Organoaluminum-Promoted Claisen Rearrangement of Allyl Vinyl Ethers

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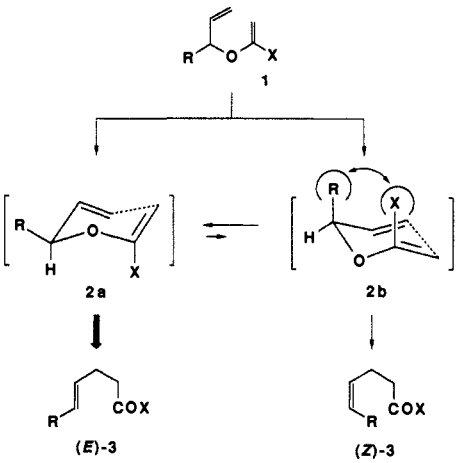
Abstract: Unprecedented stereochemical control has been achieved in the Claisen rearrangement of allyl vinyl ethers of type **4** with certain bulky organoaluminum reagents. Thus, methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (reagent A) can be utilized for obtaining the (*Z*) isomer, (*Z*)-**6**, whereas the (*E*) isomer, (*E*)-**6** was produced with methylaluminum bis(2,6-diphenylphenoxide) (reagent B). This organoaluminum-promoted Claisen rearrangement proceeds under very mild conditions with very good *E* and *Z* selectivities. On the basis of the Claisen rearrangement of optically active substrate **7** with reagent A, the *Z* selectivity would be interpreted by the intervention of the chairlike transition-state conformation with the isobutyl substituent axial. The present organoaluminum-promoted Claisen rearrangement has been successfully applied to the synthesis of (4*E*,7*Z*)-4,7-tridecadienyl acetate (**15**), a component of the sex pheromone of potato tuberworm moth, in stereoselective fashion. Furthermore, the Claisen rearrangement of bisallyl vinyl ether **16** with reagent A or B has been found to involve the more substituted allylic system to furnish dienal **18** preferentially, not obtainable in the ordinary thermal rearrangement. This chemistry has been further extended to the ionic rearrangement of dienyl vinyl ether **28** by using reagent A in a polar solvent where the previously unknown, remote transfer of the vinyloxy moiety by [3,5]-sigmatropic rearrangement via ionic intermediate **29** has been observed.

The Claisen rearrangement and its variants (Carroll, the ortho ester, Eschenmoser, and Ireland rearrangements)[1] provide an excellent stereoselective route to γ,δ-unsaturated carbonyl compounds (aldehydes, ketones, esters, amides, and acids) from allylic alcohols and offer a crucial step in the stereo- and regiochemically defined synthesis of a wide variety of natural products.[2] The reactions involve a [3,3]-sigmatropic rearrangement and take place by a concerted mechanism through a cyclic six-membered chairlike transition state.[3] The principle value of these rearrangements in organic synthesis stems from the fact that they are highly stereoselective, particularly when X ≠ H in allyl vinyl ether **1**, leading almost exclusively to the *E* configuration of the newly created double bond. Examination of the two chairlike transition-state conformations as depicted in Scheme I reveals why the *E* product (*E*)-**3** invariably predominates. Conformation **2a**, with the R substituent equatorial, leads to the (*E*)-olefinic aldehyde (*E*)-**3**, whereas the less likely conformation **2b**, with the R axial, leads to the (*Z*)-olefinic aldehyde (*Z*)-**3**. In fact, the strong preference for *E* products has been observed for Claisen as well as Carroll, the ortho ester, Eschenmoser, and Ireland rearrangements and is clearly a general attribute of the Claisen family. In simple Claisen rearrangement of **1** (X = H), the *E*/*Z* ratio in the product is approximately 90:10,[4] but when X is larger than H, as in the Eschenmoser (X = NMe_2), ortho ester (X = OEt), and Ireland (X = $OSiR_3$) rearrangements, the *E*/*Z* ratio can be greater than 99:1 due to the increased 1,3-diaxial interactions in the transition state **2b**, which dramatically decrease its participation.[5] Consequently, it is difficult to obtain the *Z* selectivity

Scheme I



by using conventional methodologies. In this context, we have been interested for some time in the development of organoaluminum-promoted Claisen rearrangement to alter the transition-state structure of the rearrangement, thereby producing the (*Z*) product (*Z*)-**6** as shown in Scheme II. This possibility is now beginning to emerge with the use of exceptionally bulky organoaluminum reagents.[6,7] Furthermore, excellent *E* selectivity has been achieved by appropriately modifying the organoaluminum ligands (Scheme II).[8]

(1) Reviews: (a) Rhosds, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1. (b) Bennett, G. B. *Synthesis* **1977**, 589. (c) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. (d) Bartlett, P. *Tetrahedron* **1980**, *36*, 2. (e) Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3B, p 503. (f) Carruthers, W. *Some Modern Methods of Organic Synthesis*, 3rd ed.; Cambridge University Press: Cambridge, 1986; p 167. (g) Blechert, S. *Synthesis* **1989**, 71.

(2) (a) Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 1155. (b) Danishefsky, S.; Tsuzuki, K. *Ibid.* **1980**, *102*, 6891. (c) Ireland, R. E.; Wuts, P. G. M.; Ernst, B. *Ibid.* **1981**, *103*, 3205. (d) Martinez, G. R.; Grieco, P. A.; Williams, E.; Kanai, K.; Srinivasan, C. V. *Ibid.* **1982**, *104*, 1436. (e) Bartlett, P. A.; Barstow, J. F. *J. Org. Chem.* **1982**, *47*, 3933. (f) Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *Ibid.* **1982**, *47*, 3941. (g) Ireland, R. E.; Daub, J. P.; Mandel, G. S.; Mandel, N. S. *Ibid.* **1983**, *48*, 1312. (h) Ireland, R. E.; Courtney, L.; Fitzsimmons, B. J. *Ibid.* **1983**, *48*, 5186. (i) Kallmerten, J.; Gould, T. J. *Ibid.* **1986**, *51*, 1155. (j) Kallmerten, J.; Balestra, M. *Ibid.* **1986**, *51*, 2857. (k) Barrish, J. C.; Lee, H. L.; Baggiolini, E. G.; Uskokovic, M. R. *Ibid.* **1987**, *52*, 1375.

(3) Vance, R. L.; Rondan, N. G.; Houk, K. N.; Jensen, F.; Borden, W. T.; Komornicki, A.; Wimmer, E. *J. Am. Chem. Soc.* **1988**, *110*, 2314.

(4) (a) Brannock, K. C. *J. Am. Chem. Soc.* **1959**, *81*, 3379. (b) Burgstahler, A. W. *Ibid.* **1960**, *82*, 4681.

(5) (a) Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1969**, *95*, 553. (b) Faulkner, D. J.; Petersen, M. R. *Tetrahedron Lett.* **1969**, 3243. (c) Katzenellenbogen, J. A.; Christy, K. J. *J. Org. Chem.* **1974**, *39*, 3315. (d) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976**, *41*, 986. (e) Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* **1943**, *65*, 1992. (f) Hill, R. K.; Synerholm, M. E. *J. Org. Chem.* **1968**, *33*, 925. (g) Wakabayashi, N.; Waters, R. M.; Church, J. P. *Tetrahedron Lett.* **1969**, 3253. (h) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.

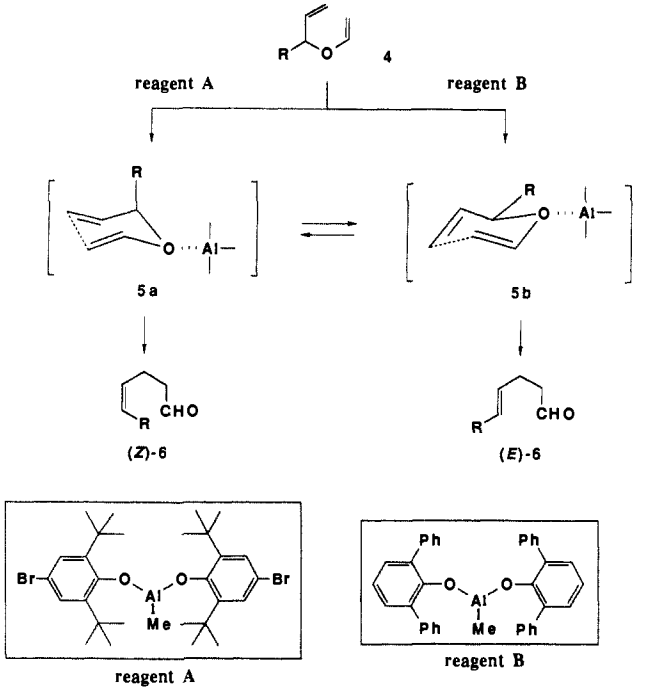
(6) The Lewis acid catalyzed Claisen rearrangements of simple allyl vinyl ethers have appeared recently. (a) Nonstereoselective rearrangement of vinyl ethers of secondary alcohols with organoaluminum reagents: Takai, K.; Mori, I.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 3985. Takai, K.; Mori, I.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 446. (b) Pd-catalyzed rearrangement of vinyl ethers of primary alcohols: van der Baan, J. L.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 6267.

