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Epoxide as an aldehyde equivalent in allyl-transfer reaction with γ-adduct of homoallylic alcohol (allyl donor) giving α-adduct of homoallylic alcohol

Junzo Nokami,* Kazuho Maruoka, Taichi Souda and Nobuo Tanaka

Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700-0005, Japan

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Abstract—Acid-catalyzed reactions of epoxides **2** with homoallylic alcohol γ-adducts, **1** [$Me_2C(OH)CHRCH{=}CH_2$], afford homoallylic alcohol α-adducts **3**–**5** via allyl-transfer reaction, sometimes being more effective than those using the corresponding aldehydes.

1. Introduction

It is well known that epoxide serves as an aldehyde in the presence of an acid catalyst as shown in Scheme 1.[1] Therefore, many reactions with aldehyde, such as allylation reaction of aldehyde, have also been carried out with epoxide, which is a synthetic equivalent of an aldehyde as shown in Scheme 2.[2]

On the other hand, we have so far discovered a new allylation reaction of aldehyde to give homoallylic alcohol α-adduct **3**, in which homoallylic alcohol γ-adduct **1** served as an allyl donor and transferred the allylic functionality into aldehyde via stereospecific oxonia[3.3]-sigmatropic rearrangement as shown in Scheme 3.[3]

Here we report an 'allyl-transfer reaction' of homoallylic alcohol γ-adduct **1** with epoxides, which are synthetic equivalents of aldehydes (Scheme 4).

2. Results and discussion

First, we tried the reaction of 2,3-dimethyl-4-penten-2-ol **1a** with stilbene oxide **2b** ($R^1{=}R^2{=}$Ph, $R^3{=}$H in Scheme 4)[4a] using an acid catalyst at 20 °C for 5 h in CH_2Cl_2. Typical results are listed in Table 1.

It seemed to be interesting for us that homoallylic alcohol α-adduct **3b** was obtained faster and in better yield (entry 7) than that in the allyl-transfer reaction of **1a** with the corresponding aldehyde, 2,2-diphenylethanal,[5] under similar reaction conditions where **3b** was obtained only in 58% yield (*E*/*Z*=6.7/1) even for 20 h.

This fact prompted us to study allyl-transfer reaction of **1a** with easily available various epoxides **2**.[4,7] Typical results are summarized in Table 2, although the reaction conditions shown in Table 2 would not be suitable to give the best result for all of the epoxides. It is noteworthy that vinyl epoxide **2i** gave the corresponding homoallylic alcohol **3i** selectively and in good yield without any migration of the double bond (Scheme 5).[6] Moreover, epoxides **2a**, **2b**, **2i**, **2d**–**f**, and **2h**, which could give more stable intermediates **T1** (Scheme 6), such as benzylic (entries 1 and 2), allylic (entry 10), and tertiary (entries 4–7 and 9) cations reacted with allyl donors more smoothly and gave better yields than those (**2c**, **2g**) giving less stable secondary cations (entries 3 and 8).

We also conducted allyl-transfer reaction with epoxides using other allyl donors **1b**, **1c** (**1b**, R=*n*-C_5H_{11}; **1c**, R=$(CH_2)_3Cl$)[8] and obtained the expected products in moderate yields (Table 3).

In conclusion, we discovered that allyl-transfer reaction of epoxides **2** took place with allyl donor, homoallylic alcohol γ-adduct **1**, to give homoallylic alcohol α-adducts **3**–**5** in a similar manner as the allylation of aldehydes, which are synthetic equivalents of the corresponding epoxides **2**. In a few cases, however, the product yields were better than those obtained from the corresponding aldehydes. This is because the hemiacetal intermediate (**T3**) can be formed directly from **2** via **T1** and **T2**. That is, the formation of **T3** from **T1** will be easier and faster than that from the corresponding aldehyde, which are unstable and sterically

