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Tetrahedron
Tetrahedron 62 (2006) 9467–9474

Highly regioselective [3,3] rearrangement of aliphatic allyl vinyl ethers catalyzed by a metalloporphyrin complex, Cr(TPP)Cl

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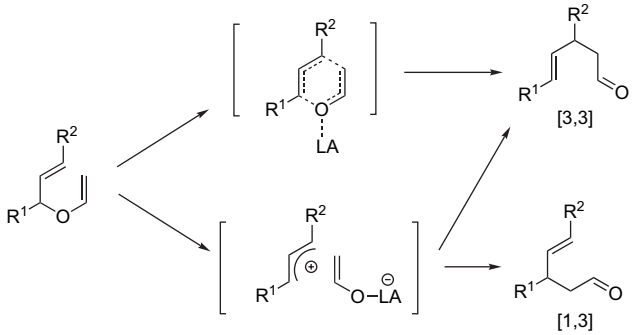
Received 2 June 2006; accepted 4 July 2006
Available online 14 August 2006

Abstract—The Claisen rearrangement of simple aliphatic allyl vinyl ethers catalyzed by a metalloporphyrin, Cr(TPP)Cl, is described. The porphyrin-based Lewis acid catalyst can effectively accelerate the rearrangement via a concerted [3,3] pathway with a minimal degree of bond ionization of the substrates, providing the corresponding Claisen products in moderate to high yields and almost perfect regioselectivity at low catalyst loading.

1. Introduction

The Claisen rearrangement, a [3,3] sigmatropic rearrangement of allyl vinyl ether, is a powerful carbon–carbon bond forming process[1,2] and its catalytic version employing a substoichiometric amount of metal catalysts is a topic of ongoing interest.[3] While the rearrangement using palladium- and related transition metal-based catalysts has been well developed,[3,4] only a few reports have appeared in the literature that utilize Lewis acids, especially in a catalytic fashion.[3,5–7] To date, several Lewis acids, including Al(III),[5] Sn(IV),[6] Cu(II),[7] and lanthanide(III)[7] Lewis acids, have been available for the Claisen rearrangement of aliphatic allyl vinyl ethers. These examples, however, require stoichiometric amounts of reagents or specific substrates such as 2-alkoxycarbonyl-substituted allyl vinyl ethers. In addition, most of these Lewis acid-mediated methods appear to suffer from a lack of regioselectivity, being troubled by the formation of the regioisomeric [1,3] rearrangement products. The reason might be that, under Lewis acid conditions, the rearrangement often proceeds through a process involving formation of an allyl cation and a metallo-enolate ion pair, which diverges from the generally accepted concerted mechanism, affording a regioisomeric mixture of [3,3]- and [1,3]-rearrangement products (Scheme 1).[8] Herein lies the difficulty with the Lewis acid-catalyzed Claisen rearrangement, as the ionic intermediates may be long-lived, to give rise to undesired regioisomeric [1,3] products. Actually, Rovis and Nasveschuk recently reported that an increase in the strength of the Lewis acid and/or in stability of the allyl cation results in increased [1,3] selectivity.[9,10] Although bulky organoaluminum Lewis acids, such as MABR, ATPH, and BINAL, developed by Yamamoto et al., are known as indeed potential reagents capable of circumventing these problems associated with the Lewis acid-mediated Claisen rearrangement. These aluminum Lewis acids are, unfortunately, a stoichiometric reagent rather than a catalyst: more than a stoichiometric amount of the reagent is usually necessary to promote the rearrangement.[5,11]



Scheme 1. Putative mechanistic scheme for the competitive formation of the [3,3] and [1,3] adducts in the Lewis acid-mediated Claisen rearrangement of aliphatic allyl vinyl ethers.

Recently, we have reported that a metalloporphyrin complex, Cr(TPP)Cl, can be used as a mild and efficient Lewis acid catalyst, and it enhances reversal *E*/*Z* selectivity in the thermal Claisen rearrangement of 4,5- and 4,6-disubstituted allyl vinyl ethers.[12–14] The purpose of this paper is to describe our results concerning the reactivity, regioselectivity, and scope of the Cr(TPP)Cl catalyst system in the Claisen rearrangement of simple aliphatic allyl vinyl ethers. This metalloporphyrin-based weak Lewis acid catalyst can

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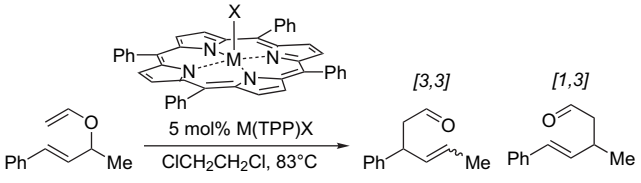
0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.07.051

effectively depress the formation of ionic intermediates, yet enhances the concerted [3,3] process, exhibiting high regioselectivity over a broad range of substrates, exclusively providing the corresponding Claisen products in good to high yields, in a fully catalytic fashion.

