hydrolyzed to afford 36 mg (53%) of **37**: IR 2900, 1450, 1100 cm^{-1}; NMR δ 4.4 (t, J = 6.3 Hz, 1), 3.3 (s, 6), 3.15 (s, 3), 3.05 (s, 3), 2.1–1.0 (m, 11); mass spectrum, *m/e* 232 (p$^+$), 217 (p$^+$ − 15). The structure of **37** was further verified by comparison with authentic material synthesized independently.[25]

1,1-Dimethoxy-3-(1-oxobutyl)cyclohexane (25). By use of the above procedure b, ketal **24** (60 mg; 0.2 mmol) was converted to **25** (35 mg; 77%) of good purity. Further purification by column chromatography resulted in some loss, affording 20 mg (44%) of **25**: IR 2890, 1710, 1450, 1160, 1050 cm^{-1}; NMR δ 3.15 (s, 3), 3.05 (s, 3), 2.6–0.8 (m, 20); mass spectrum, *m/e* 228 (p$^+$).

Exact mass calcd for $C_{13}H_{24}O_3$: 228.1725. Found: 228.1738.

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Registry No. **9**, 13683-41-5; **12**, 71785-71-2; **15**, 55339-30-5; **17**, 71785-72-3; **18**, 1489-28-7; **19**, 55339-32-7; **21**, 55339-38-3; **22**, 15040-97-8; **23**, 71785-73-4; **24**, 71785-74-5; **25**, 71785-75-6; **27**, 41309-43-7; **28**, 71785-76-7; **33**, 55339-33-8; **34**, 55339-34-9; **36**, 55339-39-4; **37**, 71785-77-8; 3-(1-ethoxyvinyl)cyclohexanone, 71785-78-9; 3-(1-ethoxy-1-vinyl)-6-methylcyclohexanone, 71785-79-0; 2-methyl-3-(1-ethoxyvinyl)cyclohexanone, 71785-80-3; 3-(1-ethoxyvinyl)-6-isopropylcyclohexanone, 71785-81-4; 3-acetyl-6-methylcyclohexanone, 56893-77-7; 3-acetyl-6-isopropylcyclohexanone, 56893-78-8; 3-acetyl-1-cyclohexene, 29372-98-3; 3-methyl-3-[1-(trimethylsilyl)-1-vinyl]cyclohexanone, 71785-82-5; 3-[1-(trimethylsilyl)-1-vinyl]-6-isopropylcyclohexanone, 71785-83-6; 3-[1-(trimethylsilyl)-1-vinyl]-2-methylcyclohexanone, 71785-84-7; 1-[1-(trimethylsilyl)-1-vinyl]bicyclo[4.3.0]nonan-3-one, 55339-35-0; 3-[1-(trimethylsilyl)-1-vinyl]-6-methylcyclohexanone, 71785-85-8; 2-cyclohexen-1-one, 930-68-7; 6-methyl-2-cyclohexen-1-one, 6610-21-5; 2-methyl-2-cyclohexen-1-one, 1121-18-2; 6-isopropyl-2-cyclohexen-1-one, 43209-90-1; 3-methyl-2-cyclohexen-1-one, 1193-18-6; 3-bromocyclohexene, 1521-51-3; (trimethylsilyl)acetylene, 1066-54-2; 1-(trimethylsilyl)-1-pentene, 56183-56-3; 1-(trimethylsilyl)-1-pentyne, 18270-17-2; ethyl vinyl ether, 109-92-2; 4-*tert*-butyl-2-cyclohexen-1-one, 937-07-5; 3-[1-(trimethylsilyl)-1-vinyl]-4-*tert*-butylcyclohexanone, 71785-86-9.