(7) The *Z* selective [2,3] Wittig rearrangement of zirconium enolates of alkenyloxyacetic acid esters: Uchikawa, M.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 4581.

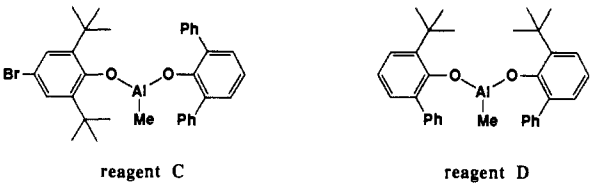
(8) A preliminary report of this work has appeared: Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 7922.

0002-7863/90/1512-316$02.50/0

Scheme II

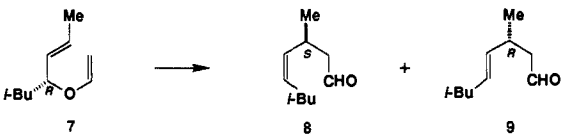


When allyl vinyl ether **4** (R = *i*-Bu) was treated with methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[9] in CH_2Cl_2 at −78 °C, the rearrangement proceeded quite reluctantly to furnish 7-methyl-4-octenal (**6**) (R = *i*-Bu) in only 43% yield. The *E*/*Z* ratio of **6** (R = *i*-Bu) was determined to be 19:81 by capillary GLC after conversion of the aldehyde to the corresponding alcohol and then to the trimethylsilyl ether. Apparently, the Lewis acidity of MAD, which is effective for the stereoselective activation of carbonyl moieties,[9] is not strong enough for activation of the ether substrate **4**. Accordingly, the more acidic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (reagent A) has been newly prepared and successfully applied to the rearrangement of **4** (R = *i*-Bu), resulting in clean generation of **6** (R = *i*-Bu) in 64% yield in the *E*/*Z* ratio of 7:93. Clearly, the less likely conformation **5a** (R = *i*-Bu), when complexed with the exceptionally bulky organoaluminum reagent, is favored over **5b** because of the severe 1,2 steric interaction between R and the aluminum reagent in **5b**, leading to the preferential formation of (*Z*)-alkene (*Z*)-**6** (Scheme II). In fact, when the bulkiness of the aluminum reagent is decreased from reagent A to dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide, the *E*/*Z* selectivity in the rearrangement of the substrate **4** (R = *i*-Bu) is changed dramatically from 7:93 to 71:29, suggesting that the population of the transition state shifts from **5a** to **5b** by decreasing the steric size of aluminum ligands. Surprisingly, treatment of **4** (R = *i*-Bu) in toluene with methylaluminum bis(2,6-diphenylphenoxide) (reagent B) at −20 °C gave rise to the *E* isomer (*E*)-**6** (R = *i*-Bu) almost exclusively (*E*/*Z* = 97:3) in 85% yield. To gain information on the exceedingly high *E* selectivity with the reagent B, the rearrangement of **4** (R = *i*-Bu) was carried out in CH_2Cl_2 at −78 °C under the influence of organoaluminum reagents C and D. The observed *E*/*Z* ratios of **6** with reagents C and D were 28:72 and 15:85, respectively, indicating the strong effect of the sterically hindered *tert*-butyl moiety on the phenoxy ligands for obtaining *Z* selectivity. Although the origin of the high *E* selectivity with reagent B remains unclear from these experiments, a series of experimental results seems to imply the importance of the electronic factor of the 2,6-diphenylphenoxy ligand as well as its steric factor.

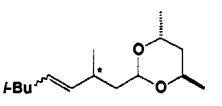


The generality of the present stereocontrolled Claisen rearrangement is indicated in Table I. Several characteristic features of the reaction have been noted: (1) In general, reagent A can be utilized to obtain the *Z* isomer, while the *E* isomer can be produced with reagent B. (2) In comparison to the conventional thermal rearrangement that requires high temperature, the organoaluminum-promoted Claisen rearrangement proceeds under very mild conditions, particularly at strikingly low temperature with very good *E* and *Z* selectivities. (3) The observed *E* and *Z* selectivities appear to increase by lowering the reaction temperature. Reaction of the substrate **4** (R = *i*-Bu) with reagent A or B at 0 °C results in the *E*/*Z* ratio of 17:83 or 83:17, respectively. (4) The *p*-bromo substituent in reagent A is indispensable for rate acceleration of the rearrangement. (5) The rearrangement using reagent A is best carried out in CH_2Cl_2. For example, rearrangement of (*E*)-1-butyl-2-butenyl vinyl ether with reagent A in toluene, $CHCl_3$, 1,2-dichloroethane, and CH_2Cl_2 gives rise to 3-methyl-4-nonenal in an *E*/*Z* ratio of 33:67, 26:74, 24:76, and 16:84, respectively (cf. entries 8 and 9). Similarly, the *E* selectivity has been lowered with reagent B in CH_2Cl_2 in lieu of toluene (the *E*/*Z* ratio of **6** (R = *i*-Bu) is 94:6 in CH_2Cl_2 and 97:3 in toluene). (6) 2-Butyl-1-methyl-2-propenyl vinyl ether gives the *E* isomer as a major product even with reagent A (entry 11). (7) The conjugated (*Z*)-enyne units, which are often present in biologically active natural product,[10] can be readily available by this approach (entry 19). (8) In the case of allyl vinyl ether **4** (R = cyclohexyl) possessing a secondary alkyl moiety, both the chemical yield and the selectivity are lowered under the standard conditions using the reagent A (entry 16).

The stereochemical aspect in the rearrangement of the optically active substrate **7** (78% ee)[11] has been examined in order to elucidate the transition state in the organoaluminum-promoted Claisen rearrangement. Thus, individual treatment of **7** with



reagent A : 74% (84 : 16)
reagent B : 90% (2 : 98)



reagents A and B under the standard conditions as described above gave the (*S*)-(*Z*)-aldehyde **8** and the (*R*)-(*E*)-aldehyde **9**, respectively as major products. The absolute configurations of the Claisen products were determined by correlation with optically active citronellal.[12] This was accomplished by catalytic hydrogenation of the Claisen products **8** and **9** with 5% Pd/C in THF under H_2 to furnish (3*R*)-3,7-dimethyloctanal ($[\alpha]_D$ +5.7° (*c* 0.97,

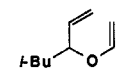
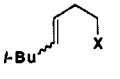
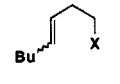
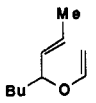
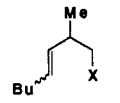
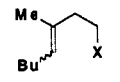
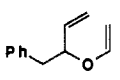
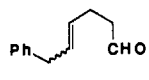
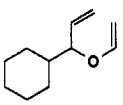
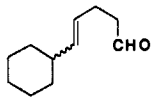
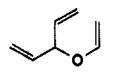
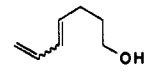
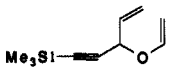
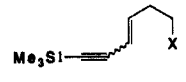
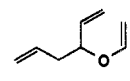
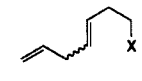
(9) For a stereoselective activation of carbonyl moieties with MAD, see: (a) Maruoka, K.; Itoh, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 4573. (b) Maruoka, K.; Sakurai, M.; Yamamoto, H. *Tetrahedron Lett.* **1985**, *26*, 3853. (c) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588. See also: (d) Maruoka, K.; Araki, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 2650. (e) Maruoka, K.; Araki, Y.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3101.

(10) (a) Witkop, B. *Experientia* **1971**, *27*, 1121. (b) Tokuyama, T.; Uenoyama, K.; Brown, G.; Daly, J. W.; Witkop, B. *Helv. Chim. Acta* **1974**, *57*, 2597. (c) Guerreno, A.; Camps, F.; Coll, J.; Riba, M.; Einhorn, J.; Descoins, Ch.; Lallemand, J. Y. *Tetrahedron Lett.* **1981**, *22*, 2013.

