6H_{11}·0.88Et_2O$	68986-19-6
28	$Mg(CH_2Ph)_2$ (2.85)	$Ph_2C(CH_3)OH$ (2.89)		1	6.0	22.5	48.7	22.8	1.00 1.16 1.05	1.25	$PhCH_2MgOC(CH_3)Ph_2·$ $1.25Et_2O$	68986-20-9
29	$Ph_2C(CH_3)$- $OMgCH_3$[e] (10.0)	HN-i-Pr_2 (39.0)	108-18-9	48 (66 °C)	5.8	23.7	46.6	23.9	1.00 0.95 0.97	1.00	$Ph_2C(CH_3)OMgN$-i-$Pr_2·$ $1.00HN$-i-Pr_2	68986-21-0
30	$(CH_3)_2Mg$ (5.24)	$(CD_3)_2CHOH$ (5.24)	3976-29-2	1	24.7	15.3	60.0	0.0	1.00 1.02 0.99	0.00	$CH_3MgOCH(CD_3)_2$	68986-22-1
31	Ph_2Mg (8.41)	$(CD_3)_2CHOH$ (8.43)		1	12.5	39.5	41.5	6.5	1.00 0.98 1.04	0.17	$PhMgOCH(CD_3)_2·0.17Et_2O$	68986-23-2
32	$(PhCH_2)_2Mg$ (3.77)	$(CD_3)_2CHOH$ (3.77)		1	10.8	40.5	36.2	12.5	1.00 0.98 1.03	0.38	$PhCH_2MgOCH(CD_3)_2·$ $0.38Et_2O$	68986-24-3

[a] Registry no.: 7693-27-8. [b] Registry no.: 2999-74-8. [c] Registry no. 555-54-4. [d] Registry no.: 6928-77-4. [e] Registry no.: 56485-23-5.

Comparisons among alkoxides having the same alkoxy group and metal but different alkyl groups indicate certain trends. For the isopropoxymagnesium compounds the order of increasing decomposition temperature was CH_3 (215 °C) < $PhCH_2$ (290 °C) < Ph (310 °C) < H (340 °C). The order for the cyclohexyloxyzinc compounds ($RZnOC_6H_{11}$) was CH_3 (295 °C) < Ph (310 °C) and that for the 1,1-diphenylethoxymagnesium and cyclohexyloxymagnesium compounds showed decomposition for the methyl and phenyl compounds at the same temperature (270 °C). Insufficient data was available to determine a trend for all aluminum compounds due to the problem of sublimation. A comparison of phenylcyclohexyloxymetal compounds in which only the identity of the metal changes exhibited an increase in decomposition temperature in the order of Al < Zn < Mg.

For alkoxides with the same alkyl group and metal there are apparently conflicting trends in the decomposition temperatures. In the case of methylmagnesium alkoxides, the order of increasing decomposition temperature parallels an approximate increase in the stability of the olefin product.[10] However, for the phenylmagnesium alkoxides the decomposition temperature follows an approximate decrease with the stability of the olefinic product. The cyclohexyloxy group appears to be out of order in both comparisons. The benzylmagnesium alkoxides show the order $OC(CH_3)PH_2$ < OEt < O-i-Pr < OC_6H_{11} and the phenylzinc alkoxides decompose in the order O-i-Pr < OEt < $OC(CH_3)Ph_2$ < OC_6H_{11}. Obviously, the order of decomposition is dependent not only on the type of alkyl or aryl groups on the metal but also on the type of metal and alkoxy group.

The dialkoxy magnesium and zinc compounds were found to decompose in two steps. The first step involves an α-hydrogen elimination to yield a ketone and the intermediate alkoxy metal hydride which is the reverse of a hydride reduction of a ketone. The intermediate then decomposes to give hydrogen and an olefin in a β-hydrogen elimination. These reactions are illustrated in eq 8 and 9 for dicyclohexyloxymagnesium (see also Table X for yield data).



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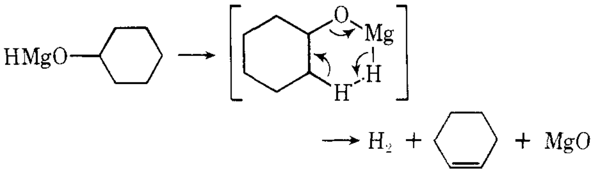


(9)

In general, there is no evidence to support the formation of an intermediate in the decomposition of the methylmetal alkoxides. The DTA–TGA traces show no break in the TGA curve. Only one compound fails to decompose completely, i.e., phenylzinc ethoxide. This compound eliminates benzene and gives a product of empirical formula $[ZnOCH_2CH_2]_x$ as determined by hydrolysis of the material remaining in the crucible after the DTA–TGA determination. The compound is not soluble in typical organic solvents and is only slowly decomposed with dilute sulfuric acid. Such behavior is typical of a polymeric material.

Stereochemistry. Our postulated mechanism for the decomposition of alkylmetal alkoxides involves the formation of a cyclic six-center transition state. This concept is illustrated for methylmagnesium *threo*-1,2-diphenyl-1-propoxide in Figure 4. An incipient methyl carbanion abstracts a β hydrogen from the alkoxy group to give methane, *cis*-1,2-diphenylpropene, and magnesium oxide. In the actual experi-

Table II. Preparation of HZnOR, CH_3ZnOR', and PhZnOR′ Compounds

expt	reactants (mmol)		reaction time,	Anal., %				Anal., ratio					registry
no.	R_2Zn	R′OH	h	Zn	R	R′O	solvent	Zn	R	R′O	solvent	product	no.
1	ZnH_2[a] (4.03)	$C_6H_{11}OH$ (4.00)	24	33.4	0.5	50.6	15.5	1.00	0.94	1.00	0.42	$HZnOC_6H_{11}\cdot 0.42THF$	68986-25-4
2	Me_2Zn[b] (4.50)	*i*-PrOH (4.48)	2	43.3	9.9	39.1	7.7	1.00	0.99	1.01	0.16	CH_3ZnO-*i*-Pr·0.16THF	10217-79-5
3	Me_2Zn (5.72)	$C_6H_{11}OH$ (5.82)	24 (40 °C)	31.5	7.2	47.7	13.6	1.00	0.71	0.95	0.39	$CH_3ZnOC_6H_{11}\cdot 0.39 THF$	68986-26-5
4	Me_2Zn (6.21)	$C_6H_{11}OH$ (12.40)		24.8	0.0	75.2	0.0	1.00	0.00	2.02	0.00	$Zn(OC_6H_{11})_2$	68986-27-6
5	Me_2Zn (4.25)	$Ph_2C(CH_3)OH$ (4.20)	2	23.6	4.0	72.2	0.0	1.00	0.77	1.02	0.00	$CH_3ZnOC(CH_3)Ph_2$	68986-28-7
6	Ph_2Zn[c] (4.35)	EtOH (4.30)	3	34.9	41.1	24.0	0.0	1.00	1.05	0.95	0.00	PhZnOEt	10217-78-4
7	Ph_2Zn (3.70)	*i*-PrOH (3.70)	2	32.5	38.2	29.3	0.0	1.00	1.01	0.99	0.00	PhZnO-*i*-Pr	10217-80-8
8	Ph_2Zn (3.68)	*t*-BuOH (3.65)	3	30.4	35.7	33.9	0.0	1.00	1.02	0.99	0.00	PhZnO-*t*-Bu	10217-82-0
9	Ph_2Zn (5.15)	$C_6H_{11}OH$ (5.12)	24	27.1	31.9	41.0	0.0	1.00	0.95	0.97	0.00	$PhZnOC_6H_{11}$	68986-29-8
10	Ph_2Zn (3.52)	$Ph_2C(CH_3)OH$ (3.50)	2	16.9	19.9	51.0	12.2	1.00	1.03	1.01	0.65	$PhZnOC(CH_3)Ph_2\cdot 0.65THF$	68986-30-1
11	Ph_2Zn (4.37)	$(CD_3)_2CHOH$ (4.38)	1	29.3	34.5	36.2	0.0	1.00	0.98	0.99	0.00	$PhZnOCH(CD_3)_2$	68986-31-2
12	Ph_2Zn (5.24)	CD_3CD_2OH[d] (5.26)	1	34.0	40.0	26.0	0.0	1.00	0.98	1.02	0.00	$PhZnOCD_2CD_3$	68986-32-3

[a] Registry no.: 14018-82-7. [b] Registry no.: 544-97-8. [c] Registry no.: 1078-58-6. [d] Registry no.: 1859-08-1.

