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Organoaluminum-Catalyzed Rearrangement of Epoxides A Facile Route to the Synthesis of Optically Active β-Siloxy Aldehydes

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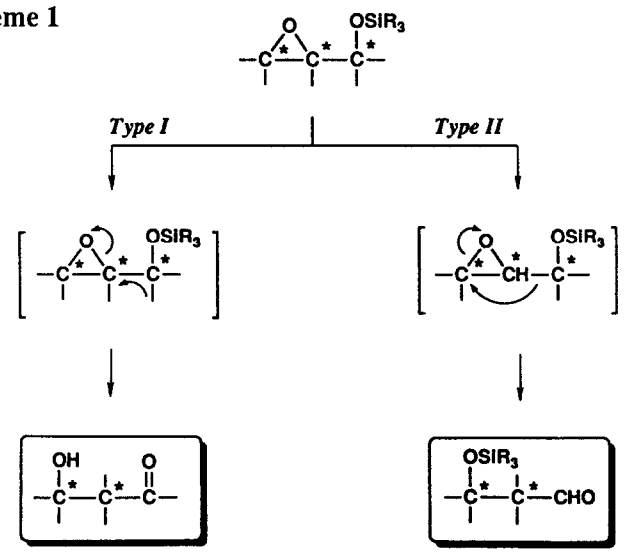
Abstract: A new, stereocontrolled rearrangement of epoxy silyl ethers leading to β-siloxy aldehydes has been effected with stoichiometric use of exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) under mild conditions Used in combination with the Sharpless asymmetric epoxidation of allylic alcohols, this rearrangement represents a new approach to the synthesis of various optically active β-hydroxy aldehydes, useful intermediates in natural product synthesis The modified organoaluminum reagent, MABR is also applicable to the transformation of a variety of simple epoxides to carbonyl compounds with high efficiency and selectivity Further, the catalytic version for the rearrangement of epoxy silyl ethers as well as simple epoxides has been newly devised The scope and limitation of this catalytic method has been clarified with various epoxy substrates

The acid-catalyzed rearrangement of epoxides to carbonyl compounds is certainly a well-known transformation and a number of reagents have been elaborated for this purpose [1] Among these, only a few reagents have been employed successfully for the rearrangement of functionalized epoxides with respect to the efficiency and selectivity of the reaction In this context, we have been interested for some time in the possibility of effecting the rearrangement of optically active epoxy silyl ethers which were readily available from allylic alcohols by Sharpless asymmetric epoxidation [2] As illustrated in Scheme I, two types of rearrangement are conceivable The type-I rearrangement of epoxy silyl ethers giving β-hydroxy carbonyl

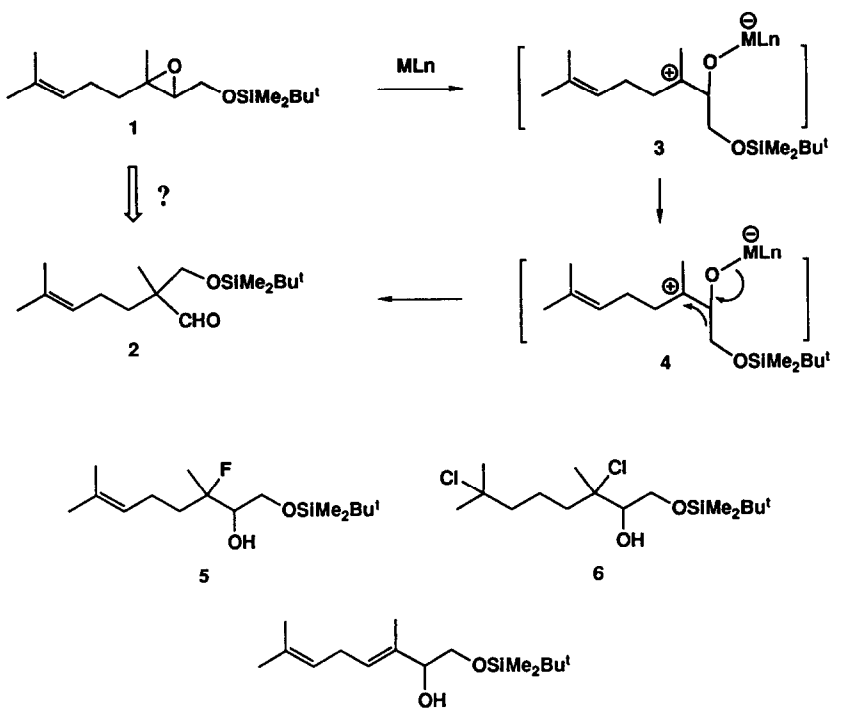
Scheme 1



compounds has been recently effected by the use of titanium tetrachloride [3] The type-II transformation, if successful, would serve as a new and highly convenient access to the synthesis of various optically active β-siloxy aldehydes, useful intermediates in natural product synthesis [4,5]

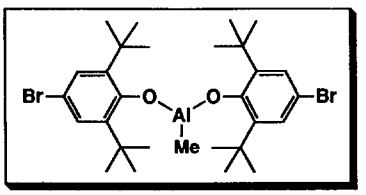
Initially, we studied the rearrangement of the *tert*-butyldimethylsilyl ether of epoxy geraniol **1** This is a challenging substrate due to its susceptibility to various side-reactions including olefinic cyclization, elimination, and nucleophilic trapping, upon formation of the intermediate carbocation **3** In fact, attempted rearrangement of **1** with several conventional Lewis acids gave rise to none of the desired β-siloxy aldehyde **2** (Scheme 2) For example, reaction of **1** with BF_3 OEt_2 (2 equiv) at low temperature afforded fluorohydrin **5** in 74% yield, while the chlorination product **6** was produced as a major product (52% yield) by $TiCl_4$ (2 equiv) We interpreted the general difficulty in obtaining the desired β-siloxy aldehyde **2** as being due to the reluctant transfer of the (*tert*-butyldimethylsiloxy)methyl moiety as shown in **4** Hence we thought that the use of a sterically hindered, oxygenophilic organoaluminum reagent might be most suitable for effecting the initial epoxide-cleavage followed by smooth alkyl transfer, in view of the steric repulsion between a bulky organoaluminum ligand and a siloxymethyl moiety The bulk of the phenoxide ligand would also inhibit it from interacting with the intermediate cation **3** as either a base or a nucleophile

Scheme 2



Attempted use of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD), which has been employed successfully for stereoselective activation of the carbonyl moiety,[6] resulted in only gradual formation of β-siloxy aldehyde **2** at -78 °C, although at -20 °C the reaction was over after 1 h In marked contrast, however, the more Lewis acidic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide),

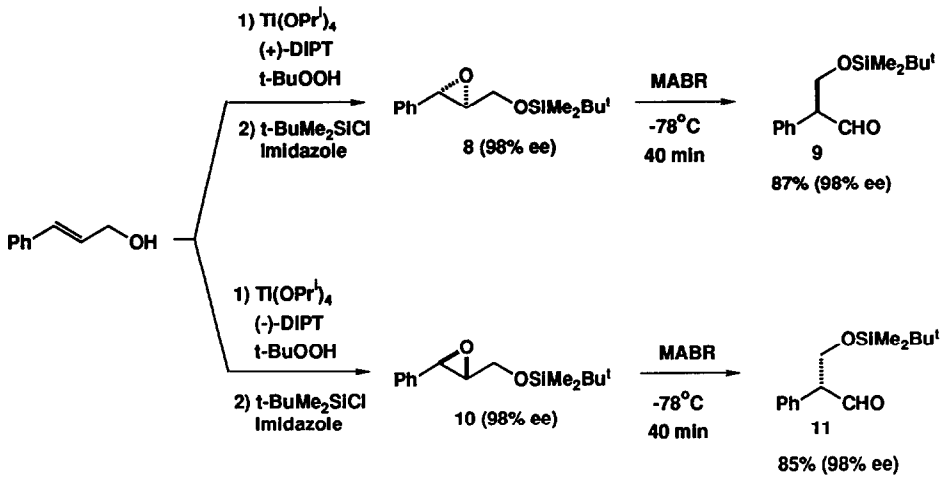
abbreviated to MABR,[7] effected the clean rearrangement of **1** to **2** (99%) at -78 °C in 1 h, showing the importance of the *p*-bromo substituent in MABR for rate acceleration of the reaction.[8] Less bulky dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide lowered the yield (63%) of the reaction (-20 °C for 90 min), while methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) afforded the elimination product **7** (16% yield) as the major product accompanied by only trace of **2**. Consequently, use of two bulky 4-bromo-2,6-di-*tert*-butylphenoxy ligands in MABR is crucial for effecting the smooth rearrangement of **1**.