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

(12) The optically active citronellal was kindly provided by the Takasago Co., Ltd.

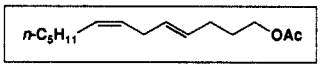
Table I. Organoaluminum-Promoted Claisen Rearrangement

entry	reagent[a]	product[b]	yield,[c] %	ratio[d,e] (E/Z)
				
1	MAD	X = CHO	43	19:81
2	A	X = CHO	64	7:93
3	B	X = CH_2OH	85	97:3 (92:8)
4	E	X = CH_2OH	55	87:13
				
5	MAD	X = CHO	37	15:85
6	A	X = CHO	41	9:91
7	B	X = CH_2OH	86	97:3
				
8	A	X = CHO	72	16:84
9	A[f]	X = CHO	70	12:88
10	B	X = CH_2OH	94	99:1 (92:8)
				
11	A	X = CHO	58	61:39
12	B	X = CH_2OH	94	95:5 (83:17)
				
13	A		12	40:60
14	B		95	92:8
15	B[g]		78	99:1
				
16	A		41	60:40
				
17	A		97	24:76
18	B		91	90:10
				
19	A	X = CHO	94	3:97
20	B	X = CH_2OH	82	69:31
				
21	A	X = CHO	40	7:93
22	B	X = CH_2OH	97	95:5
23	B[g]	X = CH_2OH	84	97:3 (93:7)

[a] Reagent E: Diisobutylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide. For structures of reagents A, B, and MAD, see text. [b] When aluminum reagent B was utilized, olefinic aldehydes were generally reduced to the corresponding alcohols with $NaBH_4$ in view of the easy product separation from 2,6-diphenylphenol. [c] Isolated yield by column chromatography. [d] Determined by GLC after conversion to the corresponding trimethylsilyl ethers. For details, see the Experimental Section. [e] The E/Z ratios in parentheses refer to those in the thermal rearrangement (250 °C). [f] At −95 °C. [g] At −78 °C.

$CHCl_3$)) and its (3*S*) isomer ($[\alpha]_D$ −8.4° (*c* 0.99, $CHCl_3$)), respectively. The authentic, optically pure (3*R*)-3,7-dimethyloctanal ($[\alpha]_D$ +13.6° (*c* 1.05, $CHCl_3$)) and its (3*S*) isomer ($[\alpha]_D$ −13.0° (*c* 1.00, $CHCl_3$)) were prepared by the catalytic hydrogenation of (*R*)- and (*S*)-citronellal, respectively. Since the Pd/C catalyst may induce partial racemization of the allylic C-3 chirality in the hydrogenation of **8** and **9** as erroneously described in the preliminary report,[8] the optical purities of the Claisen products, **8** and **9**, were rigorously established by capillary GLC analysis after conversion to the acetals **10** of (2*R*,4*R*)-2,4-pentanediol. Thus, rearrangement of **7** with reagent A gave rise to **8** and **9** in 78% ee and 64% ee, respectively (100% ee and 82% ee based on the optically pure **7**), while **7** was transformed by reagent B to **9** almost exclusively in 76% ee (98% ee based on the optically pure **7**). These results clearly indicate the rigorous conservation of chirality in the main reaction pathway of the organoaluminum-promoted Claisen rearrangement. Some loss of the optical purity (82% chiral transmission) in the conversion of **7** to **9** with reagent A would be ascribed to the participation of the ionic mechanism to some extent. Consequently, the observed selectivities are best accounted for by the two possible chairlike transition-state conformations **5a** and **5b** coordinated to the Lewis acidic aluminum reagent as depicted in Scheme II. The possibility of the boatlike transition-state conformation with the R substituent equatorial, which leads to (*Z*)-alkene, may not be excluded. However, according to the ab initio quantum mechanical calculations, the intervention of the boatlike transition structure seems to be unlikely because of the high energy compared to that of the chairlike transition structure.[3]

The synthetic utility of the present method in natural product synthesis is illustrated by a simple route to (4*E*,7*Z*)-4,7-tridecadienyl acetate (**15**), a component of the sex pheromone of potato



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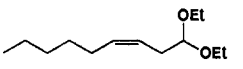

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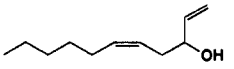

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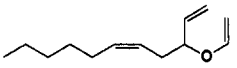

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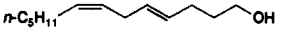


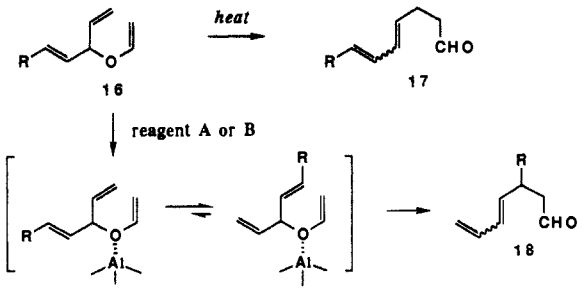
14

tuberworm moth (*Phthorimaea operculella*).[13] The requisite vinyl ether **13** was prepared from 1-heptyne via five-step sequences. Thus, lithiation of 1-heptyne with BuLi in THF at 0 °C and subsequent alkylation with bromoacetaldehyde diethyl acetal in HMPA gave rise to 3-nonynal diethyl acetal in 52% yield, which was reduced with P-2 nickel and ethylenediamine in ethanol under H_2 to furnish 3-*cis*-nonenal diethyl acetal (**11**) in 77% yield. Hydrolysis of the acetal moiety with oxalic acid in aqueous acetone followed by alkylation with vinylmagnesium bromide in THF afforded allylic alcohol **12** in 75% yield. Transetherification of **12** with ethyl vinyl ether in the presence of $Hg(OAc)_2$ produced the vinyl ether **13** in 63% yield. The Claisen rearrangement of **13** with reagent B in toluene at −20 °C and subsequent reduction with $NaBH_4$ in MeOH gave the alcohol **14** in 88% yield in the E/Z ratio of 95:5. This selectivity was further enhanced to 98:2 by lowering the reaction temperature to −78 °C. It should be noted that the thermal rearrangement of **13** resulted in the E/Z ratio of 93:7. Finally, simple acetylation of **14** gave the target compound **15** in quantitative yield.

When an allyl vinyl ether possesses alternative allylic systems, the thermal rearrangement of such a substrate **16** is reported to

(13) Previous synthesis of **15**: Roelofs, W. L.; Kochansky, J. P.; Carde, R. T.; Henrick, C. A.; Labovitz, J. N.; Corbin, V. L. *Life Sci.* **1975**, *17*, 699. (b) Voerman, S.; Rothvhild, J. *J. Chem. Ecol.* **1978**, *4*, 531. (c) Alexakis, A.; Cahiez, G.; Normant, J. F. *Tetrahedron Lett.* **1978**, 2027. (d) Fujisawa, T.; Sato, T.; Kawashima, M.; Naruse, K.; Tamai, K. *Ibid.* **1982**, *23*, 3583. (e) Nishiyama, H.; Sakuta, K.; Itoh, K. *Ibid.* **1984**, *25*, 223. (f) Vig, O. P.; Sharma, M. L.; Kumari, S.; Rani, V. *Indian J. Chem., Sect. B* **1985**, *24B*, 675. (g) Yadav, J. S.; Reddy, P. S. *Synth. Commun.* **1986**, *16*, 1119. (h) Yadav, J. S.; Kulkarni, A. D.; Reddy, P. S. *Indian J. Chem., Sect. B* **1986**, *25B*, 1220. (i) Chattopadhyay, A.; Mamdapur, V. R.; Chadha, M. S. *Ibid.* **1987**, *26B*, 187.

