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Migratory Aptitude of Alkyl Substituents in the MABR-Promoted Epoxide Rearrangement

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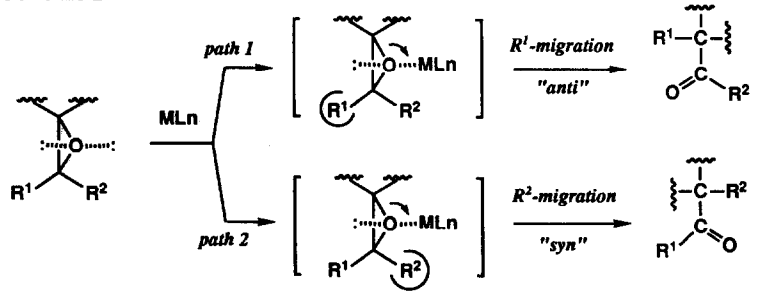
Abstract: The migratory aptitude of the Lewis acid-promoted epoxide rearrangement has been studied with exceptionally bulky, Lewis acidic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR). With α,α-disubstituted epoxides, the organoaluminum-promoted epoxide rearrangement is interpreted for by proceeding with rigorous migration of hydride *syn* to the less hindered site of the epoxide ring, while the facile *anti* migration of the alkyl groups has been observed in tri- and tetrasubstituted epoxides. The selectivity observed in various types of epoxides is found to be far superior to that with other ordinary Lewis acids such as $BF_3{\cdot}OEt_2$ and $SnCl_4$.

Despite the numerous synthetic studies of the Lewis-acid catalyzed rearrangements of epoxides to carbonyl compounds, little is understood of migratory aptitude of alkyl substituents in such rearrangements.[1] Given an unsymmetrical epoxide which is capable of being coordinated with one of the epoxide oxygen lone pairs selectively by a certain Lewis acid, the migratory aptitude of the two alkyl groups, R^1 and R^2 (*i.e.*, path 1 or 2) could be examined on the reaction course of the Lewis acid-promoted epoxide rearrangement as illustrated in Scheme I. This hypothesis in conjunction with our recent observation on the very high discriminatory ability of exceptionally bulky methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) between

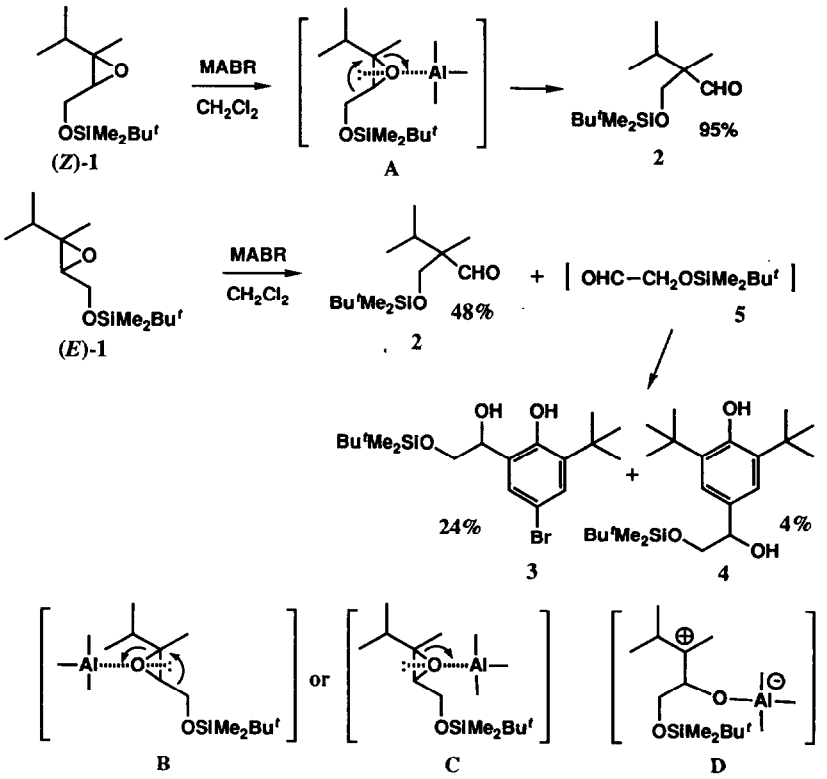
Scheme I



R = Me : MAD
R = Br : MABR

structurally and electronically similar ethers[2] has prompted us to study which of the R^1 or R^2-migration is more favorable or predominant in the MABR-promoted epoxide rearrangement. Disclosed herein are the results on this study using several representative epoxides.

