°C (in a sealed tube); $[\alpha]^{20}_D$ −118° (c 0.340, MeOH); IR (KBr) 3300, 1080, 1010 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.74; H, 10.65.

(−)-2-Acetoxytwistane (43). To a solution of (−)-**42**, $[\alpha]^{20}_D$ −118° (170 mg, 1.12 mmol), in pyridine (2 mL) was added acetic anhydride (0.3 mL) and the mixture was stirred for 6 h with ice cooling. After being allowed to stand overnight at room temperature, the mixture was poured into ice–water and extracted with ether. The extract was washed with dilute HCl, saturated $NaHCO_3$ solution, and water and dried ($MgSO_4$). After evaporation of the solvent, the residue was distilled to give 150 mg of (−)-**43** (69% yield): bp 130–135 °C (bath temperature) (20 mm); $[\alpha]^{25}_D$ −98.9° (c 0.527, MeOH); IR (neat film) 1730, 1365, 1250, 1240, 1230, 1055 cm^{-1}; NMR (CCl_4) δ 1.2–2.2 (m, 14 H), 2.93 (s, 3 H), 4.65 (d, J = 6 Hz 1 H); NMR (CCl_4; (−)-**43**/Eu(facam)$_3$ = 1:0.189) δ 4.43 and 4.53 ($OCOCH_3$).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.01; H, 9.40.

(−)-Twistan-2-one (44). To a suspension of pyridinium chlorochromate[16] (310 mg, 1.44 mmol) in methylene chloride (6 mL) was added (−)-**42**, $[\alpha]^{20}_D$ −118° (90 mg, 0.592 mmol), and the mixture was stirred for 2.5 h at room temperature. An organic phase was separated and the residue was rinsed with ether. Combined organic solutions were washed with dilute HCl, saturated $NaHCO_3$ solution, and water and dried ($MgSO_4$). After evaporation of the solvent, the residue was chromatographed on neutral alumina (Woelm, activity III). Fractions eluted with pentane gave a white solid which was sublimed at 80 °C (30 mm) to give 50 mg of (−)-**44** (56% yield), mp 184–188 °C (in a sealed tube), $[\alpha]^{22}_D$ −151° (c 0.405, EtOH). IR spectrum and VPC (stationary phase PEG-20M 10% 2 m, column temperature 180 °C) behaviors were identical with those of (+)-twistan-2-one.[3]

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.70; H, 9.35.

Registry No.—**1**, 42070-69-9; **2**, 37165-27-8; **3**, 64727-80-6; **5**, 62928-75-0; **13**, 62928-79-4; **15**, 67844-29-5; **16**, 67815-16-1; **17**, 67815-17-2; **18**, 67815-18-3; **19**, 67815-19-4; **20**, 67815-20-7; **21**, 67815-21-8; **22**, 67815-22-9; (+)-**23**, 67815-23-0; (−)-**23**, 67844-30-8; **24**, 58001-99-3; **25**, 2566-59-8; **26**, 67844-31-9; **27**, 67844-32-0; **28**, 67844-33-1; **29**, 67844-34-2; (−)-**30**, 67844-35-3; (+−)-**30**, 67844-36-4; (−)-**31**, 67815-24-1; (+−)-**31**, 67844-37-5; **32**, 67815-25-2; **33**, 67844-38-6; **34**, 20507-57-7; **35**, 54515-89-8; **36**, 67815-26-3; **37**, 67844-39-7; **38**, 54515-90-1; **39**, 67815-27-4; **40**, 67815-28-5; **41**, 67815-29-6; **42**, 67844-40-0; **43**, 67815-30-9; **44**, 37165-26-7; (−)-*exo*-3-tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decyl hydrogen phthalate, (+)-2-(1-aminoethyl)naphthalene salt, 67844-41-1; ethyl malonate, 105-53-3; phthalic anhydride, 85-44-9; (+)-2-(1-aminoethyl)naphthalene, 3886-70-2; sodium cyanide, 143-33-9.

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A New, Convenient, and Stereospecific Method for the Conversion of Secondary Amines to Primary Amines and Olefins. Thermal Decomposition of Magnesium, Zinc, and Aluminum Amides

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Magnesium, zinc, and aluminum amides of the general formula $RMNR'_2$ thermally decompose at 150–250 °C to give hydrocarbon (RH), an olefin (from R'), and a residue of empirical formula $(MNR')_x$, which can be hydrolyzed to a primary amine. Kinetic and stereochemical studies indicate that a cyclic, unimolecular six-center transition state is involved. This reaction represents the conversion of a secondary amine to a primary amine and an olefin in a syn stereochemical manner and compares favorably as an alternative to the Hoffman elimination and Cope elimination reactions.

Several methods are known for the preparation of olefins from amines.[1] These methods include the pyrolysis of quaternary ammonium hydroxides[2] (Hoffman elimination reaction) and the pyrolysis of amine oxides[3] (Cope elimination reaction). The Hoffman elimination reaction involves the thermal decomposition of a quaternary ammonium hydroxide to give an olefin, a tertiary amine, and water. The reaction usually occurs by an E_2 mechanism in an anti stereochemical manner. The yield is quite dependent upon the particular compound being decomposed with an average yield in the range 50–75%. The disadvantages of the Hoffman elimination reaction include (1) the necessity of having a tertiary amine in order to convert it to the quaternary ammonium hydroxide, (2) separation of the olefin product from the tertiary amine and water byproducts, and (3) a competing side reaction to produce an alcohol and tertiary amine due to a displacement reaction at the carbon atom.

The Cope elimination reaction involves the thermal decomposition of tertiary amine oxides to yield an olefin and a derivative of hydroxylamine in a syn stereochemical manner. The amine oxides are prepared by treating the tertiary amine with 35% aqueous hydrogen peroxide at room temperature or with stronger reagents, e.g., 40% peroxyacetic acid or monoperoxyphthalic acid. It is necessary to destroy excess peroxide

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Table I. Preparation of $HMgNR'_2$, $CH_3MgNR'_2$, $PhMgNR'_2$, and $PhCH_2MgNR'_2$ Compounds