Reaction of 2-(1,3-Butadienyl)magnesium Chloride with Carbonyl Compounds and Epoxides. A Regioselectivity Study

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The reaction of 2-(1,3-butadienyl)magnesium chloride (**1**) with carbonyl compounds and epoxides afforded a mixture of the "normal" addition product 1,3-dienyl alcohol and the "rearranged" allenic alcohol. The formation of the "rearranged" allenic alcohol was favored by lower basicity of solvent, by more covalent carbon–metal bonding, and by increased steric hindrance in ketones. The regioselectivity of the reaction was consistent with the six-membered cyclic transition state **10**.

The Grignard reagent 2-(1,3-butadienyl)magnesium chloride (**1**) was first prepared by Aufdermarsh[1] from 4-chloro-1,2-butadiene (**9**), and, later, Sultanov et al.[2] reported the synthesis of **1** from easily accessible 2-chloro-1,3-butadiene (chloroprene) (**8**) in the presence of zinc chloride catalyst (Scheme I).

Aufdermarsh showed that **1** was the 2-(1,3-butadienyl)magnesium chloride compound rather than the allenic one.

Kondo et al.[3] recently studied the reaction of **1** with carbonyl compounds and epoxides and found that a mixture of 1,3-dienyl alcohol and allenic alcohol was formed in the reaction shown in Scheme II.

We have studied the reaction in detail and found the ratios of **3** to **4** and **6** to **7** (regioselectivity of the reaction) could be influenced very much by the reaction conditions and we report the results.

Results and Discussion

Effect of Solvents. The reactions were generally carried out in tetrahydrofuran (THF) solution. The effects of adding the basic solvents hexamethylphosphoric triamide (HMPA), diglyme, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to reactions with carbonyl compounds are shown in Table I. Diglyme tends to increase the product yield but has little effect on the regioselectivity (the ratio of **3** to **4**). TMEDA has a tendency to decrease the yield, but it alters the selectivity between **3** and **4**. The reactions in the presence of TMEDA increase the ratio of **3** to **4** compared to the ratio in the presence of THF. HMPA has a great effect on the selectivity. In the reactions with acetone and methyl ethyl ketone, dienyl alcohol **3** was exclusively formed in the presence of HMPA. The effects of basic solvents on acetaldehyde and acetophenone are minor.

It is known that the solvation of a Grignard reagent by a basic solvent increases the ionic character between a carbon–magnesium bond.[4-7] The formation of dienyl alcohol **3** seems to be favored by the solvation with a basic solvent.

Effects of Alkyl Groups of Carbonyl Compounds. The effects of the bulkiness of the alkyl groups of carbonyl

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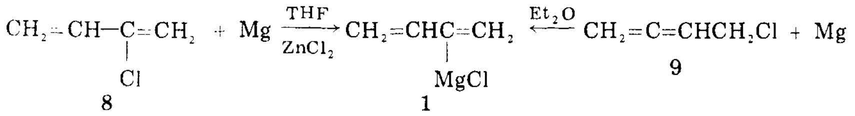
Scheme I



Scheme II

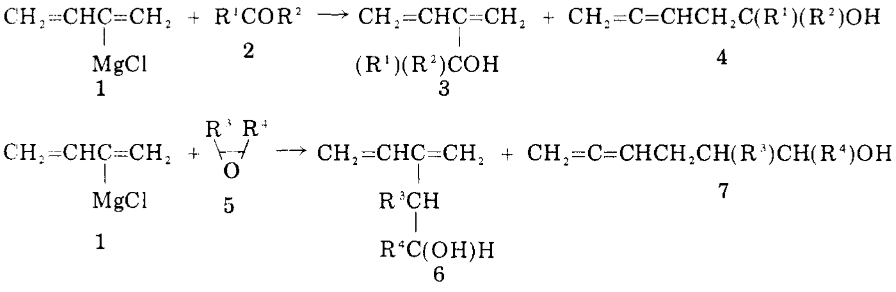


Table I. Effects of Solvents on the Reactions of 2-(1,3-Butadienyl)magnesium Chloride (1) with Carbonyl Compounds 2