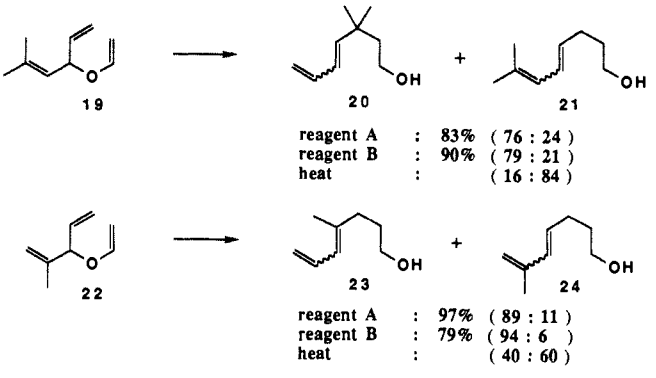
Scheme III



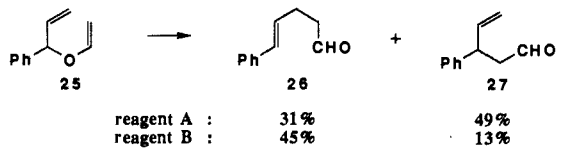
involve the less substituted allyl system to furnish dienal **17** preferentially.[14] With certain bulky organoaluminum reagents, however, the opposite regioselectivity leading to dienal **18** might be achievable in view of the steric repulsion between the more substituted allylic systems and the bulky Lewis acidic aluminum reagents as illustrated in Scheme III.[15]

Typically, bisallyl vinyl ether **16** (R = Bu) was treated with reagent A in CH_2Cl_2 at −78 °C to yield a mixture of Claisen products **17** and **18** (R = Bu) in 72% yield. The ratio of **17** and **18** (R = Bu) was determined to be 30:70 by capillary GLC after conversion of the aldehydes to the corresponding alcohols. The stereoisomeric *E*/*Z* ratios of **17** and **18** (R = Bu) were tentatively assigned to be 42:58 and 41:59, respectively. Use of other solvents exhibited similar regioselectivity so that the intervention of the ionic mechanism seems unlikely. With reagent B in toluene at −78 °C, the product ratio of **17** and **18** (R = Bu) was found to be 31:69. These results are in marked contrast with the thermal rearrangement of **16** (R = Bu), which has resulted in the reversal of selectivity (**17**:**18** = 76:24). The more bulky substrate **16** (R = *t*-Bu) on treatment with reagent A showed somewhat better selectivity (**17**:**18** = 24:76).

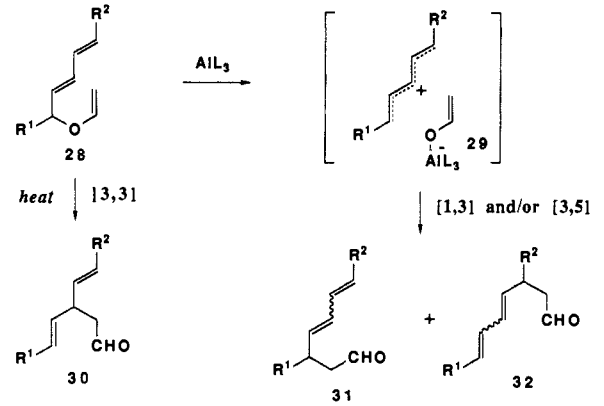
As revealed in the following examples, the course of the rearrangement appeared to be highly dependent on the substituent pattern in the allylic system of the substrates. In view of the easy product isolation, the Claisen products were directly transformed to the corresponding alcohols with $NaBH_4$ in MeOH. The bisallyl vinyl ether **19** bearing dimethyl substituents in the γ-positions gave more satisfactory results than its monoalkyl counterpart **16**. The steric difference between vinyl and isopropenyl moieties is even more clear in the second substrate **22** giving the desired Claisen product **23** with high regioselectivity.



During the course of this study, 1-phenyl-2-propenyl vinyl ether (**25**) on treatment with reagent A or B was found to undergo the unexpected [1,3]-sigmatropic rearrangement to furnish **27** in

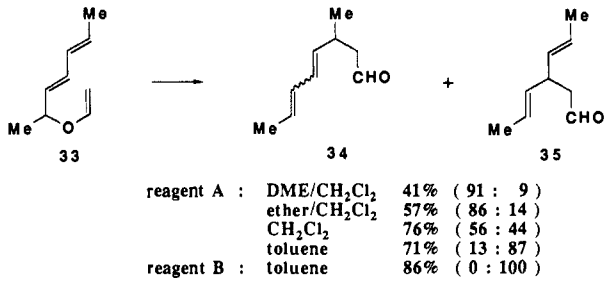


Scheme IV



competition to the normal [3,3] Claisen rearrangement, implying the intervention of the ionic mechanism in this particular case. This finding prompted us to investigate the rearrangement of dienyl vinyl ethers of type **28** under the influence of certain bulky organoaluminum reagents with the hope of observing the previously unknown, remote transfer of vinyloxy moiety by [3,5]-sigmatropic rearrangement via ionic intermediate **29**, giving dienal **32** as illustrated in Scheme IV.[16]

We examined the rearrangement of dienyl vinyl ether **33**. This system is ideal for our purpose because the extent of the concerted or ionic nature of the rearrangement is readily understandable from the product ratio. Namely, the rearranged products **28** and



29 are interpreted as derived via the ionic polar and the concerted mechanisms, respectively. The selected data clearly indicate the remarkable solvent effect on the course of the rearrangement, and the previously unknown ionic rearrangement is realized to a great extent by using reagent A in the polar solvent in order to stabilize the ionic intermediate **29** ($R^1 = R^2 = Me$). Notably, treatment of **33** with reagent B in toluene afforded the normal Claisen product **35** exclusively as the sole isolable product.

With such information in hand, various dienyl vinyl ethers were exposed to the organoaluminum–promoted rearrangement as depicted in Table II. In the substrates **28** (R^1 = Bu, R^2 = Me; R^1 = Me, R^2 = Bu; or R^1 = Ph, R^2 = Me), the remote transfer of vinyloxy moiety by [3,5]-sigmatropic rearrangement takes precedence over [1,3] and [3,3] rearrangements with reagent A in DME/CH_2Cl_2 or $ether/CH_2Cl_2$ solvents (volume ratio = 1:1) (entries 1–13). This tendency is also observed in the substrate **36** resulting in the predominant formation of the ionic rearrangement product **37** (entries 14 and 15). However, attempted reaction of the substrate **28** ($R^1 = C_5H_{11}$, R^2 = H or R^1 = H, R^2 = Me) with reagent A resulted in the exclusive formation of the normal Claisen product via [3,3]-sigmatropic rearrangement (entries 16 and 17).

Experimental Section

Preparation of Phenols. 4-Bromo-2,6-di-*tert*-butylphenol was prepared by simple bromination of 2,6-di-*tert*-butylphenol with bromine. 2-*tert*-Butyl-6-phenylphenol was prepared by Friedel–Crafts alkylation of 2-phenylphenol with isobutylene using aluminum foil.[17]

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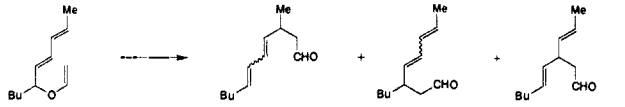
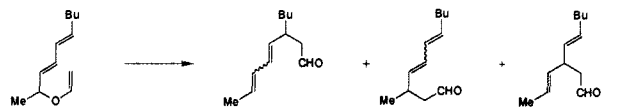
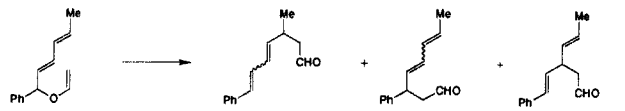
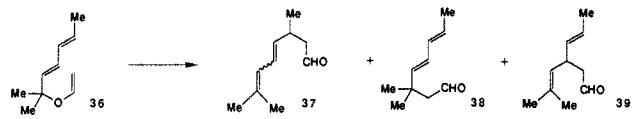
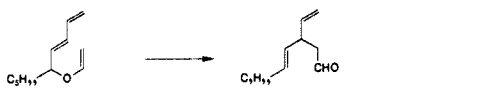
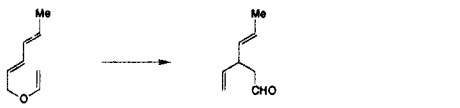
(15) For a preliminary account of this work, see: Maruoka, K.; Banno, H.; Nonoshita, K.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 1265.
(16) Gajewski, J. J.; Jurayj, J.; Kimbrough, D. R.; Gande, M. E.; Ganem, B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170.
(17) Hay, A. S. *J. Org. Chem.* **1969**, *34*, 1160.