Table III. Preparation of $(CH_3)_2AlOR'$ and PH_2AlOR' Compounds

expt	reactants (mmol)		reaction	Anal., %				Anal., ratio					registry
no.	R_3Al	R′OH	time, h	Al	R	R′O	solvent	Al	R	R′O	solvent	product	no.
1	Me_3Al[a] (4.25)	HOC_6H_{11} (4.20)	2	15.5	17.2	56.7	10.6	1.00	1.70	1.05	0.25	$Me_2AlOC_6H_{11}\cdot 0.25Et_2O$	69027-50-5
2	Ph_3Al[b] (2.36)	*i*-PrOH (2.32)	3	10.2	58.1	22.3	9.4	1.00	2.04	1.04	0.34	Ph_2AlO-*i*-Pr·$0.34Et_2O$	36164-82-6
3	Ph_3Al (3.12)	HOC_6H_{11} (3.10)	10	8.5	48.6	31.2	11.7	1.00	2.02	0.95	0.50	$Ph_2AlOC_6H_{11}\cdot 0.50Et_2O$	68986-33-4
4	Ph_3Al (2.75)	$HOC(CH_3)Ph_2$ (2.72)	3	5.2	29.8	38.2	26.8	1.00	2.10	1.02	1.87	$Ph_2AlOC(CH_3)Ph_2\cdot 1.87Et_2O$	68986-34-5
5	HAl(N-*i*-$Pr_2)_2$[c] (4.04)	$Ph_2C(CH_3)OH$ (4.05)	1	5.4	40.0	39.5	15.1	1.00	1.92	0.98	0.97	$Ph_2C(CH_3)OAl$(N-*i*-$Pr_2)_2\cdot 0.97PhH$	68986-35-6

[a] Registry no.: 75-24-1. [b] Registry No.: 841-76-9. [c] Registry no.: 2826-40-6.

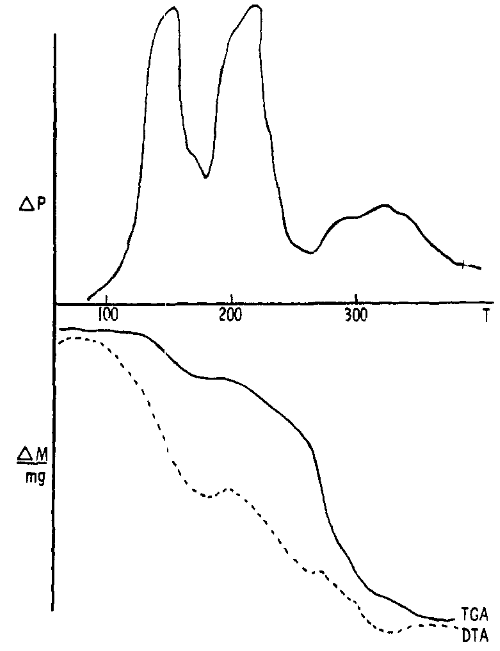


Figure 1. Vacuum DTA-TGA of $CH_3MgOC(CH_3)Ph_2\cdot1.0Et_2O$.

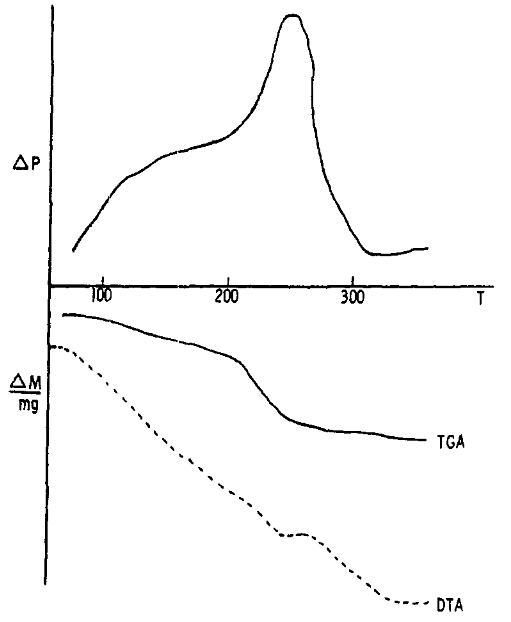


Figure 2. Vacuum DTA-TGA of PhZnO-*i*-Pr.

ment it was necessary to use triphenylphosphine to prevent isomerization of the cis olefin product by the magnesium oxide byproduct, which acts as a Lewis acid catalyst. The result of the reaction is the formation of 100% *cis*-1,2-diphenylpropene in about 70% yield. The corresponding methylmagnesium *erythro*-1,2-diphenylpropoxide gives 100% *trans*-1,2-diphenylpropene in about 65% yield.

Kinetics. (a) Kinetic Isotope Effect. Several alkoxides were prepared in which the alkoxy portion was deuterated in the β position. The deuterated and nondeuterated alkoxides were decomposed via DTA–TGA at a constant temperature (235 °C). First-order rate constants were determined by following the loss in weight of the alkoxide due to the formation of volatile reaction products. A linear least-squares plot of the natural logarithm of moles of alkoxide vs. time in minutes gave the first-order rate constants summarized in Table VII. Kinetic isotope effects (k_H/k_D) were calculated by taking the

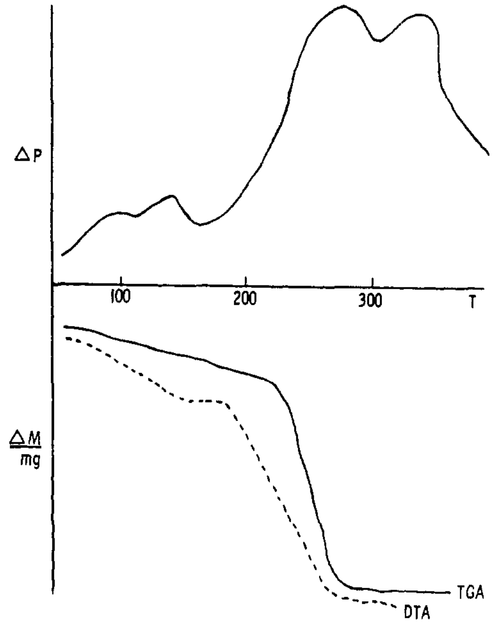


Figure 3. Vacuum DTA—TGA of $Ph_2AlOC_6H_{11}\cdot0.50Et_2O$.

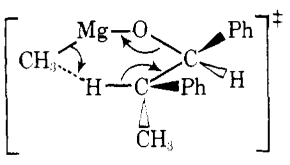


Figure 4.

ratio of the rate of decomposition of the nondeuterated alkoxide to the rate of decomposition of the deuterated alkoxide.

(b) Determination of Activation Parameters. Kinetic studies were carried out at constant temperature on several alkoxides using DTA–TGA as a means of determining the rate of decomposition. The rate constants were determined as before for several alkoxides and are summarized in Table VIII. The frequency factor (A) and experimental activation energy (E_a) were calculated from the Arrhenius equations, $k = Ae^{-E_a/RT}$ with the aid of a least-squares plot of log k vs. $1/T$, where T is the absolute temperature. The energics of activation were obtained by use of the equation $E_a = -2.303R \times$ slope, and the frequency factors were calculated from the Arrhenius equation where the intercept = log A. Having calculated E_a and A values for a given compound, it was then possible to calculate an entropy of activation ($\Delta S^{\ddagger}$) at a specific temperature using the equation of O'Connor and Nace,[11] $\Delta S^{\ddagger} = 2.303R \log A - 2.303R \log [Ke(K'T/h)]$, where K' is the Boltzman constant, h is Planck's constant, and K is the transmission coefficient (assumed to be unity). The activation parameters are listed in Table IX. The correlation coefficient, a measure of the fit of the experimental data to a straight line, is ideally unity.

