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Lewis Acid-Promoted Selective Rearrangement of Trisubstituted Epoxides to Aldehydes or Ketones

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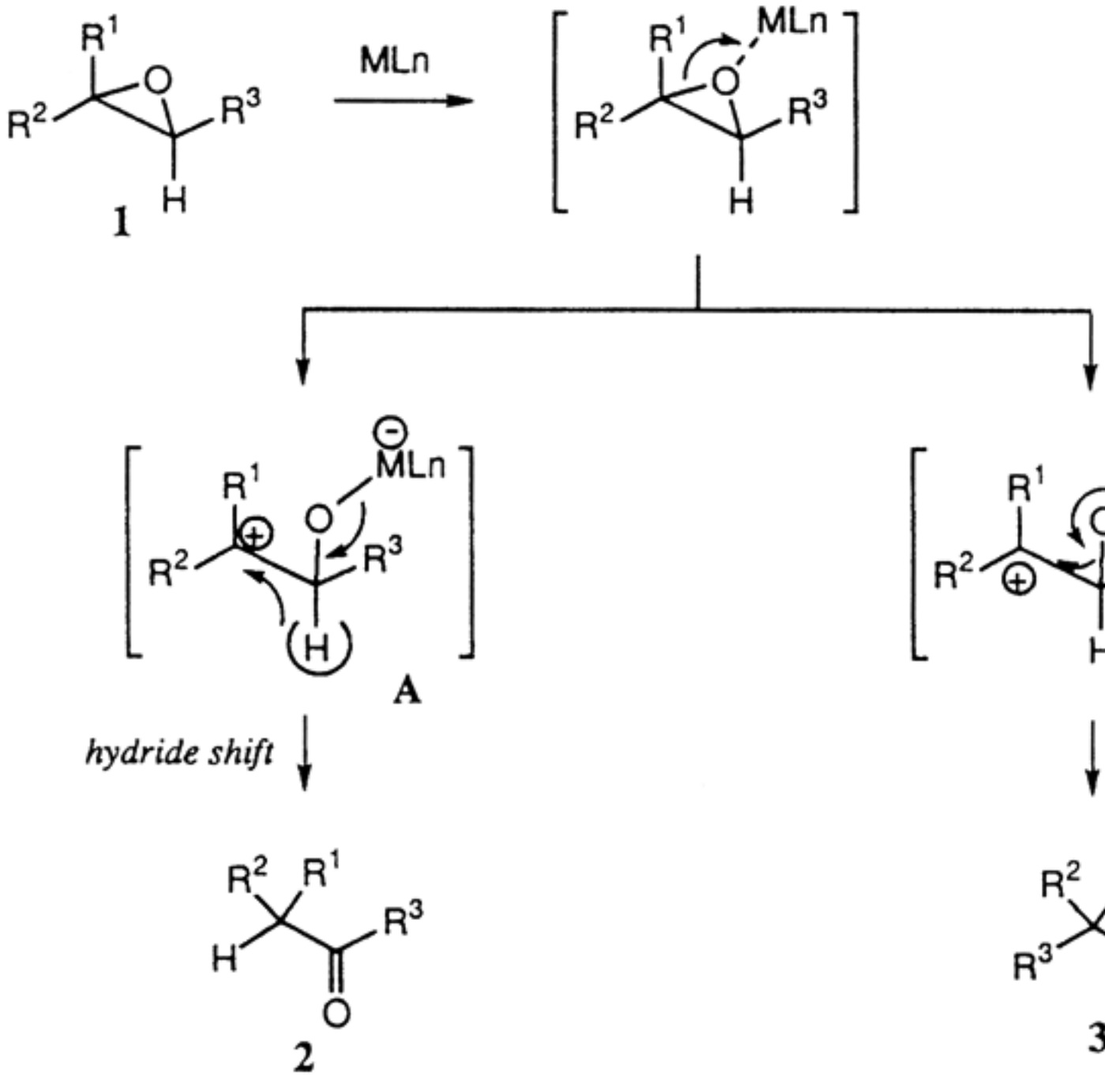
Abstract: Rearrangement of trisubstituted epoxides has been effected under the influence of various Lewis acids. Among these, methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) can be selectively rearranged from trisubstituted epoxides to aldehydes, while antimony pentafluoride is employable for selective rearrangement to ketones under mild conditions.