2. Results and discussion

We initiated our studies by subjecting the vinyl ether of 4-phenyl-3-buten-2-ol **1a** to 5 mol % of Cr(TPP)Cl in dichloroethane at 83 °C for 7 h. While only moderate regioselectivity ([3,3]:[1,3]=1:1 to 1:2) has been reported for the rearrangement of **1a** with various Lewis acids, such as $Cu(OTf)_2$, $SnCl_4$, $TiCl_4$, and $B(C_6F_5)_3$,[9,10b] under the present catalytic conditions utilizing Cr(TPP)Cl catalyst, the substrate **1a** was cleanly converted to the [3,3] adduct **2a** in 94% yield; no other products including [1,3] adduct **4a** could be identified via ^1H NMR analysis of the crude reaction mixture (Table 1, entry 1). In the absence of the metalloporphyrin catalyst, the rearrangement was quite sluggish, and did not complete over 48 h, giving the [3,3] adduct **2a** as the sole product in only 40% yield (Table 1, entry 2). Regioselective transformation of **1a** to **2a** could also be accomplished with other metalloporphyrin catalysts, such as Fe(TPP)Cl and Mn(TPP)Cl (Table 1, entries 3 and 4). Likewise, metallosalen complexes, Cr(salen)Cl and Mn(salen)Cl, could serve as a highly regioselective catalyst for the rearrangement (Table 1, entries 5 and 6).[15] In both cases, however, the highest yield never exceeded 85%. On the other hand, stronger Lewis acid catalysts, Cr(TPP)OTf and Fe(TPP)OTf, which may enhance bond ionization of the substrate, proved less effective for the [3,3] selectivity, affording the undesired [1,3] adducts **4a** as the major products in 26 and 27% yields, respectively, along with the [3,3] adducts **2a** in less than 20% yield (Table 1, entries 7 and 8). Thus, the use of porphyrin catalysts possessing weaker Lewis acidity, especially the chromium complex Cr(TPP)Cl, was found to be effective to achieve high [3,3] selectivity in the Claisen rearrangement of aliphatic allyl vinyl ethers, and these observations are consistent with the hypothesis that a weaker Lewis acid is capable of accelerating the Claisen rearrangement via a concerted [3,3] pathway, while stronger Lewis acids result in bond ionization.[9]

Table 1. Porphyrin-based Lewis acid-catalyzed Claisen rearrangement of vinyl ether of 4-phenyl-3-buten-2-ol **1a**



1a **2a** **4a**

Entry	Catalyst	Time (h)	**2a** (%) (*E*/*Z*)[a,b]	**4a** (%)[a]
1	Cr(TPP)Cl	7	94 (15:85)	—
2	None	58	40 (94:6)	—
3	Mn(TPP)Cl	24	62 (94:6)	—
4	Fe(TPP)Cl	24	83 (95:5)	—
5	Cr(salen)Cl[c]	11	59 (85:15)	—
6	Mn(salen)Cl[d]	24	62 (94:6)	—
7	Cr(TPP)OTf	24	19 (77:23)	26[e]
8	Fe(TPP)OTf	2	16 (>99:1)	27[e]

[a] Isolated yield.
[b] *E*/*Z* ratios were determined by 300 MHz ^1H NMR.
[c] Cr(salen)Cl: (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino chromium(III) chloride.
[d] Mn(salen)Cl: (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino manganese(III) chloride.
[e] An inseparable complex mixture of by-products was also produced in the catalytic rearrangement.

To assess the inherent regioselectivity of the chromium porphyrin catalyst, Cr(TPP)Cl, we then explored the reactivity of several cinnamyl vinyl ethers **1**. Although these substrates **1** are known to be less suited for the [3,3] selectivity,[9] the presence of 5 mol % of Cr(TPP)Cl[16] led to the formation of the corresponding [3,3] adducts **2** in moderate to high yields and excellent regioselectivity (Table 2). In the catalytic process, substituents on the vinyl moiety in the substrates did not affect the regioselectivity (Table 2, entries 2 and 3). Notably, even in the presence of an electron-donating substituent on the ring, the rearrangements occurred with high [3,3] selectivity, giving the Claisen adducts solely in good yields (Table 2, entries 6 and 7).

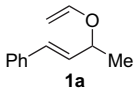
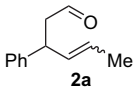
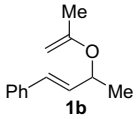
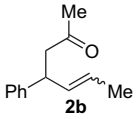
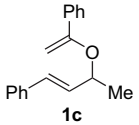
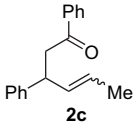
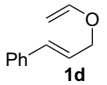
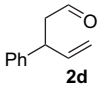
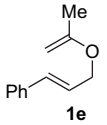
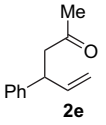
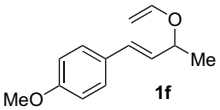
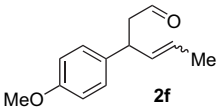
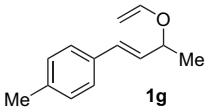
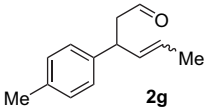
As illustrated in Table 3, allyl vinyl ethers beyond those derived from cinnamyl alcohol also underwent the catalytic [3,3] rearrangement. For example, the Cr(TPP)Cl-catalyzed rearrangement of the substrates **3a** and **3b**, which are the regio isomers of **1a** and **1d**, respectively, took place smoothly to give the corresponding [3,3] adducts, **4a** and **4b**, as the sole products in high yields (Table 3, entries 1 and 2). Replacing the Ph substituent of **1a**, **1b**, and **1c** with a Bu group (**3c**, **3d**, and **3e**) also produced the corresponding Claisen products, **4c**, **4d**, and **4e**, respectively, in high yields and excellent regioselectivity (Table 3, entries 3–5).

