On the Mechanism of Organoaluminum-Promoted Claisen Rearrangement of Allylic Vinyl Ethers

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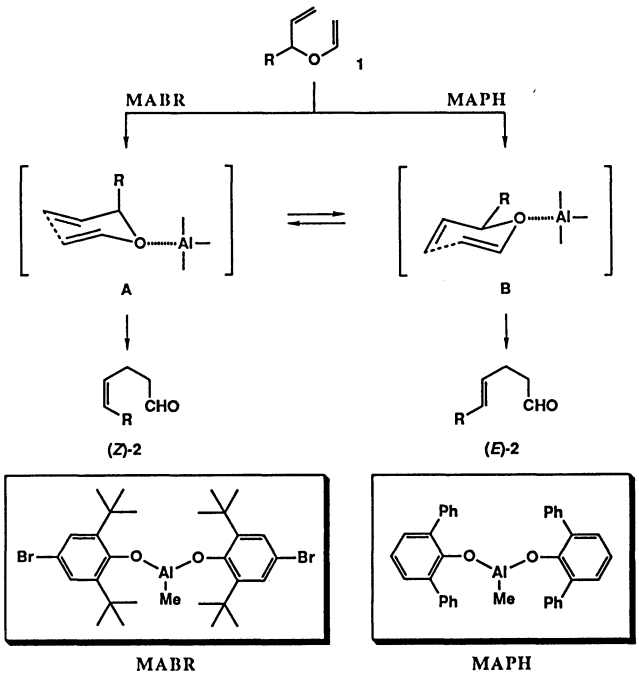
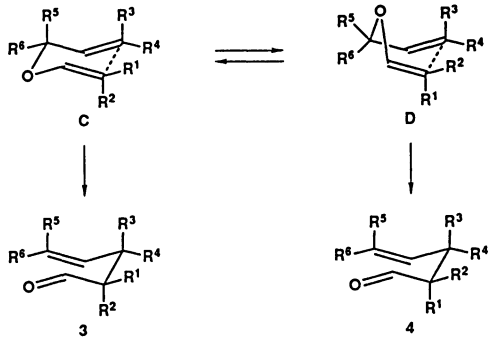
The organoaluminum-promoted Claisen rearrangement of allylic vinyl ethers has been mechanistically studied by two sets of experiments and the observed *Z* and *E* selectivity is best accounted for by two possible chair-like structures with R substituents axial and equatorial, respectively.

The organoaluminum-promoted Claisen rearrangement of allylic vinyl ethers serves as a powerful method for carbon–carbon bond formation and has proved to be highly stereoselective in many cases.[1,2] It was proposed that the observed stereoselectivity is accounted for by the two possible chair-like transition-state structures **A** and **B** coordinated to the Lewis acidic organoaluminum reagents as depicted in Scheme 1. Although some mechanistic rationales have been put forward for these reactions in our laboratory,[1b] detailed mechanistic studies have not yet appeared. In this paper, we wish to report two sets of experiments that provide firm information on the mechanism of the organoaluminum-promoted Claisen rearrangement of allylic vinyl ethers **1**.

When both termini of an allylic vinyl ether **1** are unsymmetrically substituted, Claisen rearrangement creates two chiral centers, which give rise to a pair of *erythro* and *threo* diastereomers.[3] Accordingly, structures of **C** and **D** show that the geometry of the double

