[10] R. Ahlrichs, L. Zhengyan, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1984**, *519*, 155.

[11] G. V. Girichev, A. N. Utkin, N. I. Giricheva, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **1983**, *26*, 634.

[12] The larger Al–O distance in **3** is in agreement with the values found in other highly coordinated Al compounds. For example, the Al–O bond lengths in the octahedral $[Al(O_2)(acac)_3]$ (acac = acetyl acetonate) complex is 1.89 Å (N. Ya. Turova, V. A. Kozunov, A. I. Yanovskii, N. G. Bokii, Yu. T. Struschkov, B. L. Tarnopolskii, *J. Inorg. Nucl. Chem.* **1979**, *41*, 5).

[13] The calculations give the following frequencies [in cm^{-1}] for the other isotopomers of **3** (with intensity [in $km\,mol^{-1}$] and symmetry assignment in parentheses): 1074.0 (3, a_1), 898.9 (149, a_1), 486.0 (10, a_1), 178.9 (18, a_1), 380.6 (0, a_2), 65.9 (0, a_2), 467.2 (2, b_1), 238.3 (38, b_1), 166.9 (0.03, b_1), 1071.0 (9, b_2), 694.2 (175, b_2), 199.6 (24, b_2) for $FAl(^{18}O_2)_2$, and 1136.8 (5, a_1), 899.8 (150, a_1), 496.2 (10, a_1), 182.5 (19, a_1), 390.8 (0, a_2), 67.8 (0, a_2), 479.9 (1, b_1), 240.2 (49, b_1), 171.4 (0.03, b_1), 1072.5 (6, b_2), 701.5 (177, b_2), 201.8 (24, b_2) for $FAl(^{16}O)_2(^{18}O)_2$.

[14] This relation reflects the influence of the coordination number. For example, f(Al–F) decreases from 501 in FAlO[15] to 200 $N\,m^{-1}$ in AlF_6^{3-}.[16, 17]

[15] H. Schnöckel, *J. Mol. Struct.* **1978**, *50*, 275.

[16] M. J. Reisfeld, *Spectrochim. Acta Part A* **1973**, *29*, 1923.

[17] E. J. Baran, A. E. Lavat, *Z. Naturforsch. A* **1981**, *36*, 677.

[18] C. D. Cook, P.-T. Cheng, S. C. Nyburg, *J. Am. Chem. Soc.* **1969**, *91*, 2123.

[19] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 1277.

[20] R. R. Smardzewski, L. Andrews, *J. Chem. Phys.* **1972**, *57*, 1327.

[21] L. Andrews, J. T. Yustein, *J. Phys. Chem.* **1993**, *93*, 12700.

[22] L. Andrews, J. T. Yustein, C. A. Thompson, R. D. Hunt, *J. Phys. Chem.* **1994**, *98*, 6514.

[23] L. Andrews, G. V. Chertihin, C. A. Thompson, J. Dillon, S. Byrne, C. W. Bauschlicher, Jr., *J. Phys. Chem.* **1996**, *100*, 10088.

[24] L. Andrews, G. P. Kushto, J. T. Yustein, E. Archibong, R. Sullivan, J. Leszczynski, *J. Phys. Chem. A* **1997**, *101*, 9077.

[25] L. V. Serebrennikov, S. B. Osin, A. A. Maltsev, *J. Mol. Struct.* **1982**, *81*, 25.

[26] I. V. Ovchinnikov, L. V. Serebrennikov, A. A. Maltsev, *Khim. Fak. Mosk. Gos. Univ.*, Moscow, **1984**.

[27] L. V. Serebrennikov, A. A. Mal'tsev, *Vestn. Mosk. Univ. Ser. 2: Khim.* **1985**, *26*, 137.

[28] T. R. Burkholder, J. T. Yustein, L. Andrews, *J. Phys. Chem.* **1992**, *96*, 10189.