To further explore the scope of the [3,3] rearrangement of allyl vinyl ethers, the rearrangement of the substrates **5** bearing trisubstituted alkenes in the allyl systems was examined. It has been known that the rearrangement of trisubstituted allyl vinyl ethers **5** generally provides high [1,3] selectivity with a range of Lewis acids, such as $Cu(OTf)_2$, $SnCl_4$, $TiCl_4$, Me_2AlCl, and $EtAlCl_2$: under such ionizing conditions, recombination of the metallo-enolate and allyl cation at the less hindered secondary position to give [1,3] adducts should be fast compared with [3,3] recombination to form a quaternary carbon center at the tertiary cation (Fig. 1).[9] However, when the Cr(TPP)Cl catalyst was applied to the substrates **5**, moderate to high-yielding [3,3] rearrangement to create quaternary carbon centers occurred without any formation of the corresponding [1,3] products (Table 4). In addition, under the present catalytic conditions, all the substrates examined generally rearranged more rapidly and had higher yields of the [3,3] products than those rearrangements performed under non-catalytic thermal conditions (see footnotes in Tables 2–4). These findings, thus, should lend significant support to our view that the Cr(TPP)Cl catalyst can exert its influence on accelerating the rearrangement via a concerted [3,3] pathway with a minimal degree of bond ionization (Scheme 1).

3. Conclusion

In summary, we have shown a regioselective Claisen rearrangement of simple aliphatic allyl vinyl ethers utilizing

Table 2. Cr(TPP)Cl-catalyzed Claisen rearrangement of cinnamyl vinyl ethers[a]

Entry	Substrates	Products	Time (h)	Yield (%) (*E*/*Z*)[b,c,d]
1	 **1a**	 **2a**	7	94 (15:85)
2	 **1b**	 **2b**	5	93 (69:31)
3	 **1c**	 **2c**	0.5	82 (76:24)
4	 **1d**	 **2d**	52	41
5	 **1e**	 **2e**	6	72
6	 **1f**	 **2f**	7	62 (38:62)
7	 **1g**	 **2g**	8	57 (39:61)

[a] Conditions: 5 mol % Cr(TPP)Cl, $ClCH_2CH_2Cl$, 83 °C.
[b] Isolated yield.
[c] *E*/*Z* ratios were determined by 300 MHz ^1H NMR.
[d] The reaction time, yields, and *E*/*Z* ratios obtained in the non-catalytic thermal rearrangement ($ClCH_2CH_2Cl$, 83 °C) of **1a–g** were as follows: **2a** (58 h, 40%, *E*/*Z*=94:6); **2b** (48 h, 74%, *E*/*Z*>99:1); **2c** (4 h, 43%, *E*/*Z*>99:1); **2d** (93 h, 15%); **2e** (48 h, 10%); **2f** (50 h, 76%, *E*/*Z*=94:6); **2g** (25 h, 54%, *E*/*Z*=98:2).

a metalloporphyrin-based Lewis acid catalyst, Cr(TPP)Cl, at low catalyst loading. This weak Lewis acid catalyst, Cr(TPP)Cl, is believed to accelerate the rearrangement via a concerted [3,3] pathway, and can provide the corresponding Claisen adducts in good to high yields, with almost perfect regioselectivity. The sense of regioselectivity observed in the catalytic process is hardly attainable with any other Lewis acid reagents or catalysts thus far reported for the Claisen rearrangement, where bond ionization of the substrates usually takes place to give a regioisomeric mixture of [3,3] and [1,3] adducts. Moreover, the present catalytic reaction provides a complementary method to the [1,3] selectivity obtained by Rovis and Nasveschuk.[9] Current efforts are directed at second-generation designs for the porphyrin-based Lewis acid catalysts that will lead to catalytic asymmetric Claisen rearrangement of simple aliphatic allyl vinyl ethers.

4. Experimental

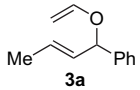
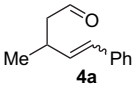
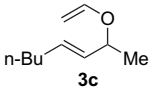
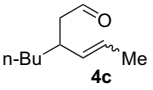
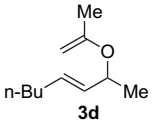
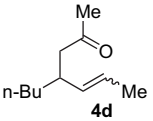
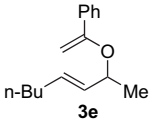
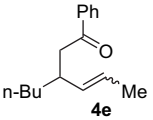
4.1. General

^1H and ^{13}C NMR spectra were recorded on JEOL JNM-EX270, JNM-AL300, and JNM-GSX400 spectrometers. The chemical shifts were reported in parts per million relative to $CHCl_3$ (δ=7.24) for ^1H NMR and relative to the central $CDCl_3$ resonance (δ=77.0) for ^{13}C NMR. IR spectra were recorded on a JASCO FT/IR-7000 spectrophotometer. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer. Column chromatography was performed on Merck silica gel 60 (230–400 mesh). 1,2-Dichloroethane was distilled from CaH_2. Chromium(III) and iron(III) tetraphenylporphyrin complexes, Cr(TPP)Cl,[17] Cr(TPP)OTf,[13a] and Fe(TPP)OTf,[13a] were prepared by the literature methods. Fe(TPP)Cl was purchased from Aldrich Chemical Co. Other chemicals were commercial products and were used without further purifications.

4.2. General procedure for the preparation of vinyl and isopropenyl ethers of allylic alcohols[18]

A mixture of allylic alcohol (30 mmol), mercury(II) acetate (6.4 g, 20 mmol), and freshly distilled ethyl vinyl ether or 2-methoxypropene (150 mL) was heated under reflux for 30 h under an argon atmosphere. The reaction mixture was quenched with 5% KOH aqueous solution (30 mL) and extracted with *n*-hexane. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on alumina (Merck Aluminum

Table 3. Cr(TPP)Cl-catalyzed Claisen rearrangement of allyl vinyl ethers[a]

Entry	Substrates	Products	Time (h)	Yield (%) (*E*/*Z*)[b,c,d]
1	 **3a**	 **4a**	9	86 (>99:1)
2	 **3b**	 **4b**	2	93 (>99:1)
3	 **3c**	 **4c**	12	62 (28:72)
4	 **3d**	 **4d**	3	89 (77:23)
5	 **3e**	 **4e**	1	93 (80:20)

[a] Conditions: 5 mol % Cr(TPP)Cl, $ClCH_2CH_2Cl$, 83 °C.
[b] Isolated yield.
[c] *E*/*Z* ratios were determined by 300 MHz ^1H NMR.
[d] The reaction time, yields, and *E*/*Z* ratios obtained in the non-catalytic thermal rearrangement ($ClCH_2CH_2Cl$, 83 °C) of **3a–e** were as follows: **4a** (30 h, 83%, *E*/*Z*>99:1); **4b** (24 h, 70%, *E*/*Z*>99:1); **4c** (24 h, 22%, *E*/*Z*=97:3); **4d** (24 h, 59%, *E*/*Z*>99:1); **4e** (6 h, 90%, *E*/*Z*>99:1).