no.	reactant	solvent	% yield	% alcohol 3	% alcohol 4
1	CH_3CHO	THF (100 mL)	70	80	20
2		THF (100 mL) + HMPA (30 mL)	50	84	16
3	CH_3COCH_3	THF (100 mL)	70	82	18
4		THF (100 mL) + diglyme (30 mL)	68	84	16
5		THF (100 mL) + HMPA (30 mL)	35	100	0
6	$CH_3COC_2H_5$	THF (100 mL)	57	72	28
7		THF (100 mL) + diglyme (30 mL)	72	73	27
8		THF (100 mL) + TMEDA (30 mL)	32	80	20
9		THF (100 mL) + HMPA (30 mL)	80	100	0
10	$CH_3COC_6H_5$	THF (100 mL)	45	12	88
11		THF (100 mL) + glyme (30 mL)	81	14	86
12		THF (100 mL) + TMEDA (30 mL)	50	18	82
13		THF (100 mL) + HMPA (30 mL)	53	18	82

Table II. Reactions of 2-(1,3-Butadienyl)magnesium Chloride (1) with Aldehydes 2

no.	RCHO	E_S value (R)	% yield	% alcohol 3	% alcohol 4	bp,[c] °C (mmHg)
14[a]	HCHO	+1.24	20	57	43	52-55 (25)
1	CH_3CHO	0	70	80	20	63-67 (20)
15[b]	CH_3CHO	0	35	17	83	
16	CH_3CH_2CHO	-0.07	39	83	17	67-70 (20)
17	$CH_3CH_2CH_2CHO$	-0.36	55	82	18	75-78 (20)
18	$CH_3CH_2CH_2CH_2CHO$	-0.40	48	80	20	62-65 (2)
19	$(CH_3)_2CHCHO$	-0.47	85	69	31	73-77 (20)
20	C_6H_5CHO	-0.90	68	30	70	86-88 (2)

[a] Gaseous formaldehyde generated by the thermolysis of paraformaldehyde was introduced with a dry N_2 stream. [b] In this run, aluminum chloride (0.03 mol) was added to reagent 1 prepared by method A. [c] Boiling point of mixture of alcohols 3 and 4.

Table III. Reactions of 2-(1,3-Butadienyl)magnesium Chloride (1) with Unsymmetric and Symmetric Ketones 2

no.	CH_3COR or RCOR	E_S value (R)	% yield	% alcohol 3	% alcohol 4	bp,[c] °C (mmHg)
6	$CH_3COC_2H_5$	-0.07	57	72	28	71-75 (25)
21	$CH_3CO(CH_2)_2CH_3$	-0.36	40	75	25	80-84 (25)
22	$CH_3CO(CH_2)_3CH_3$	-0.39	50	62	38	84-88 (5)
23	$CH_3COCH(CH_3)_2$	-0.47	68	40	60	81-86 (15)
10	$CH_3COC_6H_5$	-0.90	45	12	88	80-84 (2)
24	$CH_3COC(CH_3)_3$	-1.54	65	10	90	62-65 (2)
3	CH_3COCH_3	0	70	82	18	60-64 (15)
25[a]	CH_3COCH_3	0	54	83	17	
26[b]	CH_3COCH_3	0	40	0	100	
27	$C_2H_5COC_2H_5$	-0.07	63	68	32	73-76 (10)
28	$[CH_3CH_2CH_2]_2CO$	-0.36	47	61	39	82-85 (10)
29	$[(CH_3)_2CH]_2CO$	-0.47	55	36	64	80-84 (8)
30	$[(CH_3)_2CHCH_2]_2CO$	-0.93	50	10	90	86-90 (8)

[a] In this run, reagent 1 was prepared from active magnesium by method B. [b] In this run, aluminum chloride (0.03 mol) was added to reagent 1 prepared by method A. [c] Boiling point of mixture of alcohols 3 and 4.