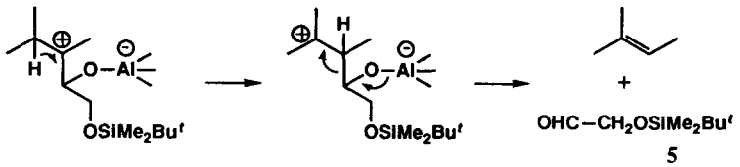
Rearrangement of Trisubstituted Epoxides. We recently reported the selective rearrangement of various trisubstituted epoxides to aldehydes under the influence of exceptionally bulky, Lewis acidic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR).[3] The distinct advantage of MABR over other Lewis acids ($BF_3{\cdot}OEt_2$, $SnCl_4$, $TiCl_4$, etc.) for the epoxide rearrangement could be partly ascribable to its efficient discrimination between the two epoxide lone pair electrons and subsequent smooth migration of alkyl groups *anti* to the MABR, in view of the steric repulsion between the bulky organoaluminum ligand and the migrating alkyl groups. Indeed, Z-isomeric epoxide (*Z*)-**1**, which possesses the bulky isopropyl and siloxymethyl moieties on the same side, was rearranged smoothly by treatment with MABR at low temperature to furnish aldehyde **2** in high yield (95%), indicating the facile migration of siloxymethyl group *anti* to the oxygen lone pair which may be selectively coordinated with the aluminum reagent *via* the intermediary complex **A**. In contrast, rearrangement of isomeric (*E*)-**1** with MABR under similar conditions gave rise to the desired aldehyde **2** (48%) accompanied by **3** (24%) and **4** (4%), probably by way of epoxide-aluminum coordination complexes **B** and **C**, respectively. The phenolic products **3** and **4** were derived by the Friedel-



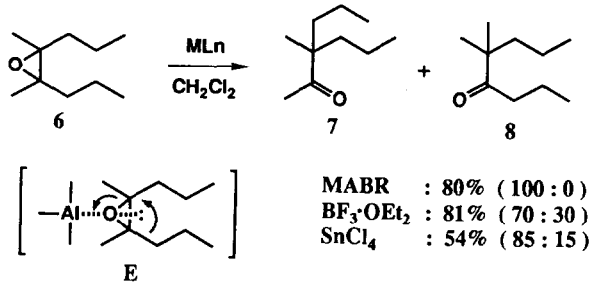
Crafts alkylation of 4-bromo-2,6-di-*tert*-butylphenoxy ligand with intermediary siloxyaldehyde **5**, the formation of which is interpreted as being by the initial epoxide opening of (*E*)-**1** *via* the complex **C**, 1,2-hydride shift and subsequent C-C bond cleavage as shown in Scheme II. Consequently, these results rule out

considerably the possibility of intervention of cationic intermediate **D** in the formation of the rearranged aldehyde **2**.

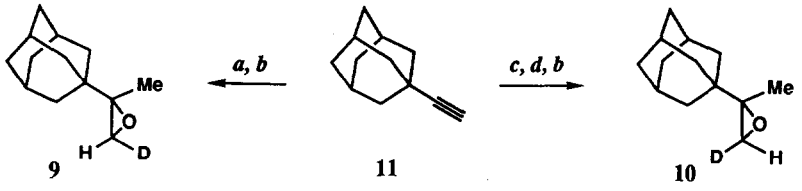
Scheme II



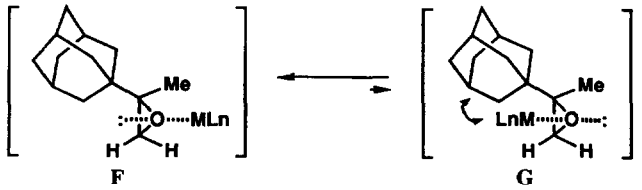
Rearrangement of Tetrasubstituted Epoxides. With the demonstration of the *anti*-selective alkyl migration of trisubstituted epoxides, our attention has been focused on the migration pattern of more-substituted epoxides. Accordingly, tetrasubstituted epoxide **6** was subjected to the MABR-promoted rearrangement giving ketone **7** as a sole isolable product. Hence, this rearrangement takes place with the migration of propyl group *anti* to the less hindered site of the epoxide ring as depicted in **E**. It should be noted that this selectivity is far superior to that with ordinary Lewis acids like $BF_3{\cdot}OEt_2$ and $SnCl_4$.