ser. no.	reactants (mmol) R_2Mg[a]	R'_2NH	registry no.	reaction time, h	analysis, % Mg	R	R'_2N	solvent	analysis ratio Mg:R:R'_2N:solvent	product	registry no.
1.	MgH_2 (3.58)	$Mg(N\text{-}n\text{-}Pr_2)_2$ (3.50)	23293-22-3	5	16.5	0.66	71.2	11.7	1.00:0.97:1.05:0.24	$HMgN\text{-}n\text{-}Pr_2\cdot 0.24THF$	65277-32-9
2.	MgH_2 (3.70)	$Mg(N\text{-}s\text{-}Bu_2)_2$ (3.70)	65277-27-2	4	12.1	0.48	64.0	23.4	1.00:0.96:1.00:0.65	$HMgN\text{-}s\text{-}Bu_2\cdot 0.65THF$	65277-33-0
3.	MgH_2 (4.00)	$Mg[N(c\text{-}C_6H_{11})_2]_2$ (4.00)	23275-86-7	6	8.63	0.35	63.9	27.1	1.00:0.98:1.01:1.06	$HMgN(c\text{-}C_6H_{11})_2\cdot 1.06THF$	67699-67-6
4.	$(CH_3)_2Mg$ (53.2)	Et_2NH (53.4)	109-89-7	1	22.7	13.6	63.8	00.0	1.00:0.97:0.95:0.00	CH_3MgNEt_2	67699-68-7
5.	$(CH_3)_2Mg$ (75.0)	$n\text{-}Pr_2NH$ (75.2)	142-84-7	1	17.7	10.4	71.9	00.0	1.00:0.98:0.99:0.00	$CH_3MgN\text{-}n\text{-}Pr_2$	67699-69-8
6.	$(CH_3)_2Mg$ (18.0)	$i\text{-}Pr_2NH$ (18.1)	108-18-9	0.5	18.9	10.9	70.2	00.0	1.00:0.95:0.90:0.00	$CH_3MgN\text{-}i\text{-}Pr_2$	67209-22-7
7.	$(CH_3)_2Mg$ (50.0)	$n\text{-}Bu_2NH$ (50.3)	111-92-2	0.5	16.1	9.20	74.6	00.0	1.00:0.93:0.88:0.00	$CH_3MgN\text{-}n\text{-}Bu_2$	67699-70-1
8.	$(CH_3)_2Mg$ (75.0)	$s\text{-}Bu_2NH$ (75.5)	626-23-3	0.5	15.7	9.90	74.4	00.0	1.00:1.02:0.90:0.00	$CH_3MgN\text{-}s\text{-}Bu_2$	67699-71-2
9.	$(CH_3)_2Mg$ (51.8)	$c\text{-}C_5H_{10}NH$ (52.0)	110-89-4	1	19.9	11.9	68.2	00.0	1.00:0.97:0.99:0.00	$CH_3Mg(NC_5H_{10}\text{-}c)$	67699-72-3
10.	$(CH_3)_2Mg$ (76.5)	$(c\text{-}C_6H_{11})_2NH$ (76.5)	101-83-7	1	10.9	6.54	82.5	00.0	1.00:0.97:1.02:0.00	$CH_3MgN(c\text{-}C_6H_{11})_2$	67699-73-4
11.	$(CH_3)_2Mg$ (46.5)	Ph(Et)NH (46.8)	103-69-5	0.5	14.4	9.27	76.3	00.0	1.00:1.04:1.07:0.00	$CH_3MgN(Et)Ph$	67711-83-5
12.	$(CH_3)_2Mg$ (6.60)	$PhCH_2CH_2(CH_3)NH$ (6.61)	589-08-2	0.5	14.3	8.47	77.2	00.0	1.00:0.95:0.98:0.00	$CH_3MgN(CH_3)CH_2CH_2Ph$	67699-74-5
13.	$(CH_3)_2Mg$ (4.36)	$HNPh_2$ (4.39)	122-39-4	1	8.6	5.3	59.3	26.8	1.00:0.85:1.21:1.03	$CH_3MgNPh_2\cdot 1.03 Et_2O$	67209-23-8
14.	Ph_2Mg (4.00)	$HNEt_2$ (4.01)		1	12.3	39.0	36.3	12.4	1.00:1.03:0.98:0.33	$PhMgNEt_2\cdot 0.33 Et_2O$	67699-75-6
15.	Ph_2Mg (4.00)	$HN\text{-}i\text{-}Pr_2$ (3.98)		1	9.1	28.8	37.4	24.7	1.00 1.03:0.93:0.89	$PhMgN\text{-}i\text{-}Pr_2\cdot 0.98 Et_2O$	67699-76-7
16.	Ph_2Mg (4.01)	$HN\text{-}n\text{-}Bu_2$ (4.05)		1	8.4	26.6	44.1	20.9	1.00:1.05:0.93:0.82	$PhMgN\text{-}n\text{-}Bu_2\cdot 0.82 Et_2O$	67711-82-4
17.	Ph_2Mg (3.99)	$HN\text{-}s\text{-}Bu_2$ (4.03)		1	7.1	22.5	37.5	32.9	1.00:1.02:0.96:1.52	$PhMgN\text{-}s\text{-}Bu_2\cdot 1.52 Et_2O$	67699-77-8
18.	Ph_2Mg (4.93)	$HN(c\text{-}C_6H_{11})_2$ (4.94)		1	6.9	21.7	50.7	20.7	1.00:1.05:1.08:0.94	$PhMgN(c\text{-}C_6H_{11})_2\cdot 0.94 PhH$	67699-78-9
19.	$(PhCH_2)_2Mg$ (2.95)	$HNEt_2$ (2.91)		1	9.9	37.3	29.5	23.3	1.00:1.10:1.05:0.77	$PhCH_2MgNEt_2\cdot 0.77 Et_2O$	67699-79-0
20.	$(PhCH_2)_2Mg$ (2.30)	$HN\text{-}i\text{-}Pr_2$ (2.32)		1	8.0	30.1	33.2	28.7	1.00:1.27:1.02:1.17	$PhCH_2MgN\text{-}i\text{-}Pr_2\cdot 1.17 Et_2O$	67699-80-3
21.	$(PhCH_2)_2Mg$ (3.00)	$HN\text{-}n\text{-}Bu_2$ (2.96)		1	8.0	29.9	42.1	20.0	1.00:0.80:0.95:0.82	$PhCH_2MgN\text{-}n\text{-}Bu_2\cdot 0.82 Et_2O$	67699-81-4
22.	$(PhCH_2)_2Mg$ (1.60)	$HN\text{-}s\text{-}Bu_2$ (1.57)		1	7.7	28.7	40.5	23.1	1.00:0.85:0.93:0.99	$PhCH_2MgN\text{-}s\text{-}Bu_2\cdot 0.99 Et_2O$	67699-82-5
23.	$(PhCH_2)_2Mg$ (2.80)	$HN(c\text{-}C_6H_{11})_2$ (2.78)		1	5.3	19.7	39.0	36.0	1.00:0.80:0.94:2.25	$PhCH_2MgN(c\text{-}C_6H_{11})_2\cdot 2.25 Et_2O$	67699-83-6
24.	$(CH_3)_2Mg$ (4.23)	$(CH_3)_2CHNHPh$ (4.23)	76-52-5	1	11.2	6.9	61.8	20.1	1.00:0.89:1.10:0.59	$(CH_3)_2CHN(Ph)MgCH_3\cdot 0.59 Et_2O$	67699-84-7
25.	$(CH_3)_2Mg$ (5.68)	$(CD_3)_2CHNHPh$ (5.70)	67699-91-6	1	11.4	7.0	65.7	15.9	1.00:1.10:0.95:0.46	$(CD_3)_2CHN(Ph)MgCH_3\cdot 0.46 Et_2O$	67699-85-8
26.	$(CH_3)_2Mg$ (4.13)	$(CH_3)_2CHNHCH_2Ph$ (4.12)	102-97-6	1	11.6	7.2	70.6	10.6	1.00:0.93:0.97:0.30	$(CH_3)_2CHN(MgCH_3)CH_2Ph\cdot 0.30 Et_2O$	67699-86-9
27.	$(CH_3)_2Mg$ (4.60)	$(CD_3)_2CHNHCH_2Ph$ (4.62)	67699-92-7	1	11.9	7.4	75.6	5.1	1.00:0.80:1.05:0.14	$(CD_3)_2CHN(MgCH_3)CH_2Ph\cdot 0.14 Et_2O$	67699-87-0
28.	$(CH_3)_2Mg$ (4.59)	*threo*-$PhCH_3CHCHPhNHPh$ (4.61)	67711-36-8	0.5	7.53	4.88	87.6	0.00	1.00 1.05:1.02:0.00	*threo*-$PhN(MgCH_3)CHPhCHCH_3Ph$	67699-88-1
29.	$(CH_3)_2Mg$ (30.0)	$H_2N\text{-}t\text{-}Bu$ (30.0)	75-64-9	1	18.2	11.2	52.4	18.3	1.00:0.92:0.95:0.33	$CH_3MgNH\text{-}t\text{-}Bu\cdot 0.33 Et_2O$	67699-89-2
30.	$(CH_3)_2Mg$ (31.7)	HNEt(Naph-1) (31.8)	118-44-5	1	13.4	8.3	78.3	0.00	1.00:0.69:0.95:0.00	$CH_3MgNH(Naph\text{-}1)$	67699-90-5

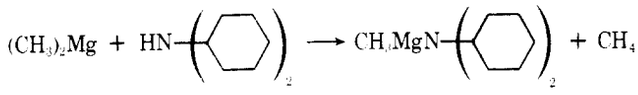
[a] Registry no.: MgH_2, 7693-27-8; $(CH_3)_2Mg$, 2999-74-8; Ph_2Mg, 2999-74-8; $(PhCH_2)_2Mg$, 6928-77-4.

before the pyrolysis is performed. The yields and disadvantages of this method of deaminating amines to olefins are similar to those of the Hoffman elimination reaction.