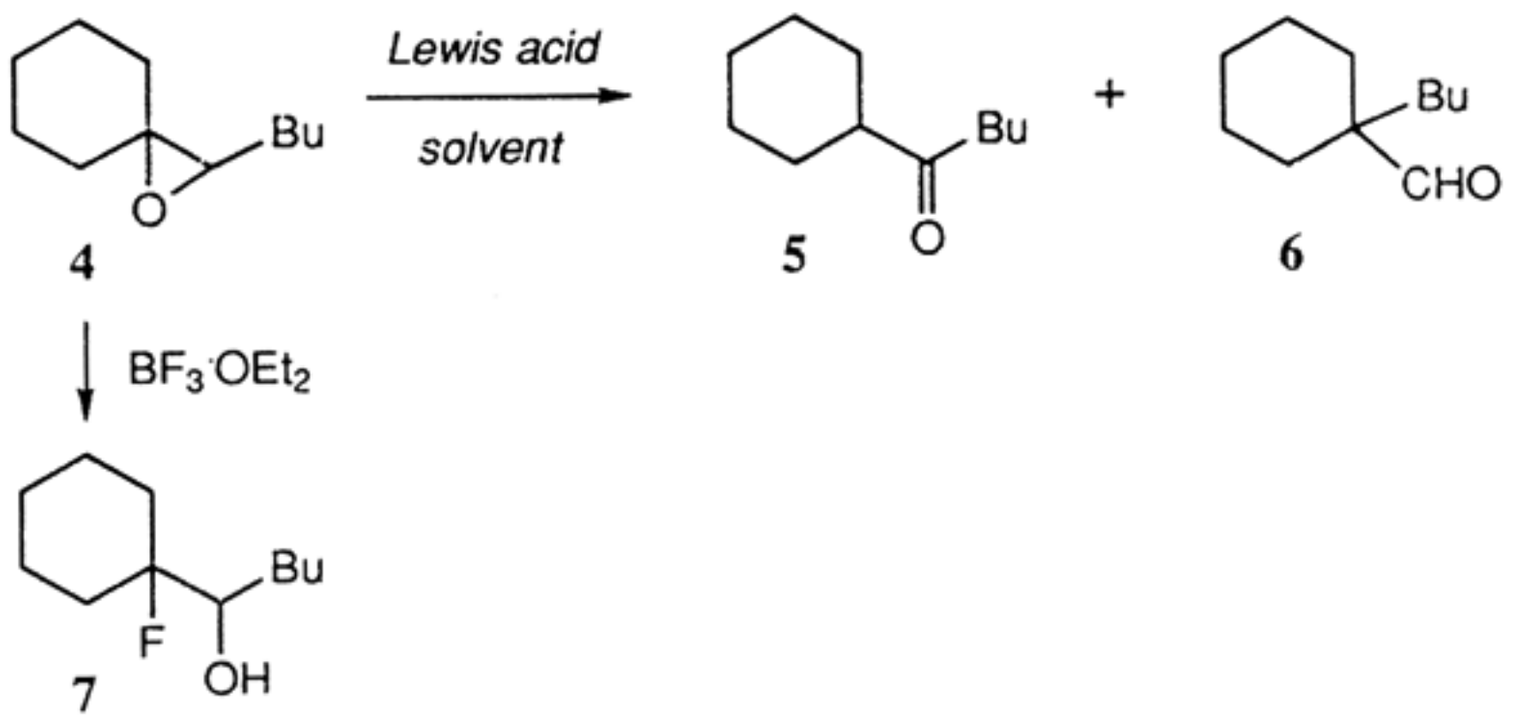
The acid-catalyzed rearrangement of epoxides to carbonyl compounds is a well-known synthetic transformation and a number of reagents have been elaborated for this purpose.[1-3] As illustrated in Scheme I, two types of rearrangement have, in principle, been conceivable for trisubstituted epoxide **1** depending on the two possible migration patterns following Lewis acid-promoted C-O bond cleavage. The rearrangement of **1** with hydrogen or alkyl (R^3) shift gives ketone **2** or aldehyde **3**, respectively. However, despite the

Scheme I



long-standing concern of the acid-catalyzed epoxide rearrangement, none of the methods has yet been found appropriate for the selective rearrangement of trisubstituted epoxides to either aldehydes or ketones depending on the choice of Lewis acids. In this context, we set out to attempt to achieve these synthetically useful transformations under mild conditions.

We have studied the Lewis acid-promoted epoxide rearrangement in detail with a model substrate **4**. Selective transformation of trisubstituted epoxide **4** to aldehyde **6** was effected with exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) which was recently developed in our laboratory (entry 1).[4,5]



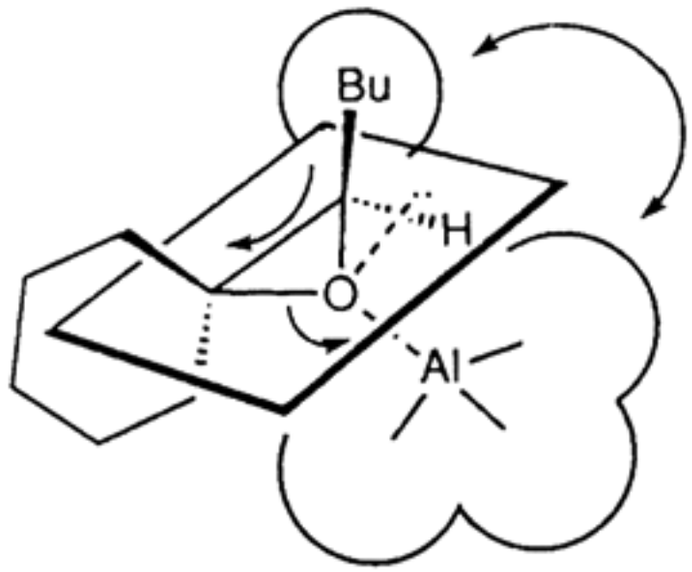
Having achieved the selective formation of aldehydes, we next focused on the possibility of obtaining the other selectivity, the selective generation of ketone **5** in the presence of certain Lewis acids. Treatment of epoxide **4** in benzene with an ordinary Lewis acid, BF_3·OEt_2 afforded a mixture of **5** and **6** in 2:1 ratio (entry 2). SnF_4 gave similar results (entries 5 and 6), while $SnCl_4$ showed no selectivity (~1:1) (entry 7). With

Table I. Effect of Lewis Acids on the Rearrangement of Epoxide **4** [a]

entry	Lewis acid	solvent	condition (°C, h)	% yield [b]	ratio of **5/6**
1	MABR	CH_2Cl_2	-20, 1	73	0 : 100
2	BF_3·OEt_2	benzene	25, 2	55	67 : 33
3	BF_3·OEt_2	toluene	-78, 2	*d*	
4	BF_3·OEt_2	ether	0, 1	*d*	
5	SnF_4	toluene	25, 4	71	67 : 33
6	SnF_4	CH_3NO_2	25, 1	71	68 : 32
7	$SnCl_4$	CH_3NO_2	-20, 1	72	50 : 50
8	SbF_3	benzene	25, 3	62	85 : 15
9	SbF_5	toluene	-78, 2	79	85 : 15
10	SbF_5	toluene/THF [c]	-78, 2	51	80 : 20
11	SbF_5	hexane	-78, 3	70	60 : 40
12	SbF_5	pentane	-100, 2	72	57 : 43

[a] Rearrangement of **4** was carried out with 1.1~2 equiv of Lewis acids under the given reaction conditions. [b] Isolated yields. [c] Volume ratio = 50:1. [d] Fluorohydrin **7** as a major product.