Table II. Organoaluminum-Promoted Rearrangement of Dienyl Vinyl Ethers

entry	reagent[a]	solvent[b]	conditions, °C h	yield,[c] %	ratio[d]
					
1	A	DME/CH_2Cl_2	−78, 0.5	57	55:34:11
2		$ether/CH_2Cl_2$	−78, 1	57	58:31:11
3		$(CH_2Cl)_2$	−20, 0.3	57	49:35:16
4		CH_2Cl_2	−78, 0.3	91	44:34:22
5		CH_2Cl_2	0, 0.3	69	31:31:38
6		toluene	−78, 0.3	82	6:5.89
7	B	toluene	−20, 0.3	89	0:0:100
8	MAD	CH_2Cl_2	−78, 0.3	92	4:3:93
9	heat	decane	200, 0.5	95	0:0:100
					
10	A	$ether/CH_2Cl_2$	−78, 1	69	37:50:13
11		CH_2Cl_2	−78, 0.3	78	24:36:40
					
12	A	DME/CH_2Cl_2	−78, 1.5	65	87:8:5
13		CH_2Cl_2	−78, 0.3	89	57:28:15
					
14	A	DME/CH_2Cl_2	−78, 0.5	75	69:10:21
15		CH_2Cl_2	−78, 0.3	85	58:20:22
					
16	A	CH_2Cl_2	−78, 0.3	86	
					
17	A	CH_2Cl_2	−78, 0.3	83	

[a] For structures of reagents A, B, and MAD, see text. [b] Volume ratio of mixed solvents is 1:1. [c] Isolated yield. [d] For determination of the regioisomeric ratios, see the Experimental Section.

Preparation of Allylic Alcohols. 1-Hepten-3-ol, 2-methyl-1-hepten-3-ol, and (*E*)-2-octen-4-ol were prepared by reaction of aldehydes (acrolein, methacrolein, and crotonaldehyde) with butyllithium. 3-Phenyl-1-propen-3-ol was prepared by treatment of acrolein with phenyllithium. 1-Cyclohexyl-2-propen-1-ol, 5-methyl-1-hexen-3-ol, and 1-phenyl-3-buten-2-ol were prepared by addition of vinylmagnesium bromide to aldehydes (cyclohexanecarbaldehyde, isovaleraldehyde, and phenylacetaldehyde). 1,5-Hexadien-3-ol was prepared by addition of allylmagnesium bromide to acrolein. Divinylcarbinol was prepared according to the literature procedure.[18] 1-(Trimethylsilyl)-4-penten-1-yn-3-ol was derived by lithiation of (trimethylsilyl)acetylene with BuLi followed by addition of acrolein.

General Method for Preparation of Allylic Vinyl Ethers.[19] A mixture of allylic alcohol (15 mmol), mercury(II) acetate (3.2 g, 10 mmol), and ethyl vinyl ether (37.5 mL) was stirred at room temperature for 3–6 h. The mixture was then poured into 5% potassium hydroxide solution (15 mL) and extracted with hexane. After drying over Na_2SO_4, the hexane extracts were concentrated. The residual crude product was purified by column chromatography using hexane as eluant to give pure allylic vinyl ether in 20–65% yield.

Preparation of Reagent A.[9c] 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 the reagent A in CH_2Cl_2 without any purification. Other modified organoaluminum reagents such as the reagents B–D and MAD were prepared in situ from Me_3Al and the corresponding phenols in either toluene or CH_2Cl_2 at room temperature for 1 h.

Preparation of Reagent E. To a solution of 4-bromo-2,6-di-*tert*-butylphenol (1 equiv) in CH_2Cl_2 was added at room temperature a 1 M hexane solution of DIBAH (1 equiv). The mixture was stirred at room temperature for 30 min and used as a solution of the reagent E in CH_2Cl_2.

Preparation of Dimethylaluminum 4-Bromo-2,6-di-*tert*-butylphenoxide. To a solution of 4-bromo-2,6-di-*tert*-butylphenol (1 equiv) in CH_2Cl_2 was added at room temperature a 2 M hexane solution of Me_3Al (1 equiv). The mixture was stirred at room temperature for 30 min and used as a solution of dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide in CH_2Cl_2.

General Method for the Claisen Rearrangement of Allylic Vinyl Ethers with Reagent A. To a solution of the reagent A (1 mmol) in CH_2Cl_2 (5 mL) was added allylic vinyl 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, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluant) gave a (*Z*)-olefinic aldehyde predominantly. The *E*/*Z* ratio of the olefinic aldehydes was determined by capillary GLC analysis by comparison with the authentic samples, which were prepared by the thermal Claisen rearrangement of the allylic vinyl ethers in tetradecane at 250 °C. In case of insufficient base-line separation on GLC, the isomeric ratio was determined after conversion of the aldehydes to the corresponding alcohols with $NaBH_4$ and then to the trimethylsilyl ethers with Me_3SiCl and NEt_3. These results are indicated in Table I. The GLC retention times of the *E*/*Z* isomers at the indicated column temperature are as follows. Trimethylsilyl ether of 7-methyl-4-octen-1-ol: t_R(*Z* isomer) = 16.6 min, t_R(*E* isomer) = 17.6 min at 50 °C. Trimethylsilyl ether of 4-nonen-1-ol: t_R(*Z* isomer) = 11.6 min, t_R(*E* isomer) = 12.6 min at 60 °C. Trimethylsilyl ether of 3-methyl-4-nonen-1-ol: t_R(*Z* isomer) = 5.5 min, t_R(*E* isomer) = 6.2 min at 80 °C. Trimethylsilyl ether of 4-methyl-4-nonen-1-ol: t_R(*Z* isomer) = 4.6 min, t_R(*E* isomer) = 5.1 min at 100 °C. Trimethylsilyl ether of 6-phenyl-4-hexen-1-ol: t_R(*Z* isomer) = 5.6 min, t_R(*E* isomer) = 6.3 min at 150 °C. 5-Cyclohexyl-4-pentenal: t_R(*Z* isomer) = 8.5 min, t_R(*E* isomer) = 9.3 min at 120 °C. 4,6-Heptadien-1-ol: t_R(*Z* isomer) = 25.7 min, t_R(*E* isomer) = 26.2 min at 80 °C. 7-(Trimethylsilyl)-4-hepten-6-yn-1-ol: t_R(*Z* isomer) = 7.1 min, t_R(*E* isomer) = 13.8 min at 140 °C. Trimethylsilyl ether of 4,7-octadien-1-ol: t_R(*Z* isomer) = 8.8 min, t_R(*E* isomer) = 9.4 min at 60 °C.

General Method for the Claisen Rearrangement of Allylic Vinyl Ethers with Reagent B. To a solution of the reagent B (1 mmol) in toluene (5 mL) was added an allylic vinyl ether (0.5 mmol) at −20 °C. The mixture was stirred at −20 °C for 15–30 min. This was poured into 10% HCl, extracted with ether, dried over Na_2SO_4, and concentrated to give a crude aldehyde, which was generally reduced to the corresponding alcohol in view of the easy product separation from 2,6-diphenylphenol. Thus, a solution of the crude aldehyde in MeOH (2 mL) was treated with $NaBH_4$ (23 mg, 0.6 mmol) at room temperature. The mixture was stirred at room temperature for 5 min, poured into water, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluant) gave the (*E*)-olefinic alcohol predominantly. The *E*/*Z* ratio of the products was determined in a similar manner as described above, and the results are shown in Table I.

Preparation of (1*R*)-(2*E*)-1-Isobutyl-2-butenyl Vinyl Ether (7).[20] Optically active (2*E*)-6-methyl-2-hepten-4-ol ($[\alpha]_D$ +7.3° (*c* 1.02, $CHCl_3$)) was prepared by the kinetic resolution of racemic (2*E*)-6-methyl-2-hepten-4-ol by the enantioselective epoxidation.[11] The absolute configuration of the allylic alcohol was assigned to be *R* by comparison with the optical rotation of an authentic sample.[19] Further, the optical yield was established to be 78% ee by capillary GLC analysis after conversion to the (−)-MTPA ester: t_R(*S* isomer) = 10.8 min, t_R(*R* isomer) = 11.4 min at the column temperature of 140 °C.