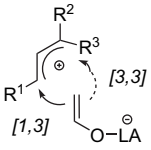
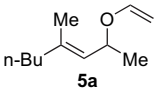
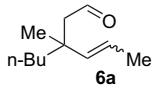
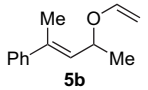
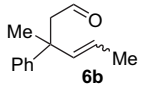
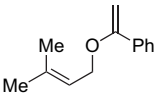
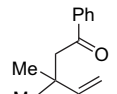


Figure 1. [1,3] Selective rearrangement of trisubstituted allyl vinyl ethers **6** under ionic conditions.

Oxide 90 active basic, activity III) using hexane as an eluent to give the corresponding allyl vinyl ethers in 95–60% yields. The following obtained allyl vinyl ethers are known compounds: (*E*)-1-phenyl-3-vinyloxybut-1-ene (**1a**),[9] (*E*)-1-phenyl-3-vinyloxyprop-1-ene (**1d**),[5i] (*E*)-1-phenyl-3-isopropenyloxyprop-1-ene (**1e**),[19] (*E*)-1-(4-methoxyphenyl)-3-vinyloxybut-1-ene (**1f**),[9] (*E*)-1-(4-methylphenyl)-3-vinyloxybut-1-ene (**1g**),[9] (*E*)-4-phenyl-4-vinyloxybut-2-ene (**3a**),[9] 3-phenyl-3-vinyloxyprop-1-ene (**3b**),[5d] (*E*)-4-methyl-2-vinyloxyoct-3-ene (**5a**),[9] and (*E*)-2-phenyl-4-vinyloxypent-2-ene (**5b**).[9]

4.2.1. (*E*)-1-Phenyl-3-isopropenyloxybut-1-ene (1b). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31–7.12 (m, 5H), 6.45 (d, *J*=16.1 Hz, 1H), 6.12 (dd, *J*=16.1 and 6.2 Hz, 1H), 4.62 (dq, *J*=6.2 and 6.2 Hz, 1H), 3.84 (br d, *J*=3.3 Hz, 2H), 1.77 (s, 3H), 1.34 (d, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$,

Table 4. Cr(TPP)Cl-catalyzed Claisen rearrangement of trisubstituted allyl vinyl ethers[a]

Entry	Substrates	Products	Time (h)	Yield (%) (*E*/*Z*)[b,c,d]
1	 **5a**	 **6a**	20	57 (>99:1)
2	 **5b**	 **6b**	50	51 (>99:1)
3	 **5c**	 **6c**	3	78

[a] Conditions: 5 mol % Cr(TPP)Cl, $ClCH_2CH_2Cl$, 83 °C.
[b] Isolated yield.
[c] *E*/*Z* ratios were determined by 300 MHz ^1H NMR.
[d] The reaction time, yields, and *E*/*Z* ratios obtained in the non-catalytic thermal rearrangement ($ClCH_2CH_2Cl$, 83 °C) of **5a–c** were as follows: **6a** (70 h, 38%, *E*/*Z*>99:1); **6b** (98 h, 30%, *E*/*Z*>99:1); **6c** (48 h, 27%).

100 MHz) δ 157.9, 136.7, 130.8, 129.8, 128.4, 127.4, 126.3, 83.0, 73.0, 21.7, 21.3. Exact EIMS calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1198.

4.2.2. (*E*)-2-Vinyloxyoct-3-ene (3c). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.30 (dd, *J*=6.4 and 14.1 Hz, 1H), 5.58–5.67 (m, 1H), 5.44–5.35 (m, 1H), 4.28 (dd, *J*=14.1 and 1.5 Hz, 1H), 4.26 (dq, *J*=6.4 and 6.4 Hz, 1H), 3.97 (dd, *J*=6.4 and 1.5 Hz, 1H), 2.05–1.99 (m, 2H), 1.27 (d, *J*=6.4 Hz, 3H), 1.40–1.26 (m, 4H), 0.88 (t, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.2, 132.9, 130.7, 88.5, 76.6, 31.9, 31.3, 22.5, 21.3, 14.0. Exact EIMS calcd for $C_{10}H_{18}O$: 154.1358. Found: 154.1356.

4.2.3. (*E*)-2-Isopropenyloxyoct-3-ene (3d). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.59 (dt, *J*=15.5 and 6.6 Hz, 1H), 5.41 (dd, *J*=15.5 and 6.2 Hz, 1H), 4.46 (dq, *J*=6.3 and 6.3 Hz, 1H), 3.86 (br s, 1H), 3.82 (br s, 1H), 2.01 (q, *J*=6.8 Hz, 2H), 1.78 (s, 3H), 1.41–1.28 (m, 4H), 1.27 (d, *J*=6.4 Hz, 3H), 0.87 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 158.6, 132.2, 131.5, 83.1, 73.5, 32.4, 31.8, 22.6, 22.1, 21.6, 14.4. Exact EIMS calcd for $C_{11}H_{20}O$: 168.1514. Found: 168.1514.