* Corresponding author. E-mail: nogami@dac.ous.ac.jp

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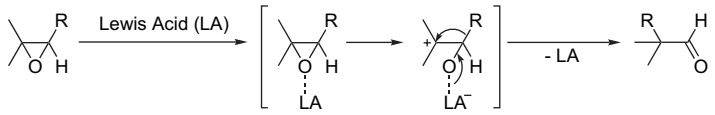
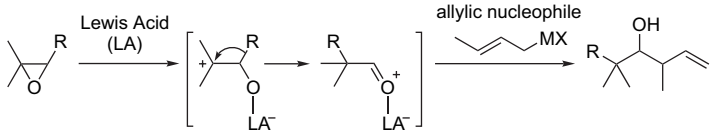
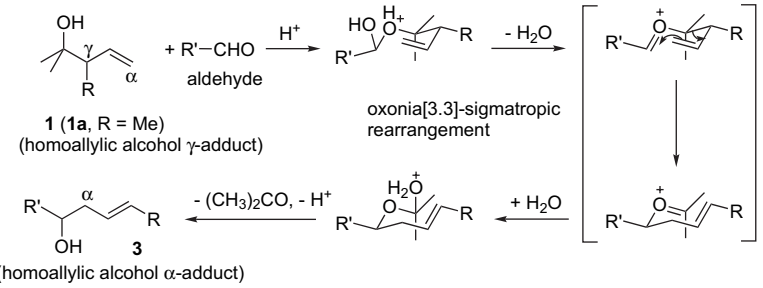


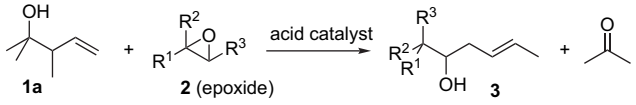
Scheme 1. Epoxide as an aldehyde equivalent.



Scheme 2. Allylation of epoxide as an aldehyde equivalent.



Scheme 3. Allylation of aldehyde via allyl-transfer reaction.



Scheme 4. Allyl-transfer reaction with epoxides.

Table 1. Crotylation of stilbene oxide **2b** via allyl-transfer reaction[a]

Entry	Catalyst[b] (mol %)	Yield of **3b**[c] (%)	*E*/*Z*[d]
1	$TSA \cdot H_2O$ (5)	0	—
2	TfOH (5)	68	4.6/1
3	$BF_3 \cdot OEt_2$ (5)	23	4.8/1
4	$Sc(OTf)_3$ (5)	54	3.7/1
5	TMSOTf (5)	67	4.7/1
6	$Sn(OTf)_2$ (5)	65	4.5/1
7	$In(OTf)_3$ (5)	70	5.2/1
8	$In(OTf)_3$ (2)	50	5.0/1
9	$In(OTf)_3$ (10)	60	5.0/1
10	$In(OTf)_3$ (5) and TfOH (5)	70	4.7/1
11	$In(OTf)_3$ (3) and TfOH (5)	82	4.6/1
12	$Bi(OTf)_3$ (5)	0	—
13	$Yb(OTf)_3$ (5)	0	—
14	$Er(OTf)_3$ (5)	Trace	—

[a] Reactions were performed with 2,3-dimethyl-4-penten-2-ol (**1a**) and stilbene oxide **2b** in the presence of an acid catalyst at 20 °C in CH_2Cl_2 for 5 h.
[b] TSA (*p*-toluenesulfonic acid); TfOH (trifluoromethanesulfonic acid).
[c] Isolated yield.
[d] Determined by ^1H NMR.

hindered (Scheme 6). It seems that the acid-catalyzed reaction of epoxide (from **2** to **T2**) is faster than the following allyl-transfer reaction (from **T2** to **3**–**5**), although the yield of **3**–**5** largely depends on the stability and steric hindrance of **T1**, **T2**, and **T3**.