[29] S. M. Sonchik, L. Andrews, K. D. Carlson, *J. Phys. Chem.* **1983**, *87*, 2004.

[30] B. Tremblay, P. Roy, L. Manceron, M. E. Alikhani, D. J. Roy, *Chem. Phys.* **1996**, *104*, 2773.

[31] A. Patyk, W. Sander, J. Gauss, D. Cremer, *Angew. Chem.* **1989**, *101*, 920; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 898.

[32] A. Patyk, W. Sander, J. Gauss, D. Cremer, *Chem. Ber.* **1990**, *123*, 89.

[33] T. Mehner, H. J. Göcke, S. Schunck, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1990**, *580*, 121.

[34] H. Schnöckel, S. Schunck, *Chem. Unserer Zeit* **1987**, *21*, 73.

[35] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[36] K. Eichhorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283.

[37] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346.

The Catalytic Enantioselective Claisen Rearrangement of an Allyl Vinyl Ether[**]

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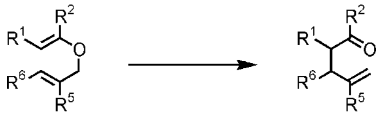
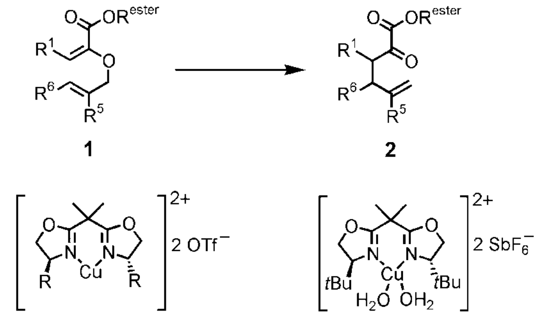
Martin Hiersemann[*]

The [3,3]-sigmatropic rearrangement of an allyl vinyl ether was described by Claisen for the first time in 1912.[1] Since then this rearrangement, which was named after him, has been developed into one of the most powerful C–C bond forming methods (Scheme 1).[2] There are various approaches to carry out the Claisen rearrangement and related [3,3]-sigmatropic rearrangements enantioselectively by using chiral reagents.[3, 4] The only catalytic enantioselective [3,3]-sigmatropic rearrangement known to date was described for allyl imidates.[5] Yamamoto et al. used chiral Lewis acids based on Al^{III} for the enantioselective Claisen rearrangement of acyclic, aliphatic allyl vinyl ethers. However, 1–2 equivalents of the chiral Lewis acid are required and the range of substrates is very select.[6]



Scheme 1. The Claisen rearrangement of an allyl vinyl ether. Which catalysts are able to catalyze this process diastereo- and enantioselectively?

In our search for a chiral catalyst for the Claisen rearrangement of 2-alkoxycarbonyl-substituted allyl vinyl ethers **1**, we found the combination of $Cu(OTf)_2$ and a molecular sieve to be suitable.[7] In an extension of this work, we now report the use of chiral copper(II) bis(oxazoline) ($[Cu^{II}(box)]$) complexes as catalysts for the Claisen rearrangement (Scheme 2).



3 (R = Ph): $[Cu\{(S,S)\text{-Ph-box}\}](OTf)_2$ **5**: $[Cu\{(S,S)\text{-}t\text{Bu-box}\}](H_2O)_2(SbF_6)_2$
4 (R = *t*Bu): $[Cu\{(S,S)\text{-}t\text{Bu-box}\}](OTf)_2$

Scheme 2. General substrate structure and the catalysts used.