BF_3·OEt_2 at low temperature or in polar solvents, fluorohydrin **7** was obtained as a major product (entries 3 and 4). For the aldehyde synthesis, the use of a sterically hindered, oxygenophilic MABR would be most suitable for effecting the initial epoxide-cleavage followed by smooth alkyl transfer, in view of the increasing steric repulsion between a bulky organoaluminum ligand and butyl group as depicted in **C**. On the other

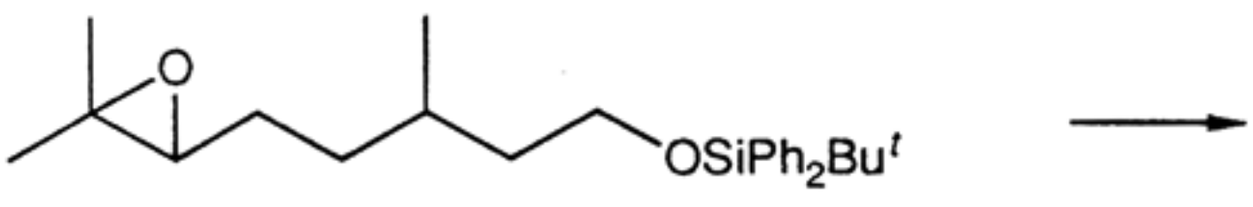
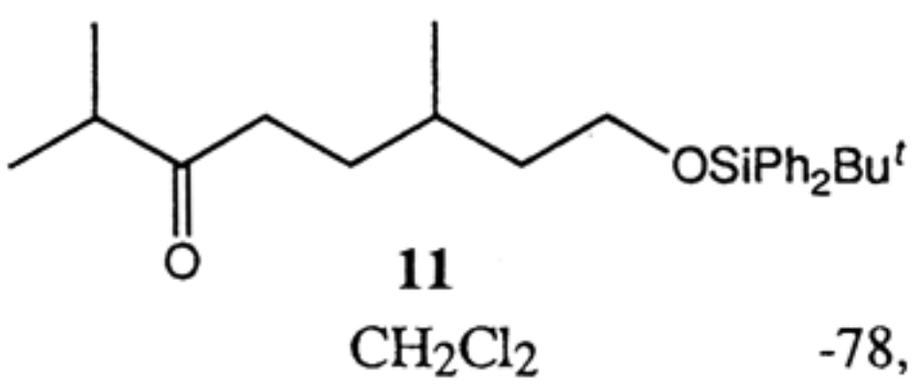
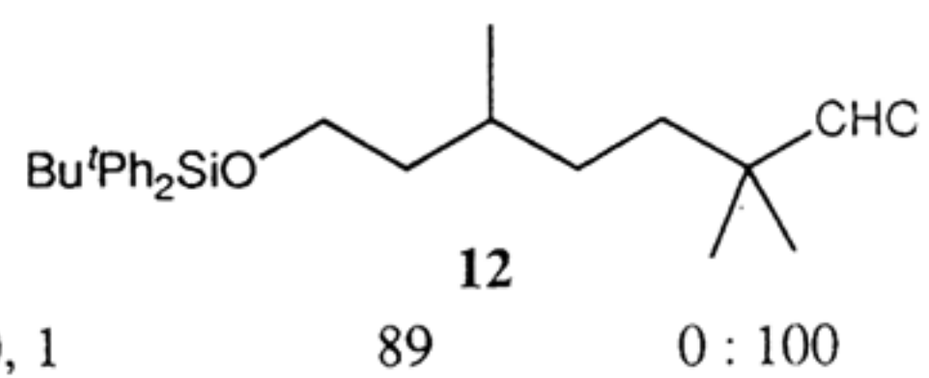
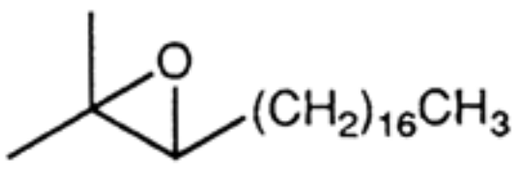
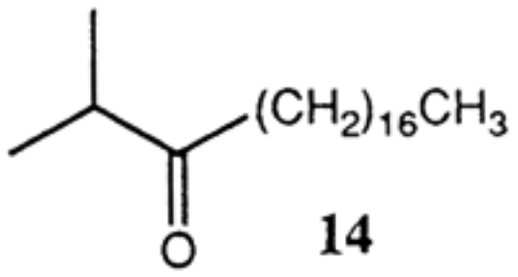
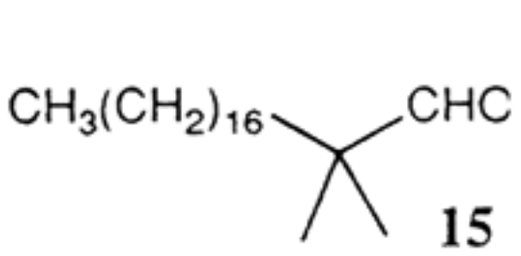
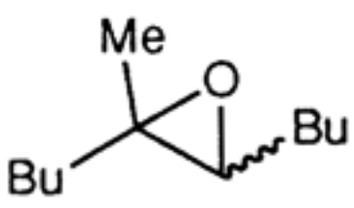
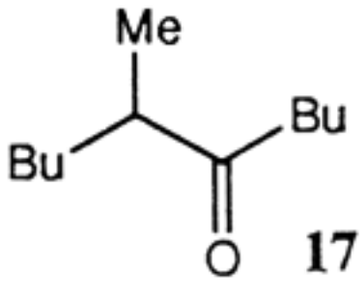
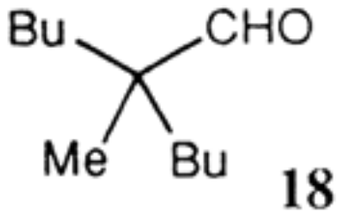
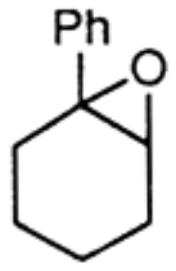
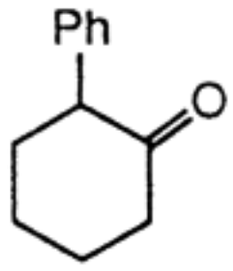
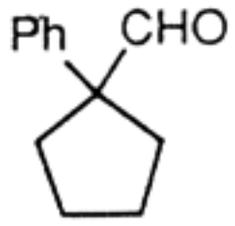