3. Experimental

3.1. General methods

Infrared spectra were recorded on a Nicolet Series II Magna-IR system 550 spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a JEOL JNMX 400 spectrometer. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-700 mass spectrometer. Elemental analyses were obtained on a Perkin–Elmer PE-2400 Series II CHN analyzer. Dichloromethane was dried over calcium hydride and distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from benzophenone ketyl. All other chemical reagents were used as supplied without further purification.

3.2. General procedure

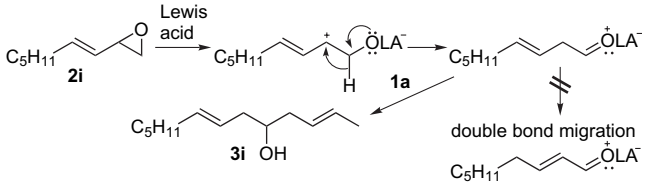
3.2.1. Allyl-transfer reaction of 2,3-dimethyl-4-penten-2-ol (1a) with styrene oxide (2a) to give 1-phenylhex-4-en-2-ol (3a). To a stirred solution of **1a** (57.1 mg, 0.5 mmol) and styrene oxide **2a** (58 μl, 0.5 mmol) in CH_2Cl_2 (2 mL) was added $In(OTf)_3$ (14.1 mg, 0.025 mmol), and the reaction mixture was warmed to 40 °C. After stirring for 6 h, saturated aqueous sodium bicarbonate (3 mL) was added to the reaction mixture at 0 °C. The resulting mixture was extracted with chloroform (3×2 mL). The combined extracts were dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc=20:1 to 3:1 as eluent) to give **3a** in 62% yield.

3.2.1.1. Compound 3a. A mixture of *E*- and *Z*-isomers; pale yellow oil; R_f 0.52 (*n*-hexane/EtOAc=3/1); IR (neat)

Table 2. Crotylation of epoxides **2** with **1a** via allyl-transfer reaction[a]

Entry	2				Temp,[b] °C	Time,[b] h	% Yield of **3**[c]			
		R^1	R^2	R^3				**A**	(**B**)	*E*/*Z*[d]
1	**a**	Ph	H	H	40 (20)	6 (15)	**a**	62	(84)	7.1/1
2	**b**	Ph	H	Ph	20 (20)	5 (5)	**b**	69	(82)	5.2/1
3	**c**	$Ph(CH_2)_2$	H	H	20	25	**c**	0		—
4	**d**	$Ph(CH_2)_2$	Me	H	20 (20)	15 (15)	**d**[e]	55	(61)	8.6/1
5	**d**	$Ph(CH_2)_2$	Me	H	40	6	**d**[e]	62		8.0/1
6	**e**	$Ph(CH_2)_2$	Et	H	20 (20)	30 (20)	**e**[e]	50	(52)	8.9/1
7	**f**	Me	Me	H	20 (20)	15 (12)	**f**	78	(80)	7/1[f]
8	**g**	C_6H_{13}	H	H	40	30	**g**	31		5.1/1
9	**h**	C_6H_{13}	Me	H	40 (20)	15 (20)	**h**[e]	49	(51)	5.4/1
10	**i**	$C_5H_{11}CH{=}CH$	H	H	20 (20)	20 (15)	**i**	46, 80[g]	(49)	4.0/1
11	**j**	$-(CH_2)_5-$		H	20 (20)	25 (20)	**j**	31	(51)	7.6/1

[a] Reactions were performed with 2,3-dimethyl-4-penten-2-ol (**1a**) (0.5 mmol) and epoxide **2** (0.5 mmol) in the presence of an acid catalyst **A**: $In(OTf)_3$ (5 mol %) in CH_2Cl_2 (2 mL) or **B**: $In(OTf)_3$ (3 mol %) and TfOH (5 mol %) in CH_2Cl_2 (4 mL), unless otherwise noted.
[b] Reaction conditions corresponding to the yields in column **B** are shown in parentheses.
[c] Isolated yield.
[d] Determined by ^1H NMR, unless otherwise noted.
[e] Ca. 1:1 of diastereomeric mixture (determined by ^{13}C NMR).
[f] Determined by ^{13}C NMR.
[g] Performed with 2 equiv of epoxide **2i** (1.0 mmol).