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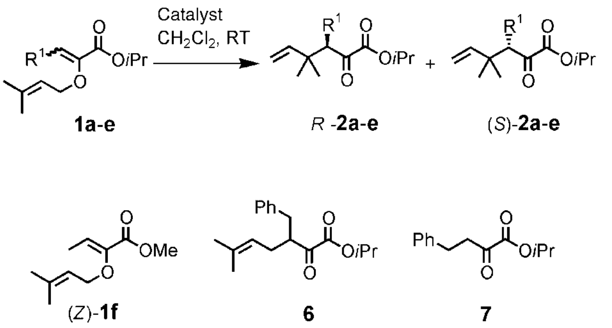
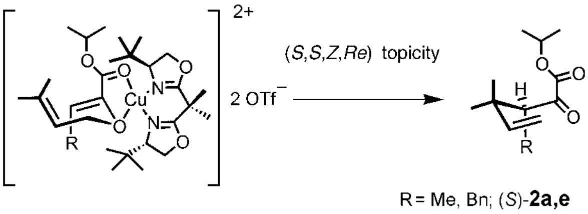
Chiral $[Cu^{II}(box)]$ complexes have proven to be suitable catalysts for a large number of reactions.[8, 9] In our investigations, we employed the commercially available Ph-BOX and *t*Bu-BOX ligands (Scheme 2). Initially, we investigated the $[Cu^{II}(box)](OTf)_2$ catalyzed Claisen rearrangement of allyl vinyl ethers in which only one center of chirality is formed during the rearrangement (Scheme 3, Table 1).[10] We could show that the catalyst (*S*,*S*)-**3** was able to catalyze the Claisen rearrangement of 1-methyl-6,6-dimethyl-substituted allyl vinyl ether **1a** with perfect chemoselectivity and very good enantioselectivity (Table 1, entries 1–5). A change in the configuration of the vinyl ether double bond or the absolute configuration of the catalyst led, as expected, to the reversal of the absolute configuration of the rearrangement product **2a** (Table 1, entries 1, 2, 5).[11] The catalyzed rearrangement was markedly slower with (*S*,*S*)-**4** as the catalyst (Table 1, entry 3). The combination of 4-Å molecular sieves and (*S*,*S*)-**4** showed a satisfactory reactivity and gave the highest enantiomeric excesses (Table 1, entry 4). Remarkably, we observed the same absolute configuration in the rearrangement product **2a** when (*S*,*S*)-**4** and (*R*,*R*)-**3** were used (Table 1, entries 2, 4). This effect was first described for the catalysis of the hetero-Diels–Alder reaction by $[Cu^{II}(box)]$ catalysts.[13]



Scheme 3. Catalytic enantioselective Claisen rearrangement. Results are given in Table 1.

In addition to the methyl group, other alkyl and alkenyl groups are tolerated on C1 of the allyl vinyl ether (Table 1). The catalyzed rearrangement of the methyl ester (*Z*)-**1f** did not lead to an improvement in the enantioselectivity (Table 1, entry 14). In the catalyzed rearrangement of the 1-benzyl-substituted allyl vinyl ether (*Z*)-**1e**, (*S*,*S*)-**4** in combination with molecular sieves showed the highest enantioselectivity, however with an unacceptable reaction time of three days (Table 1, entry 11). Use of the cationic Cu^{II} complex (*S*,*S*)-**5** resulted in a drastic reduction in the chemoselectivity;[14] in addition to the Claisen rearrangement product **2e**, the [1,3]-rearrangement product **6**, and the α-oxoester **7** were isolated (Table 1, entry 12). Clearly, the more Lewis-acidic catalyst (*S*,*S*)-**5** can cause the dissociation of the allyl vinyl ether (*Z*)-**1e**, which results in the formation of the [1,3]-rearrangement product and can lead to the hydrolysis of the vinyl ether unit. Noteworthy is that the addition of molecular sieves in this case hinders the formation of the α-oxoester **7**. The catalysis of the Claisen rearrangement is also successful on a larger scale: the rearrangement of 4 mmol of the allyl vinyl ether (*Z*)-**1e** was catalyzed with only 0.5 mol% (*R*,*R*)-**3** when the reaction time was increased to 24 h (Table 1, entry 13).