C

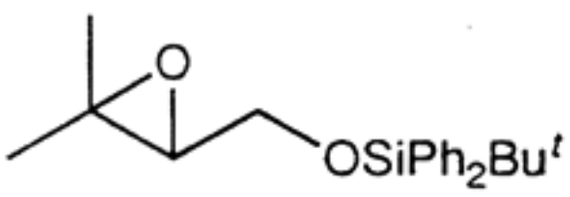
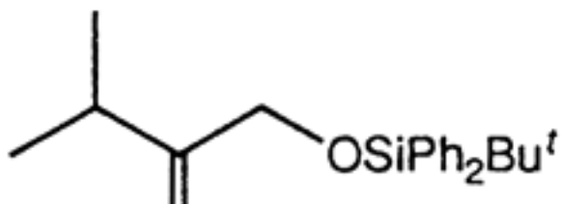
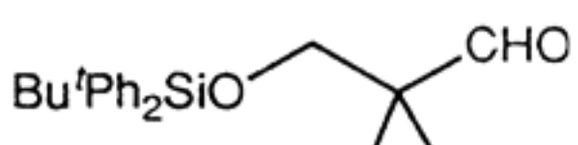
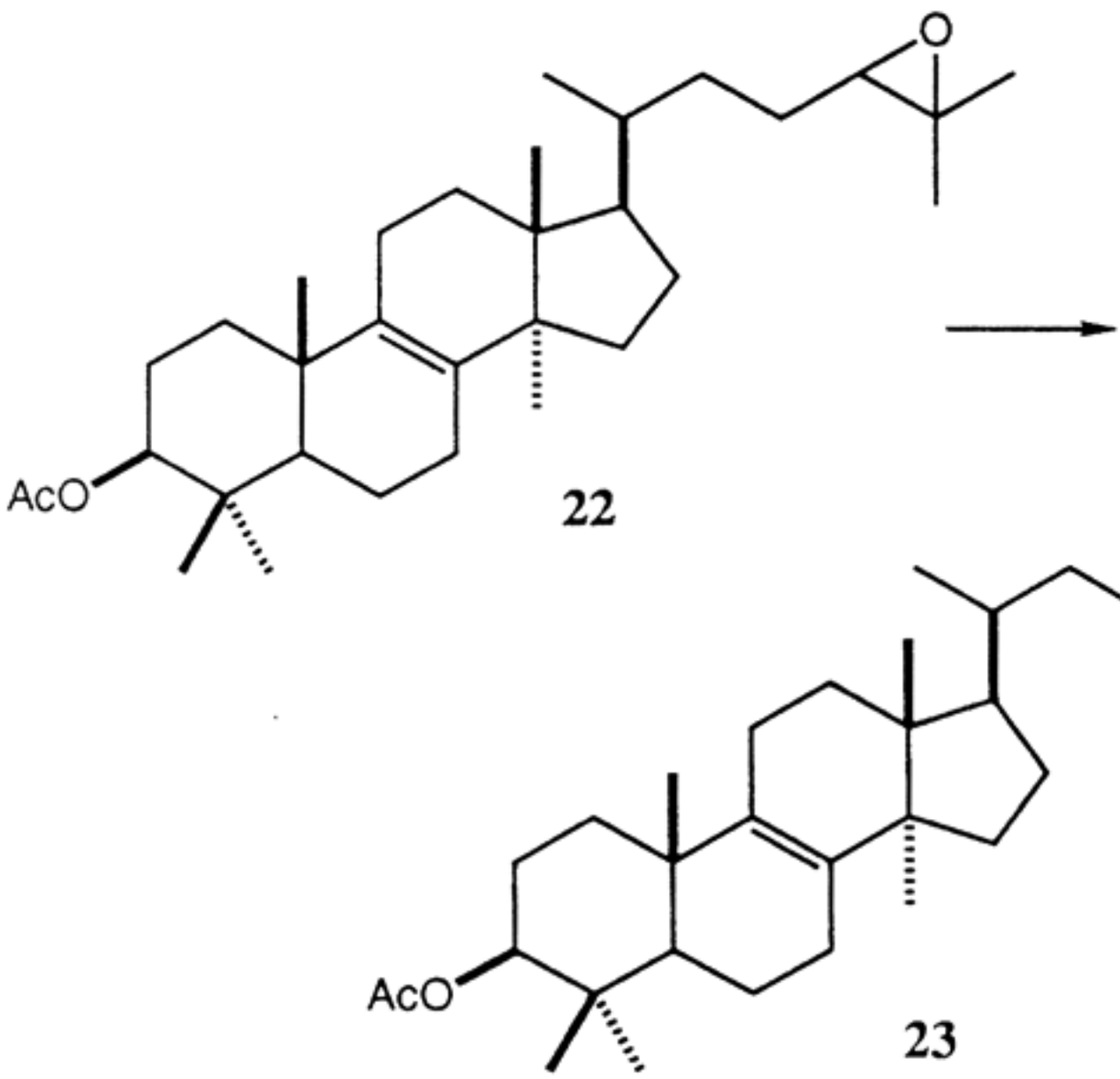
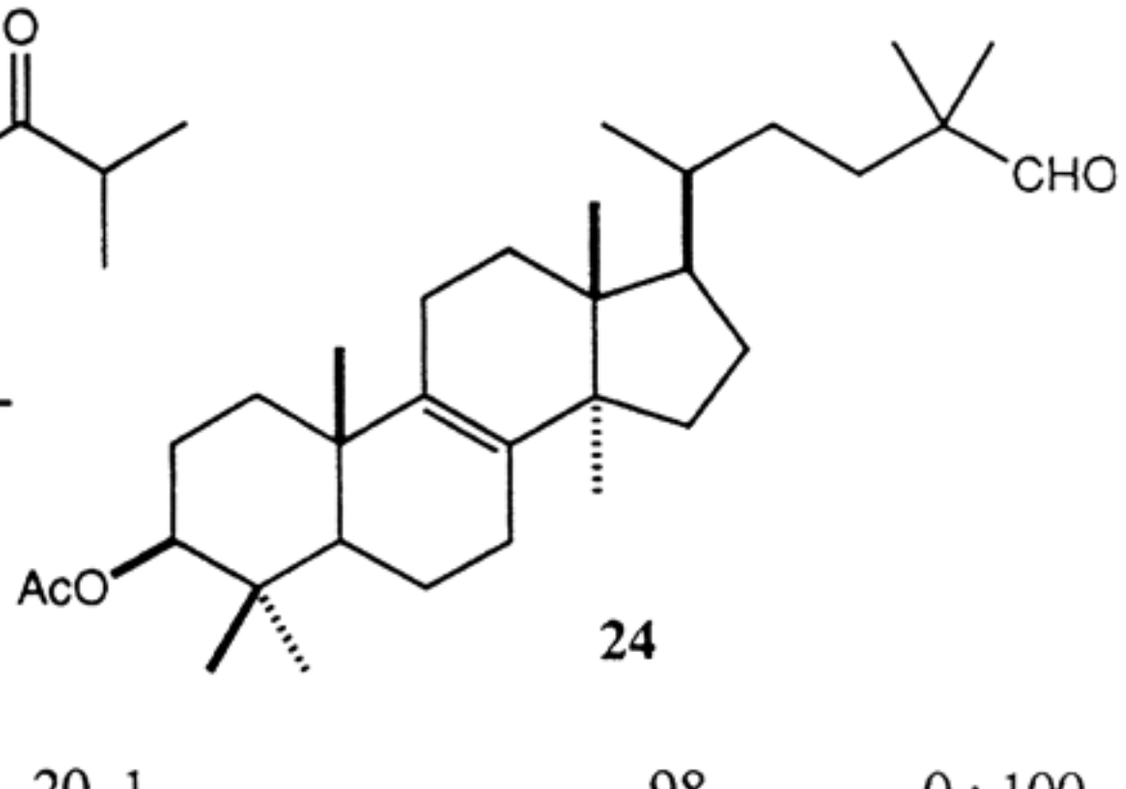
hand, several factors must be considered for selective generation of ketone **5**. First, use of a small Lewis acid would be preferable in order to minimize the steric interaction between a Lewis acid and a migrating alkyl group, thereby assuring the desired hydrogen migration, for migratory aptitudes of hydrogen are much larger than simple alkyl groups, as already reported in the migratory aptitudes of substituents in pinacol rearrangements.[6] Second, the use of fewer nucieophilic ligands for Lewis acids would inhibit them from interacting with the intermediate cation **A** as either a base or a nucleophile. This hypothesis in conjunction with the preliminary experimental findings on the rearrangement of **4** with BF_3·OEt_2, SnF_4, and $SnCl_4$ led us to examine the efficiency of various metal fluorides for the selective transformation of **4** to **5**. The results are summarized in Table I. Antimony pentafluoride (SbF_5) was found to be the most satisfactory metal fluoride in both reactivity and selectivity (entry 9).[7] Erbium(III) fluoride, magnesium(II) fluoride, and ytterbium(III) fluoride gave none of the carbonyl products and most recovery of the starting epoxide **4**.