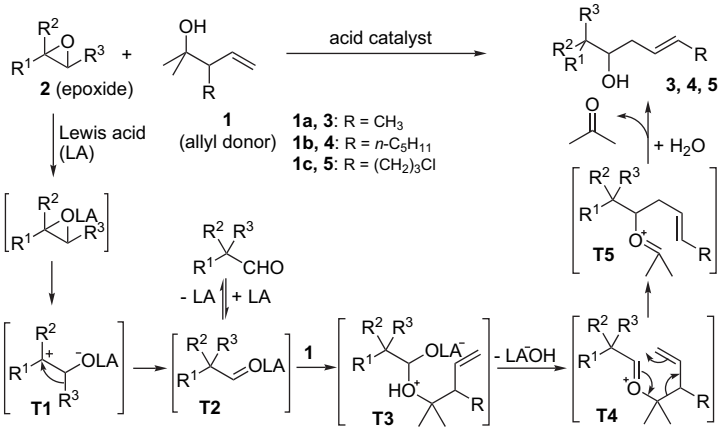


Scheme 5. Allylation of β,γ-unsaturated aldehyde equivalent **2i** with **1a** to give **3i**.

3555, 3398, 3062, 3025, 2924, 1658, 1603, 1495, 1448, 1076, 970, 743, 700 cm^{-1}; ^1H NMR (*E*-isomer) (400 MHz, $CDCl_3$) δ 1.68 (d, *J*=3.6 Hz, 1H), 1.70 (d, *J*=6.0 Hz, 3H), 2.11–2.18 (m, 1H), 2.23–2.28 (m, 1H), 2.72 (dd, *J*=7.6, 13.2 Hz, 1H), 2.82 (dd, *J*=5.2, 13.2 Hz, 1H), 3.84 (m, 1H), 5.43–5.51 (m, 1H), 5.54–5.63 (m, 1H), 7.21–7.25 (m, 3H), 7.29–7.33 (m, 2H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 18.1, 40.0, 43.2, 72.0, 126.3, 126.8, 128.4 (2), 128.9, 129.3 (2), 138.5. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.33.

3.2.1.2. 1,1-Diphenylhex-4-en-2-ol (3b). A mixture of *E*- and *Z*-isomers; pale yellow oil; R_f 0.58 (*n*-hexane/EtOAc=3:1); IR (neat) 3556, 3436, 3060, 3025, 2916, 1658, 1598, 1495, 1449, 1382, 973, 749, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (br d, *J*=5.6 Hz, 0.5H), 1.68 (d, *J*=3.6 Hz, 2.5H), 1.74 (br, 1H), 2.01–2.09 (m, 1H), 2.19–2.27 (m, 1H), 3.90 (*E*, d, *J*=8.4 Hz, 0.84H), 3.94 (d, *J*=8.4 Hz, 0.16H), 4.37 (m, 1H), 5.45–5.53 (m, 2H), 7.15–7.42 (m, 10H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 18.1, 38.3, 57.8, 73.0, 126.4, 126.6, 126.9 (2), 128.2, 128.50 (2), 128.52, 128.6 (2), 128.7 (2), 141.4, 142.3. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.57; H, 8.02.