Product Distributions and Yields. The alkoxides were decomposed under vacuum at 270–275 °C using a Woods' metal bath and a dry ice condenser. The olefinic products were distilled from the reaction mixture and product ratios and yields were determined by GLC and NMR comparisons of authentic samples. An alternative method of decomposition involved reflux of the compounds in a diluent such as n-dodecane. The data are contained in Table X.

Several alkoxides possessed more than one type of β hydrogen, leading to mixtures of olefins. These compounds are the methylmagnesium alkoxides of 1-methyl-1-cyclohexanol,

Table IV. Thermal Decomposition of HMgOR, CH_3MgOR, PhMgOR, and $PhCH_2MgOR$ Compounds

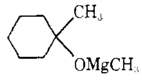
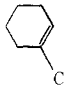
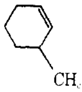
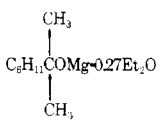
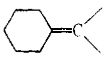
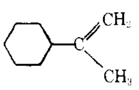
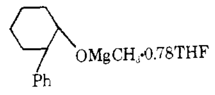
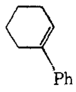
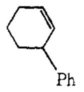
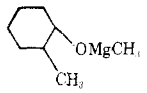
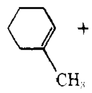
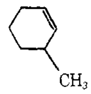
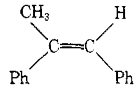
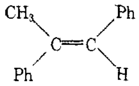
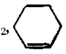
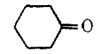
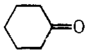
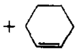
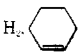
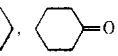
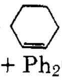
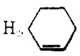
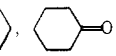
compd (sample wt, mg)	thermometric change	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
CH_3MgOEt (18.9)	endo	165–200 (185)	14.0 (74.1)	$CH_4 + CH_2{=}CH_2$, sublimation
$PhMgOEt{\cdot}0.06Et_2O$	endo	60–140 (100)	1.5 (3.3)	Et_2O
(45.1)	endo	260–440 (315)	30.0 (66.5)	$PhH + CH_2{=}CH_2$
$PhCH_2MgOEt{\cdot}0.48Et_2O$	endo	65–175 (140)	8.2 (18.1)	Et_2O
(45.4)	endo	190–355 (270)	28.3 (62.3)	$PhCH_3 + CH_2{=}CH_2$
HMgO-*i*-Pr·0.30 THF	endo	60–140 (90)	3.3 (10.6)	THF
(31.1)	endo	140–275	3.9 (12.5)	THF + some H_2
	endo	275–366 (340)	11.9 (38.3)	$H_2 + CH_3CH{=}CH_2$
CH_3MgO-*i*-Pr (27.5)	endo	200–280 (215)	25.0 (90.9)	$CH_4 + CH_3CH{=}CH_2$, sublimation
PhMgO-*i*-Pr·$0.16Et_2O$	endo	50–140 (95)	3.9 (6.7)	Et_2O
(58.1)	endo	225–425 (310)	38.6 (66.4)	$PhH + CH_3CH{=}CH_2$
$PhCH_2MgO$-*i*-Pr·$0.56Et_2O$	endo	45–157 (95)	16.0 (20.3)	Et_2O
(79.0)	endo	205–350 (290)	44.5 (56.3)	$PhCH_3 + CH_3CH{=}CH_2$
HMgO-*t*-Bu·0.45THF	endo	50–180 (115)	10.2 (21.2)	THF
(48.2)	endo	180–275	4.2 (8.7)	THF + H_2
	endo	275–365 (335)	18.9 (39.2)	$H_2 + (CH_3)_2C{=}CH_2$
CH_3MgO-*t*-Bu (96.7)	endo	110–235 (195)	91.8 (94.9)	$CH_4 + (CH_3)_2C{=}CH_2$, sublimation
$CH_3MgOC_8H_{17}{\cdot}0.10Et_2O$ (97.2)	endo	220	82.0 (84.4)	sublimation only
$HMgOC_6H_{11}{\cdot}0.05THF$	endo	60–170 (105)	1.8 (2.9)	THF
(62.3)	endo	255–430 (375)	42.0 (67.4)	H_2 + 
$CH_3MgOC_6H_{11}$ (39.2)	endo	225–380 (340)	28.5 (72.7)	CH_4 + 
$PhMgOC_6H_{11}{\cdot}2.39Et_2O$	endo	50–200 (105)	25.0 (37.8)	Et_2O
(66.2)	endo	200–395 (345)	28.0 (42.3)	PhH + 
$PhCH_2MgOC_6H_{11}{\cdot}0.88Et_2O$	endo	55–190 (120)	21.0 (23.3)	Et_2O
(90.2)	endo	245–400 (335)	53.0 (58.8)	$PhCH_3 + C_6H_{12}$
$HMgOCH_2CH_2Ph{\cdot}1.03THF$	endo	45–160 (95)	13.7 (29.2)	THF
(46.9)	endo	205–290 (270)	0.5 (10.7)	H_2
	endo	290–385 (315)	22.0 (45.9)	$PhCH{=}CH_2$
$CH_3MgOCH_2CH_2Ph$ (54.6)	endo	90–335 (270)	41.2 (75.5)	$CH_4 + PhCH{=}CH_2$
$PhMgOCH_2CH_2Ph$	endo	35–180 (105)	15.0 (29.4)	PhH
(51.0)	endo	190–330 (255)	23.3 (45.7)	$PhCH{=}CH_2$
$CH_3MgOCPh_2{\cdot}1.0Et_2O$	endo	100–185 (160)	12.5 (23.1)	Et_2O
(54.2)	endo	185–345 (270)	33.7 (62.2)	$CH_4 + Ph_2C{=}CH_2$
(*i*-Pr)$_2$NMgOC(CH$_3$)Ph$_2$·1.0	endo	140–215 (205)	15.5 (30.3)	HN-*i*-Pr$_2$
HN-*i*-Pr$_2$ (51.1)	endo	215–340 (270)	31.0 (60.7)	HN-*i*-Pr$_2$ + $Ph_2C{=}CH_2$
$PhMgOC(CH_3)Ph_2{\cdot}1.14$	endo	40–170 (85)	17.5 (22.4)	Et_2O
Et_2O (78.1)	endo	170–435 (270)	60.6 (77.6)	$PhH + Ph_2C{=}CH_2$
$PhCH_2MgOC(CH_3)Ph_2{\cdot}1.25$	endo	55–180 (105)	23.0 (22.9)	Et_2O
Et_2O (100.6)	endo	180–360 (260)	65.0 (64.6)	$PhCH_3 + Ph_2C{=}CH_2$
 (58.6)	endo	230–340 (300)	44.0 (75.1)	CH_4 +  + 
	endo	50–175 (105)	4.5 (10.0)	Et_2O
 $C_6H_{11}C(CH_3)_2OMg{\cdot}0.27Et_2O$ (45.0)	endo	175–360 (290)	32.5 (72.2)	CH_4 +  + 
(*trans*)	endo	50–195 (125)	15.5 (20.8)	THF
 (74.4)	endo	230–405 (330)	49.0 (65.9)	CH_4 +  + 
(*cis*)  (68.1)	endo	260–405 (305, 345)	50.2 (73.7)	CH_4 +  + 