4.3. Preparation of α-styryl ether of allylic alcohols by methylenation of esters with a Zn–$TiCl_4$–TMEDA reagent system[20]

Under an argon atmosphere, 2.0 M solution of $TiCl_4$ (4 mmol) in dichloromethane was added to THF (10 mL) at 0 °C. After the resulting yellow suspension was warmed to 25 °C, TMEDA (1.2 mL, 8 mmol) was added. The brown solution was stirred for 10 min, and then acid washed zinc powder (1.6 g, 9 mmol) was added at 25 °C. After being stirred at 25 °C for 30 min, the color of the suspension changed from dark brown to dark greenish blue. Dibromomethane (0.15 mL, 2.1 mmol) and a solution of the ester (1.0 mmol) in THF (1 mL) were added to the mixture. The color of the resulting mixture gradually turned to dark brown while being stirred at 25 °C for 2 h. After hydrolysis with a saturated K_2CO_3 solution (1.3 mL) at 0 °C, the reaction mixture was diluted with ether (5 mL) and filtered through a short column of alumina (Merck Aluminum Oxide 90 active basic, activity III) using pentane as a solvent. The solvent was removed under a reduced pressure and the residue was purified by column chromatography on alumina (Merck Aluminum Oxide 90 active basic, activity III) using *n*-hexane/Et_3N (200:1) as an eluent to give the corresponding allyl vinyl ethers in 45–20% yields.

4.3.1. (*E*)-1-Phenyl-3-(α-styryl)oxybut-1-ene (1c). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65–7.59 (m, 2H), 7.39–7.18 (m, 8H), 6.58 (d, *J*=16.1 Hz, 1H), 6.27 (dd, *J*=16.1 and 6.2 Hz, 1H), 4.86 (dq, *J*=6.2 and 6.2 Hz, 1H), 4.70 (d, *J*=2.7 Hz, 1H), 4.29 (d, *J*=2.7 Hz, 1H), 1.52 (d, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.2, 136.8, 136.5, 130.6, 130.1, 128.4, 128.2, 127.9, 127.5, 126.3, 125.4, 84.8, 73.9, 21.5. Exact EIMS calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1357.

4.3.2. 2-(α-Styryl)oxyoct-3-ene (3e). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58–7.53 (m, 2H), 7.29–7.22 (m, 3H), 5.61 (dt, *J*=15.6 and 6.5 Hz, 1H), 5.46 (dd, *J*=15.6 and 6.2 Hz, 1H), 4.62 (d, *J*=2.4 Hz, 1H), 4.60 (dq, *J*=6.2 and 6.2 Hz, 1H), 4.18 (d, *J*=2.4 Hz, 1H), 1.99 (q, *J*=6.8 Hz, 2H), 1.36 (d, *J*=6.2 Hz, 3H), 1.31–1.21 (m, 4H), 0.84 (t, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 158.5, 137.2, 132.0, 130.9, 128.2, 128.0, 125.5, 84.4, 73.9, 31.9, 31.3, 22.2, 21.4, 13.9. Exact EIMS calcd for $C_{16}H_{22}O$: 230.1671. Found: 230.1675.

4.3.3. 2-Methyl-4-(α-styryl)oxybut-2-ene (5c). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63–7.57 (m, 2H), 7.34–7.27 (m, 3H), 5.50 (br t, *J*=6.6 Hz, 1H), 4.64 (d, *J*=2.6 Hz, 1H), 4.40 (br d, *J*=6.6 Hz, 2H), 4.21 (d, *J*=2.6 Hz, 1H), 1.79 (s, 3H), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 159.9, 137.2, 136.7, 128.3, 128.0, 125.4, 119.9, 82.4, 64.8, 25.7, 18.2. Exact EIMS calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1200.

4.4. General procedure for the Cr(TPP)Cl-catalyzed Claisen rearrangements of allyl vinyl ethers to γ,δ-unsaturated carbonyl compounds

The catalyst Cr(TPP)Cl was dried over silica gel for 10 h under a reduced pressure (1 mmHg) at 100 °C just before its use. To a round bottle flask (5 mL) equipped with a three-way stopcock and a stirring bar were successively added an allyl vinyl ether (1 mmol), a freshly distilled 1,2-dichloroethane (3 mL), and Cr(TPP)Cl (35 mg, 0.05 mmol). The mixture was stirred at 83 °C under an argon atmosphere. After completion of the reaction (monitored by TLC analysis), the solution was directly passed through a silica gel column (AcOEt/*n*-hexane = 1:50) to give the corresponding Claisen rearrangement product. The configurations of the double bonds in the products were established by comparison of their ^{1}H and ^{13}C NMR data with those of γ,δ-unsaturated aldehydes or ketones with *E*-configuration, which were prepared from non-catalytic thermal Claisen rearrangement reactions of the corresponding allyl vinyl ethers in dichloroethane at 83 °C (the reaction time, yields, and *E*/*Z* ratios are listed in the footnotes of Tables 2–4).[21] The following obtained γ,δ-unsaturated aldehydes and ketones are known compounds: (*E*)-1,3-diphenylhex-4-en-1-one (*E*-**2c**),[22] 3-phenylpent-4-enal (**2d**),[5d] 4-phenylhex-5-en-2-one (**2e**),[23] (*E*)-5-phenylpent-4-enal (**4b**),[5d] (*E*)-4-propenyloctan-2-one (*E*-**4d**),[24] and 3,3-dimethyl-1-phenylpent-4-en-1-one (**6c**).[25]