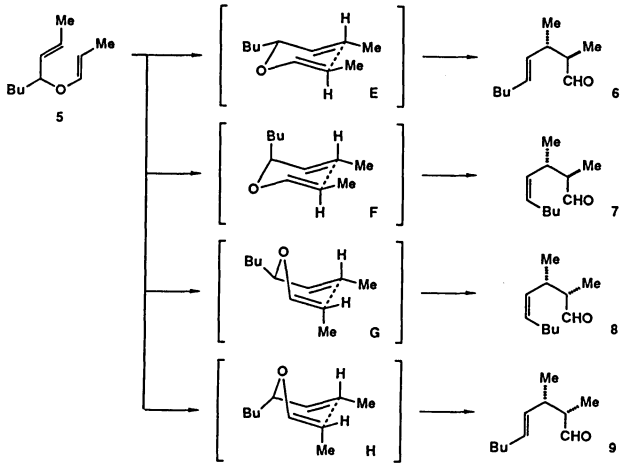


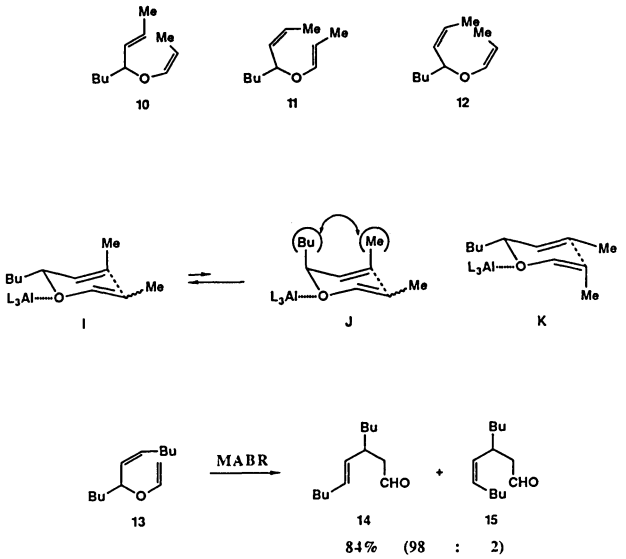
Scheme 1.



bonds in the starting material and the transition-state structures determine the *erythro*/*threo* as well as *E*/*Z* ratios in the Claisen rearrangement products **3** and **4**. For example, (*E,E*)-isomer **5** possesses four possible transition-state structures **E**—**H** giving (*E*)-*erythro*, (*Z*)-*erythro*, (*Z*)-*threo*, and (*E*)-*threo* products, **6**, **7**, **8**, and **9**, respectively.

The starting (*E,E*)-1-butyl-2-butenyl 1-propenyl ether (**5**) was prepared by transetherification of (*E*)-2-octen-4-ol with ethyl 1-propenyl ether in the presence of $Hg(OAc)_2$.[4] Treatment of the (*E,E*)-isomer **5** in CH_2Cl_2 with methylaluminum bis(4-bromo-2,6-di-*t*-butylphenoxide) (MABR) at −78 °C under conditions similar to those described previously[1b] gave a mixture of Claisen rearrangement products **6**, **7**, **8**, and **9** in 98% yield. The ratio of **6**, **7**, **8**, and **9** was determined to be 11.8 : 80.5 : 4.7 : 3.0 by capillary GLC analysis by comparison with the authentic samples, which were prepared by the thermal Claisen rearrangement of isomeric 1-butyl-2-butenyl 1-propenyl ethers **5**, **10**, **11**, and **12**. In marked contrast, however, with methylaluminum bis(2,6-diphenylphenoxide) (MAPH) in toluene at −20 °C, the product ratio of **6**, **7**, **8**, and **9** was found to be 80.6 : 11.9 : ca. 0 : 7.5. Consequently, the observed selectivities with MAPH and MABR are best accounted for by the two possible chair-like transition-state structures **E** and **F**, respectively, and the participation of the boat-like transition-state structures, **G** and **H** is rigorously excluded from the organoaluminum-promoted Claisen rearrangement.[5] The chair-like structure **F** with the *n*-Bu group axial, when complexed with the exceptionally bulky MABR, is favored over **E** owing to





the 1,2 steric interaction between *n*-Bu and the organoaluminum ligands, leading to the preferential formation of the (*Z*)-*erythro* product **7**.