The generality of the selective transformation of various epoxides to either aldehydes or ketones is indicated in Table II.[8] Only aldehydes are obtainable under the influence of MABR, whereas formation of ketones can be achieved with high selectivity using SbF_5. In the latter case, a toluene/THF mixture (volume ratio, 1:1) is preferable as solvent (entries 5 vs. 6 and 30 vs. 29). For the cyclic trisubstituted epoxide **8**, however, aldehyde **9** is a sole isolable product irrespective of kind of Lewis acid (entries 15-18).

Table II. Lewis Acid-Promoted Selective Rearrangement of Various Trisubstituted Epoxides [a]

entry	Lewis acid	solvent	condition (°C, h)	% yield [b]	ratio [c]
	 **10**		 **11**	+	 **12**
1	MABR	CH_2Cl_2	-78, 1; -20, 1	89	0 : 100
2	$BF_3{\cdot}OEt_2$	benzene	25, 1	77	74 : 26
3	$BF_3{\cdot}OEt_2$	hexane	0, 1	47	74 : 26
4	SbF_5	toluene	-78, 3	28	85 : 15
5	SbF_5	toluene/THF	-78, 3	57	92 : 8
6	SbF_5	THF	-78, 3	38	92 : 8
7	SbF_5	toluene/ether	-78, 3	51	84 : 16
	 **13**		 **14**	+	 **15**
8	MABR	CH_2Cl_2	-20, 1	99	0 : 100
9	$BF_3{\cdot}OEt_2$	benzene	25, 1	73	75 : 25
10	$SnCl_4$	toluene	-78, 2	15	83 : 17
11	SbF_5	toluene	-78, 3	47	83 : 17
	 **16**		 **17**	+	 **18**
12	MABR	CH_2Cl_2	-20, 1	75	0 : 100
13	$BF_3{\cdot}OEt_2$	benzene	25, 2	77	70 : 30
14	SbF_5	toluene	-78, 2	86	82 : 18
	 **8**			+	 **9**
15	MABR	CH_2Cl_2	-78, 0.5	98	0 : 100
16	$BF_3{\cdot}OEt_2$	benzene	25, 1	72	0 : 100
17	$BF_3{\cdot}OEt_2$	hexane	0, 3	37	0 : 100
18	SbF_5	toluene	-78, 2	17	0 : 100

(continued)

entry	Lewis acid	solvent	condition (°C, h)	% yield [b]	ratio [c]
	 **19**		 **20**	+  **21**	
19	MABR	CH_2Cl_2	-40, 1	98	0 : 100
20	$BF_3{\cdot}OEt_2$	benzene	25, 0.3	83	50 : 50
21	$BF_3{\cdot}OEt_2$	hexane	0, 1	45	42 : 58
22	$SnCl_4$	benzene	25, 1	87	22 : 78
23	SbF_5	CH_2Cl_2	-78, 3	*d*	
24	SbF_5	toluene/THF	-78, 1	30	100 : 0
25	SbF_5	toluene/THF	25, 0.2	47	82 : 18
	 **22**		**23** +  **24**		
26	MABR	CH_2Cl_2	-20, 1	98	0 : 100
27	$BF_3{\cdot}OEt_2$	benzene	25, 1	89	70 : 30
28	$BF_3{\cdot}OEt_2$	ether	25, 1	74	68 : 32
29	SbF_5	toluene	-78, 3	60	70 : 30
30	SbF_5	toluene/THF	-78, 3	66	87 : 13

[a] Rearrangement was carried out with 1.1~2 equiv of Lewis acids under the indicated conditions. [b] Isolated yields. [c] Ratio of ketone/aldehyde. [d] No isolable product.