4.4.1. 3-Phenylhex-4-enal (2a) (*E*/*Z*=15:85).[12] Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.71 (t, *J*=2.2 Hz, 1H×0.85, C*H*O in (*Z*)-**2a**), 9.70 (t, *J*=2.0 Hz, 1H×0.15, C*H*O in (*E*)-**2a**), 7.33–7.17 (m, 5H), 5.64–5.46 (m, 2H, C*H*=C*H*), 4.24 (q, *J*=8.2 Hz, 1H×0.85, PhC*H* in (*Z*)-**2a**), 3.89 (q, *J*=7.3 Hz, 1H×0.15, PhC*H* in (*E*)-**2a**), 2.87–2.69 (m, 2H), 1.67 (d, *J*=5.1 Hz, 3H×0.85, CH_3 in (*Z*)-**2a**), 1.67 (d, *J*=5.9 Hz, 3H×0.15, CH_3 in (*Z*)-**2a**); ^{13}C NMR ($CDCl_3$, 100 MHz) for (*E*)-**2a**: δ 201.3, 142.9, 132.9, 128.6, 127.3, 126.5, 125.9, 49.3, 42.9, 18.0; ^{13}C NMR ($CDCl_3$, 100 MHz) for (*Z*)-**2a**: δ 201.1, 143.2, 132.1, 128.6, 126.9, 126.4, 125.0, 50.1, 37.4, 14.3; IR (neat) 2866, 1725, 1603, 1493, 1454, 758, 719, 700 cm^{-1}. Exact EIMS calcd for $C_{12}H_{14}O$: 174.1045. Found: 174.1047.

4.4.2. 4-Phenylhept-5-en-2-one (2b) (*E*/*Z*=69:31). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30–7.14 (m, 5H), 5.60–5.37 (m, 2H, C*H*=C*H*), 4.19 (q, *J*=7.5 Hz,

1H×0.31, PhC*H* in (*Z*)-**2b**), 3.82 (q, *J*=7.2 Hz, 1H×0.69, PhC*H* in (*E*)-**2b**), 2.81–2.78 (m, 2H), 2.07 (s, 3H×0.31, COCH_3 in (*Z*)-**2b**), 2.06 (s, 3H×0.69, COCH_3 in (*E*)-**2b**), 1.68 (d, *J*=5.1 Hz, 3H×0.31, CH=CHCH_3 in (*Z*)-**2b**), 1.63 (d, *J*=6.2 Hz, 3H×0.69, CH=CHCH_3 in (*E*)-**2b**); ^{13}C NMR ($CDCl_3$, 100 MHz) for (*E*)-**2b**: δ 207.0, 143.6, 133.3, 128.4, 127.3, 126.3, 125.3, 49.8, 44.0, 30.7, 18.0; ^{13}C NMR ($CDCl_3$, 100 MHz) for (*Z*)-**2b**: δ 206.5, 143.6, 132.6, 128.5, 127.0, 126.2, 124.7, 50.5, 44.1, 31.2, 14.3; IR (neat) 2920, 1717, 1603, 1493, 1454, 1359, 1162, 969, 754, 733, 540 cm^{-1}. Exact EIMS calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1199.

4.4.3. 1,3-Diphenylhex-4-en-1-one (2c) (*E*/*Z*=76:24). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.93–7.89 (m, 2H), 7.56–7.40 (m, 3H), 7.30–7.14 (m, 5H), 5.68–5.38 (m, 2H, C*H*=C*H*), 4.40 (dt, *J*=8.3 and 6.3 Hz, 1H×0.24, PhC*H* in (*Z*)-**2c**), 4.05 (dt, *J*=7.0 and 7.0 Hz, 1H×0.76, PhC*H* in (*E*)-**2c**), 3.42–3.25 (m, 2H), 1.65 (dd, *J*=6.3 and 1.4 Hz, 3H×0.24, m, CH_3 in (*Z*)-**2c**), 1.62 (ddd, *J*=6.3, 1.5, and 1.1 Hz, 3H×0.76, CH_3 in (*E*)-**2c**); ^{13}C NMR ($CDCl_3$, 100 MHz) for (*E*)-**2c**: δ 198.2, 143.9, 137.1, 133.4, 132.8, 128.4, 128.0, 127.9, 127.4, 126.2, 125.4, 44.8, 43.9, 18.1; ^{13}C NMR ($CDCl_3$, 100 MHz) for (*Z*)-**2c**: δ 197.7, 144.3, 137.1, 133.4, 132.7, 128.5, 128.4, 127.9, 127.1, 126.1, 124.8, 45.7, 38.9, 13.3; IR (neat) 2920, 1688, 1601, 1582, 1493, 1452, 971 cm^{-1}. Exact EIMS calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1361. Anal. calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25; O, 6.39. Found: C, 86.47; H, 7.33.

4.4.4. 3-(4-Methoxyphenyl)hex-4-enal (2f) (*E*/*Z*=38:62). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.68 (t, *J*=2.2 Hz, 1H×0.62, C*H*O in (*Z*)-**2f**), 9.67 (t, *J*=2.2 Hz, 1H×0.38, C*H*O in (*E*)-**2f**), 7.13 (d, *J*=8.7 Hz, 2H), 6.83 (d, *J*=8.7 Hz, 2H), 5.58–5.46 (m, 2H, C*H*=C*H*), 4.18 (q, *J*=6.8 Hz, 1H×0.62, ArC*H* in (*Z*)-**2f**), 3.83 (q, *J*=7.1 Hz, 1H×0.38, ArC*H* in (*E*)-**2f**), 3.76 (s, 3H, OCH_3), 2.82–2.64 (m, 2H), 1.69 (d, *J*=5.1 Hz, 3H×0.62, CH=CHCH_3 in (*Z*)-**2f**), 1.64 (d, *J*=5.9 Hz, 3H×0.38, CH=CHCH_3 in (*E*)-**2f**); ^{13}C NMR ($CDCl_3$, 67.8 MHz) for (*E*)-**2f**: δ 201.9, 158.3, 135.1, 133.3, 128.3, 125.7, 114.1, 55.3, 49.3, 42.0, 17.9; ^{13}C NMR ($CDCl_3$, 67.8 MHz) for (*Z*)-**2f**: δ 201.7, 158.2, 135.5, 132.6, 128.0, 124.7, 114.0, 55.2, 50.2, 36.5, 13.1; IR (neat) 3828, 2840, 1725, 1611, 1584, 1514, 1251, 1180, 1036, 971, 830 cm^{-1}. Exact EIMS calcd for $C_{13}H_{16}O_2$: 204.1150. Found: 204.1149.