Table IV (*Continued*)

compd (sample wt, mg)	thermometric change	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
threo-$PhCHCH_3CHPhOMgMg\cdot 0.5Et_2O$ (40.8)	endo	50–145 (95)	2.0 (5.0)	Et_2O
	endo	185–260 (235)	8.2 (20.0)	CH_4
	endo	260–400 (350)	24.7 (60.6)	(*cis*) 
erythro-$PhCHCH_3CHPhOMgCH_3\cdot 0.5Et_2O$ (36.9)	endo	45–135 (85)	4.8 (13.0)	Et_2O
	endo	205–310 (240)	26.9 (72.9)	CH_4 + (*trans*) 
$Mg(OC_6H_{11})_2$ (48.1)	endo	40–400 (340)	41.1 (85.4)	H_2, , 
$C_6H_{11}OMgOPh\cdot 0.30THF$ (86.5)	endo	50–190 (95)	7.8 (9.0)	THF
	endo	190–370 (315)	38.4 (44.4)	
	endo	370–465	16.8 (19.4)	H_2 plus unknown product
$PhMgOCH(CD_3)_2\cdot 0.17Et_2O$ (91.0)	endo	50–165 (100)	6.5 (7.1)	Et_2O
	endo	165–390 (310)	58.0 (63.7)	$PhD + CD_2CH{=}CD_3$
$PhCH_2MgOCH(CD_3)_2\cdot 0.38Et_2O$ (88.3)	endo	40–160 (85)	11.0 (12.5)	Et_2O
	endo	160–390 (290)	58.0 (65.7)	$PhD + CD_2{=}CHCD_3$
$CH_3MgOCH(CH_3)_2$[a] (38.0)	endo	200–485 (305)	22.5 (59.2)	$CH_4 + CH_2{=}CHCH_3$
$CH_3MgOCH(CD_3)_2$[a] (49.1)	endo	245–480 (350)	29.0 (59.1)	$CH_3D + CD_2CHCD_3$

[a] Under static argon atmosphere.

Table V. Thermal Decomposition of CH_3ZnOR and PhZnOR Compounds

compd (sample wt, mg)	thermometric change	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
PhZnOEt (51.2)	endo	160–430 (255)	20.5 (40.0)	PhH
CH_3ZnO-*i*-$Pr\cdot 0.16THF$ (66.2)	endo	50	54.0 (81.6)	sublimation only
PhZnO-*i*-Pr (32.7)	endo	110–340 (230)	19.5 (59.6)	PhH + $CH_2{=}CHCH_3$
PhZnO-*t*-Bu (64.2)	endo	60–278 (200)	26.2 (40.8)	PhH
	endo	278–465	4.6 (7.2)	$CH_2{=}C(CH_3)_2$
$HZnOC_6H_{11}\cdot 0.42THF$ (47.8)	endo	35–105 (75)	4.5 (9.4)	THF
	endo	105–205 (150)	0.5 (1.0)	H_2
	endo	205–380 (290)	23.0 (48.1)	
$0.7CH_3ZnOC_6H_{11}\cdot 0.39THF + 0.3\ Zn(OC_6H_{11})_2$ (58.4)	endo	50–215 (150)	11.0 (18.8)	THF
	endo	215–325 (295)	9.0 (15.4)	CH_4 + 
	endo	325–415 (385)	23.0 (39.4)	H_2, , 
$PhZnOC_6H_{11}$ (100.3)	endo	195–340 (310)	64.5 (64.3)	PhH + 
$CH_3ZnOC(CH_3)Ph_2$ (71.2)	endo	55–360 (265)	49.0 (68.8)	$CH_4 + Ph_2CCH_2$
$PhZnOC(CH_3)Ph_2$ (49.6)	endo	45–125 (75)	6.0 (12.1)	THF
	endo	198–340 (260)	33.1 (66.7)	$PhH + Ph_2C{=}CH_2$
$Zn(OC_6H_{11})_2$ (42.3)	endo	310–408 (382)	28.9 (68.3)	H_2, , 
$PhZnOCH(CD_3)_2$[a] (45.2)	endo	115–485 (265)	27.5 (60.8)	$PhD + CD_2{=}CHCD_3$
$PhZnOCD_2CD_3$ (45.3)	endo	180–340 (220)	25.5 (56.3)	$PhD + CD_2{=}CD_2$

[a] Under static argon atmosphere.

dimethylcyclohexylcarbinol, *cis*-2-methyl-1-cyclohexanol, and *trans*-2-phenyl-1-cyclohexanol. The alkoxide methylmagnesium 1-methylcyclohexyl oxide decomposed in 43% yield to give a 41:59 ratio of methylenecyclohexane and 1-methyl-1-cyclohexene, respectively. This ratio represents a statistical yield of products based upon the number of available β hydrogens, which is basically what is found in other pyrolytic reactions such as Chugaev and acetate pyrolysis. Similar statistical yields of olefins were produced for the alkoxides methylmagnesium dimethylcyclohexylcarbinyl oxide and methylmagnesium *cis*-2-methyl-1-cyclohexyl oxide. However, methylmagnesium *trans*-2-phenyl-1-cyclohexyl oxide produced an 88:12 ratio of 1-phenyl-1-cyclohexene and 3-phenyl-1-cyclohexene. A statistical yield would have been 67:33. The increase in the amount of the 1-phenyl-1-cyclohexene is due to the stabilizing effect of the phenyl group to produce a conjugated olefin. The products of the Chugaev and acetate pyrolysis reactions involving the counterpart of the alkoxide also gives the above two cyclohexenes in about the same ratio due to the influence of the phenyl group in forming

Table VI. Thermal Decomposition of $(CH_3)_2AlOR$ and Ph_2AlOR Compounds

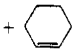
compd (sample wt, mg)	thermometric change	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
$(CH_3)_2AlOC_6H_{11}$ (68.7)	endo	80	68.7 (100)	sublimation only
Ph_2AlO-*i*-Pr·0.34Et_2O	endo	60–102 (90)	3.0 (9.7)	Et_2O
(31.1)	endo	145	25.0 (80.4)	sublimation only
$Ph_2AlOC_6H_{11}$·0.50Et_2O	endo	50–165 (110)	8.1 (11.6)	Et_2O
(69.6)	endo	195–375 (285)	35.7 (51.3)	PhH + 
$Ph_2AlOC(CH_3)Ph_2$·1.87Et_2O (108.1)	endo	55	94.0 (87.0)	sublimation only
$Ph_2C(CH_3)OAl(N$-*i*-$Pr_2)$·0.97PhH	endo	55–100 (85)	14.0 (15.1)	PhH
(92.8)	endo	110–460 (225)	61.5 (66.3)	NH-*i*-Pr_2 + $Ph_2C{=}CH_2$

Table VII. Kinetic Isotope Effects

compd	k at 235 °C min^{-1}	correlation coefficient	atmosphere	k_H/k_D
$CH_3MgOCH(CH_3)_2$	9.18×10^{-3}	0.999	Ar	0.675
$CH_3MgOCH(CD_3)_2$	1.36×10^{-2}	0.999	Ar	
$PhMgOCH(CH_3)_2$	2.10×10^{-3}	0.990	vacuum	0.712
$PhMgOCH(CD_3)_2$	2.95×10^{-3}	0.994	vacuum	
$PhZnOCH(CH_3)_2$	1.33×10^{-3}	0.987	Ar	0.226
$PhZnOCH(CD_3)_2$	5.89×10^{-3}	0.999	Ar	
$PhCH_2MgOCH(CH_3)_2$	4.60×10^{-3}	0.980	vacuum	1.300
$PhCH_2MgOCH(CD_3)_2$	3.55×10^{-3}	0.990	vacuum	
$PhZnOCH_2CH_3$[a]	1.79×10^{-3}	0.967	vacuum	0.626
$PhZnOCD_2CD_3$[a]	2.86×10^{-3}	0.967	vacuum	

[a] The temperature was 220 °C and the evolution of hydrocarbon was followed.