Rearrangement of α,α-Disubstituted Epoxides. In order to discriminate the migratory hydrogen in the rearrangement of α,α-disubstituted epoxides, we chose deuterium-labelled epoxides **9** and **10** as substrates, which are conveniently prepared from 1-adamantylacetylene (**11**) according to Negishi's



(a) Cp_2ZrCl_2, Me_3Al, CH_2Cl_2; then D_2O; (b) MCPBA; (c) BuLi, D_2O; (d) Cp_2ZrCl_2, Me_3Al, CH_2Cl_2; then H_2O.



procedure.[4] These substrates are quite suitable for our purpose since the lone pair electrons opposite the bulky adamantyl moiety are expected to coordinate selectively with a certain sterically hindered Lewis acid, giving an epoxide-Lewis acid complex **F** preferentially over **G**. Thus, treatment of **9** in CH_2Cl_2 at -78 °C with exceptionally bulky MABR gave a mixture of α-deuterated aldehyde **12** and α-protonated aldehyde **13** in a ratio of 93:7 as judged by 500 MHz ^1H NMR analysis. The isomeric epoxide **10** under similar reaction conditions, on the other hand, led to α-protonated aldehyde **13** almost exclusively (ratio of **12:13** = 5:95). Consequently, in contrast to tri- and tetrasubstituted epoxides, the MABR-promoted rearrangement of α,α-disubstituted epoxides was proven to proceed with rigorous migration of alkyl group R^2 *syn* to the Lewis acid as shown in path 2 of Scheme I. This seems to be a general tendency for various α,α-disubstituted epoxides, as also observed in the rearrangement of deuterium-labelled epoxide **14** with MABR which yielded α-deuterated aldehyde **15** as a major product (ratio of **15:16** = 72:28). Notably, attempted rearrangement of epoxides **9** and **10** with ordinary Lewis acids such as BF_3·OEt_2, $SnCl_4$, $TiCl_4$, and SbF_5 resulted in some or total scrambling between the migratory deuterium and hydrogen as indicated in Table I (entries 2-5).

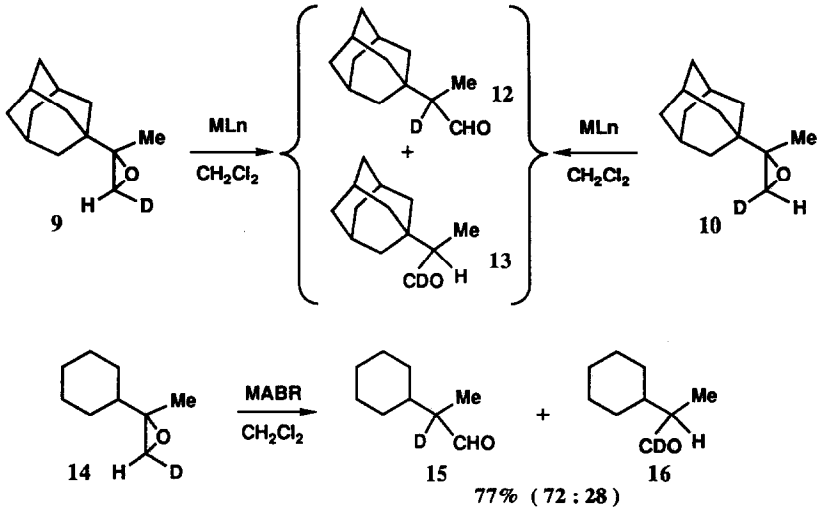
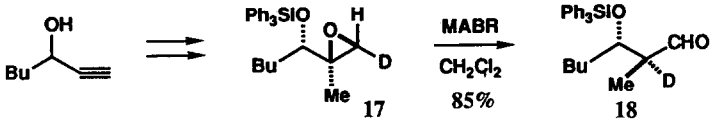