The amides of magnesium, zinc, and aluminum have been well characterized[4] and have been evaluated as stereoselective alkylating agents.[5] This report concerns a new type of deamination reaction that converts a secondary amine to a primary amine and compares favorably with the above mentioned reactions for the conversion of amines to olefins.

Results

Magnesium, zinc, and aluminum amides are prepared quantitatively by reacting a suitable hydrido, alkyl, or aryl metal compound directly with a secondary amine. This general reaction is illustrated in eq 1–3. Details of the preparation

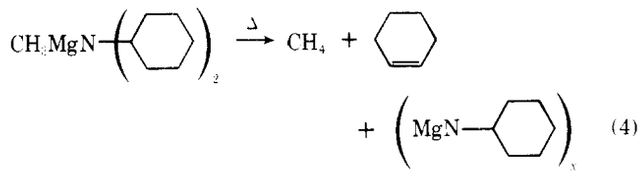


(1)

$$(Ph)_2Zn + HN\text{-}i\text{-}Pr_2 \longrightarrow PhZnN\text{-}i\text{-}Pr_2 + PhH \quad (2)$$

$$Ph_3Al + HNEt_2 \longrightarrow Ph_2AlNEt_2 + PhH \quad (3)$$

are given in the Experimental Section and are summarized in Tables I–III. Then, in a second step the amide is thermally decomposed as illustrated in reactions 4–6. The products are hydrocarbon, an olefin, and a residue of empirical formula $(MNR')_x$.



(4)

$$PhZnN\text{-}i\text{-}Pr_2 \xrightarrow{\Delta} PhH + CH_2{=}CHCH_3 + (ZnN\text{-}i\text{-}Pr)_x \quad (5)$$

$$Ph_2AlNEt_2 \xrightarrow{\Delta} PhH + CH_2{=}CH_2 + (PhAlNEt)_x \quad (6)$$

DTA–TGA Data. The decomposition reaction was studied by DTA–TGA (differential thermal analysis–thermogravimetric analysis).[6] This data is summarized in Tables IV–VI. Samples of amides 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, e.g., all decompositions are endothermic. In general, the coordinated solvent is lost first, and then the main decomposition occurs in one step without the formation of an intermediate. Both condensable and noncondensable evolved gases were identified and measured quantitatively. Further decomposition of the residue $(MgNR')_x$ occurs at higher temperature.

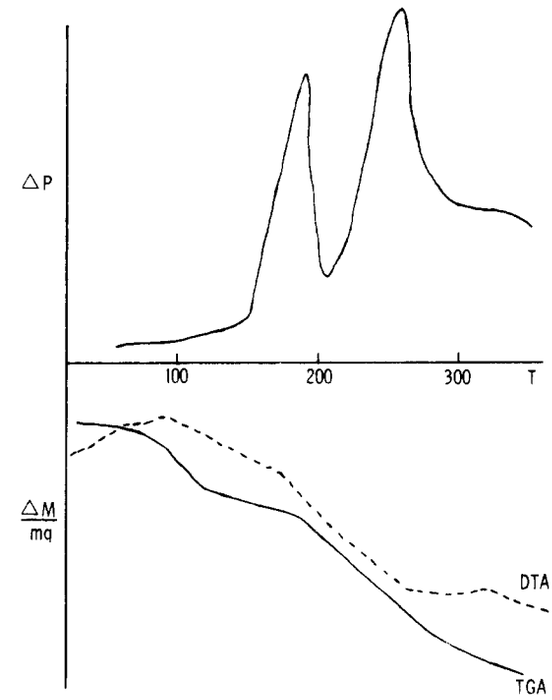


Figure 1. Vacuum DTA–TGA for $CH_3MgN(c\text{-}C_6H_{11})_2$.

Some of the compounds studied were volatile, e.g., complete sublimation occurred on heating (diethylamino)phenylzinc and (di-*n*-butylamino)diphenylaluminum. The decomposi-

Table II. Preparation of $PhZnNR'_2$ Compounds

ser. no.	Reactants (mmol) R_2Zn	Reactants (mmol) R'_2NH	reaction time, h	analysis, % Zn	R	R'_2N	solvent	analysis ratio Zn:R:R'_2N:solvent	probable product	registry no.
1.	Ph_2Zn[a] (2.55)	$HNEt_2$ (2.60)	1	25.2	29.7	27.7	17.4	1.00:0.95 1.05:0.49	$PhZnNEt_2 \cdot 0.49PhCH_3$	67699-93-8
2.	Ph_2Zn (2.65)	HN-*i*-Pr_2 (2.64)	1	22.8	26.9	34.9	15.4	1.00:0.98:1.10:0.48	PhZnN-*i*-$Pr_2 \cdot 0.48PhCH_3$	67699-94-9
3.	Ph_2Zn (2.81)	HN-*n*-Bu_2 (2.79)	1	20.1	23.6	39.3	17.0	1.00:0.97:1.02:0.60	PhZnN-*n*-$Bu_2 \cdot 0.60PhCH_3$	67699-95-0
4.	Ph_2Zn (5.09)	$HN(c\text{-}C_6H_{11})_2$ (5.14)	1	16.9	20.0	46.6	16.5	1.00:0.97:0.96:0.69	$PhZnN(c\text{-}C_6H_{11})_2 \cdot 0.69PhCH_3$	67699-96-1

[a] Registry no.: 1078-58-6.

Table III. Preparation of $Ph_2AlNR'_2$ Compounds

ser. no.	reactants (mmol) R_3Al	reactants (mmol) R'_2NH	reaction time, h	analysis, % Al	R	R'_2N	solvent	analysis ratio Al:R:R'_2N:solvent	probable product	registry no.
1.	Ph_3Al[a] (1.44)	$HNEt_2$ (1.44)	1	8.3	47.4	22.2	22.1	1.00:1.90:0.95 0.78	$Ph_2AlNEt_2 \cdot 0.78PhCH_3$	67699-97-2
2.	Ph_3Al (1.64)	HN-*i*-Pr_2 (1.63)	1	8.1	46.3	30.1	15.5	1.00:1.85:0.97:0.56	$Ph_2AlN\text{-}iPr_2 \cdot 0.56PhCH_3$	67699-98-3
3.	Ph_3Al (1.70)	HN-*n*-Bu_2 (1.72)	1	7.0	40.0	33.2	19.8	1.00:1.97:1.02:0.83	$Ph_2AlN\text{-}n\text{-}Bu_2 \cdot 0.83PhCH_3$	67699-99-4
4.	Ph_3Al (2.45)	$HN(c\text{-}C_6H_{11})_2$ (2.42)	1	4.1	23.3	27.2	45.4	1.00:1.98:1.05:3.26	$Ph_2AlN(c\text{-}C_6H_{11})_2 \cdot 3.26(PhCH_3$	67700-00-9

[a] Registry no.: Ph_3Al, 841-76-9.