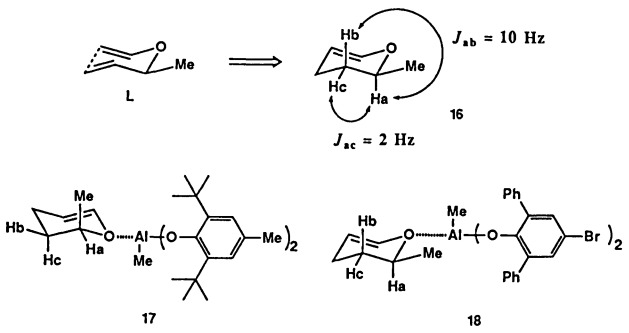
Several examples are listed in Table 1. Other (*Z,E*)-isomer **10**, (*E,Z*)-isomer **11**, and (*Z,Z*)-isomer **12** gave (*E*)-isomers as major products even with MABR. These results strongly support the intervention of the chair-like transition-state structures **I**—**K**. In substrates **11** and **12**, structure **I** with the *n*-Bu group equatorial is favored over **J** in view of the 1,3 steric interaction between *n*-Bu and axial Me. This favorable chair-like transition-state structure **I** is further supported by the following experiment. Treatment of (*Z*)-1-butyl-2-heptenyl vinyl ether (**13**) in CH_2Cl_2 with MABR at −78 °C under similar conditions gave a mixture of Claisen rearrangement products **14** and **15** in 84% yield. The isomeric ratio was determined to be 98 : 2 by capillary GLC analysis by comparison with an authentic sample, which was prepared by the thermal Claisen rearrangement of **13**. In substrate **10** the structure **K** with the *n*-Bu group equatorial is favored over that with *n*-Bu axial, where the steric interaction between axial Me and organoaluminum ligands seems to be more significant.

We also carried out NMR studies to elucidate the transition-state structures of the organoaluminum-promoted Claisen rearrangement. We chose 2-methyl-3,4-dihydro-2*H*-pyran (**16**)[6] as a model compound for a chair-like transition-state structure **L** of allylic vinyl ether substrate and executed a conformational analysis of 2-methyl-3,4-dihydro-2*H*-pyran/organoaluminum complexes by low-temperature ^1H NMR spectroscopy.[7] The ^1H NMR measurement of 2-methyl-3,4-dihydro-2*H*-pyran (**16**) in $CDCl_3$ at room temperature followed by decoupling of the signal of the methyl group on the pyran reveals that the methine proton Ha on the pyran at δ=3.93 was a double doublet and the coupling constants J_{ab} and J_{ac} were 10 and 2 Hz, respectively. This result shows a chair-like structure **16** with the methyl

Table 1. Claisen Rearrangement of Substituted Allylic 1-Propenyl Ethers[a]

Entry	Substrate	Lewis acid	Conditions	Yield[b]/%	
			°C, min	(Ratio, **6**:**7**:**8**:**9**)	
1	**5**	MABR	−78, 15	98	(11.8 : 80.5 : 4.7 : 3.0)
2		MAPH	−78, 60; −20, 30	99	(80.6 : 11.9 : ca. 0 : 7.5)
3		Heat[c]	174, 30	89	(87.1 : 5.4 : ca. 0 : 7.5)
4	**10**	MABR	−78, 15	99	(2.4 : ca. 0 : 2.6 : 95.0)
5		MAPH	−20, 60; 0, 15	89	(3.5 : ca. 0 : ca. 0 : 96.5)
6		Heat[c]	174, 30	95	(4.3 : ca. 0 : 5.3 : 90.4)
7	**11**	MABR	−78, 15	98	(4.7 : ca. 0 : ca. 0 : 95.3)
8		MAPH	−78, 30; −20, 30	88	(4.0 : ca. 0 : ca. 0 : 96.0)
9		Heat[c]	174, 30	88	(6.6 : ca. 0 : ca. 0 : 93.4)
10	**12**	MABR	−78, 15	89	(97.2 : ca. 0 : ca. 0 : 2.8)
11		MAPH	−20, 30; 0, 15	97	(95.4 : ca. 0 : ca. 0 : 4.6)
12		Heat[c]	174, 30	89	(93.5 : ca. 0 : ca. 0 : 6.5)

a) Unless otherwise noted, the Claisen rearrangement of allylic 1-propenyl ethers with 2 equiv of modified organoaluminum reagents was carried out in CH_2Cl_2 or toluene. b) Isolated yield. c) In decane.