Table I. Lewis Acid-Promoted Rearrangement of Monodeuterated Epoxides **9** and **10** [a]

entry	Lewis acid	% yield from **9** [b] (ratio of **12:13**)[c]	% yield from **10** [b] (ratio of **12:13**)[c]
1	MABR	99 (93 : 7)	100 (5 : 95)
2	BF_3·OEt_2	73 (43 : 57)	73 (14 : 86)
3	$SnCl_4$	98 (26 : 74)	87 (18 : 82)
4	$TiCl_4$	38 (27 : 73)	28 (19 : 81)
5	SbF_5	90 (35 : 65)	85 (16 : 84)

[a] Epoxide rearrangement was effected in CH_2Cl_2 with 2 equiv of Lewis acid at -78 °C for 20~60 min. [b] Isolated yield. [c] The isomeric ratios were determined by 500 MHz ^1H NMR analysis based on two different methyl signals.

The synthetic application of this *syn*-selective rearrangement is illustrated by the stereocontrolled synthesis of α-deuterio-β-triphenylsiloxy aldehyde **18** from monodeuterated *erythro*-epoxy silyl ether **17**,[5] which in turn is readily available from an acetylenic alcohol by (i) Negishi's carbometalation with Cp_2ZrCl_2/Me_3Al,[4] (ii) *erythro*-selective epoxidation with *cat.* $VO(acac)_2/t$-BuOOH,[6] and (iii) silylation with Ph_3SiCl/imidazole.[7] The rearranged β-siloxy aldehyde **18** is a valuable deuterium-labelled synthetic intermediate for further carbon-chain elongation leading to 1,3-dihydroxy functionality, a fundamental structural unit embedded in numerous natural products of acetate and propionate origin.[8] It should be noted that this selective introduction of deuterium cannot be easily attained by ordinary procedures in which the deuterium is introduced to the α-carbon of aldehydes under basic conditions in D_2O or CH_3OD solvent.



In conclusion, the organoaluminum-promoted rearrangement of α,α-disubstituted epoxides proceeds with rigorous migration of hydride *syn* to the less hindered site of the epoxide ring, while the facile *anti* migration of the alkyl groups is observed in tri- and tetrasubstituted epoxides. The origin of the unexpected *syn*-selectivity for the rearrangement of α,α-disubstituted epoxides with MABR remains unclear and awaits further research.

Experimental Section

General. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer. ^1H NMR spectra were measured on a Varian Gemini-200 (200 MHz) and VXR 500 (500 MHz) 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. 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 Department of Agricultural Chemistry, Nagoya University.

In experiments requiring dry solvents, tetrahydrofuran (THF) was freshly distilled from sodium metal using benzophenone ketyl as indicator. Hexane was dried over sodium metal. Methylene chloride and DMF were stored over 4A molecular sieves. Trimethylaluminum was obtained from Toso-Akzo Chem. Co. Ltd., Japan. Other simple chemicals were purchased and used as such.

Epoxy Silyl Ether (*E*)-1. The title compound was prepared by the $VO(acac)_2$-catalyzed epoxidation[6] of (*E*)-3,4-dimethyl-2-penten-1-ol with *t*-BuOOH in CH_2Cl_2 followed by treatment of the resulting epoxy alcohol with *tert*-butyldimethylsilyl chloride and imidazole in DMF[7]: ^1H NMR ($CDCl_3$) δ 3.73 (2H, d, J = 5 Hz, CH_2-OSi), 2.86 (1H, t, J = 5 Hz, CH-O), 1.44 (1H, septet, J = 6.5 Hz, C-CH-C), 1.15 (3H, s, CH_3C-O), 0.92 and 1.00 (6H, d, J = 6.5 Hz, $(CH_3)_2C$), 0.90 (9H, s, $SiC(CH_3)_3$), 0.08 (3H, s, $SiCH_3$), 0.07 (3H, s, $SiCH_3$); IR (liquid film) 2963, 2943, 2894, 2873, 1460, 1253, 1118, 1093, 842, 780 cm^{-1}. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.87; H, 11.55. Found: C, 63.82; H, 11.62.