Table IV. Thermal Decomposition of $HMgNR'_2$, $CH_3MgNR'_2$, $PhMgNR'_2$, and $PhCH_2MgNR'_2$ Compounds[a]

compd (sample wt, mg)	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
CH_3MgNEt_2 (79.1)	70–208 (190)	11.4 (14.4)	CH_4
	220–272 (262)	29.7 (37.5)	$CH_2{=}CH_2$
$PhMgNEt_2{\cdot}0.33Et_2O$ (19.9)	55–115 (85)	2.4 (12.1)	Et_2O
	185–330 (220)	7.9 (39.7)	PhH
	330–462 (400)	2.8 (14.1)	$CH_2{=}CH_2$
$PhCH_2MgNEt_2{\cdot}0.77Et_2O$ (60.2)	50–150 (95)	14.0 (23.3)	Et_2O
	150–445 (240)	26.2 (43.5)	$PhCH_3 + CH_2{=}CH_2$
$HMgN\text{-}n\text{-}Pr_2{\cdot}0.24THF$ (84.7)	50–190 (120)	10.0 (11.8)	THF
	190–265	5.3 (6.3)	THF cleavage product
	265–450 (340, 396)	17.6 (20.8)	$H_2 + CH_3CH{=}CH_2$
$CH_3MgN\text{-}n\text{-}Pr_2$ (89.1)	160–230 (215)	10.2 (11.4)	CH_4
	230–365 (325)	27.0 (30.3)	$CH_3CH{=}CH_2$
$CH_3MgN\text{-}i\text{-}Pr_2$ (54.4)	80–160 (125)	22.8 (42.0)	$CH_4 + CH_3CH{=}CH_2$
$PhMgN\text{-}i\text{-}Pr_2{\cdot}0.89Et_2O$ (58.7)	65–140 (110)	14.5 (24.7)	Et_2O
	140–445 (250)	26.7 (45.5)	$PhH + CH_3CH{=}CH_2$
$PhCH_2MgN\text{-}i\text{-}Pr_2{\cdot}1.17Et_2O$ (69.7)	45–150 (90)	20.0 (28.7)	Et_2O
	150–345 (210)	33.0 (47.3)	$PhCH_3 + CH_3CH{=}CH_2$
$CH_3MgN\text{-}n\text{-}Bu_2$ (42.0)	125–265 (200)	26.8 (41.7)	$CH_4 + CH_3CH_2CH{=}CH_2$
$PhMgN\text{-}n\text{-}Bu_2{\cdot}0.82Et_2O$ (43.5)	105–175 (155)	9.0 (20.7)	Et_2O
	175–462 (235)	20.0 (46.0)	$PhH + CH_3CH_2CH{=}CH_2$
$PhCH_2MgN\text{-}n\text{-}Bu_2{\cdot}0.82Et_2O$ (90.2)	50–135 (90)	18.0 (20.0)	Et_2O
	135–455 (215)	42.5 (47.1)	$PhCH_3 + CH_3CH_2CH{=}CH_2$
$HMgN\text{-}s\text{-}Bu_2{\cdot}0.65THF$ (29.7)	50–145 (90)	6.0 (20.2)	THF
	145–260	2.6 (8.8)	$THF + H_2$
	260–390 (335)	7.0 (23.6)	$H_2 + CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3$
$CH_3MgN\text{-}s\text{-}Bu_2$ (52.0)	80–175 (115)	23.0 (44.2)	$CH_4 + CH_3CH_2CHCH_2 + CH_3CHCHCH_3$
$PhMgN\text{-}s\text{-}Bu_2{\cdot}1.52Et_2O$ (86.6)	40–145 (130)	28.5 (32.9)	Et_2O
	145–450 (285)	34.5 (39.8)	$PhH + CH_2{=}CHCH_2CH_3 + CH_3CH{=}CHCH_3$
$PhCH_2MgN\text{-}s\text{-}Bu{\cdot}0.99Et_2O$ (47.7)	40–140 (75)	11.0 (23.1)	Et_2O
	140–395 (205)	24.5 (51.4)	$PhCH_3 + CH_2{=}CHCH_2CH_3 + CH_3CH{=}CHCH_3$
$HMgN(c\text{-}C_6H_{11})_2{\cdot}1.06THF$ (97.1)	50–180 (100)	26.0 (26.8)	THF
	200–390 (280)	29.2 (30.1)	H_2 + cyclohexene
$CH_3MgN(c\text{-}C_6H_{11})_2$ (28.2)	130–280 (200)	11.9 (42.1)	CH_4 + cyclohexene
$PhMgN(c\text{-}C_6H_{11})_2{\cdot}0.94PhH$ (60.3)	55–140 (100)	15.7 (26.0)	PhH
	140–455 (295)	25.4 (42.1)	PhH + cyclohexene
$PhCH_2\ MgN(c\text{-}C_6H_{11})_2{\cdot}2.25Et_2O$ (58.3)	85–210 (185)	21.0 (36.0)	Et_2O
	210–460 (295)	20.5 (35.2)	$PhCH_3$ + cyclohexene
$CH_3MgN(CH_3)CH_2CH_2Ph$ (62.9)	140–440 (275)	33.3 (52.9)	$CH_4 + PhCH{=}CH_2$
$CH_3MgNEtPh$ (37.2)	180–320 (215, 270)	10.4 (28.0)	$CH_4 + CH_2{=}CH_2$
$CH_3MgNPh_2{\cdot}1.03Et_2O$ (84.4)	45–235 (145)	22.7 (26.9)	Et_2O
	355–465 (415)	7.0 (8.3)	CH_4 + 8.7% sublimation
$CH_3Mg(NC_5H_{10}\text{-}c)$ (50.8)	60–230 (185)	6.8 (13.4)	CH_4
$CH_3MgNEt(Naph\text{-}1)$ (26.3)	65–140 (85)	5.6 (21.3)	$CH_4 + CH_2{=}CH_2$
$CH_3MgNH\text{-}t\text{-}Bu{\cdot}0.33Et_2O$ (43.3)	60–160 (105)	9.0 (20.8)	Et_2O
	200–275 (250)	5.0 (11.5)	CH_4
$(CH_3)_2CHN(Ph)MgCH_3$ (19.8)	50–160 (100)	4.5 (22.7)	Et_2O
	160–305 (210)	5.5 (27.8)	$CH_4 + CH_2{=}CHCH_3$
$(CD_3)_2CHN(Ph)MgCH_3$ (55.2)	55–160 (95)	8.8 (15.9)	Et_2O
	160–395 (215)	16.0 (30.0)	$CH_3D + CD_2{=}CHCD_3$
$(CH_3)_2CHN(MgCH_3)CH_2Ph$ (61.6)	50–150 (115)	6.5 (10.6)	Et_2O
	150–375 (240)	18.5 (30.0)	$CH_4 + CH_2{=}CHCH_3$
$(CD_3)_2CHN(MgCH_3)CH_2Ph$ (86.9)	50–140 (100)	4.5 (5.2)	Et_2O
	140–400 (195)	27.5 (31.6)	$CH_3D + CD_2{=}CHCD_3$
threo-$CH_3MgNPhCHPh\text{-}CHCH_3Ph$ (23.9)	100–155 (120)	15.8 (66.1)	$CH_4 + cis\text{-}PhC(CH_3){=}CHPh$

[a] All thermometric changes are endothermic.

tion of (diphenylamino)methylmagnesium resulted in 8.7% sublimation. All methylzinc amides and dimethylaluminum amides sublimed.