Table VIII. First-Order Rate Constants for the Thermal Decomposition of Alkoxide

compd	k, min^{-1} [a]	temp, °C	correlation coefficient
threo-$Ph(CH_3)CHCH(Ph)OMgCH_3$	7.50×10^{-4}	200	0.985
	3.18×10^{-3}	235	0.976
	1.75×10^{-2}	285	0.954
erythro-$Ph(CH_3)CHCH(Ph)OMgCH_3$	5.38×10^{-3}	200	0.982
	7.79×10^{-3}	210	0.934
	1.64×10^{-2}	235	0.988
$PhMgO$-*i*-Pr·0.16Et_2O	6.00×10^{-4}	200	0.982
	2.10×10^{-3}	235	0.990
	4.21×10^{-3}	285	0.988
$PhCH_2MgO$-*i*-Pr	6.33×10^{-4}	200	0.983
	4.60×10^{-3}	235	0.980
	3.04×10^{-2}	282	0.993
$PhZnOC_6H_{11}$	1.24×10^{-3}	215	0.988
	3.60×10^{-3}	235	0.999
	1.08×10^{-2}	278	0.976
PhZnOEt	1.50×10^{-3}	200	0.993
	1.79×10^{-3}	220	0.967
	3.43×10^{-3}	235	0.982

[a] Estimated error limit is ±2%.

Table IX. Activation Parameters for the Decomposition of Alkoxides

compd	E_a kcal/mol[a]	A, s^{-1}	correlation coefficient	$\Delta S^{\ddagger}$ at 200 °C, eu
threo-$Ph(CH_3)CH$-$CH(Ph)$-$OMgCH_3$	19.4	1.15×10^4	0.999	−42.6
erythro-$Ph(CH_3)$-$CHCH$-$(Ph)OMgCH_3$	15.5	1.26×10^3	0.999	−47.0
$PhMgO$-*i*-Pr	11.8	3.25	0.946	−58.9
$PhCH_2MgO$-*i*-Pr	24.7	2.83×10^6	0.998	−31.6
$PhZnOC_6H_{11}$	17.3	1.32×10^3	0.982	−46.9
PhZnOEt	11.4	3.91	0.912	−58.5
$PhMgOCH(CD_3)_2$	12.7	15.2	0.978	−55.8
$PHCH_2MgOCH$-$(CD_3)_2$	16.9	9.81×10^2	0.991	−47.5

[a] Estimated error limit is ±10%.

the more thermodynamically stable olefin.

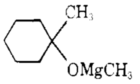
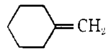
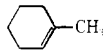
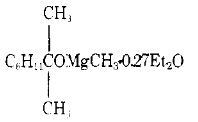
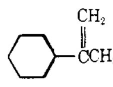
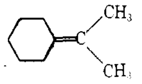
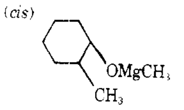
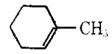
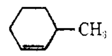
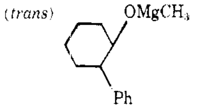
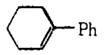
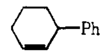
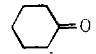
The yields from the thermal decomposition of alkoxides are usually better than those from the Chugaev and acetate pyrolysis reactions. One reason is that in the Chugaev reaction the preparation of the methyl xanthate can be a low yield reaction. The preparation of the acetate ester is not quantitative either. However, the preparation of the alkoxide takes place in quantitative yield, and the alkoxides do not have to be isolated or purified.

There are several methods for the preparation of alkoxides. Usually dimethylmagnesium, diphenylzinc, or triphenylaluminum is allowed to react with the appropriate alcohol in a 1:1 mole ratio. In addition, Grignard reagents can react directly with ketones, aldehydes, or alcohols to produce alkoxides. For example, either benzophenone or 1,1-diphenyl-1-propanol reacts with methylmagnesium bromide to produce 1,1-diphenyl-1-propoxymagnesium bromide. The thermal decomposition of this compound is best conducted in a diluent such a *n*-dodecane using an amine or triphenylphosphine as a trap for the HBr generated.

Discussion

The thermal decomposition of metal alkoxides of magnesium, aluminum, and zinc proceeds via a unimolecular, cyclic, six-center transition state involving the abstraction of a β hydrogen from the alkoxide portion by an incipient carbanion to yield a hydrocarbon, an olefin, and a metal oxide (Figure 4). Several studies support this conclusion. The first-order rate constants observed in the decomposition reaction and the fact that no intermediate is observed indicates that the reaction is unimolecular. The syn nature of the elimination reaction is suggested by the decomposition of methylmagnesium *erythro*- and *threo*-1,2-diphenyl-1-propoxide to give only *trans*- and *cis*-1,2-diphenylpropene, respectively. The transition state for the threo compound appears more hindered than that of the erythro compound, since the threo compound decomposes at a higher temperature and has a higher activation energy. The large negative entropies of activation (−32 to −59 eu) show that several degrees of freedom are restricted in the transition state and that the transition state is probably

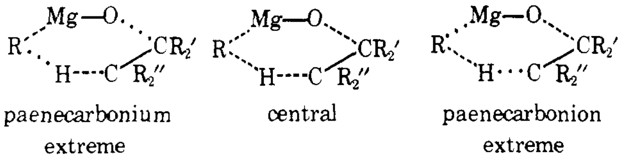
Table X. Thermal Decomposition of Alkoxides: Yields and Product Ratios

compd	olefin	% yield ratio	% yield total	method	% yield Chugaev ratio	% yield reaction total	% yield acetate ratio	% yield pyrolysis total	ref
		41	43	*a*	21	49	24	62	12, 13
		59			79		76		
 $C_6H_{11}C(CH_3)_2OMgCH_3{\cdot}0.27Et_2O$		84	85	*a*	88	29			12
		16			22				
		66	69	*a*			25	63	14
		34					75		
		88	69	*a*	88	*f*	87	53	15
		12			12		13		
threo-$PhCH(CH_3)CH(Ph)OMgCH_3$	*cis*-$PhCH{=}C(CH_3)Ph$	100	49	*a*	100	46			10
	trans-$PhCH{=}C(CH_3)Ph$	0			0				
erythro-$PhCH(CH_3)CH(Ph)OMgCH_3$	*trans*-$PhCH{=}C(CH_3)Ph$	100	48	*a*	100	54			10
	cis-$PhCH{=}C(CH_3)Ph$	0			0				
$CH_3MgOC(CH_3)Ph_2{\cdot}1.0Et_2O$	$Ph_2C{=}CH_2$		81	*a*					
			81	*b*					
$(i\text{-}Pr)_2NMgOC(CH_3)Ph_2$	$Ph_2C{=}CH_2$		70	*a*					
$BrMgOC(CH_3)Ph_2$	$Ph_2C{=}CH_2$		102	*c*					
			90	*d*					
			40	*b*					
$Mg(OC_6H_{11})_2$			88	*a*					
			58						
$(i\text{-}Pr)_2NAlOC(CH_3)Ph_2$	$Ph_2C{=}CH_2$		101	*a*					
$Ph_2AlOC(CH_3)Ph_2$	$Ph_2C{=}CH_2$		103	*a*					
$PhZnOC(CH_3)Ph_2$	$Ph_2C{=}CH_2$		76	*a*					
$PhMgOC(CH_3)Ph_2$	$Ph_2C{=}CH_2$		42	*a*					

[a] Solid decomposed using Woods' metal bath. [b] *n*-Dodecane reflux for 24 h. [c] *n*-Dodecane reflux for 24 h, excess Ph_3P added. [d] *n*-Dodecane reflux for 24 h, excess $(CH_3)_2NPh$ added. [e] Yield based on alcohol. [f] No yield given; the crude methyl xanthate was decomposed to give a product which was distilled twice to remove the odor of mercaptans.

cyclic in nature. All these observations are consistent with a cyclic, six-center transition state.

It is interesting that the kinetic isotope effect study shows that the rate-determining step of the decomposition reaction is not abstraction of the β hydrogen. Instead, the observed inverse isotope effect implies a somewhat more complicated mechanism than suggested in Figure 4. We postulate a spectrum of Ei transition states as described in Figure 5 in analogy to the E1–E2–E1cb continuum[17] to explain the results of the isotope study. The present suggestion visualizes an Ei mechanism that varies from the extreme of mostly C_α–O rupture and very little C_β–H breaking (paenecarbonium—almost carbonium like) to a central position that is essentially a synchronous breaking of C_α–O and C_β–H bonds to the extreme of mostly C_β–H rupture and very little C_α–O breaking (paenecarbanion–almost carbanion like). The variable Ei transition state as described in Figure 5 postulates that, for an Ei reaction, the lowest energy path from reactants to products is achieved by an optimum adjustment between the degrees of C_α–O and C_β–H bond rupture in the transition state. The optimum adjustment involves considerable breaking of the bond more easily broken and little breaking of the bond requiring more energy to sever. However, both bonds must be broken before the single reaction step is complete.