Epoxy Silyl Ether (*Z*)-1. To a solution of chlorodiphenylphosphine (305 μL, 1.7 mmol) in THF (5 mL) was added lithium metal (80 mg) at room temperature. The mixture was stirred at this temperature for 2 h to give a dark orange solution. This was transferred by cannula to another flask to remove excess lithium. Then the epoxy silyl ether (*E*)-**1** (264 mg, 1.1 mmol) in THF (1 mL) was added dropwise and the mixture was stirred at room temperature for 1.5 h. After addition of iodomethane (236 μL, 3.8 mmol), the mixture was stirred for additional 3 h. This was poured into water and extracted with hexane. The combined organic layers were dried over $MgSO_4$ and concentrated. Purification of the residual oil by column chromatography gave (*Z*)-1-(*tert*-butyldimethylsiloxy)-3,4-dimethyl-2-pentene (218 mg, 0.96 mmol) in 87% yield. Epoxidation of this olefin with MCPBA in CH_2Cl_2 at 0 °C gave rise to the title compound (*Z*)-**1** (232 mg) in 99% yield: ^1H NMR ($CDCl_3$) δ 3.75 (2H, d, J = 5.5 Hz, CH_2-OSi), 2.90 (1H, t, J = 5.5 Hz, CH-O), 1.53 (1H, septet, J = 7 Hz, C-CH-C), 1.19 (3H, s, CH_3C-O), 0.96 and 1.03 (6H, d, J = 7 Hz, $(CH_3)_2C$), 0.90 (9H, s, $SiC(CH_3)_3$), 0.08 (3H, s, $SiCH_3$), 0.07 (3H, s, $SiCH_3$); IR (liquid film) 2970, 2940, 2910, 2880, 1471, 1258, 1140, 1091, 845, 780 cm^{-1}. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.87; H, 11.55. Found: C, 63.93; H, 11.55.

Epoxide 6. This epoxide was prepared by the following sequences: (i) carbometalation of 4-octyne with Me_3Al/Cp_2ZrCl_2 followed by I_2 quenching; (ii) methylation of (*E*)-4-iodo-5-methyl-4-octene with $MeMgBr/NiCl_2$(dppp);[10] (iii) epoxidation of the resulting (*Z*)-4,5-dimethyl-4-octene[11] with MCPBA: ^1H NMR ($CDCl_3$) δ 1.31-1.67 (8H, m, $2(CH_2)_2$), 1.28 (6H, s, $2CH_3$-C-O), 0.85-0.99 (6H, m, $2CH_3$-C); IR (liquid film) 2965, 2940, 2889, 1465, 1380, 1191, 1160, 1125, 849 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.71; H, 12.97.

Preparation of Deuterio Epoxide 9. To a suspension of Cp_2ZrCl_2 (292 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added a 2 M hexane solution of Me_3Al (1 mL, 2 mmol) under argon at room temperature.[4] All Cp_2ZrCl_2 dissolved within 10-15 min to give a lemon-yellow solution. Then adamantylacetylene[9] (**11**) (160 mg, 1 mmol) was added at this temperature. After being stirred for 24 h, the reaction mixture was quenched with 0.3 mL of D_2O (99.9 atom %) followed by dilution with ether. The organic layer was separated by filtration and the filter cake was thoroughly extracted with ether. The combined organic layers were dried over $MgSO_4$ and the concentrated crude material was purified by column chromatography on silica gel (hexane as eluant) to furnish a carbometalation product (150 mg) in 85% yield: ^1H NMR ($CDCl_3$) δ 4.65 (1H, s, CH=C), 1.91-2.05 (3H, br s, 3CH), 1.70 (3H, s, CH_3), 1.52-1.90 (12H, m, $3CH_2$ and 6CH).

This carbometalation product (150 mg, 0.85 mmol) was oxidized with MCPBA (216 mg, 1 mmol) in CH_2Cl_2 (5 mL) at 0 °C for 1 h. The mixture was poured into saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and the concentrated crude material was purified by column chromatography on silica gel (ether/hexane = 1:15) to furnish the title epoxide **9** as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.81 (1H, s, CH-O), 1.90-2.02 (3H, br s, 3CH), 1.37-1.76 (12H, m, $3CH_2$ and 6CH), 1.22 (3H, s, CH_3); IR (liquid film) 2920, 2870, 1452, 1389, 1089, 895, 842, 820 cm^{-1}. Anal. Calcd for $C_{13}H_{19}DO$: C, 80.77; H, 10.36. Found: C, 80.81; H, 10.45.