Comparisons among amides having the same amide group and metal but different alkyl groups indicate a particular decomposition trend (Tables IV–VI). For both (di-*n*-butylamino)magnesium and (diisopropylamino)magnesium compounds, the order of increasing decomposition temperature

Table V. Thermal Decomposition of $PhZnNR'_2$ Compounds[a]

compd (sample wt, mg)	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
$PhZnNEt_2 \cdot 0.49PhCH_3$ (100.6)	70	77.0 (76.5)	sublimation only
$PhZnN\text{-}i\text{-}Pr_2 \cdot 0.48PhCH_3$ (80.3)	35–70 (60)	12.4 (15.4)	$PhCH_3$
	70–170 (120)	33.6 (41.8)	$PhH + CH_2{=}CHCH_3$
$PhZnN\text{-}n\text{-}Bu_2 \cdot 0.60PhCH_3$ (83.1)	70–205 (175)	53.0 (63.8)	$PhCH_3$, $PhH + CH_2{=}CHCH_2CH_3$
$PhZnN(c\text{-}C_6H_{11})_2 \cdot 0.69PhCH_3$ (78.0)	45–105 (95)	15.0 (19.2)	$PhCH_3$
	105–170 (145)	39.0 (50.0)	PhH + cyclohexene

[a] All thermometric changes are endothermic

Table VI. Thermal Decomposition of $Ph_2AlNR'_2$ Compounds[a]

compd (sample wt, mg)	range of transition (peak max), °C	wt loss, mg (%)	evolved gas
$Ph_2AlNEt_2 \cdot 0.78PhCH_3$ (57.9)	60–120 (90)	12.7 (21.9)	$PhCH_3$
	120–240 (205)	24.3 (42.0)	$PhH + CH_2{=}CH_2$
$Ph_2AlN\text{-}i\text{-}Pr_2 \cdot 0.56\ PhCH_3$ (40.0)	40–90 (80)	6.5 (16.3)	$PhCH_3$
	90–230 (180)	15.5 (38.8)	$PhH + CH_2{=}CHCH_3$
$Ph_2AlN\text{-}n\text{-}Bu_2 \cdot 0.83PhCH_3$ (71.5)	90–200 (180)	14.5 (20.3)	$PhCH_3$
	200	50.5 (70.6)	sublimation only
$Ph_2AlN(c\text{-}C_6H_{11})_2 \cdot 3.26PhCH_3$ (67.8)	70–250 (195)	48.8 (72.0)	$PhCH_3$, PhH + cyclohexene

[a] All thermometric changes are endothermic

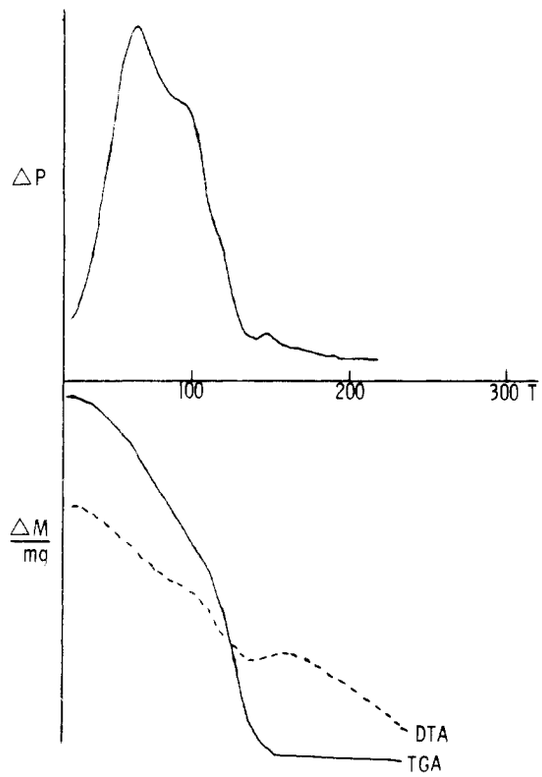


Figure 2. Vacuum DTA–TGA for $PhZnN\text{-}i\text{-}Pr_2 \cdot 0.48PhCH_3$.

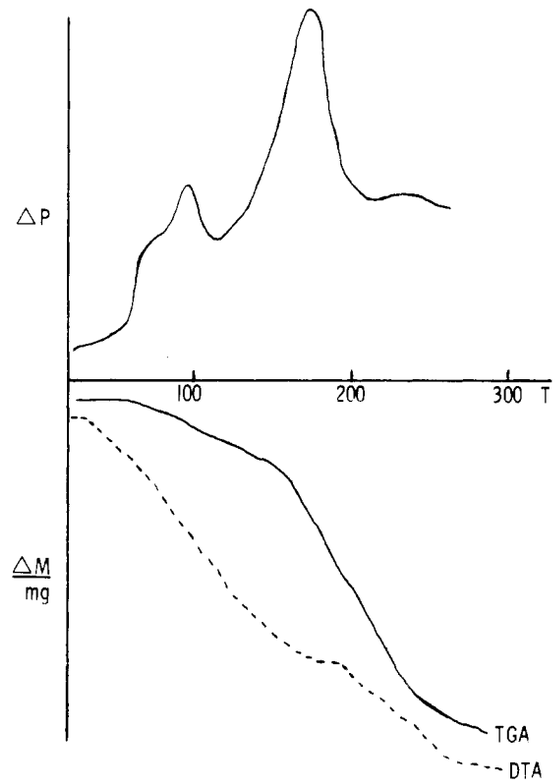


Figure 3. Vacuum DTA–TGA for $Ph_2AlNEt_2 \cdot 0.78PhCH_3$.

is $CH_3 < PhCH_3 < Ph$. However, the order for the (dicyclohexylamino)magnesium compounds is $CH_3 < PhCH_2 = Ph$. This order is not exactly what is expected for increasing stability of an incipient carbanion ($CH_3 < Ph < PhCH_2$).[7] A comparison of dicyclohexylphenyl- and diisopropylphenylamides in which only the identity of the metal changes gives an order of increasing decomposition temperature of Zn < Al < Mg.

There is a recurring trend for amides with the same alkyl group and metal but different amino groups. For methyl-, phenyl-, and benzylmagnesium amides, the order of increasing decomposition temperature parallels an approximate decrease in the stability of the olefin product. Obviously, the order of decomposition is dependent not only on the type of alkyl or aryl group on the metal but also on the type of metal and amide group.

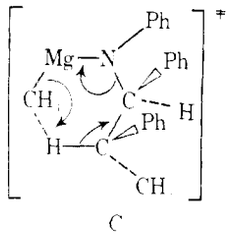
In general, there is no evidence to support the formation of an intermediate in the decomposition of the amides. The

DTA–TGA traces show no break in the TGA curve. Only one compound fails to follow this general rule, (*N*-ethylanilino)-methylmagnesium ($CH_3MgNEtPh$). This compound apparently eliminates methane at an early stage (215 °C) and then ethylene at a later stage (270 °C). A sample was refluxed in *n*-dodecane (bp 215 °C) for 24 h and quenched with deuterium oxide followed by acidic workup. Mass spectral analysis on the hydrolysis product gave a 54:46 ratio of CH_3CH_2NHPh to CDH_2CH_2NHPh as well as a large quantity of aniline. The nondeuterated *N*-ethylaniline is due to hydrolysis of the starting material. The deuterated compound is due to hydrolysis of an intermediate. Two possible structures for the intermediate are represented by A and B. Structure A repre-

A B

sents a cyclic species, whereas structure B represents a polymeric material. The aniline product is due to hydrolysis of the residue $(MgNPh)_x$ formed in the decomposition reaction.

Stereochemistry. Our postulated mechanism for the decomposition of alkyl metal amides involves the formation of a cyclic six-centered transition state. This concept is illustrated for [*N*-(*threo*-1,2-diphenyl-1-propyl)anilino]methylmagnesium in C. An incipient methyl carbanion abstracts a



C

β-hydrogen from the amide group to give methane, *cis*-1,2-diphenylpropene, and a residue $(MgNPh)_x$. In the actual experiment it was necessary to use triphenylphosphine to prevent isomerization of the cis olefin product since the by-product, $(MgNPh)_x$, acts as a Lewis acid isomerization catalyst. The result was 100% *cis*-1,2-diphenylpropene in about 75% yield.

Kinetics. (a) Kinetic Isotope Effect. Two amides were prepared in which the amino portion was deuterated in the β positions. The deuterated and nondeuterated amides were decomposed via DTA–TGA at a constant temperature (223 °C). First-order rate constants were determined by following the loss in weight of a tared sample of the amide due to the formation of volatile reaction products. A linear least-squares plot of the natural logarithm of moles of amide vs. time in minutes gives the first-order rate constants summarized in Table VII. Kinetic isotope effects (k_H/k_D) were calculated by taking the ratio of the rate of the decomposition of the nondeuterated amide to the rate of the decomposition of the deuterated amide.