(MABR)

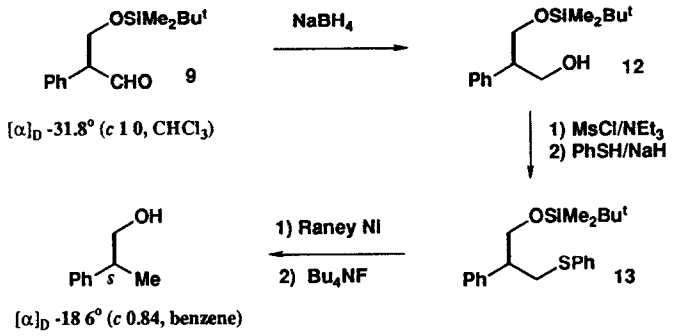
With this information in hand, our attention was focused on the rearrangement of optically active epoxy silyl ethers which were readily obtainable as both enantiomers by the Sharpless asymmetric epoxidation of allylic alcohols followed by silylation, as illustrated in Scheme 3. When the optically active epoxy *tert*-butyldimethylsilyl ether **8** (98% ee)[2b] was treated with 2 equiv of MABR in CH_2Cl_2 at -78 °C for 40 min, the

Scheme 3



corresponding β-siloxy aldehyde **9** ($[\alpha]_D$ -31.8° (*c* 1.0, $CHCl_3$)) was obtained in 87% yield. The optical purity and absolute configuration of **9** were determined from the optical rotation of 2-phenylpropanol which was derived from **9** by the following sequences (Scheme 4): (1) $NaBH_4$, MeOH, (2) MsCl, NEt_3, CH_2Cl_2, (3) PhSNa, THF-EtOH, (4) Raney Ni, EtOH, (5) Bu_4NF, THF.[9] Based on the reported optical rotation ($[\alpha]_D$ -19.0° (*c* 0.83, benzene)) of the optically pure (*S*)-2-phenylpropanol,[10] the (*S*)-2-phenylpropanol ($[\alpha]_D$ -18.6° (*c* 0.84, benzene)) derived from **9** possesses virtually the same optical purity as the starting silyl ether **8**. Hence, this organoaluminum-promoted rearrangement proceeds with rigorous transfer of the chirality of **8** and the observed stereoselectivity can be interpreted to arise from the *anti* migration of the siloxymethyl group to the epoxide moiety. Similarly, the enantiomeric epoxy silyl ether **10** (98% ee)[2b] was equally transformed to the enantiomeric β-siloxy aldehyde **11** ($[\alpha]_D$ +32.3° (*c* 1.0, $CHCl_3$)) under the same conditions.

Scheme 4



Other selected examples of the epoxy alcohol rearrangement (Table I) clearly indicate the effectiveness of our approach The migratory aptitude on the substitution patterns of epoxy alcohols should be noted As a whole, the facile migration of the alkyl group is observed in the case of γ,γ-disubstituted epoxy alcohols (entries 5, 8, 16, and 18) The γ-monosubstituted epoxy alcohols possessing aryl or alkenyl groups are also susceptible toward the rearrangement (entries 1, 4, 11, and 15) However, epoxy alcohols with other substitution patterns do not undergo the desired rearrangement For example, the *tert*-butyldimethylsilyl ether of *trans*-2,3-epoxy-1-hexanol (γ-monoalkylsubstituted epoxy alcohol) was unreactive with MABR after several hours at -78 °C or -20 °C and gradually decomposed at 0 °C The *tert*-butyldimethylsilyl ether of (*E*)-2,3-epoxy-2-methyl-1-pentanol (β,β-disubstituted epoxy alcohol) gave 2-[(*tert*-butyldimethylsiloxy)methyl]-2-methylbutanal in 57% yield with migration of the ethyl group under the standard conditions (entry 19) This rearrangement is not dependent on the configuration of the β-carbon since both epoxy geraniol and epoxy nerol gave rise to the same aldol **2** as a sole isolable product (entries 5 and 8) The stereochemistry at the migrating siloxy carbon is rigorously retained in the rearrangement (entries 11,15, 16, and 18) For example, the essentially pure *erythro* isomer **14** (>99%, >98% ee) of the optically active epoxy silyl ether, which was readily obtained by the enantioselective epoxidation of racemic (*E*)-4-phenyl-3-buten-2-ol,[11] smoothly rearranged under the influence of MABR (2 equiv) to produce the optically active, *threo* β-siloxy aldehyde **15** exclusively (entry 11) as depicted in Scheme 5

Scheme 5

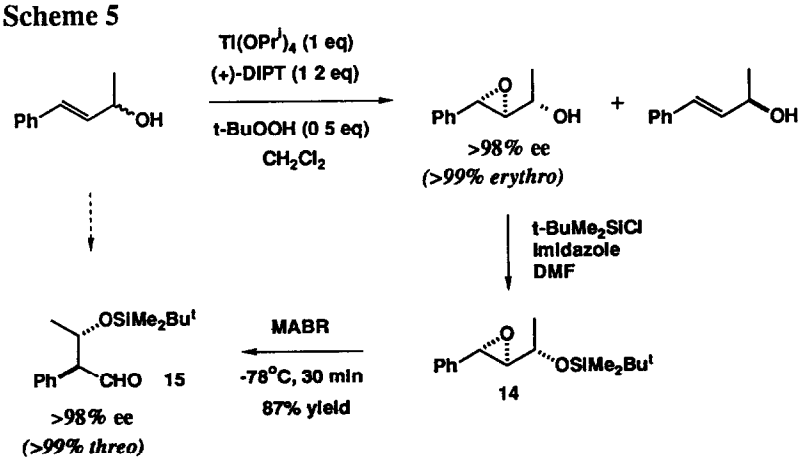
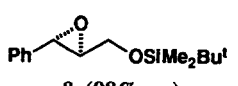
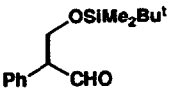
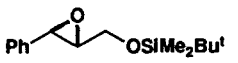
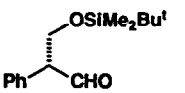
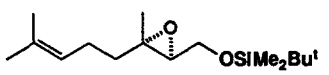
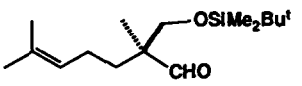
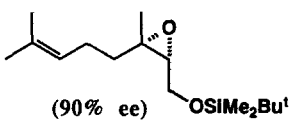
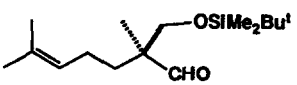
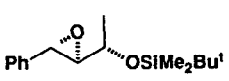
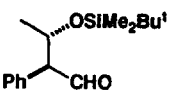
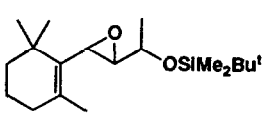
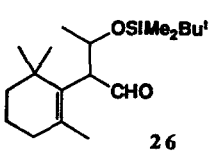
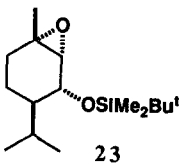
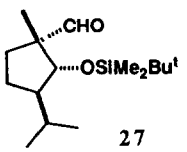
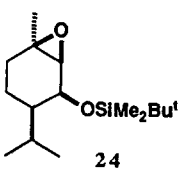
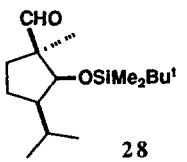
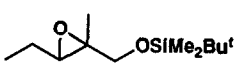
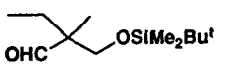


Table I Organoaluminum-Catalyzed Rearrangement of Epoxy Silyl Ethers [a]

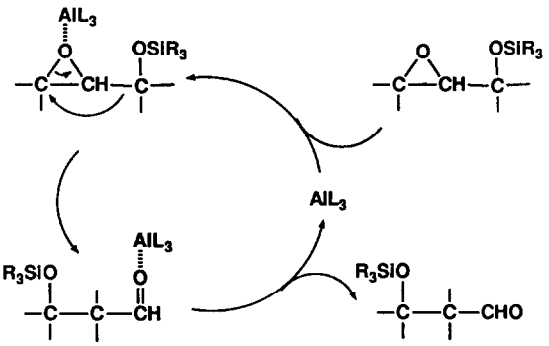
entry	epoxy silyl ether [b]	MABR (mol %)	conditions (°C, h)	β-siloxy aldehyde	% yield [c]
1		200	-78, 0 5		95
2		20	-20, 0 3		82 *d*
3	**8 (98% ee)**	10	-20, 0 3	**9 (98% ee)**	74 *d*
4		200	-78, 0 5		85
	10 (98% ee)			**11 (98% ee)**	
					