Experimental Section

General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-200 spectrometer. All experiments were carried out under an atmosphere of dry argon. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck 9385. Microanalyses were accomplished at the Faculty of Agriculture, Nagoya University.

In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were freshly distilled from sodium metal using benzophenone ketyl as indicator. Benzene, hexane, and toluene were dried over sodium metal. Methylene chloride was stored over 4Å molecular sieves. Nitromethane was freshly distilled before use. Trimethylaluminum was obtained from Toso-Akzo Chemical Co. Ltd., Japan. Other simple chemicals were purchased and used as such.

Preparation of Epoxide 4. To a suspension of pentyltriphenylphosphonium bromide (2.27g, 5.5 mmol) in THF (10 mL) at 0 °C was added a 1.6 M hexane solution of BuLi (3.44 mL, 5.5 mmol) dropwise under argon atmosphere. The resulting red solution was stirred at 0 °C for 1 h. Cyclohexanone (0.52 mL, 5 mmol) was added at 0 °C and the entire mixture was stirred at 0 °C for 2 h. This was then diluted with pentane and filtered. The combined filtrates were concentrated under vacuum and the residual oil was purified by short column chromatography on silica gel (pentane as eluant) to furnish pentylidenecyclohexane (623 mg, 82% yield) as a colorless oil.

This olefin (608 mg, 4 mmol) was added to a solution of 80% MCPBA (949 mg, 4.4 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 30 min, poured into saturated $NaHCO_3$, and extracted with ether. The combined extracts were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography on silica gel (ether/hexane = 1:20 as eluant) to furnish the title epoxide (645 mg, 96% yield) as a colorless oil:[9] ^{1}H NMR ($CDCl_3$) δ 2.68 (1H, t, J = 5.8 Hz, CH-O), 1.20-1.80 (16H, m, 8CH_2), 0.89 (3H, t, J = 7.2 Hz, CH_3); IR (liquid film) 2971, 2952, 2859, 1449, 1379, 936, 897. 849 cm^{-1}.

2-Methyl-2-eicosene Oxide (13). This epoxide was prepared from octadecanal and isopropylidenetriphenylphosphorane in 72% overall yield in a similar manner as described above: ^{1}H NMR ($CDCl_3$) δ 2.69 (1H, t, J = 6 Hz, CH-O), 1.13-1.53 (32H, m, 16CH_2), 1.28 (3H. s, CH_3-C), 1.23 (3H, s. CH_3-C), 0.85 (3H, t, J = 7 Hz, CH_3); IR (liquid film) 2924, 2858, 1466, 1377. 1123, 722 cm^{-1}. Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.64. Found: C, 81.17; H, 13.67.

5-Methyl-5-decene Oxide (16). This epoxide was prepared from 2-hexanone and pentylidenetriphenylphosphorane in 78% overall yield in a similar manner as described above: ^{1}H NMR ($CDCl_3$) δ 2.66 (1H, t, J = 6 Hz, CH-O), 1.16-1.67 (12H, m, 6CH_2), 1.21 and 1.24 (3H, s, *E*- and *Z*-CH_3-C), 0.80-0.97 (6H, m, 2CH_3); IR (liquid film) 2955, 2910, 2875, 2870, 1468, 1381, 1258, 874, 751 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.72; H, 13.07.

1-Phenylcyclohexene Oxide (8).[10] This epoxide was prepared by simple epoxidation of 1-phenylcyclohexene with MCPBA in CH_2Cl_2: ^{1}H NMR ($CDCl_3$) δ 7.20-7.41 (5H. m, Ph), 3.05 (1H, t, J = 2 Hz, CH-O), 1.93-2.35 (4H, m, 2CH_2), 1.18-1.68 (4H, m, 2CH_2).

Preparation of Epoxycitronellol *t*-Butyldiphenylsilyl Ether (10). To a solution of citronellol (781 mg, 5 mmol) in DMF (7 mL) at room temperature was added *t*-butyldiphenylsilyl chloride (1.37 g, 5

mmol) followed by imidazole (408 mg, 6 mmol). The resulting mixture was stirred at room temperature for 2 h. This was poured into water and extracted with ether. The combined ether extracts were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography on silica gel (ether/hexane = 1:100 as eluant) to furnish citronellol *t*-butyldiphenylsilyl ether (1.87 g, 95% yield) as a colorless oil.

This silyl ether (1.87g, 4.75 mmol) was added to a solution of 80% MCPBA (1.02 g, 4.75 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 30 min, poured into saturated $NaHCO_3$, and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4, evaporatively concentrated, and purified by column chromatography on silica gel (ether/hexane = 1:9 as eluant) to furnish the title epoxide (1.85g, 95% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.31–7.69 (10H, m, 2Ph), 3.67 (2H, t, J = 6 Hz, CH_2-O), 2.65 (1H, t, J = 6 Hz, CH-O), 1.06-1.70 (7H, m, CH and $3CH_2$), 1.28 (3H, s, CH_3-C), 1.23 (3H, s, CH_3-C), 1.02 (9H, s, *t*-Bu), 0.82 (3H, d, J = 6 Hz, $C\underline{H}_3$-CH); IR (liquid film) 3073, 3065, 2959, 2930, 2859, 1474, 1465, 1428, 1377, 1111, 1091, 824, 739, 702 cm^{-1}. Anal. Calcd for $C_{26}H_{38}O_2Si$: C, 76.04; H, 9.33. Found: C, 76.10; H, 9.30.