(b) Determination of Activation Parameters. Constant temperature kinetics were conducted on several amides via DTA–TGA. The rate constants were determined as before and are summarized in Table VIII for several amides. The frequency factor (A) and experimental activation energy (E_a) were calculated from the Arrhenius equation, $k = Ae^{-E_a/RT}$, with the aid of a linear least-squares plot of ln k vs. $1/T$, where T is the absolute temperature. The energies of activation were obtained by use of the equation $E_a = -K\,Cp \times$ slope, and the frequency factors were calculated from the Arrhenius equation where the intercept = ln A. Having calculated the E_a and A values for a given compound, it was then possible to calculate an entropy of activation ($S^{\pm}$) at a specific temperature (200 °C) using the equation of O'Connor and Nace,[8] $S^{\pm} = 2.303R \log A - 2.303\,R \log (KeK'T/h)$, where K' is the Boltzman constant, h is Planck's constant, and K is the transmission coefficient which is assumed to be unity. The activation parameters are listed in Table IX. The R value is a measure of the fit of the experimental data to a straight line. Ideally the R value would be unity.

Table VII. Kinetic Isotope Effects

compd	k at 223 °C, min^{-1}	R	atmosphere	k_H/k_D
$CH_3MgN(Ph)CH(CH_3)_2$	3.58×10^{-3}	0.985	vacuum	2.47
$CH_3MgN(Ph)CH(CD_3)_2$	1.45×10^{-3}	0.989	vacuum	
$CH_3MgN(CH_2PH)CH(CH_3)_2$	4.65×10^{-3}	0.945	vacuum	3.60
$CH_3MgN(CH_2Ph)CH(CD_3)_2$	1.29×10^{-3}	0.986	vacuum	

Table VIII. First-Order Rate Constants for Amides

compd	k, min^{-1}	temp, °C	R
$CH_3MgN(c\text{-}C_6H_{11})_2$	2.43×10^{-3}	170	0.984
	4.48×10^{-3}	200	0.999
	3.47×10^{-2}	235	0.987
$PhMgN(c\text{-}C_6H_{11})_2$	1.67×10^{-3}	160	0.982
	1.86×10^{-3}	182	0.996
	2.72×10^{-3}	210	0.993
$CH_3MgN\text{-}i\text{-}Pr_2$	3.40×10^{-3}	85	0.999
	4.16×10^{-2}	95	0.968
	1.40×10^{-1}	110	0.958
$PhMgN\text{-}i\text{-}Pr_2$	1.04×10^{-3}	200	0.984
	1.87×10^{-3}	235	0.991
	1.08×10^{-2}	285	0.945
$PhCH_2MgN\text{-}i\text{-}Pr_2$	5.05×10^{-4}	70	0.968
	1.51×10^{-3}	90	0.992
	1.64×10^{-2}	155	0.996
$(CH_3)_2CHN(MgCH_3)CH_2Ph$	2.33×10^{-3}	175	0.997
	3.35×10^{-3}	200	0.999
	4.65×10^{-3}	223	0.945
$(CD_3)_2CHN(MgCH_3)CH_2Ph$	6.74×10^{-4}	200	0.987
	1.29×10^{-3}	223	0.986
	4.88×10^{-3}	252	0.995

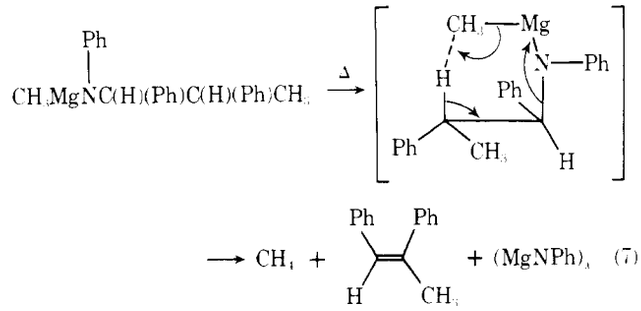
Table IX. Activation Parameters for Amides

compd	E_a, kcal/mol	A, s^{-1}	R	$\Delta S^{\pm}$ at 200 °C, eu
$CH_3MgN(c\text{-}C_6H_{11})_2$	18.1	2.55×10^{4}	0.947	−41.0
$PhMgN(c\text{-}C_6H_{11})_2$	4.1	2.96×10^{-3}	0.970	−72.8
$CH_3MgN\text{-}i\text{-}Pr_2$	39.4	8.75×10^{19}	0.947	+30.2
$PhMgN\text{-}i\text{-}Pr_2$	14.7	8.61×10^{1}	0.978	−52.3
$PhCH_2MgN\text{-}i\text{-}Pr_2$	11.9	3.10×10^{2}	0.985	−49.8
$(CH_3)_2CHN(MgCH_3)CH_2Ph$	6.5	5.79×10^{-2}	0.999	−66.9
$(CD_3)_2CHN(MgCH_3)CH_2Ph$	19.0	5.54×10^{3}	0.993	−44.0
$(CH_3)_2CHN(MgCH_3)Ph$	6.5	3.70×10^{2}	0.999	−49.4
$(CD_3)_2CHN(MgCH_3)Ph$	11.0	3.2	0.967	−58.9

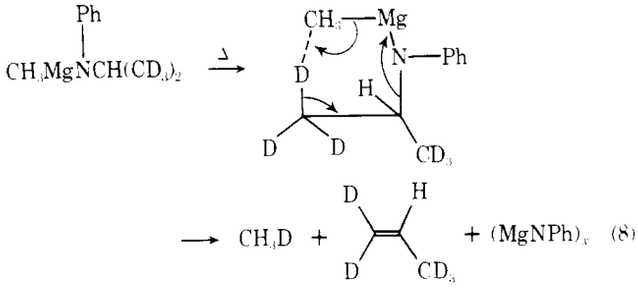
Discussion

The thermal decomposition of magnesium, zinc, and aluminum amides at 150–250 °C proceeds via a unimolecular, cyclic, six-center transition state involving the abstraction of a β-hydrogen by an incipient carbanion to yield a hydrocarbon, an olefin, and a residue of empirical formula $(MNR')_x$. The first-order rate constant (Table VIII) and the fact that no intermediate is observed (by DTA–TGA) indicate that the

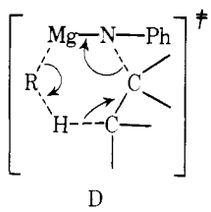
reaction is unimolecular. The large negative entropies of activation ($\Delta S^{\ddagger}$) listed in Table IX indicate that several degrees of freedom are lost in going from reactant to the transition state. These values suggest that a cyclic transition state is present in the rate-determining step of the reaction. The syn nature of the elimination reaction as implied in C is suggested by the decomposition of [*N*-(*threo*-1,2-diphenyl-1-propyl)-anilino]methylmagnesium to give only *cis*-1,2-diphenylpropene (eq 7).



The kinetic isotope effect study (Table VII) shows that the rate-determining step involves the abstraction of the β-hydrogen (eq 8). In our previous study[9] on the thermal decom-



position of the alkoxides of magnesium, zinc, and aluminum, we found an inverse kinetic isotope effect ($k_H/k_D \leq 1$) and suggested a variable E_i mechanism to explain the results. For the amides, the transition state is close to a central, synchronous E_i transition state, since the k_H/k_D ratio is about three.



D

An intermediate was detected in the decomposition of (*N*-ethylanilino)methylmagnesium ($CH_3MgNEtPh$). The two-stage decomposition was indicated by DTA–TGA and by quenching a partially decomposed sample. Isolation of an intermediate in this case only can be explained in terms of the stability of the incipient olefin and the instability of the potential residue $(MgNPh)_x$. The olefin product, ethylene, is unsubstituted and hence is the least stable olefin possible, thus explaining its difficulty in formation. A phenyl group on nitrogen is electron withdrawing, thus it removes electron density from the Mg–N bond, thus lessening any resonance stabilization of the partial positive charge on magnesium by donation of the lone pair on nitrogen onto magnesium. A decision between the two possible structures for the intermediate (A and B) cannot be made on the basis of the data available.