	(2*S*,3*S*)-1 (95% ee)			**(*S*)-2 (95% ee)**	
5		200	-78, 1		99 *e*
6		20	-78, 0 2, 0, 0 5		82 *e*
7		10	-78, 0.2, 0, 1		74 *e*
					
	(90% ee)			**(*S*)-2 (90% ee)**	
8		200	-78, 1, -40, 0 5		98 *e*
9		20	-78, 0 2, 0, 1		79 *e*
10		10	-78, 0 2, 0, 3		68 *e*
					
	14 (>98% ee)			**15 (>98% ee)**	
11		200	-78, 0 5		87
12		20	-78, 1, -40, 1, -20, 1		74 (2) *f*
13		20	-40, 0 5		75 (7) *f*
14		10	-78, 0 2, -20, 0 5, 0, 0 5		71 (7) *f*
15		200	-78, 0 3		93 *g h*
	22			**26**	

entry	epoxy silyl ether [b]	MABR (mol %)	conditions (^{O}C, h)	β-siloxy aldehyde	% yield [c]
16		200	-78, 0 5, -20, 2		88 [i]
17	23	20	-78, 0 2, 0, 5	27	77 [e]
18		200	-20, 2, 0, 7		82 [j]
	24			28	
19		200	-20, 1		57
	25			29	

[a] The reaction was carried out in degassed CH_2Cl_2 solvent by using 0 1~2 equiv of MABR per epoxy silyl ether under the indicated reaction conditions [b] The optically active substrates are utilized except the entries 15 and 19 [c] Isolated yield [d] The *in situ* derivatization of **9** to the alcohol **12** with DIBAH [e] With NaF-H_2O workup [f] Yield of *erythro* isomer [g] *Erythro/threo* = 3 1 for the starting epoxy silyl ether [h] The *erythro/threo* ratio of the β-siloxy aldehyde is 1 3 by ^{1}H NMR analysis [i] Optically active (+)-*trans*-piperitol (>95% ee by ^{1}H NMR analysis after conversion to its (-)- and (+)-MTPA esters) was kindly provided by the Takasago Co Ltd [j] Optically active (+)-*cis*-piperitol was prepared from (+)-*trans*-piperitol by the Swern oxidation followed by reduction with DIBAH.

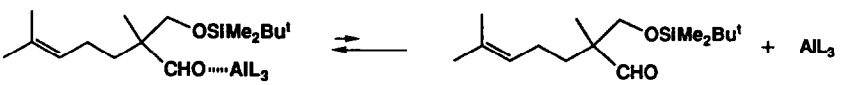
In the present rearrangement on epoxy silyl ethers, the Lewis acid could in principle be reduced to a catalytic amount if MABR can be regenerated without being inactivated by coordination to the aldehydic product or by other side reactions (Scheme 6) [12] The advantages of the catalytic version are apparent in the areas of economy, ease of large-scale preparation and isolation, and the synthetic potential for *in situ* derivatization of the carbonyl products Accordingly, we have attempted to develop the catalytic version of the epoxy silyl ether rearrangement

Scheme 6



16

Reaction of *tert*-butyldimethylsilyl ether **1** of epoxy geraniol with MABR (2 equiv) in CH_2Cl_2 at -78 °C for 1 h was already shown to give rearranged β-siloxy aldehyde **2** in 99% yield In contrast, when this epoxide was treated with the catalytic amount (20 mol%) of MABR in CH_2Cl_2 at -78 °C, the rearrangement proceeded very slowly and virtually stopped after achieving only ~20% conversion at this temperature Apparently coordination of carbonyl oxygen to an aluminum reagent is stronger than that of epoxide oxygen, thereby requiring the stoichiometric use of MABR for completion of the rearrangement Addition of Me_3SiCl or 4A molecular sieves (activated powder) was not effective in inducing attempted dissociation of the aluminum reagent-carbonyl complex **17** or in capturing the *in situ* generated aldehyde **2** However, on warming to -20 °C the rate of the rearrangement was markedly accelerated and was complete within 30 min to furnish the desired aldehyde **2** in 82% yield



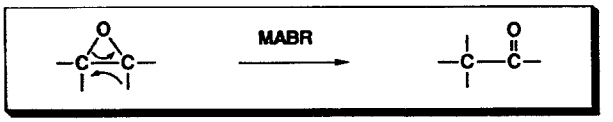
17 2

Several other examples are included in Table 1 Use of NaF-H_2O workup[13] further simplifies the experimental operation in this catalytic process. It should be noted that the *erythro/threo* stereoselection can be diminished in the case of certain optically active epoxy silyl ethers (entries 12-14) Reaction of **14** with 10-20 mol% of MABR at -78 ~ 0 °C gave rise to the desired *threo*-aldehyde **15** accompanied by isomeric *erythro*-aldehyde as a minor product (entries 12-14) Rearrangement of other optically active substrates proceeds nicely (entries 2,3, 6, 7, 9, 10, and 17)

The key element of the present modification is the use of a higher reaction temperature (though still at or below 0 °C) than with the stoichiometric reaction in order to induce the dissociation of aluminum reagent-carbonyl complex **16**, thereby allowing the regeneration of MABR for further use in the catalytic cycle of the reaction (Scheme 6) The facile dissociation of complex **16** as well as the smooth rearrangement of epoxides

is apparently ascribable to the exceptional bulkiness of MABR The less bulky methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) was found to be totally ineffective for the rearrangement of *tert*-butyldimethylsilyl ether **1** of epoxy geraniol

The bulky aluminum reagent, MABR is also applicable to the rearrangement of a variety of simple epoxides under very mild conditions with high efficiency and selectivity as indicated in Table 2 [14] For



instance, while attempted rearrangement of *tert*-butyldimethylsilyl ether of epoxy citronellol with BF_3 OEt_2 resulted in formation of a number of products, treatment with MABR produced the rearranged aldehyde (see entry 14). Certain diene monoepoxides exhibited unusual behavior under the influence of MABR (entry 18), when compared with the previously known transition metal (Pd^0 and Rh^I) catalysts [12] Once again the amount of Lewis acid, MABR can be reduced to 5 mol% for many of the epoxy substrates However, certain substrates cannot be successfully rearranged in the catalytic process (entries 7 and 15) For example, treatment of terminal epoxide **18** with catalytic MABR (20 mol%) in CH_2Cl_2 at -20 °C for 30 min afforded dimeric alcohol **19** as a major product (Scheme 7). Presumably, this side reaction proceeds by initial epoxide cleavage followed by trapping of the intermediate carbocation **21** with excess epoxide in preference to the normal rearrangement Furthermore, epoxides derived from monosubstituted olefins and internal dialkyl-substituted olefins are unreactive even with a two-fold quantity of MABR.

Scheme 7

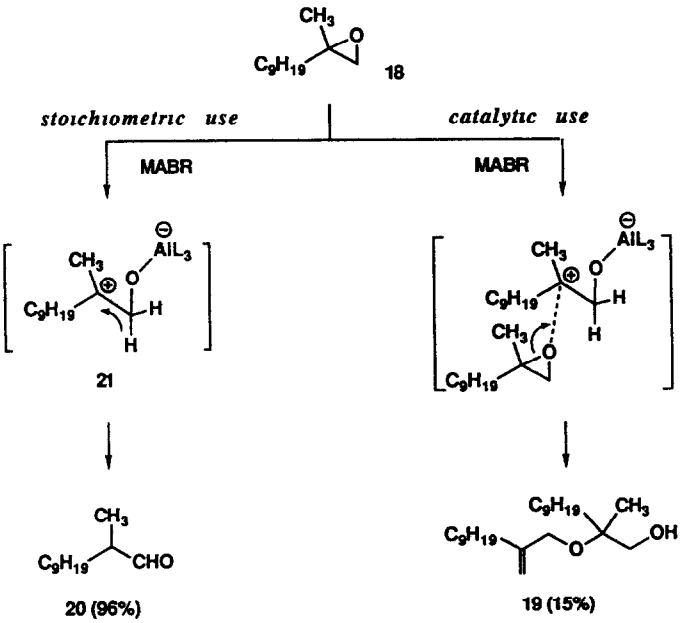
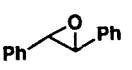
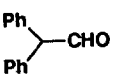
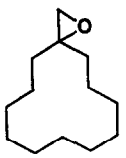
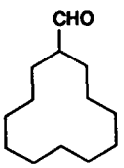
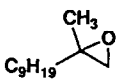
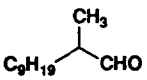
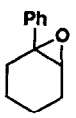
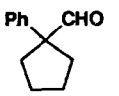
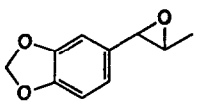
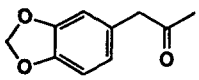
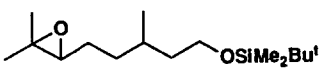
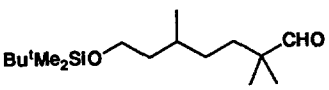
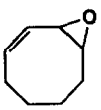
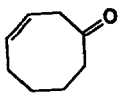
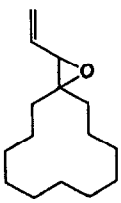
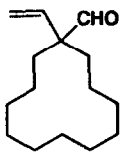