4.4.5. 3-(*p*-Tolyl)hex-4-enal (2g) (*E*/*Z*=39:61). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.68 (t, *J*=2.2 Hz, 1H×0.61, C*H*O in (*Z*)-**2g**), 9.68 (t, *J*=2.2 Hz, 1H×0.39, C*H*O in (*E*)-**2g**), 7.16–7.04 (m, 4H), 5.58–5.47 (m, 2H, C*H*=C*H*), 4.19 (q, *J*=6.6 Hz, 1H×0.61, ArC*H* in (*Z*)-**2g**), 3.84 (q, *J*=7.3 Hz, 1H×0.39, ArC*H* in (*E*)-**2g**), 2.84–2.66 (m, 2H), 2.30 (s, 3H, ArCH_3), 1.69 (d, *J*=5.1 Hz, 3H×0.61, CH=CHCH_3 in (*Z*)-**2g**), 1.64 (d, *J*=5.9 Hz, 3H×0.39, CH=CHCH_3 in (*E*)-**2g**); ^{13}C NMR ($CDCl_3$, 67.8 MHz) for (*E*)-**2g**: δ 201.9, 140.0, 136.2, 133.2, 129.4, 127.2, 125.8, 49.2, 42.4, 21.0, 17.9; ^{13}C NMR ($CDCl_3$, 67.8 MHz) for (*Z*)-**2g**: δ 201.7, 158.6, 135.9, 128.3, 128.0, 124.7, 114.1, 55.2, 50.2, 36.5, 13.1; IR (neat) 2924, 2728, 1721, 1516, 1452, 1417, 1381, 1112, 1044, 1021, 969, 816 cm^{-1}. Exact EIMS calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1202.

4.4.6. (*E*)-3-Methyl-5-phenylpent-4-enal (4a). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.76 (t, *J*=2.2 Hz, 1H, C*H*O), 7.34–7.17 (m, 5H), 6.40 (d, *J*=15.9 Hz, 1H, CH=C*H*–Ph), 6.14 (dd, *J*=15.9 and 7.3 Hz, 1H, C*H*=CH–Ph), 2.99–2.89 (m, 1H, MeC*H*), 2.59–2.38 (m, 2H), 1.16 (d, *J*=6.8 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 202.1, 137.1, 133.9, 129.1, 128.5, 127.3, 126.1, 50.4, 31.9, 20.4; IR (neat) 694, 750, 969, 1073, 1450, 1493, 1601, 1725, 2968 cm^{-1}. Exact EIMS calcd for $C_{12}H_{14}O$: 174.1045. Found: 174.1048.

4.4.7. 3-Propenylheptanal (4c) (*E*/*Z*=28:72).[5d,12] Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 (t, *J*=2.4 Hz, 1H×0.28, C*H*O in (*E*)-**4c**), 9.66 (t, *J*=2.4 Hz, 1H×0.72, C*H*O in (*Z*)-**4c**), 5.49 (ddq, *J*=10.4, 6.8, and 0.9 Hz, 1H×0.72, CH=C*H*–Me in (*Z*)-**4c**), 5.45 (ddq, *J*=15.2, 5.9, and 0.7 Hz, 1H×0.28, CH=C*H*–Me in (*E*)-**4c**), 5.24 (ddq, *J*=15.2, 8.3, and 1.5 Hz, 1H×0.28, C*H*=CH–Me in (*E*)-**4c**), 5.13 (ddq, *J*=10.4, 10.4, and 1.8 Hz, 1H×0.72, C*H*=CH–Me in (*Z*)-**4c**), 2.97–2.84 (m, 1H×0.72, BuC*H* in (*Z*)-**4c**), 2.58–2.48 (m, 1H×0.28, BuC*H* in (*E*)-**4c**), 2.44–2.23 (m, 2H), 1.63 (dd, *J*=5.9 and 1.7 Hz, 3H×0.32, CH=CH–CH_3 in (*E*)-**4c**), 1.62 (dd, *J*=6.8 and 1.6 Hz, 3H×0.72, CH=CH–CH_3 in (*Z*)-**4c**), 1.36–1.14 (m, 6H), 0.86 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) for (*E*)-**4c**: δ 202.7, 133.6, 125.7, 49.2, 37.6, 35.1, 29.3, 22.7, 18.0, 14.2; ^{13}C NMR ($CDCl_3$, 100 MHz) for (*Z*)-**4c**: δ 202.4, 133.2, 124.7, 49.7, 37.6, 35.4, 29.4, 22.8, 18.0, 14.2; IR (neat) 1729, 1460, 1408, 1379, 1263, 1067, 969, 932, 803, 729 cm^{-1}. Exact EIMS calcd for $C_{10}H_{18}O$: 154.1358. Found: 154.1353.