Comparisons can be made between the Hoffman elimination and Cope elimination reactions and the thermal decomposition of amides. The advantages of the newer method include (1) higher yields of olefin and equally good stereochemistry, (2) a simpler method in that the amide is easily prepared and does not have to be isolated or purified, and (3) the method is selective for secondary amines. The major disadvantage is the limited number of functional groups compatible with an organometallic compound.

The nature of the residue $(MgNR')_x$ formed in the thermal decomposition of the magnesium amides is the subject of a report to be published at a later date.

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[10] or on the bench using Schlenk tube techniques.[11] Glassware was flash flamed and flushed with dry nitrogen prior to use. DTA–TGA analysis was performed on a Mettler thermoanalyzer II equipped to run under vacuum.[12] Powdered amide samples were loaded into a cylindrical aluminum crucible with fritted disk and cap (preheated to 250 °C and cooled to room temperature) in the glovebox using a vibrator to ensure uniform particle size when possible. Samples were transferred to the DTA–TGA machine under nitrogen and were heated at 4 °C/min at 10^{-6} mmHg from 25 to 450 °C and at a chart speed of 6 in./h.

Analyses. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid or methanol on a standard vacuum line equipped with a Toepler pump.[11] Magnesium and zinc were determined by EDTA titration at pH 10 using Eriochrome Black T as the 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.

Diethylamine (Baker), di-*n*-propylamine, isopropylbenzylamine, methylphenethylamine (Aldrich), diisopropylamine, di-*n*-butylamine, dicyclohexylamine, *N*-ethylaniline (Eastman), *tert*-butylamine, piperdine (Fisher), *N*-ethyl-1-naphthylamine (Eastman), and di-*sec*-butylamine (Pfaltz and Bauer) were predried over NaOH and fractionally distilled prior to use. Diphenylamine (Fisher) and triphenylphosphine (Aldrich) were used without further purification.

Preparation of Dialkyl- and Diarylmagnesium Compounds. Dimethylmagnesium was prepared from dimethylmercury. 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 egg-shaped stirring bar. The apparatus was 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 glovebox. The active methyl/magnesium ratio = 2.02:1.00.

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

Dibenzylmagnesium was prepared from dibenzylmercury.[13] 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. The product was isolated by decantation of the ether layer from mercury followed by the distillation of ether. The ratio of benzyl/magnesium = 1.98:1.00.

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 to four times and finally made a slurry in THF. The analysis of this slurry showed that it contained a magnesium/hydrogen ratio = 1.00:2.02.

Preparation of Dimethyl- and Diphenylzinc. Dimethylzinc was prepared by the procedure of Noller.[14] 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 atmospheric pressure under nitrogen. The neat dimethylzinc was diluted with diethyl ether to facilitate handling. The ratio of methyl/zinc = 2.10:1.00.

Diphenyzinc was prepared from diphenylmercury.[15] To a 500-mL flask equipped with a reflux condenser and three-way stopcock sidearm was added granular zinc (23.2, 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. Ratio phenyl/zinc = 2.03:1.00.

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

Triphenylaluminum was prepared from diphenylmercury.[16] 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 for 39 h. The supernatant solution gave a phenyl/aluminum ratio = 3.05:1.00.

Preparation of *N*-(*threo*-1,2-Diphenyl-1-propyl)aniline. *N*-(*threo*-1,2-Diphenyl-1-propyl)aniline was prepared in five steps from *d,l*-benzoin.[17]

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. The mixture was then refluxed 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, $PhCH_3COHCHOHPh$, was crystallized from CS_2 (33.6 g, 80.9% yield). Analysis: mp 103–104 °C; IR 3400 cm^{-1}. 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 diethyl ether extracted. The diethyl ether was dried over $MgSO_4$ and reduced under vacuum to give an oil which slowly crystallized (26.6 g, 90.5% yield). The solid ketone product, $PhCHCH_3COPh$, 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, $PhCHCH_3COPh$ (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; the latter was then dried over $MgSO_4$, filtered, and evaporated under vacuum to give an oil. The oil was crystallized from pentane to give white needles (30.2 g, 47.8% yield). Analysis: 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.

The erythro alcohol $PhCHCH_3CHPhOH$ was converted to the brosylate by the following procedure. A solution of the erythro alcohol (8.8 g) in 150 mL of dry pyridine was cooled to −3 °C, and 12.5 g of *p*-bromobenzenesulfonyl chloride was added such that the temperature was kept below 0 °C. The solution was stored at 0 °C for 6 days. At that time the mixture was poured onto ice and water. The solid that separated was filtered and combined with the benzene extract of the aqueous layer. The benzene solution was washed with water, ice-cold 10% H_2SO_4, water again, $NaHCO_3$ solution, and then water again. The benzene solution was dried over anhydrous $MgSO_4$ and reduced in volume. Pentane was added to give a solid (4.7 g, 26.5% yield, mp 71–72 °C).

The erythro brosylate (12.4 g) and freshly distilled aniline (2.60 mL of aniline, 10:1 excess) were dissolved in 300 mL of benzene and refluxed for 20 h. The benzene solution was filtered to remove the white solid and then concentrated under vacuum. HCl was bubbled through the solution to form a white solid, which was removed by filtration. The benzene solution was treated with HCl gas again and the resultant solid was collected. The HCl salt was dissolved in water, basified, and extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$ and reduced in volume. The *threo*-$PhCHCH_3CHPhNHPh$ was crystallized three times from ether to give 0.6 g of material (7.2% yield): mp 118–119 °C dec; ($CDCl_3$) δ 1.20 (d, 3 H, CH_3), 3.07 (m, 1 H), 4.38 (d, 1 H), 7.27 (m, 15 H); IR (Nujol) 3400 (NH), 1600, 750, 695 cm^{-1} (Ph); mass spectrum *m/e* 287 (M^+), 182, 105, 77. Anal. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.37; N, 4.87. Found: C, 87.54; H, 7.45; N, 4.81. A mixture of threo and erythro anilines gave a methyl doublet at δ 1.23 (threo) as well as methyl doublet at δ 1.10 (erythro).

Preparation of Isopropylaniline.[18] Sodium borohydride (10 g, excess) was added to a mixture of 4.7 mL of aniline (50 mmol), 13.5 g of sodium acetate trihydrate, 42 mL of acetic acid, 125 mL of water, 30 mL of ethanol, and 10 mL (excess) of acetone at 0 °C with stirring. The solution was made basic with NaOH, and the aqueous layer was extracted with diethyl ether. The ether extract was dried over anhydrous $MgSO_4$ and reduced under vacuum to give 5.7 g of oil (crude yield 84.4%). The oil was distilled under nitrogen (bp 199–200 °C; lit. 198–207 °C[19]): NMR ($CDCl_3$) δ 1.18 (d, 6 H, CH_3), 3.47 (m, 2 H, NH + CH), and 6.88 (m, 5 H, Ph); IR (neat) 3410 (NH), 1600, 1505, 750, 690 cm^{-1} (Ph); n^{25}_D 1.5458 (lit. 1.5298, 1.5331[20]); mass spectrum *m/e* 135 (M^+), 120 ($M^+ - CH_3$), 93, 77, 42. Anal. Calcd for $C_9H_{13}N$: C, 79.96; H, 9.69; N, 10.35. Found: C, 79.80; H, 9.71; N, 10.31.

Preparation of Isopropyl-d_6-aniline. The procedure for the preparation of isopropylaniline was repeated substituting acetone-d_6 for acetone. The resultant oil (crude yield 76.8%) was distilled under nitrogen (bp 199–201 °C). The percent isotopic purity was determined by mass spectroscopic comparison to the nondeuterated isopropylaniline and was found to be 99 atom %: NMR in ($CDCl_3$) δ 3.35 (s, 1 H, NH), 3.49 (s, 1 H, CH), and 6.85 (m, 5 H, Ph); IR (neat) 3200 (NH), 1510, 655, 595 cm^{-1} (Ph); n^{25}_D 1.5390; mass spectrum *m/e* 141 (M^+), 123 ($M^+ - CD_3$), 94, 77. Anal. Calcd for $C_9H_7D_6N$: C, 77.03. Found: C, 76.55.