Table 2. Organoaluminum-Catalyzed Rearrangement of Epoxides to Carbonyl Compounds [a]

entry	epoxide	MABR (mol %)	conditions (^{O}C, h)	product	% yield [b]
1		200	-78, 0 5		93
2		10	-20, 0 3		95
3		200	-78, 2, -20, 0 3		94
4		30	-20, 0 5		77
5		20	-20, 0 5		58
6		200	-78, 0 5		96
7		20	-20, 0 3		0
	18			**20**	
8		200	-78, 0 5		98
9		10	-20, 1		96
10		5	-20, 1		91
11		200	-78, 0 3		87
12		10	-20, 0 5		90
13		5	-20, 0 2		84
					
14		200	-78, 1, -20, 1		98
15		20	-20, 1, 0, 2		0
16		200	-78, 1, -20, 4 5		73
17		20	-20, 1, 0, 2		0
18		200	-78, 1, -20, 1 5		90

[a] The rearrangement was carried out in degassed CH_2Cl_2 by using 0 05~2 equiv of MABR per epoxide under the indicated conditions [b] Isolated yield by column chromatography

Experimental Section

General. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer ^{1}H NMR spectra were measured on a Varian Gemini-200 spectrometer Analytical gas-liquid phase chromatography (GLC) was performed on Gasukuro Kogyo Model 370 and Shimadzu GC-8A instruments equipped with a flame ionization detector and a capillary column of PEG-HT (0 25 X 25,000 mm) using nitrogen as carrier gas Optical rotations were measured on a JASCO DIP-140 digital polarimeter 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 Institute of Applied Organic Chemistry, Faculty of Engineering, 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 and DMF were stored over 4A molecular sieves In the catalytic process, methylene chloride as solvent was freshly distilled before use Pyridine and triethylamine were stored over KOH pellets Trimethylaluminum was obtained from Toso-Akzo Chem Co Ltd , Japan Other simple chemicals were purchased and used as such

Preparation of Epoxides. Various epoxides were prepared according to one of the following procedures (1) simple epoxidation of olefins with MCPBA, (2) $VO(acac)_2$-catalyzed epoxidation of allylic alcohols with *tert*-BuOOH, (3) Sharpless asymmetric epoxidation of allylic alcohols [2]

Preparation of Epoxy Silyl Ethers. *tert*-Butyldimethylsilyl ethers of various epoxy alcohols were obtained by treatment of the epoxy alcohols with *tert*-butyldimethylsilyl chloride (1 1~2 equiv) and imidazole (2~3 equiv) in DMF at -20 ~ 0 °C for several hours

Epoxy Silyl Ether (2*S*,3*S*)-1: $[\alpha]_D^{24}$ -4 57° (*c* 1 00, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 5 08 (1H, t, *J* = 7 5 Hz, C=CH), 3 72 (2H, d, *J* = 5 Hz, CH_2-OSi), 2 88 (1H, t, *J* = 5 Hz, CH-O), 2 06 (2H, q, *J* = 10 Hz, C=C-CH_2), 1 58 and 1 67 (6H, s, $(CH_3)_2$C=), 1 42 (2H, m, C-CH_2-C), 1 23 (3H, s, CH_3-C-O), 0 89 (9H, s, *t*-Bu), 0 07 (6H, s, Me_2Si), IR (liquid film) 2960, 2940, 2865, 1450, 1380, 1250, 1130, 1090, 830, 770 cm^{-1} Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 50, H, 11 39

Epoxy Silyl Ether 8: $[\alpha]_D^{24}$ -26 8° (*c* 1 04, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 7 23–7 37 (5H, m, Ph), 3 95 (1H, dd, *J* = 4, 14 Hz, CH-OSi), 3 80 (1H, dd, *J* = 6, 14 Hz, CH-OSi), 3 78 (1H, d, *J* = 2 Hz, Ph-CH), 3 12 (1H, m, CH-O), 0 89 (9H, s, *t*-Bu), 0 08 (6H, s, Me_2Si), IR (liquid film) 2955, 2940, 2865, 1465, 1255, 1140, 1105, 840, 780, 700 cm^{-1} Anal Calcd for $C_{15}H_{24}O_2Si$ C, 68 11, H, 9 17 Found C, 67 85, H, 9 30

Epoxy Silyl Ether 10. $[\alpha]_D^{24}$ +27 6° (*c* 1 10, $CHCl_3$) Anal Calcd for $C_{15}H_{24}O_2Si$ C, 68 11, H, 9 17 Found C, 67 97, H, 9 26

Silyl Ether of (2*R*,3*S*)-2,3-Epoxynerol: $[\alpha]_D^{26}$ +4 03° (*c* 1 07, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 5 08 (1H, m, C=CH), 3 76 (1H, dd, *J* = 6, 14 Hz, CH-OSi), 3 67 (1H, dd, *J* = 6, 12 Hz, CH-OSi), 2 87 (1H, t, *J* = 6 Hz, CH-O), 2 08 (2H, q, *J* = 8 5 Hz, C=C-CH_2), 1 58 and 1 66 (6H, s, $(CH_3)_2$C=), 1 46 (2H, m, C-CH_2-C), 1 30 (3H, s, CH_3-C-O), 0 88 (9H, s, *t*-Bu), 0 06 (6H, s, Me_2Si), IR (liquid film) 2960, 2935, 2865, 1455, 1377, 1249, 1085, 831, 771 cm^{-1} Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 71, H, 11 43

Epoxy Silyl Ether 14: $[\alpha]_D^{24}$ -23 9° (*c* 1 22, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 7 21-7 37 (5H, m, Ph), 3 87 (1H, dq, *J* = 4 2, 8 Hz, CH-OSi), 3 80 (1H, d, *J* = 2 Hz, Ph-CH), 2 90 (1H, dd, *J* = 2, 4 2 Hz, CH-O), 1 26 (3H, d, *J* = 8 Hz, CH_3), 0 88 (9H, s, *t*-Bu), 0 07 (6H, s, Me_2Si), IR (liquid film) 2980, 2945,

2880, 1455, 1250, 1145, 1110, 1095, 830, 770, 685 cm^{-1} Anal Calcd for $C_{16}H_{26}O_2Si$ C, 69 00, H, 9 43 Found C, 68 83, H, 9 71 The optical purity of the erythro epoxy alcohol was found to be >98% ee by ^1H NMR analysis after conversion to the (-)-α-methoxy-α-(trifluoromethyl)phenylacetic acid ((-)-MTPA) ester

Epoxy Silyl Ether 22 (*erythro/threo* ratio = 3 1)[15]: ^1H NMR ($CDCl_3$) δ 3 64 and 3 79 (1H, quintet, J = 6 4 Hz, *erythro* and *threo* CH-OSi), 3 34 (1H, s, =C-CH-O), 2 76 and 2 81 (1H, dd, J = 6 4, 6 4 Hz, *erythro* and *threo* CH-O), 1 64 and 1 68 (3H, s, *threo* and *erythro* CH_3-C=), 1 21 and 1 26 (3H, d, J = 6 4 Hz, *threo* and *erythro* CH_3C-O), 1 04 and 1 13 (6H, s, $(CH_3)_2C$), 0 85 (9H, s, *t*-Bu), 0 03 (6H, s, Me_2Si), IR (liquid film) 2960, 2938, 2865, 1456, 1356, 1250, 1106, 990, 900, 830, 770 cm^{-1} Anal Calcd for $C_{19}H_{36}O_2Si$ C, 70 29, H, 11 20 Found C, 70 04, H, 11 20