3.2.1.3. 3-Methyl-1-phenyloct-6-en-4-ol (3d). A mixture of *syn* and *anti*, and *E*- and *Z*-isomers; colorless oil; R_f 0.56 (*n*-hexane/EtOAc=3:1); IR (neat) 3404, 3026, 2962, 2932, 2879, 2858, 1605, 1496, 1453, 1378, 970, 748, 699 cm^{-1}; ^1H NMR (*E*-isomer) (400 MHz, $CDCl_3$) δ 0.97 and 0.99 (each d, *J*=6.0, 6.4 Hz, resp., 3H), 1.4–1.7 (m, 6H), 1.69 (d, *J*=6.0 Hz, 3H), 1.82 (m, 1H), 2.06 (m, 1H), 2.20 (m, 1H), 2.50–2.63 (m, 1H), 2.67–2.79 (m, 1H), 3.44



Scheme 6. Allyl-transfer reaction with epoxides: a plausible reaction mechanism.

Table 3. Allyl-transfer reaction of epoxides **2** with allyl donor **1b**, **1c**[a]

Entry	**1**[b]	**2**				Temp,[c] °C	Time,[c] h	% Yield of **4**, **5**[d]			
			R^1	R^2	R^3				**A**	(**B**)	*E*/*Z*[e]
1	**1b**	**a**	Ph	H	H	40 (20)	15 (10)	**4a**	60	(54)	*E*
2	**1b**	**b**	Ph	H	Ph	20 (20)	8 (3)	**4b**	70[h]	(81)	8/1[f]
3	**1b**	**d**	$Ph(CH_2)_2$	Me	H	20 (20)	20 (20)	**4d**[g]	47	(56)	*E*
4	**1b**	**f**	Me	Me	H	20 (20)	20 (13)	**4f**	74[h]	(81)	11/1[f]
5	**1b**	**h**	C_6H_{13}	Me	H	40	20	**4h**[g]	55		*E*
6	**1b**	**i**	$C_5H_{11}CH{=}CH$	H	H	20 (20)	20 (20)	**4i**	33[i]	(52)	*E*
7	**1c**	**a**	Ph	H	H	40	15	**5a**	50		*E*
8	**1c**	**b**	Ph	H	Ph	20	20	**5b**	74		5/1
9	**1c**	**d**	$Ph(CH_2)_2$	Me	H	20	20	**5d**[g]	55		26/1
10	**1c**	**f**	Me	Me	H	20	20	**5f**	70		12/1[f]
11	**1c**	**h**	C_6H_{13}	Me	H	20	20	**5h**[g]	50		26/1
12	**1c**	**i**	$C_5H_{11}CH{=}CH$	H	H	20	20	**5i**	37[i]		*E*

[a] **A**: reactions were performed with allyl donor **1** (0.5 mmol) and epoxide **2** (0.5 mmol) in the presence of $In(OTf)_3$ (5 mol %) in CH_2Cl_2 (2 mL) or **B**: in the presence of $In(OTf)_3$ (3 mol %) and TfOH (5 mol %) in CH_2Cl_2 (4 mL) unless otherwise noted.
[b] **1b**, R=*n*-C_5H_{11}; **1c**, R=$(CH_2)_3Cl$ in Scheme 6.
[c] Reaction conditions corresponding to the yields in column (**B**) are shown in parentheses.
[d] Isolated yield.
[e] Determined by ^1H NMR of the products obtained in the system **A**, unless otherwise noted.
[f] Determined by ^{13}C NMR.
[g] Ca. 1:1 of diastereomeric mixture (determined by ^{13}C NMR).
[h] Performed in the presence of TfOH (5 mol %) instead of $In(OTf)_3$.
[i] Epoxide **2i** (1.0 mmol) was used.

and 3.52 (each m, 0.4H and 0.6H, resp.), 5.41 (m, 1H), 5.55 (m, 1H), 7.15–7.30 (m, 5H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 14.0 and 15.2, 18.11 and 18.12, 33.5 and 33.6, 34.1 and 35.1, 37.0 and 37.3, 37.72 and 37.73, 73.9 and 74.6, 125.5 (2), 127.5 and 127.6, 128.17 (4), 128.25 (4), 128.6 and 128.9, 142.58 and 142.6. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.54; H, 10.52.