Preparation of Isopropyl-d_6-benzylamine. The procedure for the preparation of isopropylaniline was repeated substituting acetone-d_6 and 5.46 mL (50 mmol) of benzylamine. The resultant oil (crude yield 66.1%) was distilled under nitrogen (bp 193–194 °C). The percent isotopic purity was determined by mass spectroscopic comparison of it with the nondeuterated isopropylbenzylamine and was found to be 93.6 atom %: NMR ($CDCl_3$) δ 1.28 (s, 2 H, CH_2), 3.75 (s, 1 H, NH), 3.82 (s, 1 H, CH), and 7.27 (s, 5 H, Ph); IR (neat) 3300 (NH), 2120 (CD), 1665, 1605, 1495, 735, 700 cm^{-1} (Ph); n^{25}_D 1.5269; mass spectrum *m/e* 155 (M^+), 137 ($M^+ - CD_3$), 108, 91, 77. Anal. Calcd for $C_9H_7D_6H$: C, 76.99. Found: C, 77.38.

General Preparation of an Amide. The general method for the preparation of an amide is illustrated for (diisopropylamino)phenylmagnesium.

A dry, weighted 100-mL flask is fitted with a rubber septum cap, purged with dry nitrogen, and fitted with a needle connected to a nitrogen bubbler. A measured quantity of diisopropylamine is added to the flask via syringe and the flask is reweighed (0.402 g, 3.98 mmol). Then the flask is cooled to −78 °C and the calculated amount of diphenylmagnesium diethyl ether solution (4.00 mmol) is added via syringe. The flask is warmed to 25 °C and a solid forms with corresponding formation of benzene. The septum is replaced with a three-way stopcock and the solvent is distilled out under vacuum. The solid (diisopropylamino)phenylmagnesium is transferred to the glovebox for further manipulation and analysis. Ratio magnesium/benzene/diisopropylamine/diethyl ether = 1.00:1.03:0.93:0.89.

General Methods of Decomposition. (a) Decomposition in the Solid State. The method of decomposing amides in the solid state is illustrated for the thermal decomposition of [*N*-(*threo*-1,2-diphenyl-1-propyl)anilino]methylmagnesium.

[*N*-(*threo*-1,2-diphenyl-1-propyl)anilino]methylmagnesium and excess triphenylphosphine were placed in a dry 10-mL flask dequipped 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-diphenylpropene product distilled onto the cold finger and was removed by rinsing with diethyl ether for GLC analysis after addition of the internal standard. The pot was anlayzed for magnesium to determine the yield (75%).

(b) Decomposition in *n*-Dodecane Diluent. The decomposition of an amide in *n*-dodecane diluent is illustrated for (diethylamino)methylmagnesium.

The reagent (4.3 mmol) is prepared in the usual manner in a 100-mL flask equipped with a Teflon sidearm, magnetic stirring bar, and reflux condenser with a three-way stopcock. The diethyl ether solvent is removed under vacuum, and 25 mL of *n*-dodecane is added via syringe. The apparatus is connected via the three-way stopcock to a gas evolution apparatus designed to collect evolved gases at at-

mospheric pressure. The n-dodecane solution is refluxed with stirring for 3 h, and the evolved gases are measured. The quantitative yield is 8.6 mmol of gases identified as a mixture of methane and ethylene by mass spectroscopy.

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Registry No.—Magnesium, 7439-95-4; dimethylmercury, 593-74-8; diphenylmercury, 587-85-9; diethylmagnesium, 557-18-6; *d,l*-benzoin, 579-44-2; 1,2-diphenyl-1,2-propylene glycol, 41728-16-9; 1,2-diphenyl-1-propanone, 67737-73-9; *erythro*-1,2-diphenyl-1-propanol, 56844-75-8; *p*-bromobenzenesulfonyl chloride, 98-58-8; *erythro*-1,2-diphenyl-1-propanol brosylate, 67700-01-0; aniline, 62-53-3; acetone-d_6, 666-52-4; benzylamine, 100-46-9; methyl iodide, 74-88-4.

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Total Synthesis of (±)-Ferruginol and (±)-Hinokione

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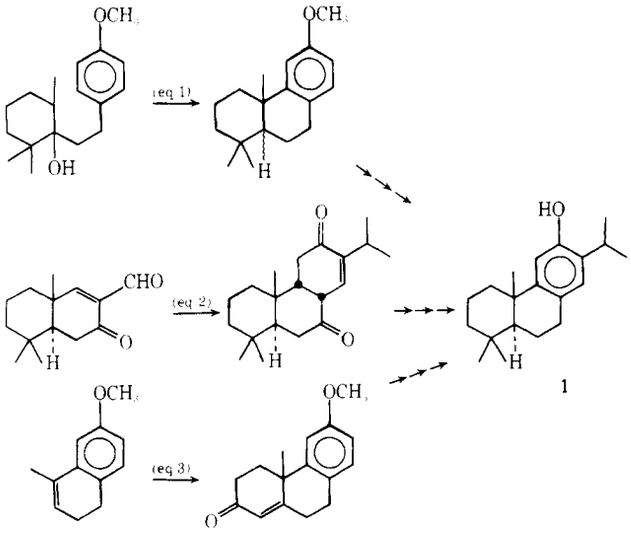
Stereospecific syntheses of (±)-ferruginol and (±)-hinokione were achieved in which the tricyclic ring system was assembled in the order C → BC → ABC. The key features of the approach involve: (1) the utilization of a lactone bridge as part of an enone protecting group in ring A; (2) the installation of an isopropyl group by the regioselective addition of lithium dimethylcuprate to a cross-conjugated dienone; (3) the elimination of the lactone bridge with concomitant aromatization of ring C; and (4) the reductive methylation of the enone in ring A to install the C-4 geminal dimethyl group and to guarantee the trans fusion of the AB rings.

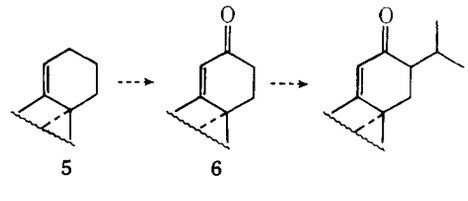
The isolation and structure elucidation[1] of ferruginol (**1**), a major constituent of New Zealand's Miro tree (*Podocarpus ferruginea*), actuated interest in the total synthesis of this phenolic diterpene. Synthetic efforts directed toward ferruginol (**1**) have employed various permutations of the order in which the three rings are assembled. The earliest approach by King[2] utilized the AC → ABC closure shown below (eq 1),



but suffered from a lack of stereoselectivity in the A/B ring fusion.[3] Later approaches by Meyer,[4] who employed an AB → ABC sequence (eq 2), and by Rao,[5] who employed a BC → ABC sequence (eq 3), culminated in stereospecific syntheses of ferruginol (**1**).

In connection with our interest in diterpenoid synthesis, we recently prepared the tricyclic acid **4** by two successive Robinson annelations of 2-carboethoxycyclohexanone and ethyl vinyl ketone.[6] The cis orientation of the angular methyl and carboxy groups in **4** was in accord with the stereoselective trapping of the enolate of the octalone **2** with ethyl vinyl ketone at the α face of **2** as a result of the directing influence of the C-8β carboethoxy group. To demonstrate the utility of this intermediate acid **4** in diterpenoid synthesis, we wish to report a total synthesis of (±)-ferruginol (**1**) and (±)-hinokione (**18**) as shown in Scheme I.

Having constructed the basic skeleton, we sought to introduce the appropriate functionality in the C ring in a sequential fashion. Prior to generating the enone functionality in the C ring (**5** → **6**), it was necessary to protect the enone



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