group equatorial. Next, the ^{1}H NMR measurement of a 1 : 1 complex of 2-methyl-3,4-dihydro-2*H*-pyran and methylaluminum bis(2,6-di-*t*-butyl-4-methylphenoxide) (MAD), which possesses a structure similar to MABR, in $CDCl_3$ at −50 °C followed by decoupling of the signal of the methyl group on the pyran, shows that the original signal of the methine proton Ha on the pyran at δ=3.93 shifted downfield to δ=4.34 and the methine proton Ha was a singlet. This means that the coupling constants J_{ab} and J_{ac} were almost zero. Hence, the chair-like structure **17** with the methyl group axial is favored when complexed with the exceptionally bulky MAD. Similarly, the ^{1}H NMR measurement of a 1 : 1 complex of the pyran and methylaluminum bis(4-bromo-2,6-diphenylphenoxide), which possesses a structure similar to MAPH, in $CDCl_3$ at −50 °C followed by decoupling of the signal of the methyl group on the pyran, revealed that the methine proton Ha at δ=3.93 shifted upfield to δ=3.87 with a broad doublet. The coupling constant was about 6.5 Hz. This result shows that the chair-like structure **18** with the methyl group equatorial is favored over the chair-like structure with the methyl group axial, although the coupling constant J_{ab} in **18** was smaller than J_{ab}=10 Hz in the free **16**.

In summary, the observed selectivity is best accounted for by two possible chair-like transition-state structures in the organoaluminum-promoted Claisen rearrangement of allylic vinyl ethers. The chair-like structure **A** with the R substituent axial, when complexed with the exceptionally bulky MABR, is favored over **B** in view of the severe 1,2 steric interaction between R and the aluminum reagent in **B**, leading to the preferential formation of (*Z*)-alkene. This tendency is also supported by ^{1}H NMR analysis using 2-methyl-3,4-dihydro-2*H*-pyran (**16**) as a model compound for a chair-like transition-state structure **L** of allylic vinyl ether substrate.

Experimental

Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on Varian Gemini-200 and VXR 500 spectrometers. 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 (0.25×25000 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 Art. 9385. Microanalyses were accomplished at the Faculty of Agriculture, Nagoya University.

In experiments requiring dry solvents, ether and tetrahydrofuran (THF), are freshly distilled from sodium metal using benzophenone ketyl as indicator. Hexane and toluene are dried over sodium metal. Dichloromethane is stored over 4A molecular sieves. Pyridine is stored over potassium hydroxide pellets. Me_3Al is obtained from Toso-Akzo Chem. Co., Ltd., Japan. Other chemicals are purchased and used as such.

Preparation of Allylic Alcohols. (*E*)-2-Octen-4-ol was prepared by reaction of crotonaldehyde with butyllithium. (*Z*)-2-Octen-4-ol and (*Z*)-6-undecen-5-ol were prepared by lithiation of propyne and 1-hexyne, respectively, with *n*-BuLi followed by addition of valeraldehyde, then partial hydrogenation of alkyne with P-2 Ni and ethylenediamine.[8]

Preparation of (*E*)-1-Butyl-2-butenyl (*E*)-1-Propenyl Ether (5) and (*E*)-1-Butyl-2-butenyl (*Z*)-1-Propenyl Ether (10).[4] A mixture of (*E*)-2-octen-4-ol (3.85 g, 30 mmol), mercury(II) acetate (4.78 g, 15 mmol), and ethyl 1-propenyl ether (6.64 mL, 60 mmol) was stirred at room temperature for 2 d. The mixture was then poured into 5% potassium hydroxide solution (30 mL) and extracted with hexane. After drying over Na_2SO_4, the hexane extracts were concentrated. The residual crude products were purified by column chromatography (hexane to ether–hexane=1 : 20 as eluant) three times to give (*E*)-1-butyl-2-butenyl (*Z*)-1-propenyl ether (**10**) (2.11 g, 42% yield) and (*E*)-1-butyl-2-butenyl (*E*)-1-propenyl ether (**5**) (349 mg, 7% yield).