Epoxy Silyl Ether 23: $[\alpha]_D^{24}$ +58 0° (*c* 1 22, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 3 78 (1H, dd, J = 2 5, 10 Hz, CH-OSi), 2 94 (1H, d, J = 2 5 Hz, CH-O), 2 05 (1H, m, CH), 1 72 (2H, m, CH_2), 1 29 (3H, s, CH_3-C-O), 0 88 (9H, s, *t*-Bu), 0 68 and 0 85 (6H, d, J = 7 Hz, $(CH_3)_2C$), 0 08 and 0 11 (6H, s, Me_2Si), IR (liquid film) 2965, 2940, 2870, 1460, 1255, 1095, 1075, 890, 835, 770 cm^{-1}, MS, *m/e* (rel intensity) 268 (8), 267 (8), 227 (100) Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 33, H, 11 36

Epoxy Silyl Ether 24: $[\alpha]_D^{24}$ -115 2° (*c* 1 10, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 4 19 (1H, t, J = 5 Hz, CH-OSi), 2 96 (1H, d, J = 5 Hz, CH-O), 2 00 (1H, d, J = 16 Hz, CH), 1 28 (3H, s, CH_3-C-O), 0 89 (9H, s, *t*-Bu), 0 85 and 0 86 (6H, d, J = 7 Hz, $(CH_3)_2C$), 0 08 and 0 13 (6H, s, Me_2Si), IR (liquid film) 2960, 2935, 2865, 1463, 1456, 1245, 1140, 1097, 983, 875, 827, 767 cm^{-1} Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 39, H, 11 25

Epoxy Silyl Ether 25: ^1H NMR ($CDCl_3$) δ 3 55 (2H, s, CH_2-OSi), 2 79 (1H, t, J = 6 4 Hz, CH-O), 1 56 (2H, quintet, J = 7 Hz, CH_2C-O), 1 24 (3H, s, CH_3C-O), 1 00 (3H, t, J = 7 4 Hz, $C\underline{H}_3CH_2$), 0 87 (9H, s, *t*-Bu), 0 02 and 0 03 (6H, s, Me_2Si), IR (liquid film) 2955, 2935, 2860, 1465, 1450, 1245, 1095, 835, 770 cm^{-1} Anal Calcd for $C_{12}H_{26}O_2Si$ C, 62 53, H, 11 39 Found C, 62 38, H, 11 54

Rearrangement of 1 with BF_3·OEt_2. Treatment of **1** (142 mg, 0 5 mmol) in CH_2Cl_2 (5 mL) with BF_3 OEt_2 (123 μL, 1mmol) at -78°C for 15 min afforded 1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-3-fluoro-6-octen-2-ol (**5**) (112 mg, 74% yield) as a major product ^1H NMR ($CDCl_3$) δ 5 09 (1H, br t, J = 7 Hz, C=CH), 3 52-3 78 (3H, m, O-$CHCH_2$-OSi), 2 60 (1H, s, OH), 2 07 (2H, m, CH_2-C=), 1 58 and 1 67 (6H, s, $(CH_3)_2C$=), 1 31 (3H, d, J = 22 4 Hz, CH_3-C-F), 0 88 (9H, s, *t*-Bu), 0 07 (6H, s, Me_2Si), IR (liquid film) 3540, 2950, 2930, 2850, 1460, 1380, 1250, 1110, 980, 835, 775, 730 cm^{-1}, MS, *m/e* (rel intensity) 285 (3), 267 (4), 227 (43), 209 (33), 171 (30), 157 (40), 145 (100) Anal Calcd for $C_{16}H_{33}O_2SiF$ C, 63 09, H, 10 94 Found C, 62 79, H, 11 01 Authentic **5** was prepared by treatment of epoxy geraniol with Py HF in THF followed by selective monosilylation with *tert*-$BuMe_2SiCl$/Py in CH_2Cl_2 in the presence of catalytic 4-dimethylaminopyridine (DMAP)

Rearrangement of 1 with $TiCl_4$. Treatment of **1** (142 mg, 0 5 mmol) in CH_2Cl_2 (5 mL) with a 1 M CH_2Cl_2 solution of $TiCl_4$ (1mmol) at -78°C for 15 min afforded 1-(*tert*-butyldimethylsiloxy)-3,7-dichloro-3,7-dimethyl-2-octanol (**6**) (84 mg, 52% yield) as a major product ^1H NMR ($CDCl_3$) δ 3 82 (1H, m, CH-O), 3 70 (2H, m, CH_2-OSi), 2 80 (1H, d, J = 2 Hz, OH), 1 60-1 92 (6H, m, CH_2), 1 52 and 1 54 (9H, s, CH_3-C-Cl), 0 87 (9H, s, *t*-Bu), 0 07 (6H, s, Me_2Si), ^{13}C NMR ($CDCl_3$) δ77 56 (CH-O), 71 09 and 75 68 (C-Cl), 63 59 (CH_2-O), 40 32 and 46 30 (CH_2), 32 58 and 32 78 (CH_3-C-Cl), 26 05 (CH_3-C-Si), 20 26 (CH_2), 18 41 (C-Si), IR (liquid film) 3600, 2970, 2940, 2870, 1460, 1385, 1370, 1250, 1110, 975, 835, 775 cm^{-1}, MS, *m/e* (rel intensity) 264 (13), 228 (33), 136 (100) Anal Calcd for $C_{16}H_{34}O_2SiCl_2$ C, 53 76, H, 9 59 Found C, 53 49, H, 9 71

The product **6** was further converted to its acetate with Ac_2O-Py ^1H NMR ($CDCl_3$) δ 5 12 (1H, dd, J = 4, 7 Hz, CH-OAc), 3 94 (1H, dd, J = 4, 11 Hz, CH-OSi), 3 73 (1H, dd, J = 7, 11 Hz, CH-OSi), 2 10 (3H, s, $COCH_3$), 1 60-1 80 (6H, m, $(CH_2)_3$), 1 56 (9H, s, CH_3-C-Cl), 0 85 (9H, s, *t*-Bu), 0 03 (6H, s, Me_2Si)

Rearrangement of the Epoxy Silyl Ether 1 with Methylaluminum Bis(4-bromo-2,6-diisopropylphenoxide). Treatment of **1** (142 mg, 0 5 mmol) in CH_2Cl_2 (5 mL) with methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) (1 mmol) at -78 °C for 1 5 h and at -20 °C for 1 5 h yielded 1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-3,6-octadien-2-ol (**7**) (23 mg, 16% yield) as a major product ^1H NMR ($CDCl_3$) δ 5 42 (1H, br t, J = 7 Hz, C=CH), 5 08 (1H, br t, J = 7 Hz, C=CH), 4 02 (1H, m, CH-O), 3 61 (1H, dd, J = 4, 7 5 Hz, CH-OSi), 3 46 (1H, dd, J = 2 5, 7 5 Hz, CH-OSi), 2 70 (2H, br t, J = 7 Hz, =C-CH_2-C=), 2 59 (1H, d, J = 2 5 Hz, OH), 1 68 (3H, s, CH_3-C=), 1 61 (3H, s, CH_3-C=),0 88 (9H, s, *t*-Bu), 0 06 (6H, s, Me_2Si), IR (liquid film) 3394, 2969, 2944, 2874, 1467, 1256, 1114, 839, 779 cm^{-1} Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 70, H, 11 52 Authentic **7** was prepared by treatment of epoxy nerol with $Ti(OPr^i)_4$ in CH_2Cl_2 followed by selective monosilylation with *tert*-$BuMe_2SiCl$/Py in CH_2Cl_2 in the presence of catalytic DMAP [5]

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 any purification Other modified organoaluminum reagents such as MAD, methylaluminum bis(4-bromo-2,6-diisopropylphenoxide), and dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide were prepared *in situ* from Me_3Al and the corresponding phenols in CH_2Cl_2 at room temperature for 1 h

Stoichiometric Procedure for the Rearrangement of Epoxy Silyl Ethers with MABR. To a solution of the MABR (1 mmol) in CH_2Cl_2 (5 mL) was added an epoxy silyl ether (0 5 mmol) at -78 °C and the resulting mixture was stirred under the indicated 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) gave β-siloxy aldehyde in the yields shown in Table I