3.2.1.4. 3-Ethyl-1-phenyloct-6-en-4-ol (3e). A mixture of *syn* and *anti*, and *E*- and *Z*-isomers; colorless oil; R_f 0.61 (*n*-hexane/EtOAc=3:1); IR (neat) 3414, 3085, 3026, 2933, 2875, 1604, 1496, 1454, 1378, 969, 748, 698 cm^{-1}; ^1H NMR (*E*-isomer) (400 MHz, $CDCl_3$) δ 0.93 (t, *J*=7.2 Hz, 3H), 1.37–1.78 (m, 10H), 2.05–2.09 (m, 1H), 2.20 (m, 1H), 2.57–2.71 (m, 2H), 3.63 (m, 1H), 5.41–5.44 (m, 1H), 5.52–5.57 (m, 1H), 7.16–7.30 (m, 5H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 11.65 and 11.67, 18.1 (2), 21.7 and 22.6, 30.8 and 31.5, 33.7 (2), 37.3 and 37.7, 43.98 and 44.04, 72.07 and 72.10, 125.53 and 125.55, 127.62 and 127.67, 128.18 (4), 128.24 (4), 128.79 and 128.84, 142.7 and 142.8. Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.91; H, 10.42.

3.2.1.5. 2-Methylhept-5-en-3-ol (3f). A mixture of *E*- and *Z*-isomers; colorless oil; R_f 0.56 (*n*-hexane/EtOAc=3:1); IR (neat) 3371, 3019, 2960, 1655, 1462, 1380, 971 cm^{-1}; ^1H NMR (*E*-isomer) (400 MHz, $CDCl_3$) δ 0.93 (d, *J*=6.4 and 9.2 Hz, 6H), 1.63–1.70 (m, 2H), 1.69 (d, *J*=5.2 Hz, 3H), 2.04 (dt, *J*=8.0, 14.8 Hz, 1H), 2.20–2.28 (m, 1H), 3.33 (ddd, *J*=3.2, 5.2, 8.8 Hz, 1H), 5.40–5.48 (m, 1H), 5.52–5.59 (m, 1H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 17.64, 18.1, 18.8, 33.0, 37.6, 75.6, 127.6, 128.6; (*Z*-isomer) (100 MHz, $CDCl_3$) δ 17.57, 18.1, 18.9, 33.1, 37.6, 76.2, 126.6, 127.0. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.06; H, 12.55.

3.2.1.6. Dodec-2-en-5-ol (3g). A mixture of *E*- and *Z*-isomers; colorless oil; R_f 0.60 (*n*-hexane/EtOAc=3:1); IR (neat) 3361, 3018, 2926, 2858, 1658, 1458, 1375, 1125, 969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.29 (br, 10H), 1.44–1.49 (br m, 2H), 1.65 (br d, *J*=6.8 Hz, 0.5H), 1.70 (dd, *J*=0.8, 6.4 Hz, 2.5H), 2.05 (dt, *J*=7.6, 13.6 Hz, 1H), 2.19–2.27 (m, 1H), 3.54–3.62 (br m, 1H), 5.39–5.48 (m, 1H), 5.51–5.61 (m, 1H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 14.2, 18.2, 22.7, 25.8, 29.3, 29.7, 31.9, 36.8, 40.7, 71.0, 127.1, 128.9. HRMS (EI) *m*/*z* calcd for $C_{12}H_{24}O$ 184.1827. Found 184.1821.