(*E*)-1-Butyl-2-butenyl (*E*)-1-Propenyl Ether (5): R_f=0.24 (hexane); IR (neat) 3038, 2959, 2934, 2860, 1674, 1657, 1456, 1379, 1271, 1171, 1129, 967, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.10 (1H, d, *J*=12.4 Hz, O–CH=C), 5.65 (1H, dq, *J*=15.4, 6.4 Hz, O–C–C=CH), 5.37 (1H, dd, *J*=15.4, 6.6 Hz, O–C–CH=C), 4.88 (1H, dq, *J*=12.4, 6.4 Hz, O–C=CH), 3.93 (1H, q, *J*=6.6 Hz, O–CH–C=C), 1.73 (3H, d, *J*=6.4 Hz, O–C–C=C–CH_3), 1.54 (3H, d, *J*=6.4 Hz, O–C=C–CH_3), 1.14—1.81 (6H, m, $CH_2CH_2CH_2$), 0.90 (3H, t, *J*=6.8 Hz, CH_2CH_3). Found: C, 78.95; H, 12.25%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

(*E*)-1-Butyl-2-butenyl (*Z*)-1-Propenyl Ether (10): R_f=0.33 (hexane); IR (neat) 3044, 2959, 2936, 2863, 1667, 1453, 1404, 1379, 1343, 1256, 1117, 1069, 967, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.99 (1H, d, *J*=6.5 Hz, O–CH=C), 5.64 (1H, dq, *J*=15.4, 6.4 Hz, O–C–C=CH), 5.38 (1H, dd, *J*=15.4, 6.8 Hz,O–C–CH=C), 4.35 (1H, quintet, *J*=6.5 Hz, O–C=CH), 3.89 (1H, q, *J*=6.8 Hz, O–CH–C=C), 1.70 (3H, d, *J*=6.5 Hz, O–C–C=C–CH_3), 1.58 (3H, d, *J*=6.4 Hz, O–C=C–CH_3), 1.18—1.79 (6H, m, $CH_2CH_2CH_2$), 0.89 (3H, br t, CH_2CH_3). Found: C, 79.00; H, 12.33%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

Preparation of (*Z*)-1-Butyl-2-butenyl (*E*)-1-Propenyl Ether (11) and (*Z*)-1-Butyl-2-butenyl (*Z*)-1-Propenyl Ether (12). (*Z*)-1-butyl-2-butenyl (*E*)-1-propenyl ether (**11**) and (*Z*)-1-butyl-2-butenyl (*Z*)-1-propenyl ether (**12**) were prepared in a similar manner as described in the preparation of (*E*)-1-butyl-2-butenyl (*E*)-1-propenyl ether (**5**) and (*E*)-1-butyl-2-butenyl (*Z*)-1-propenyl ether (**10**).

(*Z*)-1-Butyl-2-butenyl (*E*)-1-Propenyl Ether (11): 6% yield. R_f=0.25 (hexane); IR (neat) 3021, 2959, 2934, 2863, 1676,

1657, 1458, 1379, 1316, 1271, 1171, 1125, 968, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.09 (1H, d, J=12.6 Hz, O-CH=C), 5.65 (1H, dq, J=11.0, 7.0 Hz, O-C-C=CH), 5.32 (1H, dd, J=11.0, 6.8 Hz, O-C-CH=C), 4.86 (1H, dq, J=12.6, 6.8 Hz, O-C=CH), 4.39 (1H, q, J=6.8 Hz, O-CH-C=C), 1.69 (3H, d, J=6.8 Hz, O-C-C=C-CH_3), 1.53 (3H, d, J=7.0 Hz, O-C=C-CH_3), 1.12—1.84 (6H, m, $CH_2CH_2CH_2$), 0.90 (3H, t, J=6.8 Hz, CH_2CH_3). Found: C, 78.79; H, 12.28%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