A mixture of (4*R*)-(2*E*)-6-methyl-2-hepten-4-ol (674 mg, 5.25 mmol), mercury(II) acetate (1.12 g, 3.5 mmol), and ethyl vinyl ether (20 mL)

(18) Ramsden, H. E.; Leebrick, J. R.; Rosenberg, S. D.; Miller, E. H.; Walburn, J. J.; Balint, A. E.; Cserr, R. *J. Org. Chem.* **1957**, *22*, 1602.
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was stirred at room temperature for 5 h. The mixture was poured into 5% potassium hydroxide solution (5 mL) and extracted with hexane. After drying over Na_2SO_4, the hexane extracts were concentrated. Purification of the residual crude product by column chromatography (pentane as eluant) gave the title compound **7** (522 mg, 65% yield, $[\alpha]_D$ −2.89° (*c* 1.02, $CHCl_3$)): IR (liquid film) 2950, 2920, 1625, 1610, 1465, 1175, 1125, 1035, 960, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.33 (1 H, dd, *J* = 14, 7 Hz, C=CHO), 5.59–5.77 (1 H, m, C=CHMe), 5.37 (1 H, dd, *J* = 15, 7 Hz, HC=CMe), 4.30 (1 H, dd, *J* = 14, 1 Hz, *cis*-HC=CO), 4.15 (1 H, q, *J* = 7 Hz, C=CCHO), 3.97 (1 H, dd, *J* = 7, 1 Hz, *trans*-HC=CO), 1.72 (3 H, d, *J* = 7 Hz, C=CCH_3), 1.60–1.79 (2 H, m, CH_2), 1.26–1.57 (1 H, m, C*H*Me_2), 0.91 (6 H, d, *J* = 7 Hz, C-$(CH_3)_2$).

Claisen Rearrangement of Allylic Vinyl Ether 7 with Reagent A. To a solution of the reagent A (1.5 mmol) in CH_2Cl_2 (7.5 mL) was added allylic vinyl ether **7** (116 mg, 0.75 mmol) at −78 °C. The mixture was stirred at −78 °C for 30 min, poured into 10% HCl, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane = 1:20 to 1:10 as eluant) gave a mixture of (3*S*)-(4*Z*)-3,7-dimethyl-4-octenal (**8**) and (3*R*)-(4*E*)-3,7-dimethyl-4-octenal (**9**) (74 mg, 67% combined yield). The ratio of the Claisen products, **8** and **9**, was determined to be 84:16 by capillary GLC analysis after conversion of the aldehydes to the corresponding alcohols with $NaBH_4$ and then to the trimethylsilyl ethers with Me_3SiCl and NEt_3: t_R(*Z* isomer) = 4.8 min, t_R(*E* isomer) = 5.4 min at the column temperature of 70 °C. The absolute configuration of the major Claisen product was determined by correlation to optically active citronellal. This was accomplished by catalytic hydrogenation of the Claisen products with 5% Pd/C in THF under H_2 at room temperature to furnish (3*R*)-3,7-dimethyloctanal ($[\alpha]_D$ +5.7° (*c* 0.97, $CHCl_3$)). The authentic, optically pure (3*R*)-3,7-dimethyloctanal ($[\alpha]_D$ +13.6° (*c* 1.05, $CHCl_3$)) and its (3*S*) isomer ($[\alpha]_D$ −13.0° (*c* 1.00, $CHCl_3$)) were prepared by the catalytic hydrogenation of optically pure (*R*)- and (*S*)-citronellal, respectively. Therefore, the major *Z* isomer **8** possesses the *S* configuration. Since the Pd/C catalyst resulted in partial racemization of the allylic C-3 chirality in the hydrogenation of **8** and **9** as predicted by the relatively low value of the optical rotation of (3*R*)-3,7-dimethyloctanal,[8] the optical purities of the Claisen products, **8** and **9** were rigorously established to be 78% ee and 64% ee, respectively (100% ee and 82% ee based on the optically pure **7**) by capillary GLC analysis after conversion to the acetals **10** of (2*R*,4*R*)-2,4-pentanediol with $CH(OEt)_3$ and catalytic *p*-TsOH in benzene at room temperature: *Z*-3*R* isomer, t_R = 43.5 min (7.9%); *E*-3*R* isomer, t_R = 52.3 min (14.9%); *Z*-3*S* isomer, t_R = 57.0 min (73.9%); *E*-3*S* isomer, t_R = 59.0 min (3.3%) at the column temperature of 70 °C. Furthermore, hydrogenation of **10** with Raney Ni in EtOH under H_2 at room temperature yielded (3*R*)- and (3*S*)-3,7-dimethyloctanal acetal of (2*R*,4*R*)-2,4-pentanediol in a ratio of 76:24, showing conservation of the allylic C-3 chirality in the hydrogenation step: t_R(*R* isomer) = 16 min, t_R(*S* isomer) = 16.5 min at the column temperature of 95 °C. (3*S*)-(4*Z*)-3,7-Dimethyl-4-octenal (**8**).[20] IR (liquid film) 2955, 2870, 2715, 1725, 1460, 1380, 1365, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.71 (1 H, t, *J* = 2 Hz, CHO), 5.18–5.44 (2 H, m, HC=CH), 2.94–3.16 (1 H, m, C=CCH), 2.36 (2 H, dd, *J* = 7, 2 Hz, O=CCH_2), 1.96 (2 H, t, *J* = 7 Hz, C=CCH_2), 1.55–1.72 (1 H, m, C*H*Me_2), 1.03 (3 H, d, *J* = 7 Hz, CCH_3), 0.90 (6 H, d, *J* = 7 Hz, C-$(CH_3)_2$).

Claisen Rearrangement of Allylic Vinyl Ether 7 with Reagent B. To a solution of the reagent B (1.5 mmol) in toluene (20 mL) was added allylic vinyl ether **7** (116 mg, 0.75 mmol) at −78 °C. The resulting mixture was stirred at −78 °C for 45 min and at −20 °C for 30 min. The reaction mixture was poured into 10% HCl, extracted with ether, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (benzene as eluant) gave a mixture of (3*S*)-(4*Z*)-3,7-dimethyl-4-octenal (**8**) and (3*R*)-(4*E*)-3,7-dimethyl-4-octenal (**9**) (130 mg, 90% combined yield). The ratio of the Claisen products, **8** and **9**, was determined to be 2:98 in a similar manner as described above. The absolute configuration of the major Claisen product **9** was determined by catalytic hydrogenation of the Claisen products with 5% Pd/C in THF under H_2 to furnish (3*S*)-3,7-dimethyloctanal ($[\alpha]_D$ −8.4° (*c* 0.99, $CHCl_3$)). The optical purity of the major Claisen product **9** was established to be 76% ee (98% ee based on the optically pure **7**) by capillary GLC analysis after conversion to the acetal **10** of (2*R*,4*R*)-2,4-pentanediol: ratio of *E*-3*R* isomer, *Z*-3*S* isomer, and *E*-3*S* isomer = 85.0:3.3:11.7. Furthermore, hydrogenation of **10** with Raney Ni in EtOH under H_2 at room temperature yielded (3*R*)- and (3*S*)-3,7-dimethyloctanal acetal of (2*R*,4*R*)-2,4-pentanediol in a ratio of 15:85, again indicating retention of the allylic C-3 chirality. (3*R*)-(4*E*)-3,7-Dimethyl-4-octenal (**9**).[20] ^1H NMR ($CDCl_3$) δ 9.72 (1 H, t, *J* = 2 Hz, CHO), 5.27–5.51 (2 H, m, HC=CH), 2.62–2.82 (1 H, m, C=CCH), 2.25–2.48 (2 H, m, O=CCH_2), 1.86 (2 H, t, *J* = 6 Hz, C=CCH_2), 1.48–1.67 (1 H, m, C*H*Me_2), 1.06 (3 H, d, *J* = 7 Hz, CCH_3), 0.85 (6 H, d, *J* = 7 Hz, C-$(CH_3)_2$).

(*Z*)-3-Nonenal Diethyl Acetal (11).[21] To a solution of 1-heptyne (7.9 mL, 60 mmol) in THF (60 mL) was added a 1.7 M hexane solution of BuLi (37 mL, 63 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h, and a solution of bromoacetaldehyde diethyl acetal (10 g, 50.7 mmol) in HMPA (20 mL) was added dropwise at 0 °C over 20 min. The reaction mixture was stirred at 0 °C for 30 min, at room temperature overnight. Then this was poured into water, extracted with hexane, and dried over Na_2SO_4. Evaporation of solvents and distillation of the residue gave 3-nonynal diethyl acetal (70–78 °C (3 mmHg), 5.6 g, 52% yield).