3.2.1.7. 6-Methyldodec-2-en-5-ol (3h). A mixture of *syn* and *anti*, and *E*- and *Z*-isomers; colorless oil; R_f 0.67 (*n*-hexane/EtOAc=3:1); IR (neat) 3380, 3021, 2926, 2856, 1457, 1378, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87–0.92 (m, 6H), 1.10–1.58 (m, 13H), 1.65 (*Z*, d, *J*=6.8 Hz, 0.5H), 1.70 (*E*, d, *J*=6.4 Hz, 2.5H), 1.99–2.11 (m, 1H), 2.17–2.25 (m, 1H), 3.40–3.42 (m, 0.4H), 3.46–3.49 (m, 0.6H), 5.43–5.45 (m, 1H), 5.53–5.57 (m, 1H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 14.0 and 15.2, 14.2 (2), 18.12 and 18.13, 22.7 (2), 27.2 and 27.3, 29.66 and 29.68, 31.9 (2), 32.2 and 33.2, 36.9 and 37.77, 37.84 and 38.1, 74.2 and 74.7, 127.7 and 127.8, 128.5 and 128.8. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.95; H, 13.39.

3.2.1.8. Trideca-2,7-dien-5-ol (3i). A mixture of 2*E*- and 2*Z*-isomers; pale yellow oil; R_f 0.60 (*n*-hexane/EtOAc=3:1); IR (neat) 3393, 2928, 2858, 1457, 1377, 969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=7.0 Hz, 3H), 1.2–1.4 (m, 6H), 1.64 (*Z*, d, *J*=7.2 Hz, 0.6H), 1.69 (*E*, d, *J*=6.2 Hz, 2.4H), 2.01 (q, *J*=6.8 Hz, 2H), 2.05–2.15 (m, 2H), 2.17–2.26 (m, 2H), 3.59 (m, 1H), 5.35–5.49 (m, 2H), 5.50–5.60 (m, 2H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 14.1, 18.1, 22.5, 29.1, 31.4, 32.7, 39.9, 40.0, 70.5, 125.6, 127.0, 128.4, 134.3. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.55; H, 12.39.

3.2.1.9. 1-Cyclohexylpent-3-en-1-ol (3j). A mixture of *E*- and *Z*-isomers; colorless oil; R_f 0.60 (*n*-hexane/

EtOAc=3:1); IR (neat) 3378, 3018, 2925, 2855, 1657, 1448, 1088, 1065, 1031, 969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95–1.40 (m, 7H), 1.63–1.90 (m, 5H), 1.64 (*Z*, d, *J*=7.2 Hz, 0.6H), 1.70 (*E*, d, *J*=6.4 Hz, 2.4H), 2.04 (dt, *J*=8.4, 13.6 Hz, 1H), 2.21–2.29 (m, 1H), 3.33 (m, 1H), 5.39–5.48 (m, 1H), 5.52–5.60 (m, 1H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 18.2, 26.2, 26.4, 26.6, 28.3, 29.1, 37.5, 43.0, 75.0, 127.6, 128.8. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.57; H, 12.06.

3.2.1.10. 1-Phenyldec-4-en-2-ol (4a). Colorless oil; R_f 0.40 (*n*-hexane/EtOAc=3:1); IR (neat) 3557, 3405, 3062, 3027, 2925, 2857, 1665, 1603, 1495, 1454, 1381, 1074, 972, 742, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*= 6.8 Hz, 3H), 1.2–1.4 (m, 6H), 1.73 (br, 1H), 2.03 (q, *J*= 7.2 Hz, 2H), 2.14 (dt, *J*=6.8, 13.5 Hz, 1H), 2.20–2.30 (m, 1H), 2.71 (dd, *J*=7.6, 13.6 Hz, 1H), 2.80 (dd, *J*=5.0, 13.6 Hz, 1H), 3.82 (br, 1H), 5.41–5.48 (m, 1H), 5.51–5.60 (m, 1H), 7.20–7.26 (m, 3H), 7.27–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 31.4, 32.7, 40.1, 43.2, 72.0, 125.5, 126.3, 128.4 (2), 129.3 (2), 134.7, 138.5. HRMS (EI) *m/z* calcd for $C_{16}H_{24}O$ 232.1827. Found 232.1804.