Scheme III

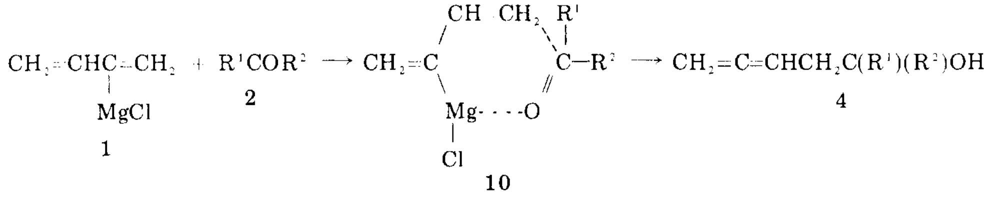


Table IV. Reactions of 2-(1,3-Butadienyl)magnesium Chloride (1) with Epoxides 5

no.	epoxide	% yield	% alcohol 6	% alcohol 7	bp,[b] °C (mmHg)
31	propylene oxide	40	100	0	56-60 (20)
32[a]	propylene oxide	35	60	40	
33	1,2-butylene oxide	45	100	0	66-69 (20)
34	cyclohexene oxide	80	91	9	62-66 (2)
35[a]	cyclohexene oxide	60	48	52	
36	isobutylene oxide	40	74	26	60-64 (20)
37	2,3-butylene oxide	60	60	40	63-66 (22)

[a] In this run, aluminum chloride (0.03 mol) was added to reagent 1 prepared by method A. [b] Boiling point of mixture of alcohols 6 and 7.

compounds on the selectivity are shown in Tables II and III.

In the reactions with aldehydes or methyl *n*-alkyl ketones, the bulkiness of the alkyl groups has little effect on the ratio of **3** to **4**.

However, as shown in Table III, in the reactions with branched ketones and symmetrically substituted ketones, the proportion of **4** remarkably increased with the increase in steric hindrance (more negative value of E_s).[8] There must be a significant steric crowding in the transition state for the formation of **3** in the case of symmetrically substituted ketones.

In the reaction with acetone, both Grignard reagents prepared by methods A and B (see Experimental Section) gave similar selectivity (nos. 3 and 25 of Table III).

Effect of Aluminum Chloride. The effect of adding aluminum chloride to **1** is shown in Tables II–IV (nos. 15, 25, 32, 25). The addition of aluminum chloride to **1** tends to decrease the yield; however, it transposes the selectivity of **4** over **3**, and the effect is remarkable.

When magnesium is exchanged for aluminum,[9,10] the metal–carbon bond becomes more covalent, which seems to be favorable for the formation of **4**. In the case of epoxides, shown in Table IV, more **7** was formed than **6** when magnesium was replaced by aluminum.

Reaction with Epoxides. The epoxides coordinated with the Grignard reagent less strongly than did the carbonyl compounds.[11,12]

It was interesting to investigate the selectivity of the reactions with epoxides in order to obtain more knowledge about the reaction mechanism.

The results are shown in Scheme II and Table IV. In the reactions with less hindered epoxides, like propylene oxide and 1,2-butylene oxide, dienyl alcohol **6** was selectively formed.

The reactions with more hindered epoxides, such as cyclohexene oxide, isobutylene oxide, and 2,3-butylene oxide, gave both dienyl alcohol **6** and allenic alcohol **7**. The steric factor seems to be important in determining the product selectivity.

Apparently, the reaction seems to have proceeded by the attack on the less hindered carbon of the epoxide ring by **1**.

In 1,2-disubstituted epoxides, the reaction by the allenyl form of **1** becomes favored. When magnesium was replaced by aluminum, more allenic alcohol **7** was formed; the same tendency was observed in the case of carbonyl compounds.

Reaction Mechanism. The characteristic of the reaction is that more "rearranged" allenic alcohols **4** and **7** were favored by less basic solvents, by more covalently bonded organometallic, and by increased steric hindrance in the substrates. These observations could be reasonably rationalized by a six-membered transition state which has been postulated in the reactions of benzyl Grignard reagent (Scheme III), although there are arguments against the cyclic mechanism for allylic Grignard reagents.[13-17]

Such a chelated cyclic transition would be difficult in basic solvents like HMPA or TMEDA, and hence more **3** or **6** would be formed. On the contrary, such a mechanism would be favored with large alkyl groups (R^1 and R^2) and more covalent character of the carbon–metal bond. Even in the case of epoxides, which, compared to the case of the carbonyl compounds, would be poorly coordinated to the metal, more allenic alcohol **7** was formed with aluminum as a metal component.