Catalytic Procedure for the Rearrangement of Epoxy Silyl Ethers with MABR. To a solution of the MABR (0 2 mmol) in degassed CH_2Cl_2 (5 mL) was added an epoxy silyl ether (1 mmol) at -78 °C The mixture was stirred under the indicated conditions in Table 1 Then the mixture was treated with NaF (17 mg, 0 4 mmol) followed by water (5 4 μL, 0 3 mmol) at -20 ~ 0 °C [13] The entire mixture was vigorously stirred at -20 ~ 0 °C for 20 min and filtered with the aid of CH_2Cl_2 The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ether/hexane = 1 10 to 1 5 as eluants) to give β-siloxy aldehyde in the yields shown in Table 1

(*S*)-3-(*tert*-Butyldimethylsiloxy)-2-phenylpropanal (9): $[\alpha]_D^{21}$ -31 8° (*c* 1 00, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 9 80 (1H, d, J = 2 Hz, CHO), 7 17–7 40 (5H, m, Ph), 4 21 (1H, dd, J = 7, 10 Hz, CH-OSi), 3 94 (1H, dd, J = 5 5, 10 Hz, CH-OSi), 3 72 (1H, br t, J = 7 5 Hz, PhCH), 0 82 (9H, s, *t*-Bu), -0 04 and -0 06 (6H, s, Me_2Si), IR (liquid film) 2965, 2940, 2870, 1725, 1250, 1110, 830, 770, 695 cm^{-1}, MS, *m/e* (rel intensity) 207 (100), 178 (66), 162 (16), 133 (12), 115 (10) Anal Calcd for $C_{15}H_{24}O_2Si$ C, 68 11, H, 9 17 Found C, 67 84, H, 9 30 Since the aldehyde **9** was readily susceptible to partial racemization in the presence of concentrated acidic 4-bromo-2,6-di-*tert*-butylphenol at ~30 °C, concentration of the crude extracts and application of the crude residue to column chromatography should be executed at low temperature (0 ~ 10 °C) Hence, the *in situ* derivatization of **9** to the alcohol **12** is recommended Thus, treatment of epoxy silyl ether **8** with MABR at -78 °C for 30 min and subsequent addition of DIBAH (2

equiv) at this temperature gave rise to the alcohol **12** ($[\alpha]_D^{23}$ +14 6° (*c* 1 03, $CHCl_3$)) after acidic workup with 1*N* HCl

(*R*)-3-(*tert*-Butyldimethylsiloxy)-2-phenylpropanal (11): $[\alpha]_D^{22}$ +32 3° (*c* 1 00, $CHCl_3$) Anal. Calcd for $C_{15}H_{24}O_2Si$ C, 68 11, H, 9 17 Found· C, 68.29, H, 9 10.

β-Siloxy Aldehyde (*S*)-2 from (2*S*,3*S*)-1: $[\alpha]_D^{24}$ +6 45° (*c* 1 00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 9.53 (1H, s, CHO), 5 03 (1H, br t, *J* = 6 5 Hz, C=CH), 3 67 (1H, d, *J* = 10 Hz, CH-OSi), 3 54 (1H, d, *J* = 10 Hz, CH-OSi), 1 88 (2H, m, C=C-CH_2), 1 55 and 1 64 (6H, s, $(CH_3)_2C$=), 1 02 (3H, s, CH_3), 0 85 (9H, s, *t*-Bu), 0 02 (6H, s, Me_2Si), IR (liquid film) 2950, 2920, 2850, 1730, 1455, 1255, 1100, 840, 775 cm^{-1} Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 32, H, 11 53

β-Siloxy Aldehyde (*S*)-2 from Silyl Ether of (2*R*,3*S*)-2,3-Epoxy Nerol: $[\alpha]_D^{26}$ +6 02° (*c* 1 08, $CHCl_3$)

(2*S*,3*S*)-3-(*tert*-Butyldimethylsiloxy)-2-phenylbutanal (15): $[\alpha]_D^{22}$ +64 8° (*c* 1 12, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 9 84 (1H, d, *J* = 3 4 Hz, CHO), 7 16-7 39 (5H, m, Ph), 4 48 (1H, dq, *J* = 5 5, 8 5 Hz, CH-OSi), 3 50 (1H, dd, *J* = 3 4 and 8 5 Hz, CH-C=O), 1 03 (3H, d, *J* = 5 5 Hz, CH_3), 0.85 (9H, s, *t*-Bu), 0 05 and 0 07 (6H, s, Me_2Si), IR (liquid film) 2946, 2924, 1724, 1268, 1137, 1094, 988, 837, 771, 695 cm^{-1} Anal Calcd for $C_{16}H_{26}O_2Si$ C, 69.00, H, 9 43. Found C, 68 78, H, 9 73

β-Siloxy Aldehyde 26 (*erythro*/*threo* ratio = 1 3): ^1H NMR ($CDCl_3$) δ 9 46 and 9 63 (1H, s, *erythro* and *threo* CHO), 4 44 and 4 63 (1H, m, *erythro* and *threo* CH-OSi), 3 07 (1H, d, *J* = 10 Hz, CH-C=O), 1 92 (2H, br t, =C-CH_2), 1.46 (3H, s, =C-CH_3), 1 08 and 1 23 (3H, d, *J* = 8 Hz, *threo* and *erythro* CH_3-C-O), 0 80 and 1.01 (6H, s, $(CH_3)_2C$), 0 82 (9H, s, *t*-Bu), -0 04 and 0 06 (3H, d, *J* = 8 0 Hz, *erythro* and *threo* Me_2Si), IR (liquid film) 2970, 2935, 2874, 1721, 1455, 1247, 1099, 1080, 825, 764 cm^{-1} Anal Calcd for $C_{19}H_{36}O_2Si$. C, 70 29, H, 11 20 Found C, 70 22, H, 11 47

β-Siloxy Aldehyde 27: $[\alpha]_D^{24}$ -2 33° (*c* 1 18, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 9 70 (1H, s, CHO), 3 69 (1H, d, *J* = 8 Hz, CH-OSi), 2.08 (1H, m, CH), 1 12 (3H, s, CH_3), 0 92 (3H, d, *J* = 6.5 Hz, CH_3), 0 83 (9H, s, *t*-Bu), 0 79 (3H, d, *J* = 6 5 Hz, CH_3), 0 02 and 0 04 (6H, s, Me_2Si), IR (liquid film) 2955, 2930, 2855, 1730, 1460, 1385, 1365, 1255, 1110, 1070, 850, 835, 775 cm^{-1}, MS, *m/e* (rel intensity) 243 (17), 227 (100), 213 (74) Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11.36 Found C, 67 22, H, 11 50

β-Siloxy Aldehyde 28: $[\alpha]_D^{24}$ +50 9° (*c* 1 00, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 9 65 (1H, s, CHO), 3 98 (1H, d, *J* = 2 Hz, CH-OSi), 2 29 (1H, m, CH), 1 47-1 87 (4H, m, CH_2CH_2), 1 23 (1H, m, CH), 1 01 (3H, s, CH_3), 0 86 (3H, d, *J* = 6 5 Hz, CH_3), 0 83 (3H, d, *J* = 6 5 Hz, CH_3), 0 81 (9H, s, *t*-Bu), 0 00 and 0 03 (6H, s, Me_2Si), IR (liquid film) 2950, 2930, 2850, 1720, 1450, 1380, 1360, 1250, 1120, 1080, 990, 830, 775 cm^{-1} Anal Calcd for $C_{16}H_{32}O_2Si$ C, 67 53, H, 11 36 Found C, 67 37, H, 11 30

β-Siloxy Aldehyde 29: ^1H NMR ($CDCl_3$) δ 9 53 (1H, s, CHO), 3 65 (1H, d, *J* = 10 Hz, CH-OSi), 3 53 (1H, d, *J* = 10 Hz, CH-OSi), 1 52 (2H, m, $C\underline{H}_2CH_3$), 0 98 (3H, s, CH_3), 0 84 (9H, s, *t*-Bu), 0 80 (3H, t, *J* = 7.6 Hz, $CH_2C\underline{H}_3$), -0 03 (6H, s, Me_2Si), IR (liquid film) 2970, 2935, 2865, 1731, 1457, 1255, 1100, 835, 775 cm^{-1} Anal. Calcd for $C_{12}H_{26}O_2Si$ C, 62 53, H, 11 39 Found C, 62 33, H, 11 68