To a solution of nickel(II) acetate (498 mg, 2 mmol) in EtOH (15 mL) was added a solution of $NaBH_4$ (76 mg, 2 mmol) in EtOH (2 mL) over 30 s at room temperature, and the mixture was stirred there for a few minutes. The reactor was purged with H_2, and ethylenediamine (0.27 mL, 4 mmol) was added, followed by 3-nonynal diethyl acetal (3.4 g, 16 mmol). When H_2 uptake was quantitative, H_2 was released. The reaction mixture was filtered through active carbon, washed with THF, and concentrated. The residue was purified by column chromatography (ether/hexane = 1:40 as eluant) to give (*Z*)-3-nonenal diethyl acetal (**11**) (2.64 g, 77% yield): IR (liquid film) 2975, 2920, 1365, 1340, 1120, 1055, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.32–5.54 (2 H, m, HC=CH), 4.46 (1 H, t, *J* = 6 Hz, C*H*$(OEt)_2$), 3.41–3.71 (4 H, m, $(OCH_2)_2$), 2.36 (2 H, t, *J* = 6 Hz, C*H*$_2$C$(OEt)_2$), 2.01 (2 H, q, *J* = 6 Hz, CH_2C=C), 1.18 (6 H, t, *J* = 7 Hz, $(OCCH_3)_2$), 0.86 (3 H, br t, CH_3).

(5*Z*)-1,5-Undecadien-3-ol (12).[22] To a solution of (*Z*)-3-nonenal diethyl acetal (**11**) (2.26 g, 10.5 mmol) in acetone (16 mL) was added oxalic acid dihydrate (630 mg, 5 mmol) followed by water (13 mL), and the resulting mixture was refluxed for 1 h. Then the mixture was cooled to room temperature, poured into saturated $NaHCO_3$, extracted with ether, and dried over Na_2SO_4. Evaporation of solvents left crude (*Z*)-3-nonenal.

To a 0.6 M THF solution of vinylmagnesium bromide (40 mL, 24 mmol) was added a solution of the crude (*Z*)-3-nonenal in ether (8 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min, poured into aqueous NH_4Cl, extracted with ether, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane = 1:4 as eluant) gave (5*Z*)-1,5-undecadien-3-ol (**12**) (1.33 g, 75% yield): IR (liquid film) 3325, 2960, 2920, 2855, 990, 910, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.88 (1 H, ddd, *J* = 17, 10, 6 Hz, C=CHCO), 5.30–5.78 (2 H, m, CCH=CHC), 5.24 (1 H, d, *J* = 17 Hz, *cis*-HC=CCO), 5.11 (1 H, d, *J* = 10 Hz, *trans*-HC=CCO), 4.08–4.16 (1 H, m, OCH), 2.30 (2 H, t, *J* = 7 Hz, $OCCH_2$), 2.01 (2 H, br t, C*H*$_2$Bu), 1.62 (1 H, d, *J* = 4 Hz, OH), 1.18–1.42 (6 H, m, $CH_2CH_2CH_2$), 0.86 (3 H, t, *J* = 6 Hz, CH_3).

(3*Z*)-1-Vinyl-3-nonenyl Vinyl Ether (13). A mixture of (5*Z*)-1,5-undecadien-3-ol (**12**) (505 mg, 3 mmol), mercury(II) acetate (637 mg, 2 mmol), and ethyl vinyl ether (10 mL) was stirred at room temperature for 5.5 h. The mixture was poured into 5% potassium hydroxide solution, extracted with hexane, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (hexane as eluant) gave the title compound **13** (366 mg, 63% yield): IR (liquid film) 2945, 2905, 2840, 1630, 1610, 1315, 1190, 1175, 1050, 985, 925, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.31 (1 H, dd, *J* = 14, 7 Hz, C=CHO), 5.75 (1 H, ddd, *J* = 17, 10, 6 Hz, C=CHCO), 5.27–5.56 (2 H, m, CCH=CHC), 5.21 (1 H, d, *J* = 17 Hz, *cis*-HC=CCO), 5.19 (1 H, d, *J* = 10 Hz, *trans*-HC=CCO), 4.29 (1 H, dd, *J* = 14, 1 Hz, *cis*-HC=CO), 4.15 (1 H, q, *J* = 6 Hz, C=CCHO), 3.99 (1 H, dd, *J* = 7, 1 Hz, *trans*-HC=CO), 2.23–2.50 (2 H, m, $OCCH_2$), 2.05 (2 H, br q, C*H*$_2$Bu), 1.15–1.40 (6 H, m, $CH_2CH_2CH_2$), 0.86 (3 H, t, *J* = 7 Hz, CH_3). Anal. ($C_{13}H_{22}O$) C, H.

(4*E*,7*Z*)-4,7-Tridecadien-1-ol (14).[13] To a solution of the reagent B (1 mmol) in toluene (7 mL) was added (3*Z*)-1-vinyl-3-nonenyl vinyl ether (**13**) (97 mg, 0.5 mmol) at −20 °C. The mixture was stirred at −20 °C for 30 min and poured into 10% HCl. The crude product was extracted with ether, dried over Na_2SO_4, and concentrated to furnish crude (4*E*,7*Z*)-4,7-tridecadienal.

To a solution of the crude (4*E*,7*Z*)-4,7-tridecadienal in MeOH (2 mL) was added $NaBH_4$ (23 mg, 0.6 mmol) at room temperature. The mixture was stirred at room temperature for 5 min, poured into water, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane = 1:2 to 1:1 as eluant) gave (4*E*,7*Z*)-4,7-tridecadien-1-ol (**14**) (86 mg, 88% yield): IR (liquid film) 3300, 2910, 2845, 1450, 1055, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29–5.51 (4 H, m, CH=CHCH=CH), 3.63 (2 H, t, *J* = 6 Hz, CH_2O), 2.68–2.79 (2 H, m, C=CCH_2C=C), 1.92–2.15 (4

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H, m, $CH_2C{=}CCC{=}CCH_2$), 1.54–1.68 (2 H, m, CH_2CO), 1.17–1.42 (7 H, m, $CH_2CH_2CH_2$ and OH), 0.86 (3 H, br t, CH_3).

(4*E*,7*Z*)-4,7-Tridecadienyl Acetate (15).[13] To a solution of (4*E*,7*Z*)-4,7-tridecadien-1-ol (**14**) (35 mg, 0.18 mmol) in CH_2Cl_2 (3 mL) were added pyridine (73 μL, 0.9 mmol), Ac_2O (85 μL, 0.9 mmol), and a catalytic amount of DMAP at room temperature. The mixture was stirred at room temperature for 30 min, poured into saturated $NaHCO_3$, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane = 1:10 as eluant) gave (4*E*,7*Z*)-4,7-tridecadienyl acetate (**15**) (42 mg, 100% yield): IR (liquid film) 2945, 2910, 1735, 1445, 1355, 1230, 1035, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29–5.43 (4 H, m, CH=CHCCH=CH), 4.03 (2 H, t, *J* = 7 Hz, CH_2O), 2.70 (2 H, br t, $C{=}CCH_2C{=}C$), 1.95–2.09 (4 H, m, $CH_2C{=}CCC{=}CCH_2$), 2.02 (3 H, s, $COCH_3$), 1.66 (2 H, quint, *J* = 5 Hz, CH_2CO), 1.18–1.37 (6 H, m, $CH_2CH_2CH_2$), 0.86 (3 H, br t, CH_3). The *E*/*Z* ratio of the acetate was determined to be 95:5 by capillary GLC analysis: t_R(*Z* isomer) = 9.1 min, t_R(*E* isomer) = 9.7 min at the column temperature of 150 °C.

Preparation of Bisallylic Alcohols. (4*E*)-1,4-Nonadien-3-ol, (4*E*)-6,6-dimethyl-1,4-heptadien-3-ol, and 2-methyl-1,4-pentadien-3-ol were prepared by lithiation of alkenyl halides ((*E*)-1-iodo-1-hexene, (*E*)-3,3-dimethyl-1-iodo-1-butene, and isopropenyl bromide)[23] with *t*-BuLi followed by addition of acrolein. 5-Methyl-1,4-hexadien-3-ol was derived from alkylation of 3-methyl-2-butenal with vinylmagnesium bromide.

Preparation of Bisallylic Vinyl Ethers.[24] Bisallylic vinyl ethers were prepared in 38–91% yield in a similar manner as described in the general method for preparation of allylic vinyl ethers.

Claisen Rearrangement of Bisallylic Vinyl Ethers with Reagent A or B. To a solution of the reagent A (1 mmol) in CH_2Cl_2 (5 mL) or the reagent B (1 mmol) in toluene (15 mL) was added a bisallylic vinyl ether (0.5 mmol) at −78 °C. The mixture was stirred at −78 °C for 0.5–1.5 h, poured into 10% HCl, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated to give crude aldehydes **17** and **18**.