Epoxyprenol *t*-butyldiphenylsilyl ether (**19**) was prepared from prenol in 92% overall yield in a similar manner as described above.

Epoxide 19: ^{1}H NMR ($CDCl_3$) δ 7.35–7.76 (10H, m, 2Ph), 3.82 (1H, dd, J = 5.4 Hz, CH-O), 3.75 (1H, dd, J = 5.4 Hz, CH-O), 3.01 (1H, t, J = 5.4 Hz, CH-O), 1.32 (3H, s, CH_3-C), 1.13 (3H, s, CH_3-C), 1.07 (9H, s, *t*-Bu); IR (liquid film) 3073, 3055, 2953, 2920, 2859, 1474, 1428, 1379, 1258, 1140, 1118, 1082, 866, 824, 741, 702 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29. Found: C, 74.11; H, 8.35.

Epoxide 22 of Lanosterol Acetate:[11] ^{1}H NMR ($CDCl_3$) δ 4.48 (1H, dd, J = 5, 11 Hz, C$\underline{H}$-OAc), 2.66 (1H, t, J = 6.2 Hz, CH-O), 2.02 (3H, s, CH_3-C=O), 1.28 (3H, s, CH_3-C-O), 1.23 (3H, s, CH_3-C-O), 0.97 (3H, s, CH_3-C), 0.89 (3H, d, J = 6 Hz, CH_3-CH), 0.85 (9H, s, $3CH_3$), 0.66 (3H, s, CH_3-C); IR ($CHCl_3$ solution) 2953, 2875, 1721, 1380, 1375, 1260, 1221, 777, 752, 742 cm^{-1}.

Preparation of Fluorohydrin 7. Treatment of epoxide **4** (118 mg, 0.7 mmol) in toluene (7 mL) with BF_3·OEt_2 (172 μL, 1.4 mmol) at -78 °C for 2 h afforded the title compound **7** (50 mg, 42% yield) as a semisolid: ^{1}H NMR ($CDCl_3$) δ 3.40-3.57 (1H, m, CH-O), 1.06-2.01 (16H, m, $8CH_2$), 0.91 (3H, t, J = 7 Hz, CH_3); IR (liquid film) 3310, 2940, 2850, 1465, 1440, 1165, 959, 920, 831. 752 cm^{-1}. Anal. Calcd for $C_{11}H_{21}OF$: C, 70.17; H, 11.24. Found: C, 70.11; H, 11.00.

Preparation of MABR. To a solution of 4-bromo-2,6-di-*tert*-butylphenol (2 equiv) in CH_2Cl_2 was added at room temperature a 2 *M* hexane solution of Me_3Al (1 equiv). The methane gas evolved immediately. The resulting colorless solution was stirred at room temperature for 1 h and used as a solution of MABR in CH_2Cl_2 without purification.

General Procedure for the Rearrangement of Trisubstituted Epoxides with MABR. To a solution of the MABR (1 mmol) in CH_2Cl_2 (5 mL) was added an epoxide (0.5 mmol) at -78 °C and the resulting mixture was stirred under the given reaction conditions in Table 1. The solution was then poured into diluted HCl and extracted with CH_2Cl_2. The combined extracts were washed with saturated $NaHCO_3$ and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluants) afforded an aldehyde in the yield shown in Table I.

General Procedure for the Rearrangement of Trisubstituted Epoxides with Ordinary Lewis Acids. BF_3·OEt_2, MgF_2, ErF_3, and YbF_3 were directly added to a solution of an epoxide under the

given reaction conditions in Table I. SnF_4, $SnCl_4$, SbF_3, and SbF_5 were utilized as 1M CH_2Cl_2 solutions. The rearrangement of an epoxide was carried out in the presence of 1.1~2 equiv of these Lewis acids in a similar manner as described above.

Butyl Cyclohexyl Ketone (5):[12] ^1H NMR ($CDCl_3$) δ 2.41 (2H, t, J = 7.2 Hz, CH_2-C=O), 2.32 (1H, m, CH-C=O), 1.05-1.89 (14H, m, $7CH_2$), 0.89 (3H, t, J = 7.2 Hz, CH_3); IR (liquid film) 2932, 2857, 1709, 1451, 1377, 1148, 990 cm^{-1}.

α-Butylcyclohexanecarboxaldehyde (6):[13] ^1H NMR ($CDCl_3$) δ 9.41 (1H, s, CH=O), 1.78-1.93 (2H, m, CH_2), 1.04-1.67 (14H, m, $7CH_2$), 0.86 (3H, t, J = 7.2 Hz, CH_3); IR (liquid film) 2932, 2859, 2685, 1728, 1453, 831, 743 cm^{-1}.

8-(*t*-Butyldiphenylsiloxy)-2,6-dimethyl-3-octanone (11): ^1H NMR ($CDCl_3$) δ 7.29–7.68 (10H, m, 2Ph), 3.65 (2H, t, J = 6.4 Hz, CH_2-O), 2.57 (1H, heptet, J = 7.2 Hz, CH-C=O), 2.39 (2H, t, J = 7.2 Hz, CH_2-C=O), 1.10-1.67 (5H, m, CH and $2CH_2$), 1.05 (6H, d, J = 7.2 Hz, $2CH_3$), 1.02 (9H, s, *t*-Bu), 0.80 (3H, d, J = 6 Hz, CH_3); IR (liquid film) 3073, 3065, 2959, 2931, 2902, 1715, 1473, 1468, 1428, 1385, 1113, 1093, 824, 739, 702 cm^{-1}. Anal. Calcd for $C_{26}H_{38}O_2Si$: C, 76.04; H, 9.33. Found: C, 76.11; H, 9.30.