(*Z*)-1-Butyl-2-butenyl (*Z*)-1-Propenyl Ether (12): 24% yield. R_f=0.34 (hexane); IR (neat) 3044, 3019, 2959, 2934, 2862, 1669, 1453, 1402, 1379, 1323, 1258, 1117, 1076, 967, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.97 (1H, d, J=6.4 Hz, O-CH=C), 5.65 (1H, dq, J=11.0, 6.8 Hz, O-C-C=CH), 5.33 (1H, dd, J=11.0, 7.4 Hz, O-C-CH=C), 4.29—4.42 (2H, m, CH-O-C=CH), 1.66 (3H, d, J=6.8 Hz, O-C-C=C-CH_3), 1.57 (3H, d, J=6.8 Hz, O-C=C-CH_3), 1.10—1.81 (6H, m, $CH_2CH_2CH_2$), 0.89 (3H, br t, CH_2CH_3). Found: C, 78.65; H, 12.33%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

Preparation of MABR. To a solution of 4-bromo-2,6-di-*t*-butylphenol (2 equiv) in degassed CH_2Cl_2 was added at room temperature a 2 mol cm^{-3} 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. MAPH was prepared in situ from Me_3Al and 2,6-diphenylphenol in degassed toluene at room temperature for 1 h.

General Method for the Claisen Rearrangement of Allylic 1-Propenyl Ethers with MABR. To a solution of MABR (1 mmol) in CH_2Cl_2 (5 mL) was added allylic 1-propenyl ether (0.5 mmol) at −78 °C. The solution was stirred at −78 °C for 15 min. The reaction mixture was poured into 10% HCl and extracted with CH_2Cl_2. The combined extracts were washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Evaporation of solvent and purification of the residue by column chromatography (ether-hexane as eluant) gave the olefinic aldehyde. The *erythro*/*threo* and *E*/*Z* ratio of the olefinic aldehydes was determined by capillary GLC analysis by comparison with authentic samples, which were prepared by the thermal Claisen rearrangement of allylic 1-propenyl ethers **5**, **10**, **11**, and **12** in decane at 174 °C. The *erythro*/*threo* ratio was also determined by capillary GLC analysis by comparison with the saturated alcohols obtained by the hydrogenation of the rearrangement products **6**—**9** with Raney Ni in EtOH. These results are shown in Table 1. The GLC retention times of the isomers at the indicated column temperature are as follows. t_R((*Z*)-*threo* isomer **9**)=35.7 min, t_R((*Z*)-*erythro* isomer **7**)=37.6 min, t_R((*E*)-*threo* isomer **8**)=38.7 min, and t_R((*E*)-*erythro* isomer **6**)=40.8 min at 60 °C. 2,3-Dimethyl-1-nonanol: t_R(*threo* isomer)=9.7 min and t_R(*erythro* isomer)=10.0 min at 130 °C.

General Method for the Claisen Rearrangement of Allylic 1-Propenyl Ethers with MAPH. To a solution of MAPH (1 mmol) in toluene (5 mL) was added allylic 1-propenyl ether (0.5 mmol) at −78 °C. The mixture was stirred at −20—0 °C for 15—30 min. This was poured into 10% HCl, extracted with ether, washed with sat. $NaHCO_3$, and dried over Na_2SO_4. Evaporation of solvent and purification of the residue by column chromatography (ether-hexane as eluant) gave the olefinic aldehyde. The *erythro*/*threo* and *E*/*Z* ratio of the products was determined in a similar manner as described above, and the results are shown in Table 1.