To a solution of the crude aldehydes **17** and **18** in MeOH (2 mL) was added $NaBH_4$ (23 mg, 0.6 mmol) at room temperature. The mixture was stirred at room temperature for 5 min, poured into water, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluant) gave a mixture of alcohols. The isomeric ratio was determined by capillary GLC analysis by comparison with the authentic samples, which were prepared by the thermal Claisen rearrangement of bisallylic vinyl ethers in toluene under reflux. The GLC retention times of the alcohols derived from **17** and **18** at the indicated column temperature are as follows: t_R(*E* and *Z* isomeric alcohols from **18** (R = Bu)) = 12.1 and 13.0 min, t_R(*E* and *Z* isomeric alcohols from **17** (R = Bu)) = 20.5 and 23.2 min at 160 °C; t_R(*E* and *Z* isomeric alcohols from **18** (R = *t*-Bu)) = 10.0 and 10.8 min, t_R(*E* and *Z* isomeric alcohols from **17** (R = *t*-Bu)) = 13.1 and 16.6 min at 150 °C; t_R(*E* and *Z* isomers of **20**) = 7.9 and 10.2 min, t_R(*E* and *Z* isomers of **21**) = 18.7 and 19.8 min at 140 °C; t_R(*E* and *Z* isomers of **23**) = 14.8 and 16.5 min, t_R(*E* and *Z* isomers of **24**) = 15.5 and 15.8 min at 130 °C.

Dienyl alcohols 20 and 21: Anal. ($C_9H_{16}O$) C, H.

Dienyl alcohols 23 and 24: Anal. ($C_8H_{14}O$) C, H.

Claisen Rearrangement of 1-Phenyl-2-propenyl Vinyl Ether (25) with Reagent A. To a solution of the reagent A (1 mmol) in CH_2Cl_2 (5 mL) was added 1-phenyl-2-propenyl vinyl ether (**25**) (80 mg, 0.5 mmol) at −78 °C. The mixture was stirred at −78 °C for 15 min, poured into 10% HCl, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane = 1:10 to 1:5 as eluant) gave a mixture (64 mg, 80% yield) of (4*E*)-5-phenyl-4-pentenal (**26**) and 3-phenyl-4-pentenal (**27**). The ratio of **26** and **27** was determined to be 31:49 by ^1H NMR analysis based on the integration of two aldehyde peaks: ^1H NMR ($CDCl_3$) δ 9.83 (t, *J* = 1 Hz) and 9.73 (t, *J* = 2 Hz). These products can be separated by column chromatography (ether/hexane = 1:10 to 1:5 as eluant).

(4*E*)-5-Phenyl-4-pentenal (26):[6a] ^1H NMR ($CDCl_3$) δ 9.83 (1 H, t, *J* = 1 Hz, CHO), 7.19–7.38 (5 H, m, C_6H_5), 6.45 (1 H, d, *J* = 16 Hz, C=CHPh), 6.21 (1 H, dt, *J* = 16, 6 Hz, HC=CPh), 2.51–2.67 (4 H, m, CH_2CH_2).

3-Phenyl-4-pentenal (27): IR (liquid film) 2820, 2720, 1725, 1640, 1605, 1490, 1450, 1405, 990, 915, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.73 (1 H, *J* = 2 Hz, CHO), 7.19–7.38 (5 H, m, C_6H_5), 6.00 (1 H, ddd, *J* = 17, 10, 7 Hz, PhCCH=C), 5.12 (1 H, d, *J* = 10 Hz, *trans*-PhCC=CH), 5.08 (1 H, d, *J* = 17 Hz, *cis*-PhCC=CH), 3.96 (1 H, q, *J* = 7 Hz, PhCH), 2.73–2.96 (2 H, m, $CH_2C{=}O$). Anal. ($C_{11}H_{12}O$) C, H.

Claisen Rearrangement of 25 with Reagent B. The rearrangement of **25** (80 mg, 0.5 mmol) was effected with the reagent B (1 mmol) in toluene (15 mL) at −78 °C for 1 h and at −20 °C for 15 min. Purification of the residue by column chromatography (CH_2Cl_2/hexane = 1:4 to 1:2 and to 1:1 as eluant) gave a mixture (46 mg, 58% yield) of **26** and **27**, the ratio of which was determined to be 45:13 in a similar manner as described above.

Preparation of Dienylic Alcohols. (3*E*,5*E*)-3,5-Heptadien-2-ol, (6*E*,8*E*)-6,8-decadien-5-ol, and (2*E*,4*E*)-1-phenyl-2,4-hexadien-1-ol were prepared by reaction of 2,4-hexadienal with methyllithium, butyllithium, and phenyllithium, respectively. (3*E*,5*E*)-3,5-Decadien-2-ol was synthesized by conversion of (*E*)-2-heptenal to homologated (2*E*,4*E*)-2,4-nonadienal[25] followed by methylation with methyllithium. (3*E*,5*E*)-2-Methyl-3,5-heptadien-2-ol was prepared by treatment of methyl sorbate with methyllithium. (3*E*)-1,3-Decadien-5-ol was derived from the coupling reaction of *tert*-butyldimethylsilyl ether of (1*E*)-1-iodo-1-octen-3-ol with vinylmagnesium bromide in the presence of $Pd(PPh_3)_4$ catalyst followed by desilylation with Bu_4NF.[26]

Preparation of Dienylic Vinyl Ethers. Dienylic vinyl ethers were prepared in 34–81% yield in a similar manner as described in the general method for preparation of allylic vinyl ethers.

Rearrangement of Dienylic Vinyl Ethers with Reagent A. The rearrangement was carried out in a similar manner as described in the general method for the Claisen rearrangement of allylic vinyl ethers. The isomeric ratios of the dienal products were determined by ^1H NMR analysis or capillary GLC analysis after conversion to the saturated aldehydes of the dienals by the catalytic hydrogenation with 5% Pd/C under H_2. The results are indicated in Table II. The characteristic ^1H NMR chemical shifts or the GLC retention times of the mixtures at the indicated column temperature are as follows. **34** and **35**: ^1H NMR ($CDCl_3$) δ 1.73 (d, *J* = 7 Hz, $C{=}CCH_3$ of **34**), 1.66 (d, *J* = 6 Hz, CH_3 of **35**). Saturated aldehyde derived from **30–32** (R^1 = Bu, R^2 = Me; R^1 = Me, R^2 = Bu): t_R(**31**) = 4.8 min, t_R(**30**) = 4.9 min, t_R(**32**) = 5.7 min at 110 °C. Saturated aldehyde derived from **30–32** (R^1 = Ph, R^2 = Me): t_R(**31**) = 12.1 min, t_R(**30**) = 15.7 min, t_R(**32**) = 18.9 min at 140 °C. **37–39**: ^1H NMR ($CDCl_3$) δ 9.85 (br t, CHO of **39**), 9.77 (br t, CHO of **37**), 9.67 (br t, CHO of **38**).

Thermal Rearrangement of (2*E*,4*E*)-1-Butyl-2,4-hexadienyl Vinyl Ether 28 (R^1 = Bu; R^2 = Me). A solution of the dienylic vinyl ether (90 mg, 0.5 mmol) in decane (1 mL) was refluxed for 30 min and was, after cooling to room temperature, subjected to column chromatography (ether/hexane = 1:20 to 1:10 as eluant) to furnish the [3,3] rearrangement product **30** (R^1 = Bu; R^2 = Me) (86 mg, 95% yield): ^1H NMR ($CDCl_3$) δ 9.70 (1 H, t, *J* = 1 Hz, CHO), 5.16–5.61 (4 H, m, =CH), 3.25 (1 H, quint, *J* = 6 Hz, C=CCH), 2.46 (2 H, dd, *J* = 7, 2 Hz, $O{=}CCH_2$), 2.01 (2 H, br q, $C{=}CCH_2$), 1.67 (3 H, d, *J* = 6 Hz, $C{=}CCH_3$), 1.19–1.42 (4 H, m, CH_2CH_2), 0.89 (3 H, t, *J* = 6 Hz, CH_3). Anal. ($C_{12}H_{20}O$) C, H.

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Supplementary Material Available: General experimental section and physical and analytical data for all new compounds not included in the experimental section (7 pages). Ordering information is given on any current masthead page.

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