Conclusion

In the reactions of 1,3-dienyl Grignard reagent **1** with carbonyl compounds and epoxides, the ratio of dienyl alcohol **3** or **6** and allenic alcohol **4** or **7** can be controlled by employing appropriate reaction conditions.

Experimental Section

Preparation of 2-(1,3-Butadienyl)magnesium Chloride (1). Method A. In a 300-mL four-necked flask were charged 4.0 g (0.15 mol) of thoroughly dried flaky magnesium (Merck), 1 mL of 1,2-dibromoethane,[18] and 2 mL of THF. The contents were heated to activate the magnesium surface, 1–3 mol % of zinc chloride[2,3] was added, and the magnesium was covered with additional THF (50 mL).

To this, 9 g (0.10 mol) of chloroprene (Toyo Soda Manufacturing Co.) and 4 g (0.02 mol) of 1,2-dibromoethane were added

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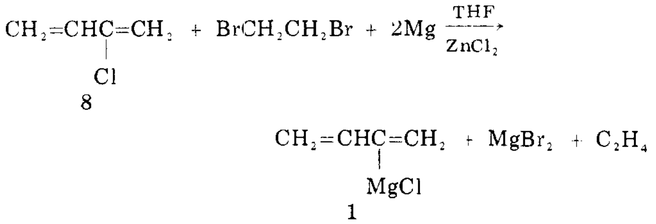
dropwise as a THF (50 mL) solution during 40 min under a nitrogen atmosphere.

An exothermic reaction occurred during the addition, and the color of the contents changed gradually from grayish white to grayish black.

After the completion of the addition, stirring was continued for 30 min under reflux. In the IR spectrum of about a 0.1 M solution of the Grignard reagent (1) thus prepared was observed a strong absorption of a conjugated diene at 1600 cm^{-1}.

Diglyme, TMEDA, and HMPA were slowly added to the above solution to prepare the reagent 1 in different solvent systems.



$$\underset{\textstyle\mathbf{8}}{\underset{Cl}{CH_2{=}CH\overset{}{C}{=}CH_2}} + BrCH_2CH_2Br + 2Mg \xrightarrow[ZnCl_2]{THF} \underset{\textstyle\mathbf{1}}{\underset{MgCl}{CH_2{=}CHC{=}CH_2}} + MgBr_2 + C_2H_4$$

Method B. A 500-mL four-necked flask equipped with a stirrer, a nitrogen inlet, and exhaust was charged with 11 g (0.12 mol) of anhydrous magnesium chloride, 9 g (0.05 mol) of potassium iodide, 8 g (0.20 mol) of metallic potassium, and 100 mL of THF, and the contents were heated under reflux with stirring under a nitrogen stream.

After about 10 min, potassium metal was melted and the reduction of magnesium started.[19] The heating was continued for 50 min. More chloroprene (9 g, 0.10 mol) in 50 mL of THF was added dropwise during 20 min. An exothermic reaction occurred during the addition and the system was refluxed for an additional 10 min after completion of the addition.

Preparation of Reagent 1 Used for the Reaction with Epoxides. In the preparation of Grignard reagent 1, 1,2-dibromoethane was not used for activation of magnesium. The reaction was started by using a small amount of iodine and methyl iodide and was carried out in a manner similar to that of the procedure of method A except for the start of the reaction.

Addition of Aluminum Chloride to 2-(1,3-Butadienyl)magnesium Chloride (1). A 4.4-g (0.03 mol) portion of powdered anhydrous aluminum chloride was added to the ice-cooled Grignard reagent 1 prepared by method A.

An exothermic reaction gradually occurred, and when the reaction became gentle, the mixture was heated under reflux for about 20 min.