Determination of the Optical Purity and the Absolute Configuration of Aldehyde 9: To a solution of the aldehyde **9** (59 mg, 0 22 mmol) in MeOH (3 mL) was added $NaBH_4$ (8 mg, 0 2 mmol) at 0 °C The mixture was stirred at 0 °C for 30 min, poured into brine, and extracted with ether The concentrated crude material was purified by column chromatography on silica gel (ether/hexane = 1 2) to furnish (*R*)-3-(*tert*-butyldimethylsiloxy)-2-phenyl-1-propanol (**12**) (53 mg, 90% yield) $[\alpha]_D$ +14 7° (*c* 1 00, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7 15–7 36 (5H, m, Ph), 4 05 (1H, ddd, *J* = 4 5, 7, 9 Hz, CH-O), 3 90 (2H,

d, J = 9 Hz, CH_2-OSi), 3 86 (1H, ddd, J = 4 5, 7, 9 Hz, CH-O), 3 07 (1H, quintet, J = 9 Hz, PhCH), 2 73 (1H, dd, J = 4 5, 7 Hz, OH), 0 87 (9H, s, t-Bu), 0 03 (6H, s, Me_2Si)

This alcohol (53 mg, 0 20 mmol) was dissolved in CH_2Cl_2 (1 5 mL) and triethylamine (32 μL, 0 22 mmol) followed by methanesulfonyl chloride (18 μL, 0 22 mmol) was added at 0 °C The mixture was stirred at 0 °C for 30 min and poured into saturated $NaHCO_3$ The crude product was extracted with CH_2Cl_2, concentrated, and dissolved in EtOH (2 mL) This solution was added at 0 °C to a THF solution (2 mL) of sodium phenylthiolate which was prepared from NaH (50% in oil, 21 mg, 0 6 mmol) and thiophenol (70 mL, 0 68 mmol) The whole mixture was stirred at room temperature for 41 h After usual workup, the crude material was purified by column chromatography on silica gel (ether/hexane = 1 100 to 1 50) to give *tert*-butyldimethylsilyl ether **13** of (*S*)-2-phenyl-3-(phenylthio)propanol (65 mg, 90 % yield) ^{1}H NMR ($CDCl_3$) δ 7 10–7 45 (5H, m, Ph), 3 88 (1H, dd, J = 5, 10 Hz, CH-OSi), 3 76 (1H, dd, J = 6, 10 Hz, CH-OSi), 3 53 (1H, dd, J = 6, 13 Hz, CH-SPh), 3 12 (1H, dd, J = 8, 13 Hz, CH-SPh), 2 99 (1H, m, PhCH), 0 83 (9H, s, t-Bu), -0 03 (6H, s, Me_2Si)

The phenylthio derivative **13** (65 mg, 0 18 mmol) was dissolved in EtOH (3 mL) and hydrogenated with Raney Ni (Aldrich) in water (3 mL) under H_2 at 0°C for 30 min Filtration followed by removal of solvents *in vacuo* left the crude material which was purified by column chromatography on silica gel (ether/hexane = 1 100) to furnish *tert*-butyldimethylsilyl ether of (*S*)-2-phenylpropanol (33 mg, 72% yield) ^{1}H NMR ($CDCl_3$) δ 7 11–7 33 (5H, m, Ph), 3 68 (1H, dd, J = 5 5, 10 Hz, CH-OSi), 3 57 (1H, dd, J = 7, 10 Hz, CH-OSi), 2 88 (1H, quintet, J = 6 Hz, PhCH), 1 27 (3H, d, J = 7 Hz, CH_3), 0 84 (9H, s, t-Bu), -0 05 (6H, s, Me_2Si)

The silyl ether (33 mg, 0 13 mmol) was treated with tetrabutylammonium fluoride (0 2 mL of a 1M THF solution) in THF (3 mL) at room temperature for 2 h Aqueous workup and purification of the residue by column chromatography on silica gel (ether/hexane = 2 3 to 1 1) afforded (*S*)-2-phenylpropanol (9 3 mg, 53% yield) $[\alpha]_D$ -18 6° (*c* 0 84, benzene) Since the optical rotation value of the optically pure (*S*)-2-phenylpropanol is reported to be $[\alpha]_D$ - 19° (*c* 0 83, benzene)[10] , the optical purity of the aldehyde **9** was found to be ~98% ee with the *S* configuration

Determination of the Optical Purity of (*S*)-2. The β-siloxy aldehyde (*S*)-**2** derived from the rearrangement of (2*R*,3*S*)-**1** was converted to the acetal of (-)-2(*R*),4(*R*)-pentanediol with triethyl orthoformate (2 4 equiv) and catalytic *p*-TsOH in benzene at room temperature overnight Its optical purity was established to be 95% ee by capillary GLC analysis (PEG-HT column 0 25 X 25,000 mm) based on separated two peaks t_R = 80 7 and 81 8 min at the column temperature of 120 °C

Stereochemical Assignment of the *threo*-Aldehyde 15. Authentic *erythro*- and *threo*-3-(*tert*-butyldimethylsiloxy)-2-phenylbutanals were prepared in two-step sequence from methyl *erythro*-3-hydroxy-2-phenylbutanoate and its *threo*-isomer, respectively [16]

To a solution of lithium diisopropylamide (2 4 mmol) in THF (10 mL) was added at -78 °C methyl phenylacetate (287 μL, 2 mmol) After 5 min, acetaldehyde (186 μL, 3 mmol) was added at this temperature The mixture was stirred at -78 °C for 30 min and worked up in a usual manner Purification of the crude material by column chromatography on silica gel (ether/hexane = 1 1 to 2 1) afforded methyl *erythro*-3-hydroxy-2-phenylbutanoate (125 mg, 32% yield) and its *threo*-isomer (72 mg, 19% yield)[16] methyl *erythro*-3-hydroxy-2-phenylbutanoate ^{1}H NMR ($CDCl_3$) δ 7 33 (5H, s, Ph), 4 33 (1H, dq, J = 6 2 and 6 8 Hz, CH-O), 3 65 (3H, s, OCH_3), 3 50 (1H, d, J = 6 8 Hz, CH-C=O), 2 34 (1H, d, J = 3 2 Hz, OH), 1 17 (3H, d, J = 6 2 Hz, CH_3), methyl *threo*-3-hydroxy-2-phenylbutanoate ^{1}H NMR ($CDCl_3$) δ 7 27 (5H, m, Ph),

4 32 (1H, dq, J = 6 2 and 9 2 Hz, CH-O), 3 66 (3H, s, OCH_3), 3 48 (1H, d, J = 9 2 Hz, CH-C=O), 2 92 (1H, d, J = 4 4 Hz, OH), 1 01 (3H, d, J = 6 2 Hz, CH_3)

The *erythro*-hydroxy ester (98 mg, 0 5 mmol) was treated with *tert*-butyldimethylsilyl chloride (151 mg, 1 mmol) and imidazole (102 mg, 1 5 mmol) in DMF (5 mL) at room temperature for 1 day Usual workup and purification of the residue by column chromatography (ether/hexane = 1 15 to 1 10) gave methyl *erythro*-3-(*tert*-butyldimethylsiloxy)-2-phenylbutanoate (151 mg, 98% yield) ^{1}H NMR ($CDCl_3$) δ 7 31 (5H, m, Ph), 4 29 (1H, dq, J = 6 2 and 8 2 Hz, CH-OSi), 3 64 (3H, s, OCH_3), 3 48 (1H, d, J = 8 2 Hz, CH-C=O), 1 19 (3H, d, J = 6 2 Hz, CH_3), 0 68 (9H, s, *t*-Bu), -0 12 (6H, s, Me_2Si)

To a solution of the β-siloxy ester (145 mg, 0 47 mmol) in toluene (5 mL) was added a 1M hexane solution of DIBAH (0 47 mL, 0 47 mmol) at -78 °C The mixture was stirred at -78°C for 30 min and worked up with diluted HCl The crude product was extracted with ether and washed with saturated $NaHCO_3$ Purification of the concentrated crude material by column chromatography (ether/hexane = 1 20 as eluant) furnished *erythro*-3-(*tert*-butyldimethylsiloxy)-2-phenylbutanal (111 mg, 85% yield) ^{1}H NMR ($CDCl_3$) δ 9 83 (1H, d, J = 1 6 Hz, CHO), 7 29 (5H, m, Ph), 4 50 (1H, quintet, J = 6 2 Hz, CH-OSi), 3 43 (1H, dd, J = 1 6 and 6 2 Hz, CH-C=O), 1 13 (3H, d, J = 6 2 Hz, CH_3), 0 77 (9H, s, *t*-Bu), -0 04 (6H, s, Me_2Si)