The absolute configuration of the products that results from the use of (*S*,*S*)-**4** can be understood on the basis of known models (Scheme 4):[9] we assume that the allyl vinyl ether is coordinated to the Cu^{II} ion in a bidentate fashion. The formation of a chelate between the $[Cu^{II}(box)]$ catalyst and the substrate is generally accepted as the prerequisite for a high enantioselectivity.[9] This chelation should lead to a relatively rigid, ideally planar arrangement of the box ligand,



Scheme 4. Model for the stereochemical pathway of the catalyzed Claisen rearrangement.

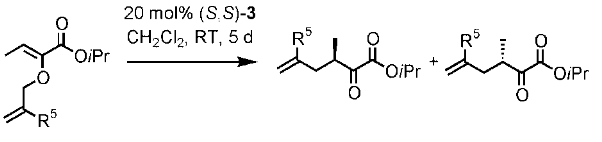
Table 1. Catalytic enantioselective Claisen rearrangements.

Entry	Substrate	R1	*Z*:*E*	Catalyst	*t* [h]	Yield [%][a]	*R*:*S*[b]
1	(*Z*)-**1a**	methyl	96:4	5 mol% (*S*,*S*)-**3**	1	100	91:9
2	(*Z*)-**1a**	methyl	96:4	5 mol% (*R*,*R*)-**3**	1	100	9:91
3	(*Z*)-**1a**	methyl	96:4	10 mol% (*S*,*S*)-**4**	24	47[c]	6:94
4	(*Z*)-**1a**	methyl	96:4	10 mol% (*S*,*S*)-**4**[d]	24	99	6:94
5	(*E*)-**1a**	methyl	4:96	5 mol% (*S*,*S*)-**3**	1	99	9:91
6	(*Z*)-**1b**	ethyl	100:0	5 mol% (*S*,*S*)-**3**	2	99	92:8
7	(*Z*)-**1c**	2-propyl	90:10	5 mol% (*S*,*S*)-**3**	24	98	89:11
8	(*Z*)-**1d**	2-propenyl	100:0	5 mol% (*S*,*S*)-**3**	1	100	93:7
9	(*Z*)-**1e**	benzyl	97:3	5 mol% (*S*,*S*)-**3**	1	99	88:12
10	(*Z*)-**1e**	benzyl	97:3	10 mol% (*S*,*S*)-**4**	72	7[e]	–
11	(*Z*)-**1e**	benzyl	97:3	10 mol% (*S*,*S*)-**4**[d]	72	94[f]	8:92
12	(*Z*)-**1e**	benzyl	97:3	10 mol% (*S*,*S*)-**5**	24	62[g]	27:73
13	(*Z*)-**1e**	benzyl	97:3	0.5 mol% (*R*,*R*)-**3**[h]	24	100	12:88
14	(*Z*)-**1f**	methyl	100:0	5 mol% (*S*,*S*)-**3**	3	99	90:10

[a] Yield of isolated, analytically pure product after removal of the catalyst by filtration through a column of silica gel (4 × 0.5 cm). Reactions were carried out with 0.4 mmol substrate. [b] Determined by HPLC: Chiracel OD 14025, hexane:*i*PrOH 99.9:0.1. [c] In a mixture with 52% substrate. [d] Additionally with 4-Å molecular sieves. [e] In a mixture with 93% substrate. [f] In a mixture with 6% substrate. [g] In a mixture with 24% [1,3]-rearrangement product **6** and 13% α-oxoester **7**. [h] On a 4 mmol scale.

the Cu^{II} ion, and the vinyl ether unit. For a chair-shaped conformation of the allyl vinyl ether, the allyl unit would then approach the vinyl-ether double bond on the side opposite to the *tert*-butyl group of the BOX ligand. This direction of aproach leads to the favored *Re* attack on the *Z*-configured vinyl ether double bond during catalysis with (*S*,*S*)-**4**. Ultimately, this is, an enantiotopos-differentiating reaction in which the catalyst can distinguish between the two enantiotopic lone pairs on the oxygen atom of the allyl vinyl ether.