The IR spectrum of the solution exhibited a strong absorption due to a conjugated diene at 1600 cm^{-1}.

Reaction of 2-(1,3-Butadienyl)magnesium Chloride (1) with Carbonyl Compounds. Unless otherwise specified, the carbonyl compound in 25 mL of THF was slowly added into an equimolar amount of Grignard reagent 1 prepared by method A.

An exothermic reaction occurred, and the reaction system was refluxed for about 30 min. The reaction system was hydrolyzed with 6 N HCl. The organic layer was separated, and the aqueous layer was extracted twice with 80 mL of ethyl ether.

The combined ether solution was washed with 5% sodium hydrogen carbonate, followed by water, dried over anhydrous Na_2SO_4, and distilled. The reactions with carbonyl compounds were also carried out similarly for Grignard reagent 1 prepared from active magnesium (method B) and for the Grignard reagent to which aluminum chloride had been added according to the procedure described above.

The reactions with epoxides were also carried out similarly.

Analysis of Reaction Products. After separation by gas chromatography using 4-ft columns (25% PEG 20 M on Chromosorb W), the corresponding dienyl alcohol **3** or **6** and allenic alcohol **4** or **7** were mainly identified by IR and NMR spectra by comparison with the reported data.[1,3]

IR spectra were taken on a Hitachi 515 spectrophotometer, and NMR spectra were recorded on a JEOL MH-100 spectrometer.

The quantitative analyses of the products **3** or **6** and **4** or **7** were carried out with a Yanagimoto G-1800 gas chromatograph by using 4-ft columns of 25% PEG 20 M on Chromosorb W.