7-(*t*-Butyldiphenylsiloxy)-2,2,5-trimethylheptanal (12): ^1H NMR ($CDCl_3$) δ 9.42 (1H, s, CHO), 7.32-7.71 (10H, m, 2Ph), 3.67 (2H, m, CH_2-OSi), 1.07-1.65 (7H, m, CH and $3CH_2$), 1.04 (9H, s, *t*-Bu), 1.01 (6H, s, $(CH_3)_2C$), 0.82 (3H, d, J = 7 Hz, CH_3); IR (liquid film) 3073, 3066, 2971, 2935, 2859, 2693, 1728, 1472, 1428, 1394, 1362, 1113, 895, 824, 739, 702 cm^{-1}. Anal. Calcd for $C_{26}H_{38}O_2Si$: C, 76.04; H, 9.33. Found: C, 76.23; H, 9.40.

2-Methyl-3-eicosanone (14): ^1H NMR ($CDCl_3$) δ 2.60 (1H, heptet, J = 7 Hz, CH-C=O), 2.43 (2H, t, J = 7.4 Hz, CH_2-C=O), 1.11-1.63 (30H, m, $15CH_2$), 1.08 (6H, d, J = 7 Hz, $2CH_3$), 0.87 (3H, br t, J = 7 Hz, CH_3); IR (liquid film) 2924, 2835, 1717, 1466, 1383, 722 cm^{-1}. Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.64. Found: C, 81.36; H, 13.59.

2,2-Dimethylnonadecanal (15): ^1H NMR ($CDCl_3$) δ 9.44 (1H, s, CH=O), 1.13-1.51 (32H, m, $16CH_2$), 1.03 (6H, s, $2CH_3$), 0.87 (3H, br t, J = 7 Hz, CH_3); IR (liquid film) 2928, 2835, 1728, 1468, 909, 735 cm^{-1}. Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.64. Found: C, 81.27; H, 13.79.

6-Methyl-5-decanone (17):[14] ^1H NMR ($CDCl_3$) δ 2.50 (1H, sextet, J = 7 Hz, CH-C=O), 2.42 (2H, t, J = 7.2 Hz, CH_2-C=O), 1.13-1.73 (10H, m, $5CH_2$), 1.04 (3H, d, J = 7 Hz, $C\underline{H}_3$-CH), 0.89 (3H, t, J = 7.2 Hz, CH_3), 0.87 (3H, t, J = 7 Hz, CH_3); IR (liquid film) 2955, 2915, 2875, 2870, 1713, 1460, 1379 cm^{-1}.

2-Butyl-2-methylhexanal (18): ^1H NMR ($CDCl_3$) δ 9.43 (1H, s, CH=O), 1.02-1.62 (12H, m, $6CH_2$), 1.00 (3H, s, CH_3), 0.89 (6H, t, J = 7 Hz, $2CH_3$); IR (liquid film) 2955, 2941. 2877, 2873, 2685, 1728, 1468, 1375, 889, 729 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.61; H, 13.05.

α-Phenylcyclopentanecarboxaldehyde (9):[15] ^1H NMR ($CDCl_3$) δ 9.39 (1H, s, CHO), 7.19-7.41 (5H, m, Ph), 2.43-2.59 (2H, m, CH_2), 1.50-1.95 (6H, m, $3CH_2$).

1-(*t*-Butyldiphenylsiloxy)-3-methyl-2-butanone (20): ^1H NMR ($CDCl_3$) δ 7.34–7.73 (10H, m, 2Ph), 4.29 (2H, s, CH_2-O), 2.86 (1H, heptet, J = 7 Hz, CH-C=O), 1.12 (9H, s, *t*-Bu), 1.06 (3H, d, J = 7 Hz, $C\underline{H}_3$-CH), 1.04 (3H, d, J = 7 Hz, $C\underline{H}_3$-CH); IR (liquid film) 3073, 3055, 2965, 2934, 2859, 1734,

1474, 1428, 1113, 1028, 826, 741, 702 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29. Found: C, 74.08; H, 8.35.

3-(*t*-Butyldiphenylsiloxy)-2,2-dimethylpropanal (21): ^1H NMR ($CDCl_3$) δ 9.62 (1H, s, CHO), 7.34–7.71 (10H, m, 2Ph), 3.65 (2H, s, CH_2-O), 1.08 (6H, s, $2CH_3$-C), 1.05 (9H, s, *t*-Bu); IR (liquid film) 3075, 3054, 2961, 2932, 2858, 1734, 1474, 1428, 1113, 826, 741, 702 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29. Found: C, 74.00; H, 8.21.

Ketone 23:[11b] ^1H NMR ($CDCl_3$) δ 4.48 (1H, dd, *J* = 5, 11 Hz, C<u>H</u>-OAc), 2.59 (1H, heptet, *J* = 7 Hz, CH-C=O), 2.33-2.49 (1H, m, CH-C=O), 2.03 (3H, s, CH_3-C=O), 1.06 (6H, d, *J* = 7 Hz, $2CH_3$), 1.01 (3H, s, CH_3-C), 0.97 (3H, s, CH_3-C), 0.89 (3H, d, *J* = 6 Hz, C<u>H</u>$_3$-CH), 0.85 (9H, s, $3CH_3$), 0.65 (3H, s, CH_3-C); IR ($CHCl_3$ solution) 2953, 2878, 1723, 1471, 1374, 1260, 1221, 1209, 1028, 781, 756, 746, 731, 669 cm^{-1}.

Aldehyde 24:[11b] ^1H NMR ($CDCl_3$) δ 9.42 (1H, s, CH=O), 4.46 (1H, dd, *J* = 5, 11 Hz, C<u>H</u>-OAc), 2.03 (3H, s, CH_3-C=O), 0.99 (6H, s, $2CH_3$-C), 0.96 (3H, s, CH_3), 0.89 (3H, d, *J* = 6 Hz, CH_3-CH), 0.87 (6H, s, $2CH_3$), 0.85 (3H, s, CH_3), 0.66 (3H, s, CH_3-C); IR ($CHCl_3$ solution) 2958, 2878, 1721, 1468, 1374, 1260, 1028, 1011, 980, 754, 747 cm^{-1}.

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