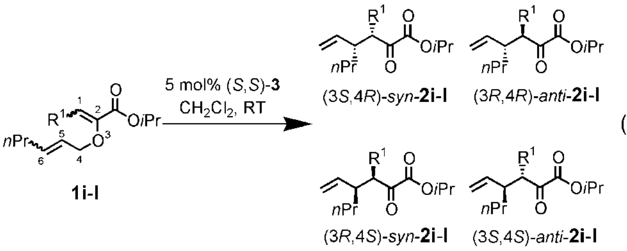
When we used the allyl vinyl ethers (*Z*)-**1g** and (*Z*)-**1h**, which are not substituted in the 6-position, we found that considerably greater concentrations of catalyst and longer reaction times were necessary, and lower enantioselectivities were obtained [Eq. (1)]. The diasteroselective construction of two neighboring centers of chirality is one of the strengths of the thermal Claisen rearrangement.[2] Therefore, we investigated the conditions under which the inherent diastereoselectivity of the thermal Claisen rearrangement can be combined with the enantioselectivity of the catalyzed Claisen rearrangement [Eq. (2)]. Once again, in agreement with our results with the Cu(OTf)$_2$/molecular sieve catalyzed Claisen rearrangement, the diastereoselectivity of the Claisen rearrangement was dependent on the configuration of the allyl ether double bond (Table 2). Allyl vinyl ethers with a *Z*-configured allyl ether double bond rearranged with very good diastereo- and enantioselectivities (Table 2, entries 3–5, 7, 9, 10). The relative configuration of the rearrangement product can be determined by the choice of the configuration of the vinyl ether double bond (Table 2, entries 3, 4). The relationship between the configuration of the double bond in the allyl vinyl ether and the relative configuration of the rearrangement product is the same in this case as for the thermal rearrangement ("(*Z*,*Z*) to *syn*" and "(*E*,*Z*) to *anti*").[2] This observation indicates a chair-shaped transition state in the catalyzed Claisen rearrangement of the allyl vinyl ethers **1i**–**l** which have a *Z*-configured allyl ether double bond.



(1)

R^5 = H: (*Z*)-**1g**
R^5 = Me: (*Z*)-**1h**

R^5 = H: 95 %, (*R*)-**2g**:(*S*)-**2g** = 84:16
R^5 = Me: 79 %, (*R*)-**2h**:(*S*)-**2h** = 75:25



(2)

The catalyzed Claisen rearrangement of allyl vinyl ethers with an *E*-configured allyl ether double bond is generally not completely diastereoselective. The extent of the diastereoselectivity is dependent on the configuration of the vinyl ether double bond and on the substituent at C1 (Table 2, entries 1, 2, 6, 8). The preference for the *syn* diastereomer in the catalyzed rearrangement of the *Z*,*E*-configured 1-isopropyl-substituted allyl vinyl ether (*Z*,*E*)-**1k** is particularly remarkable because, on the basis of a chair-type transition state, the formation of an *anti* diastereomer is expected (Table 2, entry 8).[15]

We have presented here the first catalytic enantioselective Claisen rearrangement. We exploited the potential of chiral, Lewis-acidic, [Cu^{II}(box)] catalysts and the ability of our 2-alkoxycarbonyl-sustituted allyl vinyl ethers to complex in a bidentate mode and thus, were able to achieve excellent chemoselectivities and acceptable enantioselectivities. Our current work focuses on the improvement of the enantiomeric excesses and substrate tolerances by variation of the substrate structure and the catalyst.