(the strength of the bond increases in the order: ··· < --- < —)

Figure 5.

The variable Ei transition state picture predicts the *maximum kinetic isotope effect for the central transition state* (Figure 5). A value for $k_H/k_D > 1$ would be expected for the essentially synchronous breaking of C_α–O and C_β–H bonds. The Chugaev reaction ($k_H/k_D \simeq 2.0$)[14] and the acetate pyrolysis reaction ($k_H/k_D \simeq 2$)[14] appear to have a transition state more closely related to this central one.

The kinetic isotope effect for the paenecarbanion transition state would be smaller than that for the central transition state and, in fact, would lead to an inverse isotope effect ($k_H/k_D < 1$) in the extreme case.[18] An explanation for the observed inverse isotope effects is based on the following model. In the *paenecarbanion transition state* considerable C–H bond breaking has occurred due to the abstraction of a proton (or deuterium) from the β carbon by the incipient carbanion on the metal. This leaves a carbanion at the β carbon with two C–H(D) bonds. One of these remaining C–H(D) bonds is taken as a hypothetical reactant molecule. It has only a single vibrational frequency (V) which can be calculated for each isotopic species from the expression for a simple harmonic oscillator, namely $V = (1/2\pi)\sqrt{f/m}$, where f is the force constant, a measure of the stiffness of the bond, and m is the reduced mass. The one vibrational mode becomes the motion along the *reaction coordinate* in the transition state. Since carbon makes a small contribution to the reduced mass compared to hydrogen or deuterium, the isotopic ratio of frequencies becomes $V_D/V_H = 1\sqrt{2}$. The assumption is made that the force constants for a C–H and C–D bond both in the ground state and in the transition state are essentially the same. Of course, there is a change in force constants in going to the transition state, since the comparison is between an aliphatic and a vinylic C–H (C–D) bond due to rehybridization at the carbanionic carbon. Therefore, the difference in zero-point vibration energy between the transition state and the ground state for the deuterated compound is lower than the corresponding energy difference for the hydrogen compound, giving rise to a larger rate constant for the deuterated compound and thus an inverse isotope effect.

The paenecarbonium transition state resembles an E1-type mechanism and would have a similar isotope effect. That is, the isotope effect would be less than that for the central transition state, but greater than unity (k_H/k_D for E1 = 1–3).[19] No example of this extreme Ei transition state is known as yet.

One kinetic isotope effect was found to be greater than unity. The benzylmagnesium isopropoxide compounds gave $k_H/k_D = 1.30$. Evidently, in this case the transition state lies closer to the synchronous transition state.

The variable Ei mechanism explains the apparent conflict in trends in decomposition temperatures. The series of 1,1-diphenylzinc and -magnesium compounds shows that the decomposition temperature is independent of the nature of the incipient carbanion base. Apparently, there is considerable carbanion character in these cases, and the decomposition rate is determined by the rate of rehybridization of the carbanion to give the olefin product. The isoproxymagnesium and cyclohexyloxyzinc compounds show a lower decomposition temperature when the incipient carbanion is methyl. In this case the transition state must lie more toward the central one in that the breakage of the C_β–H bond becomes more important. The stronger base (methyl carbanion) can remove the proton from the β carbon more easily. The nature of the transition state also depends on the type of metal, since the cyclohexyloxymagnesium compounds decompose at the same temperature (compared to the cyclohexyloxyzinc compounds). The phenylmagnesium alkoxides give the lowest decomposition temperatures for formation of the most stable carbanion at the β carbon, while the methylmagnesium alkoxides show the reverse order. The explanation here is that for the phenylmagnesium alkoxides there is more carbanion character in the transition state due to a greater portion of C_β–H bond breaking, whereas for the methylmagnesium alkoxides there is less C_β–H bond rupture and less carbanion character. The reversal in decomposition order can then be explained in terms of steric hindrance in the transition state. It is more difficult for bulky alkoxy groups to achieve the correct geometry in the transition state. Therefore, the simplest olefins are formed at the lowest decomposition temperature.

Eclipsing effects were studied for the case of the methylmagnesium *erythro*- and *threo*-1,2-diphenyl-1-propoxides. In the transition state describing the formation of the cis olefin from erythro substrate, the phenyl groups in C_α and C_β are brought into a partially eclipsed arrangement. The extent of eclipsing depends on the degree of C=C character. Because phenyl groups are large, steric strain is introduced into the transition state when they eclipse. Obviously, the adverse energy effect is greater the flatter the transition state. On the other hand, the eclipsing of a methyl group and a phenyl group in the formation of trans olefin from erythro substrate has a smaller adverse effect, since a methyl group is smaller than a phenyl group. Therefore, the erythro/threo rate ratio is a measure of the C=C character in the transition state.[20] The calculation at 200 °C gives an erythro/threo ratio equal to 7.19. The magnitude of the result shows some C=C character in the transition state. Hence, the paenecarbanion transition state appears to apply here. The paenecarbonium extreme would require the ratio to be near unity, and the central mechanism would require a larger number than 7.

Comparisons can be made between the Chugaev and acetate pyrolysis reactions and the thermal decomposition of alkoxides. The advantages of the newer method include: (1) higher yields and equally good stereochemistry and (2) a simpler method in that the alkoxide is easily prepared and does not have to be isolated or purified. The major disadvantage is the limited number of functional groups compatible with an organometallic compound. However, this disadvantage can be overcome to some extent. The alkoxide can be formed by reaction of the alcohol with a base, e.g., (diisopropylamino)-magnesium bromide as shown in eq 10 and 11. The resultant alkoxide is the same as that prepared from the reaction of methylmagnesium bromide with the alcohol except that the problem of an active organometallic compound has been avoided. In some cases the problem can be employed to advantage as in the preparation of the alkoxide methylmagnesium 1,1-diphenylethoxide directly by the reaction of dimethylmagnesium with benzophenone.

$$CH_3MgBr + HN\text{-}i\text{-}Pr_2 \rightarrow CH_4 + i\text{-}Pr_2NMgBr \quad (10)$$

$$i\text{-}Pr_2NMgBr + R'OH \rightarrow HN\text{-}i\text{-}Pr_2 + R'OMgBr \quad (11)$$

Experimental Section

Apparatus. All operations were performed under a nitrogen atmosphere using either a nitrogen-filled glove box equipped with a special recirculating system to remove oxygen and moisture[21] or at the bench using Schlenk tube techniques.[22] Glassware was flash flamed and flushed with dry nitrogen prior to use. DTA–TGA analyses were performed on a Mettler Thermoanalyzer II equipped to operate under vacuum.[23] Powdered alkoxide samples were loaded into a cylindrical crucible (preheated to 250 °C and cooled to room temperature) in the glove box using a vibrator to ensure uniform particle size. Samples were heated at 4 °C/min at 10^{-6} mmHg from 25 to 450 °C and at a 6 in./h chart speed.

Analyses. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid or methanol on a standard vacuum line equipped with a Toepler pump.[22] Magnesium and zinc were determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum was determined by reaction with excess EDTA and back titration with zinc acetate at pH 4 using dithiazone as an indicator. GLC analyses were performed on an F and M Model 720 gas chromatograph.