Preparation of Deuterio Epoxide 10. 2-Dueterio-1-adamantylacetylene was prepared by treatment of adamantylacetylene[9] (**11**) with butyllithium followed by addition of D_2O (99.9% atom %). The isotopic purity of the compounds was estimated to be >99% by ^1H NMR analysis. Its carbometalation with Me_3Al/Cp_2ZrCl_2, product isolation, and subsequent oxidation with MCPBA were carried out as described above[4] to give the title epoxide **2**: ^1H NMR ($CDCl_3$) δ 2.34 (1H, s, CH-O), 1.90-2.01 (3H, br s, 3CH), 1.45-1.77 (12H, m), 1.22 (3H, s, CH_3); IR (liquid film) 2912, 2852, 1450, 1391, 1072, 852, 768 cm^{-1}. Anal. Calcd for $C_{13}H_{19}DO$: C, 80.77; H, 10.36. Found: C, 81.18; H, 10.62.

Deuterio Epoxide 14: ^1H NMR ($CDCl_3$) δ 2.58 (1H, s, CH-O), 1.57-1.90 (5H, m, CH_2 and CH), 0.97-1.35 (6H, m, $3CH_2$), 1.22 (3H, s, CH_3); IR (liquid film) 2980, 2941, 2870, 2250, 1450, 1407, 1382, 924, 882, 850, 831 cm^{-1}. Anal. Calcd for $C_9H_{15}DO$: C, 76.64; H, 11.42. Found: C, 76.34; H, 11.68.

Deuterio Epoxide 17. 1-Heptyn-3-ol was converted to (*E*)-1-deuterio-2-methyl-1-hepten-3-ol by the carbometalation with Me_3Al/Cp_2ZrCl_2 followed by D_2O quenching. Subsequent $VO(acac)_2$-catalyzed epoxidation[6] of this allylic alcohol with *t*-BuOOH in CH_2Cl_2 followed by the silylation of the resulting epoxy alcohol with triphenylsilyl chloride and imidazole in DMF[7] gave the title epoxide **17**: ^1H NMR ($CDCl_3$) δ 7.32–7.72 (15H, m, $SiPh_3$), 3.35(1H, t, J = 6 Hz, CH-OSi), 2.18 (1H, s, CH-O), 1.54-1.74 (2H, m, CH_2C-OSi), 1.35 (3H, s, CH_3C-O), 1.04-1.44 (4H, m, $(CH_2)_2$), 0.78 (3H, t, J = 6.5 Hz, CH_3C-C); IR (liquid film) 3069, 2957, 2934, 1429, 1117, 1090, 741, 712, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{29}DO_2Si$: C, 77.37; H, 7.24. Found: C, 77.29; H, 7.38.

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.

General Method for the Epoxide Rearrangement with MABR. To a solution of MABR (1 mmol) in CH_2Cl_2 (5 mL) was added an epoxide (0.5 mmol) at -78 °C. The mixture was stirred at -78 ~ -20 °C for several hours. The solution was poured into diluted HCl and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluant) gave the rearranged carbonyl products.

Physical properties and analytical data of the rearranged products are as follows.

β-Siloxy Aldehyde 2: ^{1}H NMR ($CDCl_3$) δ 9.59 (1H, s, CHO), 3.75 (1H, d, *J* = 10 Hz, CH-OSi), 3.53 (1H, d, *J* = 10 Hz, CH-OSi), 2.13 (1H, septet, *J* = 7 Hz, C-CH-C), 0.90 (3H, s, CH_3), 0.88 (3H, d, *J* = 6.5 Hz, CH_3), 0.83 (9H, s, $SiC(CH_3)_3$), 0.79 (3H, d, *J* = 6.5 Hz, CH_3), 0.02 (6H, s, $Si(CH_3)_2$); IR (liquid film) 2959, 2932, 2859, 1727, 1471, 1258, 1109, 1090, 837, 777 cm^{-1}. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.87; H, 11.55. Found: C, 63.81; H, 11.82.