4.4.8. 4-Propenyloctan-2-one (4d) (*E*/*Z*=77:23). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.51–5.34 (m, 1H, CH=C*H*–Me), 5.19 (ddq, *J*=15.2, 8.3, and 1.6 Hz, 1H×0.77, C*H*=CH–Me in (*E*)-**4d**), 5.08 (ddq, *J*=9.9, 9.9, and 1.8 Hz, 1H×0.23, C*H*=CH–Me in (*Z*)-**4d**), 2.93–2.80 (m, 1H×0.23, BuC*H* in (*Z*)-**4d**), 2.50–2.43 (m, 1H×0.77, BuC*H* in (*E*)-**4d**), 2.42–2.26 (m, 2H), 2.09 (s, 3H×0.23, COCH_3 in (*Z*)-**4d**), 2.08 (s, 3H×0.77, COCH_3 in (*E*)-**4d**), 1.61 (dd, *J*=6.2 and 1.6 Hz, 3H×0.77, CH=CH–CH_3 in (*E*)-**4d**), 1.61 (dd, *J*=7.0 and 1.5 Hz, 3H×0.23, CH=CH–CH_3 in (*Z*)-**4d**), 1.31–1.18 (m, 6H), 0.86 (t, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) for (*E*)-**4d**: δ 208.3, 133.9, 125.2, 49.9, 38.8, 35.1, 30.6, 29.4, 22.8, 18.0, 14.2; ^{13}C NMR ($CDCl_3$, 100 MHz) for (*Z*)-**4d**: δ 208.2, 133.7, 124.4, 50.2, 38.8, 35.4, 30.7, 29.5, 22.9, 18.0, 13.3; IR (neat) 729, 969, 1166, 1359, 1458, 1717, 2930 cm^{-1}. Exact EIMS calcd for $C_{11}H_{20}O$: 168.1514. Found: 168.1514.

4.4.9. 1-Phenyl-3-propenylheptan-1-one (4e) (*E*/*Z*=80:20). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92–7.89 (m, 2H), 7.55–7.40 (m, 3H), 5.48–5.34 (m, 1H, CH=C*H*–Me), 5.26 (ddq, *J*=15.1, 7.9, and 1.5 Hz, 1H×0.8, C*H*=CH–Me in (*E*)-**4e**), 5.14 (ddq, *J*=10.8, 10.8, and 1.8 Hz, 1H×0.2, C*H*=CH–Me in (*Z*)-**4e**), 3.11–3.00 (m, 1H×0.2, BuC*H* in (*Z*)-**4e**), 2.91 (d, *J*=7.4 Hz, 2H, PhCOCH_2), 2.70–2.59 (m, 1H×0.8, BuC*H* in (*E*)-**4e**), 1.59 (dd, *J*=6.2 and 1.3 Hz, 3H×0.8, CH=CH–CH_3 in (*E*)-**4e**), 1.54 (dd, *J*=6.8 and 1.8 Hz, 3H×0.2, CH=CH–CH_3 in (*E*)-**4e**), 1.45–1.17 (m, 6H), 0.86 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) for (*E*)-**4e**: δ 199.6, 137.4, 134.2, 132.6, 128.3, 128.0, 125.1, 44.7, 39.0, 35.0, 29.5,

22.8, 18.0, 14.2; ^{13}C NMR ($CDCl_3$, 100 MHz) for (*Z*)-**4e**: δ 199.5, 137.4, 134.1, 133.9, 132.5, 125.0, 124.3, 44.8, 38.9, 35.5, 29.5, 22.9, 18.0, 13.3; IR (neat) 3018, 2808, 1688, 1599, 1582, 1450, 967, 752, 690, 572 cm^{-1}. Exact EIMS calcd for $C_{16}H_{22}O$: 230.1671. Found: 230.1672.

4.4.10. (*E*)-3-Methyl-3-propenylheptanal (6a). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.69 (t, *J*=3.2 Hz, 1H, C*H*O), 5.46 (d, *J*=15.6 Hz, C*H*=CH–Me), 5.38 (dq, *J*=15.6 and 4.9 Hz, CH=C*H*–Me), 2.32 (dd, *J*=14.7 and 3.2 Hz, 1H), 2.22 (dd, *J*=14.7 and 3.2 Hz, 1H), 1.67 (d, *J*=4.9 Hz, 3H, CH=CH–CH_3), 1.36–1.08 (m, 6H), 1.08 (s, 3H), 0.87 (t, *J*=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 204.1, 138.1, 123.2, 53.7, 41.8, 38.1, 26.1, 24.2, 23.3, 18.1, 14.1; IR (neat) 2934, 1723, 1458, 1381, 975 cm^{-1}. Exact EIMS calcd for $C_{11}H_{20}O$: 168.1514. Found: 168.1510.

4.4.11. (*E*)-3-Methyl-3-phenylhex-4-enal (6b). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.56 (t, *J*=3.0 Hz, 1H), 7.39–7.17 (m, 5H), 5.71 (dq, *J*=15.5 and 1.5 Hz, 1H, C*H*=CH–Me), 5.51 (dq, *J*=15.5 and 6.3 Hz, 1H, CH=C*H*–Me), 2.78 (dd, *J*=15.2 and 2.9 Hz, 1H), 2.71 (dd, *J*=15.2 and 2.9 Hz, 1H), 1.73 (dd, *J*=6.3 and 1.5 Hz, 3H, CH=CH–CH_3), 1.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 203.3, 146.4, 138.0, 128.5, 126.4, 126.2, 123.7, 53.8, 42.1, 26.8, 18.1; IR (neat) 2972, 1721, 1448, 1495, 1379, 1035, 975, 762, 700 cm^{-1}. Exact EIMS calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1200.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (KAKENHI) from JSPS and a Special Grant (GAKUCHO-GRANT) from Meiji Pharmaceutical University.

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