Materials. Diethyl ether (Fisher Anhydrous Reagent Grade) was distilled from $LiAlH_4$ (Ventron) prior to use. Tetrahydrofuran and benzene (Fisher Certified Reagent Grade) were distilled from $NaAlH_4$ (Ventron). *n*-Dodecane (Eastman) was predried over NaOH and fractionally distilled. Toluene (Fisher) was distilled from CaH_2. Dimethylmercury, diphenylmercury, and dibenzylmercury were obtained commercially (Orgmet). Magnesium (Ventron chips), zinc (Baker Analyzed Reagent, granular), and aluminum (Alcoa Grade 101 Atomized Powder) were dried by flash flaming under vacuum before use. Cyclohexanol (Fisher), cyclohexyl methyl ketone (Chemical Samples), cyclohexanone (Matheson Coleman and Bell), 1-octanol (Fisher), phenol (Baker), diisopropylamine (Aldrich), and *N,N*-dimethylaniline (Columbia Organic Chemicals) were distilled prior to use. Ethanol (Fisher) was dried by azeotropic distillation with benzene and 2-propanol (Baker) was distilled from triisopropoxyaluminum. 2-Phenyl-1-ethanol (Eastman) was distilled from CaH_2 at reduced pressure, and benzophenone (Fisher) was sublimed under vacuum. 1,1-Diphenyl-1-ethanol (Eastman), 2-methyl-2-propanol (Fisher), *trans*-2-phenylcyclohexanol (Aldrich), *cis*-2-methylcyclohexanol (Aldrich), triphenylphosphine (Eastman) and ethanol-d_6 (Pfaltz and Bauer) were used without further purification.

Preparation of Dialkyl- and Diarylmagnesium Compounds. Dimethylmagnesium. Magnesium chips (20 g, 0.833 mol) were rinsed with diethyl ether and placed in a 1-L flask with a three-way stopcock and an egg-shaped stirring bar. The magnesium and apparatus were evacuated, flame heated, and purged with dry nitrogen. Dimethylmercury (30 mL, 0.400 mol) was added and the reaction mixture was allowed to stir at 25 °C for 48 h until the magnesium became white and powderlike. The flask was placed under vacuum for 15 min to remove any unreacted dimethylmercury. The dimethylmagnesium was extracted with diethyl ether and filtered through a fritted filter funnel in the glove box. The active methyl/magnesium ratio = 2.02:1.00.

Diphenylmagnesium was prepared from diphenylmercury in a similar manner to the dimethylmagnesium except that the solid–solid reaction mixture was heated at 140 °C for 24 h. The ratio of phenyl/magnesium = 2.04:1.00.

Dibenzylmagnesium.[24] To a dry 1-L flask equipped with a three-way stopcock and stirring bar was added magnesium (19.5 g, 0.882 mol, flame dried under vacuum), dibenzylmercury (25.0 g, 0.065 mol), and diethyl ether (400 mL). The reaction mixture was stirred for 26 h under a nitrogen atmosphere, filtered, and analyzed. The ratio of benzyl/magnesium = 1.98:1.00. The benzyl group content was measured by GLC as toluene produced on hydrolysis.

Preparation of Active Magnesium Hydride in THF. When 15.0 mmol of $LiAlH_4$ solution in diethyl ether (30 mL) was added dropwise to a magnetically well-stirred solution of Et_2Mg (15.0 mmol) in diethyl ether (35 mL), an exothermic reaction occurred and an immediate precipitate appeared. This reaction mixture was allowed to stir for 1 h at room temperature followed by centrifugation of the insoluble white solid. The supernatant solution was separated by syringe and the insoluble white solid was washed with diethyl ether three or four times and finally made a slurry in THF. The analysis of this slurry showed that it contained Mg and H in the ratio 1.00:2.02.

Preparation of Dimethyl- and Diphenylzinc. Dimethylzinc was prepared by the procedure of Noller.[25] Methyl iodide (Fisher) was dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc–copper couple was obtained from Alfa Inorganics. The reaction of zinc–copper couple with methyl iodide was allowed to proceed overnight, and the dimethylzinc was distilled from the reaction mixture at atmosphere pressure under nitrogen. The neat dimethylzinc was diluted with diethyl ether to facilitate handling. The ratio of methyl/zinc = 2.10:1.00.

Diphenylzinc.[26] To a 500-mL flask equipped with a reflux condenser and three-way stopcock sidearm was added granular zinc (23.2 g, 0.355 mol, dried by flaming under vacuum), diphenylmercury (20.0 g, 0.056 mol), and toluene (100 mL). The reaction mixture was refluxed 39 h. The solution was cooled and analyzed. The ratio of phenyl/zinc = 2.03:1.00.

Preparation of Zinc Hydride. The method of Schlesinger[27] was used to prepare zinc hydride. $(CH_3)_2Zn$ was added to $LiAlH_4$ in 1:2 ratio in diethyl ether solution. The resultant precipitate of zinc hydride was removed by filtration. The ratio of hydrogen/zinc = 1.95:1.00.

Preparation of Trimethyl- and Triphenylaluminum. **Trimethylaluminum** is commercially available (Ethyl Corp.) and was diluted with diethyl ether to facilitate handling. The ratio of methane/aluminum = 2.97:1.00.

Triphenylaluminum.[28] To a 500-mL flask equipped with a reflux condenser and a three-way stopcock sidearm was added powdered aluminum (12.3 g, 0.456 mol, dried by flaming under vacuum), diphenylmercury (21.9 g, 0.062 mol), and toluene (120 mL). The reaction mixture was refluxed 39 h. The supernatant solution gave a phenyl/aluminum ratio = 3.05:1.00.

Preparation of Alane and Bis(diisopropylamino)alane. Alane (AlH_3) was prepared from $LiAlH_4$ and 100% sulfuric acid in THF according to the procedure of Brown.[29] Bis(diisopropylamino)alane, $HAl(NPi_2)_2$, was prepared from AlH_3 and diisopropylamine in 1:2 ratio. Alane in THF was cooled to −78 °C and the amine was added. The reaction mixture was allowed to warm to room temperature with stirring. The THF was removed by vacuum distillation and benzene was added. The ratio of hydrogen/aluminum = 1.00:1.00.

Preparation of *threo*-1,2-Diphenyl-1-propanol.[16] *threo*-1,2-Diphenyl-1-propanol was prepared by the reaction of phenylmagnesium bromide with 2-phenylpropanal (Aldrich).

A three-neck 500-mL flask was equipped with a reflux condenser, an addition funnel, a stirring bar, and a three-way stopcock. Magnesium (15.2 g, 0.626 mol) was added and the apparatus was flamed under vacuum. The apparatus was purged with dry nitrogen and diethyl ether (250 mL) was added. Bromobenzene (Aldrich, 98.0 g, 0.624 mol) was then added dropwise to prepare the corresponding Grignard reagent. 2-Phenylpropanal (67.0 g, 0.550 mol) was diluted with diethyl ether (100 mL) and added dropwise to the phenylmagnesium bromide cooled in an ice bath. The reaction was quenched by hydrolysis with saturated ammonium chloride solution followed by diethyl ether extraction of the aqueous layer. The diethyl ether was dried over $MgSO_4$ and distilled at reduced pressure to yield an oily residue. The oil distilled at 137–139 °C (4 mmHg) to give 79.7 g (75.2% yield) of crude *threo*-1,2-diphenyl-1-propanol (17% erythro isomer present).

The crude threo alcohol (79.7 g, 0.376 mol) and freshly prepared *p*-nitrobenzoyl chloride (70.0 g, 0.377 mol) were dissolved in pyridine (150 mL) and heated on a steam bath for 2 h. A precipitate formed. The slurry was poured onto ice and 20% H_2SO_4. The solid material was separated from the aqueous layer. The solid *p*-nitrobenzoyl ester was dissolved in ethyl acetate and dried over $MgSO_4$. The *p*-nitrobenzyl ester was crystallized from the ethyl acetate to give 52.4 g (0.145 mol, 38.6% yield), mp 143–144 °C.