Reaction of Epoxide (*E*)-1 with MABR. To a solution of MABR (1 mmol) in CH_2Cl_2 (5 mL) was added (*E*)-**1** (0.5 mmol) at -78°C. The mixture was stirred at -78 °C for 1 h and at -40 °C for 40 min. The solution was 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 = 1:40 to 1:8 as eluants) gave the rearranged aldehyde **2** in 48% yield along with the Friedel-Crafts alkylation products **3** (24%) and **4** (4%).

Friedel-Crafts Product 3: ^{1}H NMR ($CDCl_3$) δ 8.66 (1H, s, Ar-OH), 7.29 (1H, d, *J* = 2.6 Hz, Ar-H), 6.98 (1H, d, *J* = 2.6 Hz, Ar-H), 4.80 (1H, dd, *J* = 5.0, 7.5 Hz, Ar-CH-O), 3.69-3.84 (2H, m, CH_2-OSi), 3.45 (1H, s, OH), 1.37 (9H, s, Ar-$C(CH_3)_3$), 0.92 (9H, s, $SiC(CH_3)_3$), 0.10 (6H, s, $Si(CH_3)_2$); IR (liquid film) 3300, 2955, 2930, 2861, 1472, 1422, 1256, 1227, 1100, 837, 781 cm^{-1}.

This product was further converted to its acetate with Ac_2O-Py in CH_2Cl_2: ^{1}H NMR ($CDCl_3$) δ 7.95 (1H, s, Ar-OH), 7.32 (1H, d, *J* = 2.4 Hz, Ar-H), 7.19 (1H, d, *J* = 2.4 Hz, Ar-H), 5.86 (1H, dd, *J* = 4.7, 6.0 Hz, Ar-CH-O), 4.04 (1H, dd, *J* = 4.7, 10 Hz, CH-OSi), 3.87 (1H, dd, *J* = 6, 10 Hz, CH-OSi), 2.12 (3H, s, CH_3-C=O), 1.37 (9H, s, Ar-$C(CH_3)_3$), 0.89 (9H, s, $SiC(CH_3)_3$), 0.08 (3H, s, $SiCH_3$), 0.06 (3H, s, $SiCH_3$); IR (liquid film) 3260, 2955, 2930, 2861, 1752, 1709, 1420, 1372, 1258, 1227, 1117, 837, 781 cm^{-1}.

Friedel-Crafts Product 4: ^{1}H NMR ($CDCl_3$) δ 8.44 (1H, s, Ar-OH), 7.25 (1H, d, *J* = 2.4 Hz, Ar-H), 6.83 (1H, d, *J* = 2.4 Hz, Ar-H), 4.83 (1H, dd, *J* = 4, 8 Hz, Ar-CH-O), 3.70-3.89 (2H, m, CH_2-OSi), 3.47 (1H, s, OH), 1.41 (9H, s, Ar-$C(CH_3)_3$), 1.27 (9H, s, Ar-$C(CH_3)_3$), 0.93 (9H, s, $SiC(CH_3)_3$), 0.10 (6H, s, $Si(CH_3)_2$); IR (liquid film) 3347, 2955, 2932, 2861, 1482, 1362, 1256, 1231, 1100, 839, 779 cm^{-1}.

This product was further converted to its acetate with Ac_2O-Py in CH_2Cl_2: ^{1}H NMR ($CDCl_3$) δ 7.75 (1H, s, Ar-OH), 7.30 (1H, d, *J* = 2.4 Hz, Ar-H), 7.03 (1H, d, *J* = 2.4 Hz, Ar-H), 5.90 (1H, t, *J* = 5 Hz, Ar-CH-O), 4.08 (1H, dd, *J* = 5.0, 10.6 Hz, CH-OSi), 3.94 (1H, dd, *J* = 5.2, 10.6 Hz, CH-OSi), 2.12 (3H, s, CH_3-C=O), 1.41 (9H, s, Ar-$C(CH_3)_3$), 1.28 (9H, s, Ar-$C(CH_3)_3$), 0.89 (9H, s, $SiC(CH_3)_3$), 0.07 (3H, s, $SiCH_3$), 0.05 (3H, s, $SiCH_3$); IR (liquid film) 3318, 2959, 2930, 2858, 1742, 1713, 1480, 1464, 1391, 1364, 1258, 1231, 1121, 839 cm^{-1}.