(*E*)-*erythro*-2,3-Dimethyl-4-nonenal (6): IR (neat) 2963, 2930, 2874, 2701, 1727, 1456, 1379, 972 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.68 (1H, d, J=2.0 Hz, CHO), 5.49 (1H, dt, J=15.4, 6.2 Hz, C=CH-Bu), 5.36 (1H, dd, J=15.4, 6.8 Hz, H-C=C-Bu), 2.55 (1H, sextet, J=6.8 Hz, C=C-CH), 2.33 (1H, double quintet, J=6.8, 2.0 Hz, H-C-C=O), 2.02 (2H, br q, C=C-CH_2), 1.19—1.42 (4H, m, C=C-C-CH_2CH_2), 1.05 (3H, d, J=6.8 Hz, CH_3), 1.02 (3H, d, J=6.8 Hz, CH_3), 0.91 (3H, br t, CH_2CH_3). Found: C, 79.04; H, 12.28%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

(*Z*)-*erythro*-2,3-Dimethyl-4-nonenal (7): IR (neat) 2963, 2930, 2874, 2703, 1728, 1456, 1397, 1377, 972, 914, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.64 (1H, d, J=2.2 Hz, CHO), 5.40 (1H, dt, J=10.6, 6.8 Hz, C=CH-Bu), 5.24 (1H, dd, J=10.6, 9.6 Hz, H-C=C-Bu), 2.80 (1H, double quintet, J=9.6, 6.8 Hz, C=C-CH), 2.25 (1H, double quintet, J=6.8, 2.2 Hz, H-C-C=O), 1.92—2.11 (2H, m, C=C-CH_2), 1.17—1.43 (4H, m, C=C-C-CH_2CH_2), 1.06 (3H, d, J=6.8 Hz, CH_3), 1.00 (3H, d, J=6.8 Hz, CH_3), 0.84—0.94 (3H, m, CH_2CH_3). Found: C, 78.84; H, 12.30%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

(*E*)-*threo*-2,3-Dimethyl-4-nonenal (9): IR (neat) 2961, 2930, 2874, 2701, 1728, 1456, 1379, 972 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.64 (1H, d, J=2.4 Hz, CHO), 5.46 (1H, dt, J=15.4, 6.6 Hz, C=CH-Bu), 5.25 (1H, dd, J=15.4, 7.0 Hz, H-C=C-Bu), 2.55 (1H, sextet, J=7.0 Hz, C=C-CH), 2.26 (1H, double quintet, J=7.0, 2.4 Hz, H-C-C=O), 1.99 (2H, br q, C=C-CH_2), 1.16—1.42 (4H, m, C=C-C-CH_2CH_2), 1.06 (3H, d, J=7.0 Hz, CH_3), 1.02 (3H, d, J=7.0 Hz, CH_3), 0.89 (3H, br t, CH_2CH_3). Found: C, 78.07; H, 12.22%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

Preparation of (*E*)-1-Butyl-2-heptenyl Vinyl Ether (13). (*E*)-1-butyl-2-heptenyl vinyl ether (**13**) was prepared in 70% yield in a similar manner as described previously.[1b] IR (neat) 2959, 2932, 2874, 2862, 1634, 1609, 1468, 1320, 1196, 1183, 1125, 1044, 824, 751 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.32 (1H, dd, J=14, 6.6 Hz, C=CH-O), 5.56 (1H, dt, J=11.2, 7.2 Hz, C=CH-Bu), 5.29 (1H, dd, J=11.2, 8.8 Hz, H-C=C-Bu), 4.48 (1H, dt, J=8.8, 7.2 Hz, C=C-CH-O), 4.26 (1H, dd, J=14, 1.4 Hz, cis H-C=C-O), 3.97 (1H, dd, J=6.6, 1.4 Hz, trans H-C=C-O), 1.93—2.21 (2H, m, C=C-CH_2), 1.11—1.83 (10H, m, CH_2CH_2 and $CH_2CH_2CH_2$), 0.82—0.99 (6H, m, CH_3). Found: C, 79.64; H, 12.48%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

Rearrangement of (*E*)-1-Butyl-2-heptenyl Vinyl Ether (13) with MABR. The rearrangement was carried out in a similar manner as described in the general method for the Claisen rearrangement of allylic 1-propenyl ethers. The isomeric ratio of the olefinic aldehydes was prepared by the thermal Claisen rearrangement of **13** in decane at 174 °C. The GLC retention times of the isomers at the indicated column temperature are as follows. t_R((*Z*)-isomer **15**)=17.1 min and t_R((*E*)-isomer **14**)=19.6 min at 100 °C.