The purified *p*-nitrobenzoyl ester (52.4 g, 0.145 mol), KOH (8.1 g), NaOH (5.8 g), methanol (104 mL), and H_2O (104 mL) were refluxed for 12 h. The aqueous layer was extracted with diethyl ether. The diethyl ether was dried over $MgSO_4$ and distilled under vacuum to give an oil. The oil was distilled at 139–142 °C (6 mmHg) to give 27.7 g (89.9% yield) of *threo*-1,2-diphenyl-1-propanol: NMR ($CDCl_3$) δ 1.22 (d, 3 H, CH_3), 2.25 (d, 1 H, OH), 3.00 (p, 1 H), 4.62 (d, 1 H), 7.08 (d, 10 H, Ph); mass spectrum *m/e* 212 (M^+), 107, 106, 77.

Preparation of *erythro*-1,2-Diphenyl-1-propanol.[16] *erythro*-1,2-Diphenyl-1-propanol was prepared in three steps from *d,l*-benzoin.

A 1-L three-neck flask was equipped with a solid addition tube, stirring bar, a reflux condenser, and a three-way stopcock. *d,l*-Benzoin (Aldrich, 38.6 g, 0.181 mol) was added slowly to CH_3MgI (100 g of MeI, 18.0 g of Mg, 0.704 mol) in diethyl ether (500 mL) cooled in an ice bath. Then the mixture was refluxed for 3 h, cooled to 25 °C, and quenched with NH_4Cl saturated solution. The diethyl ether layer was decanted and the aqueous layer was washed with diethyl ether. The diethyl ether extracts were combined, dried over $MgSO_4$, and filtered, and the ether was removed under vacuum to give a yellow solid. The crude glycol product, $Ph(CH_3)COHCH(OH)Ph$, was crystallized from CS_2 (33.6 g, 80.9% yield): mp 103–104 °C; IR 3400 cm^{-1} (s). The glycol (32.0 g, 0.140 mol) was added to H_2SO_4 (200 mL) at 0 °C over a period of 1 h with constant stirring and then at 25 °C for 2 h. The material was poured onto 1000 g of ice and then extracted with diethyl ether. The diethyl ether was dried over $MgSO_4$ and reduced under vacuum to give an oil which slowly crystallized (26.6 g, 90.0% yield). The solid ketone product, $PhC(H)CH_3COPh$, was crystallized from cold ethanol to give white, fluffy crystals (4.0 g, 13.5% yield, mp 49–50 °C).

A 500-mL three-neck flask was equipped with an addition funnel, stirring bar, reflux condenser, and three-way stopcock. To the pot was added $LiAlH_4$ (0.094 mol) in diethyl ether. The ketone, PhC(H)-CH_3COPh, (0.298 mol) in diethyl ether was added dropwise and the solution was refluxed for 30 min. The reaction was quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted with diethyl ether, which was then dried over $MgSO_4$, filtered, and distilled under vacuum to give an oil. The oil was crystallized from pentane to give white needles (30.2 g, 47.8% yield): mp 50–52 °C; NMR ($CDCl_3$) δ 1.06 (d, 3 H, CH_3), 1.87 (s, 1 H, OH), 2.01 (p, 1 H), 4.62 (d, 1 H), and 7.27 (d, 10 H, Ph); mass spectrum m/e 212 (M^+), 197, 77.

Preparation of 2-Propanol-d_6. Acetone-d_6 (Fisher, 10.0 g, 0.190 mol) was placed in a 50-mL flask and $LiAlH_4$ (0.0474 mol) in 95 mL of diethyl ether was added at room temperature. The reaction mixture was stirred for 1 h, quenched with a minimum amount of water, and filtered. The filtrate was dried over $MgSO_4$ and the ether was removed by distillation. The 2-propanol-d_6 was distilled at 80–82 °C under nitrogen to give 3.91 g (34.3% yield).

General Preparation of an Alkoxide. The general method for the preparation of an alkoxide is illustrated for methylmagnesium cyclohexyl oxide.

A dry, weighed 100-mL flask was fitted with a rubber septum cap, purged with dry nitrogen, and fitted with a needle connected to a nitrogen bubbler. A measured quantity of cyclohexanol was added to the flask via syringe and the flask was reweighed (0.498 g, 4.98 mmol). Then the flask was cooled to −78 °C, and the calculated amount of dimethylmagnesium diethyl ether solution (5.02 mmol) was added via syringe. The flask was warmed to 25 °C and a solid formed with corresponding evolution of methane. The septum was replaced with a three-way stopcock, and the diethyl ether was distilled under vacuum. The solid methylmagnesium cyclohexyl oxide was transferred to the glove box for further manipulation and analysis. The ratio of magnesium/methane/cyclohexanol = 1.00:1.00:0.96.

General Methods of Decomposition. (a) Decomposition in the Solid State. The decomposition of diphenylaluminum 1,1-diphenyl-1-ethoxide illustrates the method of decomposing a solid alkoxide. In the glove box a sample of the alkoxide is loaded into a 10-mL flask connected to an apparatus consisting of a dry ice cold finger and three-way stopcock. The apparatus is removed from the glove box and evacuated. The flask is immersed in a Woods' metal bath preheated to 270–275 °C for 5 min. The olefin, 1,1-diphenylethene, distills onto the dry ice cold finger from which it is washed with diethyl ether for GLC analysis after the addition of a suitable internal standard.

(b) Decomposition in *n*-Dodecane Diluent. The decomposition of methylmagnesium 1,1-diphenyl-1-ethoxide represents the general method for the decomposition of an alkoxide in *n*-dodecane diluent. In the glove box a sample of alkoxide is transferred to a 25-mL flask equipped with a reflux condenser and rubber septum. On the bench *n*-dodecane (10 mL) is added via syringe and the reaction mixture is refluxed for 24 h. The reaction mixture is then quenched with a saturated solution of NH_4Cl and extracted with ether. The ether layer is dried over $MgSO_4$ and analyzed by GLC. The aqueous layer is analyzed for magnesium to determine the yield.

Decomposition of 1,1-Diphenyl-1-ethoxymagnesium Bromide. 1,1-Diphenyl-1-ethanol (2.19 g, 0.0111 mmol) was placed in a 30-mL flask equipped with a stirring bar, reflux condenser, and three-way stopcock. Methylmagnesium bromide (0.0111 mol) in diethyl ether was added slowly. The solution was stirred 30 min, the diethyl ether was removed under vacuum, and *n*-dodecane (4 mL) and *N,N*-dimethylaniline (1 mL) were added. The solution was refluxed 24 h, quenched with a saturated solution of NH_4Cl, and extracted with diethyl ether. The diethyl ether was washed with NaOH solution, dried over $MgSO_4$, and analyzed by GLC. The aqueous layer was analyzed for magnesium to determine the yield (89.6%).

Decomposition of Methylmagnesium *threo*- and *erythro*-1,2-Diphenyl-1-propoxide. Methylmagnesium *threo*-1,2-diphenyl-1-propoxide and excess triphenylphosphine were placed in a dry 10-mL flask equipped with a dry ice cold finger and three-way stopcock. The apparatus was evacuated and the flask was placed in a Woods' metal bath preheated to 270–275 °C. The *cis*-1,2-diphenyl-1-propene product distilled onto the cold finger and was rinsed off with diethyl ether for GLC analysis after addition of the internal standard.

A similar experiment was performed on the methylmagnesium *erythro*-1,2-diphenyl-1-propoxide to produce *trans*-1,2-diphenyl-1-propene.

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Registry No.—Dimethylmercury, 593-74-8; diphenylmercury, 587-85-9; dibenzylmercury, 780-24-5; bromobenzene, 108-86-1; 2-phenylpropanal, 93-53-8; *threo*-1,2-diphenyl-1-propanol, 7693-95-0; *d,l*-benzoin, 579-44-2; methyl iodide, 74-88-4; 1,2-diphenyl-1,2-propanediol, 41728-16-9; 1,2-diphenyl-1-propanone, 67737-73-9; *cis*-1,2-diphenyl-1-propene, 1017-22-7; *trans*-1,2-diphenyl-1-propene, 833-81-8; 1,1-diphenyl-1-ethoxymagnesium bromide, 68986-36-7; methylmagnesium bromide, 75-16-1.

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