Registry No. **1**, 126-99-8; **2** ($R^1 = CH_3$; $R^2 = H$), 75-07-0; **2** ($R^1 = R^2 = CH_3$), 67-64-1; **2** ($R^1 = CH_3$; $R^2 = C_2H_5$), 78-93-3; **2** ($R^1 = CH_3$; $R^2 = C_6H_5$), 98-86-2; **2** ($R^1 = R^2 = H$), 50-00-0; **2** ($R^1 = C_2H_5$; $R^2 = H$), 123-38-6; **2** ($R^1 = CH_2CH_2CH_3$; $R^2 = H$), 123-72-8; **2** ($R^1 = CH_2CH_2CH_2CH_3$; $R^2 = H$), 110-62-3; **2** ($R^1 = CH(CH_3)_2$; $R^2 = H$), 78-84-2; **2** ($R^1 = C_6H_5$; $R^2 = H$), 100-52-7; **2** ($R^1 = CH_3$; $R^2 = CH_2CH_2CH_3$), 107-87-9; **2** ($R^1 = CH_3$; $R^2 = CH_2CH_2CH_2CH_3$), 591-78-6; **2** ($R^1 = CH_3$; $R^2 = CH(CH_3)_2$), 563-80-4; **2** ($R^1 = CH_3$; $R^2 = C(CH_3)_3$), 75-97-8; **2** ($R^1 = R^2 = C_2H_5$), 96-22-0; **2** ($R^1 = R^2 = CH_2CH_2CH_3$), 123-19-3; **2** ($R^1 = R^2 = CH(CH_3)_2$), 565-80-0; **2** ($R^1 = R^2 = CH_2CH(CH_3)_2$), 108-83-8; **3** ($R^1 = CH_3$; $R^2 = H$), 61230-76-0; **3** ($R^1 = R^2 = CH_3$), 59163-80-3; **3** ($R^1 = CH_3$; $R^2 = C_2H_5$), 71885-77-3; **3** ($R^1 = CH_3$; $R^2 = C_6H_5$), 61201-25-0; **3** ($R^1 = R^2 = H$), 13429-21-5; **3** ($R^1 = C_2H_5$; $R^2 = H$), 71885-78-4; **3** ($R^1 = CH_2CH_2CH_3$; $R^2 = H$), 71885-79-5; **3** ($R^1 = CH_2CH_2CH_2CH_3$; $R^2 = H$), 71885-80-8; **3** ($R^1 = CH(CH_3)_2$; $R^2 = H$), 59163-78-9; **3** ($R^1 = C_6H_5$; $R^2 = H$), 59163-81-4; **3** ($R^1 = CH_3$; $R^2 = CH_2CH_2CH_3$), 71885-81-9; **3** ($R^1 = CH_3$; $R^2 = CH_2CH_2CH_2CH_3$), 71885-82-0; **3** ($R^1 = CH_3$; $R^2 = CH(CH_3)_2$), 71885-83-1; **3** ($R^1 = CH_3$; $R^2 = C(CH_3)_3$), 71885-84-2; **3** ($R^1 = R^2 = C_2H_5$), 71885-85-3; **3** ($R^1 = R^2 = CH_2CH_2CH_3$), 71885-86-4; **3** ($R^1 = R^2 = CH(CH_3)_2$), 71885-87-5; **3** ($R^1 = R^2 = CH_2CH(CH_3)_2$), 71885-88-6; **4** ($R^1 = CH_3$; $R^2 = H$), 23431-36-9; **4** ($R^1 = R^2 = CH_3$), 61201-28-3; **4** ($R^1 = CH_3$; $R^2 = C_2H_5$), 71885-89-7; **4** ($R^1 = CH_3$; $R^2 = C_6H_5$), 61201-30-7; **4** ($R^1 = R^2 = H$), 5557-87-9; **4** ($R^1 = C_2H_5$; $R^2 = H$), 31516-32-2; **4** ($R^1 = CH_2CH_2CH_3$; $R^2 = H$), 71885-90-0; **4** ($R^1 = CH_2CH_2CH_2CH_3$; $R^2 = H$), 71885-91-1; **4** ($R^1 = CH(CH_3)_2$; $R^2 = H$), 31516-33-3; **4** ($R^1 = C_6H_5$; $R^2 = H$), 61201-27-2; **4** ($R^1 = CH_3$; $R^2 = CH_2CH_2CH_3$), 71885-92-2; **4** ($R^1 = CH_3$; $R^2 = CH_2CH_2CH_2CH_3$), 71885-93-3; **4** ($R^1 = CH_3$; $R^2 = CH(CH_3)_2$), 71885-94-4; **4** ($R^1 = CH_3$; $R^2 = C(CH_3)_3$), 61201-29-4; **4** ($R^1 = R^2 = C_2H_5$), 71885-95-5; **4** ($R^1 = R^2 = CH_2CH_2CH_3$), 71885-96-6; **4** ($R^1 = R^2 = CH(CH_3)_2$), 71885-97-7; **4** ($R^1 = R^2 = CH_2CH(CH_3)_2$), 71901-56-9; **5** ($R^3 = H$; $R^4 = CH_3$), 75-56-9; **5** ($R^3 = H$; $R^4 = C_2H_5$), 106-88-7; **5** ($R^3 = R^4 = -(CH_2)_4-$), 286-20-4; **5** ($R^3 = H$; $R^4 = (CH_3)_2$), 558-30-5; **5** ($R^3 = R^4 = CH_3$), 3266-23-7; **6** ($R^3 = H$; $R^4 = CH_3$), 71885-98-8; **6** ($R^3 = H$; $R^4 = C_2H_5$), 59163-76-7; **6** ($R^3 = R^4 = -(CH_2)_4-$), 61201-32-9; **6** ($R^3 = H$; $R^4 = (CH_3)_2$), 71885-99-9; **6** ($R^3 = R^4 = CH_3$), 71886-00-5; **7** ($R^3 = H$; $R^4 = CH_3$), 25033-96-9; **7** ($R^3 = R^4 = -(CH_2)_4-$), 71886-01-6; **7** ($R^3 = H$; $R^4 = (CH_3)_2$), 71886-02-7; **7** ($R^3 = R^4 = CH_3$). 71886-03-8.

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[19] R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974).