Experimental Section

General procedure: A mixture of the ligand (6–22 mol%) and Cu(OTf)$_2$ (5–20 mol%) in CH$_2$Cl$_2$ (2 mL) was stirred in a round-bottomed flask under argon at room temperature for 1–3 h. Subsequently, the corresponding allyl vinyl ether (0.4 mmol) in CH$_2$Cl$_2$ (2 mL) was added. After stirring for a suitable reaction time, the catalyst was removed by filtration of the reaction solution through a short column of silica gel (4 × 0.5 cm). The solvent was removed and the residue dried in a high vacuum to give the rearrangement product, which was generally an analytically pure colorless oil.

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Table 2. Diastereo- and enantioselectivity of the catalyzed Claisen rearrangement.

Entry	Substrate	R^1	Config.	*t* [h][a]	Yield [%][b]	*syn*:*anti*[c]	*ee* [%][d]
1	(*E*,*E*)-**1i**	methyl	1*E*,5*E*	12	100	86:14	82 (3*S*,4*R*)
2	(*Z*,*E*)-**1i**	methyl	1*Z*,5E	4	100	28:72	72 (3*R*,4*R*)
3	(*E*,*Z*)-**1i**	methyl	1*E*,5*Z*	38	99	3:97	88 (3*S*,4*S*)
4	(*Z*,*Z*)-**1i**	methyl	1*Z*,5*Z*	38	98	99:1	84 (3*R*,4*S*)
5	(*Z*,*Z*)-**1i**	methyl	1*Z*,5*Z*	12[e]	99	96:4	84 (3*R*,4*S*)
6	(*Z*,*E*)-**1j**	benzyl	1*Z*,5*E*	6	100	44:56	n.d.[f]
7	(*Z*,*Z*)-**1j**	benzyl	1*Z*,5*Z*	48	100	95:5	82 (3*R*,4*S*)
8	(*Z*,*E*)-**1k**	2-propyl	1*Z*,5*E*	7	96[g]	85:15	n.d.[f]
9	(*Z*,*Z*)-**1k**	2-propyl	1*Z*,5*Z*	24[h]	97	94:6	n.d.[f]
10	(*Z*,*Z*)-**1l**	2-propenyl	1*Z*,5*Z*	24	98	92:8	86 (3*R*,4*S*)

[a] Reaction time not optimized. [b] Yield of isolated, analytically pure product after removal of the catalyst by filtration through a column of silica gel (4 × 0.5 cm). Reactions were carried out with 0.4 mmol substrate. [c] Determined from the ^{1}H NMR spectra. [d] Determined by HPLC: Chiracel OD1 14025, hexane:*i*PrOH 99.9:0.1. Absolute configuration assigned by assumption of a (*S*,*S*,1*Z*,1*Si*) or (*S*,*S*,1*E*,1*Re*) topicity of a chair-shaped transition state. The *ee* value of the minor diastereomer could not be determined. [e] With 10 mol% catalyst. [f] n.d. = not determined. [g] In a mixture with 4% substrate. [h] With 7.5 mol% catalyst.

[1] L. Claisen, *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3157–3166.

[2] Reviews: a) F. E. Ziegler, *Chem. Rev.* **1988**, *88*, 1423–1452; b) H. Frauenrath in *Methods Org. Chem.* (*Houben-Weyl*) *4th ed. 1952–*, *Vol. E21d*, **1995**, pp. 3301–3756.

[3] T. P. Yoon, D. W. C. McMillan, *J. Am. Chem. Soc.* **2001**, *123*, 2911–2912.

[4] Reviews: a) H. Ito, T. Taguchi, *Chem. Soc. Rev.* **1999**, *28*, 43–50; b) D. Enders, M. Knopp, R. Schiffers, *Tetrahedron: Asymmetry* **1996**, *7*, 1847–1882.