(*E*)-3-Butyl-4-nonenal (14): IR (neat) 2959, 2928, 2874, 2859, 2714, 1728, 1466, 1379, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.70 (1H, t, J=2.4 Hz, CHO), 5.45 (1H, dt, J=15.4, 6.6 Hz, C=CH-Bu), 5.21 (1H, dd, J=15.4, 8.0 Hz, H-C=C-Bu), 2.41—2.64 (1H, m, C=C-CH), 2.33—2.39 (2H, m, H-C-C=O), 1.99 (2H, br q, C=C-CH_2), 1.12—2.45 (10H, m, CH_2CH_2 and $CH_2CH_2CH_2$) 0.88 (6H, t, J=6.4 Hz, CH_3). Found: C, 80.02; H, 12.66%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

Preparation of 2-Methyl-3,4-dihydro-2*H*-pyran (16).[6] 2-Methyl-3,4-dihydro-2*H*-pyran (**16**) was prepared by reduction of acrylaldehyde dimer with $NaBH_4$ in MeOH followed by

tosylation with *p*-toluenesulfonyl chloride and pyridine, then reduction with $LiAlH_4$ in ether: ^1H NMR ($CDCl_3$) δ=6.36 (1H, dt, J=6.5, 2.0 Hz, O-CH=C), 4.64—4.67 (1H, m, O-C=CH), 3.90—3.96 (1H, m, CH-Me), 2.04—2.12 (1H, m), 1.93—1.99 (1H, m), 1.81—1.86 (1H, m), 1.50—1.61 (1H, m), 1.27 (3H, d, J=6.5 Hz, CH_3). After decoupling of the signal of the methyl group on the pyran **16**: ^1H NMR ($CDCl_3$) δ=3.93 (1H, dd, J=10, 2 Hz, CH-Me).

Preparation of MAD. To a solution of 2,6-di-*t*-butyl-4-methylphenol (6.61 g, 30 mmol) in degassed hexane (20 mL) was added a 2 mol cm^{-3} hexane solution of Me_3Al (7.5 mL, 15 mmol) at room temperature. The white precipitate appeared immediately. After 1 h, this mixture was heated until the precipitate redissolved in hexane. The resulting solution was stood for 3 h, yielding colorless crystals which were filtered in an argon box: ^1H NMR ($CDCl_3$) δ=7.04 (4H, s, C_6H_2), 2.28 (6H, s, CH_3), 1.53 (36H, s, $C(CH_3)_3$), −0.35 (3H, s, Al-CH_3).

Preparation of Methylaluminum Bis(4-bromo-2,6-diphenylphenoxide). To a solution of 4-bromo-2,6-diphenylphenol in degassed CH_2Cl_2 was added a 2 mol cm^{-3} hexane solution of Me_3Al at room temperature. After 1 h, the solvent was evaporated to dryness. Attempted recrystallization from toluene was unsuccessful.

^1H NMR Measurement of a Complex 17 of 2-Methyl-3,4-dihydro-2*H*-pyran and MAD. A 1 : 1 mixture of 2-methyl-3,4-dihydro-2*H*-pyran (**16**) and MAD in $CDCl_3$ was measured at −50 °C followed by decoupling of the signal of the methyl group on the pyran: ^1H NMR ($CDCl_3$) δ=4.34 (1H, s, CH-Me).

^1H NMR Measurement of a Complex 18 of 2-Methyl-3,4-dihydro-2*H*-pyran and Methylaluminum Bis(4-bromo-2,6-diphenylphenoxide). A 1 : 1 mixture of 2-methyl-3,4-dihydro-2*H*-pyran (**16**) and methylaluminum bis(4-bromo-2,6-diphenylphenoxide) in $CDCl_3$ was measured at −50 °C followed by decoupling of the signal of the methyl group on the pyran: ^1H NMR ($CDCl_3$) δ=3.87 (1H, d, J=6.5 Hz, CH-Me).

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