The *threo*-3-(*tert*-butyldimethylsiloxy)-2-phenylbutanal was prepared in a similar manner as described above

Determination of the Optical Purity of 15. The *threo*-aldehyde **15** was converted to the acetal of (-)-2(*R*),4(*R*)-pentanediol or (+)-2(*S*),4(*S*)-pentanediol with triethyl orthoformate (2 4 equiv) and catalytic *p*-TsOH in benzene at room temperature overnight Its optical purity was established to be >98% ee by capillary GLC analysis (PEG-HT column 0 25 X 25,000 mm) based on separated two peaks t_R = 35 7 and 36 5 min at the column temperature of 150 °C

General Procedure for the Rearrangement of Various Simple Epoxides with MABR. To a solution of the MABR (0 05 ~ 2 mmol) in degassed CH_2Cl_2 (5 mL) was added an epoxide (1 mmol) at -78 °C The mixture was stirred under the indicated conditions in Table 2 Then the mixture was worked up either with diluted HCl or with NaF-H_2O according to the stoichiometric or catalytic procedure for the rearrangement of epoxy silyl ethers with MABR Purification of the crude products by column chromatography on silica gel (ether/hexane as eluant) gave carbonyl compounds in the yields shown in Table 2

7-(*tert*-Butyldimethylsiloxy)-2,2,5-trimethylheptanal: ^{1}H NMR ($CDCl_3$) δ 9 42 (1H, s, CHO), 3 59 (2H, m, CH_2-OSi), 1 00 (6H, s, $(CH_3)_2C$), 0 86 (9H, s, *t*-Bu), 0 85 (3H, d, J = 7 Hz, CH_3), 0 02 (6H, s, Me_2Si) Anal Calcd for $C_{16}H_{34}O_2Si$ C, 67 05, H, 11 98 Found C, 66 75, H, 11 86

(1-Vinylcyclododecyl)carboxaldehyde: ^{1}H NMR ($CDCl_3$) δ 9 43 (1H, s, CHO), 5 49-5 70 (1H, m, C=CH), 4 96-5 09 (2H, m, $=CH_2$), 2 19 (2H, d, J = 7 5 Hz, CH), 1 21-1 75 (20H, m, CH_2) Anal Calcd for $C_{15}H_{26}O$ C, 81 02, H, 11 78 Found C, 81 22, H, 11 65

Alkoxy Alcohol 19: ^{1}H NMR ($CDCl_3$) δ 4 83, 5 01 (2H, s, $C=CH_2$), 3 80 (2H, s, $=C-CH_2O$), 3 46 (2H, dq, J = 6 5, 10 0 Hz, $-CH_2O$), 2 04 (2H, t, J = 6 5 Hz, $-CH_2-C=$), 1 92 (1H, t, J = 6 5 Hz, OH), 1 16 (3H, s, O-C-CH_3), IR (liquid film) 3450, 2970, 2940, 2870, 2370, 2330, 1655, 1470, 1380, 1060, 900 cm^{-1} Anal Calcd for $C_{24}H_{48}O_2$ C, 78 19, H, 13 12 Found C, 77 98, H, 13 00

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References and Notes

(1) Reviews on the Lewis acid-mediated rearrangement of epoxides (a) Parker, R E , Isaacs, N S *Chem Rev* **1959**, *59*, 737 (b) Rao, A S , Paknikar, S K , Kirtane, J G *Tetrahedron* **1983**, *39*, 2323 See also Rickborn, B , Gerkin, R M *J Am Chem Soc* **1971**, *93*, 1693, Milstein, D , Buchman, O , Blum, J *Tetrahedron Lett* **1974**, 2257 For the transformation of 2,3-epoxy alcohols and their derivatives, see Bahrens, C H , Sharpless, K B *Aldrichimica Acta* **1983**, *16*, 67

(2) (a) Hill, J G , Sharpless, K B *Org Synth* **1984**, *63*, 66 (b) Gao, Y , Hanson, R M , Klunder, J M , Ko, S. Y , Masamune, H., Sharpless, K B *J Am Chem Soc* **1987**, *109*, 5765

(3) (a) Maruoka, K , Hasegawa, M , Yamamoto, H , Suzuki, K , Shimazaki, M , Tsuchihashi, G *J Am Chem Soc* **1986**, *108*, 3827. See also (b) Suzuki, K , Miyazawa, M , Tsuchihashi, G *Tetrahedron Lett* **1987**, *28*, 3515 (c) Shimazaki, M , Hara, H , Suzuki, K , Tsuchihashi, G *ibid* **1987**, *28*, 5891.

(4) (a) Masamune, S , Choy, W *Aldrich Acta* **1982**, *15*, 47 (b) Masamune, S , Choy, W , Petersen, J S , Sita, L R *Angew Chem Int Ed Engl* **1985**, *24*, 1 (c) Danishefsky, S J *Aldrich Acta* **1986**, *19*, 59

(5) For another type of the epoxy alcohol rearrangement with Ti(O-*i*-Pr)$_4$, see Morgans, D J , Sharpless, K B , Traynor, S G *J Am Chem Soc* **1981**, *103*, 462

(6) (a) Maruoka, K., Itoh, T , Yamamoto, H *J Am Chem Soc* **1985**, *107*, 4573 (b) Maruoka, K , Sakurai, M., Yamamoto, H *Tetrahedron Lett* **1985**, *26*, 3853 (c) Maruoka, K , Nonoshita, K , Yamamoto, H *Tetrahedron Lett* **1987**, *28*, 5723 (d) Nonoshita, K , Maruoka, K , Yamamoto, H *Bull Chem Soc Jpn* **1988**, *61*, 2241 (e) Maruoka, K , Itoh, T , Sakurai, M , Nonoshita, K , Yamamoto, H *J Am Chem Soc* **1988**, *110*, 3588

(7) For other synthetic applications of MABR to the regio- and stereocontrolled Claisen rearrangements, see (a) Maruoka, K., Nonoshita, K , Banno, H , Yamamoto, H *J Am Chem Soc* **1988**, *110*, 7922 (b) Maruoka, K , Banno, H , Nonoshita, K , Yamamoto, H *Tetrahedron Lett* **1989**, *30*, 1265 (c) Nonoshita, K , Banno, H Maruoka, K , Yamamoto, H *J Am Chem Soc* **1990**, *112*, 316 (d) Maruoka, K , Sato, J., Banno, H , Yamamoto, H *Tetrahedron Lett* **1990**, *31*, 377

(8) Preliminary report Maruoka, K , Ooi, T , Yamamoto, H *J Am Chem Soc* **1989**, *111*, 6431

(9) Harada, T , Hayashiya, T , Wada, I , Iwa-ake, N , Oku, A *J Am Chem Soc* **1987**, *109*, 527

(10) Suzuki, K , Kitayama, E , Matsumoto, T , Tsuchihashi, G *Tetrahedron Lett* **1984**, *25*, 828

(11) Martin, V S , Woodard, S S , Kastuki, T , Yamada, Y , Ikeda, M , Sharpless, K B *J Am Chem Soc* **1981**, *103*, 6237

(12) Recent catalytic procedures for the epoxide rearrangement (a) Isomerization of diene monoepoxide with Pd^0 catalyst Suzuki, M , Oda, Y., Noyori, R *J Am Chem Soc.* **1979**, *101*, 1623 (b) 1,3-Diketone synthesis from epoxy ketones with Pd^0 catalyst Suzuki, M , Watanabe, A , Noyori, R *J Am Chem Soc* **1980**, *102*, 2095 (c) Isomerization of diene monoepoxide with Rh^I catalyst Sato, S , Matsuda, I , Izumi, Y *Tetrahedron Lett* **1985**, *26*, 1527 (d) Aldol synthesis from epoxy silyl ethers with Me_3SiOTf See ref 3b

(13) Yamamoto, H , Maruoka, K *J Am Chem Soc* **1981**, *103*, 4186

(14) Maruoka, K , Nagahara, S , Ooi, T , Yamamoto, H *Tetrahedron Lett* **1989**, *30*, 5607

(15) For the *erythro/threo* structural assignments, see Rossiter, B E , Verhoeven, T R , Sharpless, K B *Tetrahedron Lett* **1979**, 4733

(16) Mulzer, J , Lammer, O *Chem Ber* **1986**, *119*, 2178