3-Methyl-3-propyl-2-hexanone (7): ^{1}H NMR ($CDCl_3$) δ 2.07 (3H, s, CH_3-C=O), 0.90-1.62 (8H, m, $4CH_2$), 1.04 (3H, s, CH_3), 0.87 (6H, t, *J* = 7 Hz, $2CH_3$); IR (liquid film) 2964, 2944, 2884, 1704, 1463, 1382, 1352, 1136 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.80; H, 12.96.

5,5-Dimethyl-4-octanone (8): ^{1}H NMR ($CDCl_3$) δ 2.40 (2H, t, *J* = 7.5 Hz, CH_2-C=O), 1.42-1.62 (4H, m, $2CH_2$), 1.10-1.28 (2H, m, CH_2), 1.08 (6H, s, $2CH_3$), 0.89 (3H, t, *J* = 8 Hz, CH_3), 0.87 (3H, t, *J* = 8 Hz, CH_3); IR (liquid film) 2971, 2951, 2891, 1706, 1462, 1386, 1365, 1121 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.81; H, 12.73.

α-Deuterio Aldehyde 12: ^{1}H NMR ($CDCl_3$) δ 9.82 (1H, s, CHO), 1.90-2.05 (3H, br s, 3CH), 1.40-1.79 (12H, m, 6CH and $3CH_2$), 0.98 (3H, s, CH_3); IR (liquid film) 2915, 2860, 1720, 1448 cm^{-1}. Anal. Calcd for $C_{13}H_{19}DO$: C, 80.77; H, 10.36. Found: C, 80.71; H, 10.44.

Deuterio Aldehyde 13: ^{1}H NMR ($CDCl_3$) δ 1.90-2.05 (3H, br s, 3CH), 1.47-1.80 (12H, m, 6CH and $3CH_2$), 1.00 (3H, d, J = 7 Hz, CH_3); IR (liquid film) 2915, 2860, 1711, 1450 cm^{-1}. Anal. Calcd for $C_{13}H_{19}DO$: C, 80.77; H, 10.36. Found: C, 80.62; H, 10.32.

The isomeric ratios of **12** and **13** in Table 1 were determined by 500 MHz ^{1}H NMR analysis based on the integration of the two different methyl peaks at δ 0.98 and δ 1.00.

Deuterio Aldehydes 15 and 16: ^{1}H NMR ($CDCl_3$) δ 9.64 (s, CHO), 2.20 (quintet, J = 6 Hz, CH-C=O), 1.52-1.82 (m, CH and CH_2), 0.98-1.43 (m, CH_2), 1.03 (d, J = 6 Hz, CH_3), 1.02 (s, CH_3); IR (liquid film) 2950, 2880, 1720, 1455 cm^{-1}. Anal. Calcd for $C_9H_{15}DO$: C, 76.54; H, 11.42. Found: C, 76.66; H, 11.54.

The isomeric ratios of **15** and **16** were determined by 500 MHz ^{1}H NMR analysis based on the integration of the aldehydic peak at δ 9.64 and the α-methine proton of carbonyl at δ 2.20.

α-Deuterio-β-siloxy aldehyde 18:[5] ^{1}H NMR ($CDCl_3$) δ 9.73 (1H, s, CHO), 7.34–7.68 (15H, m, $SiPh_3$), 4.10 (1H, t, J = 5.6 Hz, CH-OSi), 1.39-1.72 (2H, m, CH_2-C-OSi), 0.99-1.31 (4H, m, $2CH_2$), 1.05 (3H, s, CH_3C-C=O), 0.76 (3H, t, J = 7.2 Hz, CH_3); IR (liquid film) 3069, 2957, 2934, 1727, 1485, 1429, 1117, 1026, 929, 741 cm^{-1}. Anal. Calcd for $C_{26}H_{29}DO_2Si$: C, 77.37; H, 7.24. Found: C, 77.24; H, 7.41.

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