[5] a) Y. Jiang, J. M. Longmire, X. Zhang, *Tetrahedron Lett.* **1999**, *40*, 1449–1450; b) Y. Donde, L. E. Overman, *J. Am. Chem. Soc.* **1999**, *121*, 2933–2934; c) Y. Uozumi, K. Kato, T. Hayashi, *Tetrahedron: Asymmetry* **1998**, *9*, 1065–1072; d) F. Cohen, L. E. Overman *Tetrahedron: Asymmetry* **1998**, *9*, 3213–3222; e) T. K. Hollis, L. E. Overman, *Tetrahedron Lett.* **1997**, *38*, 8837–8840; f) M. Calter, T. K. Hollis, L. E. Overman, J. Ziller, G. G. Zipp, *J. Org. Chem.* **1997**, *62*, 1449–1456.

[6] a) K. Maruoka, H. Banno, H. Yamamoto, *J. Am. Chem. Soc.* **1990**, *112*, 7791–7793; b) K. Maruoka, H. Yamamoto, *Synlett* **1991**, 793–794; c) K. Maruoka, H. Banno, H. Yamamoto, *Tetrahedron: Asymmetry* **1991**, *2*, 647–662.

[7] M. Hiersemann, L. Abraham, *Org. Lett.* **2001**, *3*, 49–52.

[8] See the cited literature in W. Zhuang, N. Gathergood, R. G. Hazell, K. A. Jørgensen, *J. Org. Chem.* **2001**, *66*, 1009–1013.

[9] Reviews: a) J. S. Johnson, D. A. Evans, *Acc. Chem. Res.* **2000**, *33*, 325–335; b) D. A. Evans, T. Rovis, J. S. Johnson, *Pure Appl. Chem.* **1999**, *71*, 1407–1415; c) A. K. Gosh, P. Mathivanan, J. Cappiello, *Tetrahedron: Asymmetry* **1998**, *9*, 1–45.

[10] The synthesis of the 2-alkoxycarbonyl-substituted allyl vinyl ethers corresponding to our procedure and subsequent separation of the vinyl ether double bond isomers by preparative HPLC: M. Hiersemann, *Synthesis* **2000**, 1279–1290.

[11] The absolute configuration was determined for, among others, the rearrangement product **2e** by chemical correlation using the auxiliary method of Evans et al.[12] Alkylation of (*S*)-3-(3,3-dimethyl-pent-4-enoyl)-4-isopropyl-oxazolidine-2-one (lithium diisopropylamide (LDA), THF, −78 °C, then benzyl bromide; 76 %), and subsequent reductive cleavage of the auxiliary group ($LiAlH_4$), THF, −78 °C → RT; 16 %) gave the alcohol (*S*)-(−)-2-benzyl-3,3-dimethyl-pent-4-en-1-ol with > 95 % *ee*. The reduction of **2e** (Table 1, entry 13) to the diol ($LiAlH_4$, THF, −78 °C → RT) and subsequent oxidative cleavage ($NaIO_4$, THF/H_2O, RT, 20 min) followed by a second reduction ($NaBH_4$, EtOH) gave (*S*)-(−)-2-benzyl-3,3-dimethyl-pent-4-en-1-ol with 79 % *ee* (85 % over the three steps).

[12] D. A. Evans, M. D. Ennis, D. J. Mathre, *J. Am. Chem. Soc.* **1982**, *104*, 1737–1739.

[13] a) M. Johannsen, K. A. Jørgensen, *J. Org. Chem.* **1995**, *60*, 5757–5762; b) D. A. Evans, J. S. Johnson, C. S. Burgey, K. R. Campos, *Tetrahedron Lett.* **1999**, *40*, 2879–2828; b) K. A. Jørgensen, *Angew. Chem.* **2000**, *112*, 3702–3733; *Angew. Chem.* **2000**, *39*, 3558–3588.

[14] D. A. Evans, S. W. Tregay, C. S. Burgey, N. A. Paras, T. Vojkovsky, *J. Am. Chem. Soc.* **2000**, *122*, 7936–7943.

[15] The thermal rearrangement of all the allyl vinyl ethers described here led, with very high to complete diastereoselectivity, to the diastereomer with the relative configuration that can be explained by the assumption of a chair-shaped transition state during the rearrangement.

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