3.2.1.11. 1,1-Diphenyldec-4-en-2-ol (4b). A mixture of *E*- and *Z*-isomers; pale yellow oil; R_f 0.65 (*n*-hexane/EtOAc=3:1); IR (neat) 3562, 3454, 3060, 3027, 2924, 2857, 1662, 1598, 1494, 1452, 1381, 1064, 973, 752, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.84–0.89 (m, 3H), 1.24–1.38 (m, 6H), 1.77 (br, 1H), 1.88–2.09 (m, 3H), 2.20–2.27 (m, 1H), 3.91 (*E*, d, *J*=8.4 Hz, 0.9H), 3.94 (*Z*, d, *J*=8.4 Hz, 0.1H), 4.35–4.37 (br m, 1H), 5.42–5.54 (m, 2H), 7.19–7.40 (m, 10H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.1, 31.4, 32.7, 38.4, 57.8, 73.0, 125.5, 126.4, 126.5, 128.2 (2), 128.45 (2), 128.48 (2), 128.7 (2), 134.5, 141.4, 142.3. Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.88; H, 8.85.

3.2.1.12. 2-Methyl-1-phenyldodec-6-en-4-ol (4d). A mixture of *syn* and *anti* isomers; colorless oil; R_f 0.69 (*n*-hexane/EtOAc=3:1); IR (neat) 3421, 3085, 3026, 2926, 2857, 1605, 1501, 1457, 1377, 970, 747, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=7.2 Hz, 3H), 0.96 and 0.97 (each d, *J*=7.2, 6.4 Hz, resp., 3H), 1.24–1.70 (m, 9H), 1.75–1.90 (m, 1H), 1.97–2.13 (m, 3H), 2.15–2.27 (br m, 1H), 2.50–2.64 (m, 1H), 2.65–2.70 (m, 1H), 3.42 and 3.51 (each m, 1H), 5.37 (m, 1H), 5.53 (m, 1H), 7.14–7.22 (m, 3H), 7.23–7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 and 15.3, 14.1 (2), 22.5 (2), 29.2 (2), 31.4 (2), 32.64 and 32.66, 33.55 and 33.67, 34.1 and 35.1, 37.1 and 37.3, 37.7 and 37.8, 73.9 and 74.3, 125.5 (2), 126.1 and 126.2, 128.2 (4), 128.3 (4), 134.5 and 134.8, 142.60 and 142.64. Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.20; H, 10.88.

3.2.1.13. 2-Methylundec-5-en-3-ol (4f). A mixture of *E*- and *Z*-isomers; colorless oil; R_f 0.63 (*n*-hexane/EtOAc=3:1); IR (neat) 3388, 2958, 2926, 2868, 1660, 1463, 1381, 973 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=7.2 Hz, 3H), 0.93 (dd, *J*=6.8 Hz, 6H), 1.22–1.40 (m, 6H), 1.58 (br, 1H), 1.64–1.72 (m, 1H), 1.99–2.08 (m, 3H), 2.18–2.29 (m, 1H), 3.33 (m, 1H), 5.37–5.45 (m, 1H), 5.52–5.60 (m, 1H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 14.1, 17.7, 18.8, 22.5, 29.2, 31.4, 32.7, 32.97, 37.6, 75.5, 126.1, 134.5; (*Z*-isomer) (100 MHz, $CDCl_3$) δ 14.2, 17.6, 18.9, 27.4, 29.4, 31.5, 32.2, 33.04, 37.6, 76.1, 125.5, 133.3. HRMS (EI) *m/z* calcd for $C_{12}H_{24}O$ 184.1827. Found 184.1789.

3.2.1.14. 7-Methylhexadec-10-en-8-ol (4h). A mixture of *syn* and *anti* isomers; colorless oil; R_f 0.70 (*n*-hexane/EtOAc=3:1); IR (neat) 3377, 2955, 2925, 2858, 1461, 1378, 973 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 9H), 1.08–1.64 (m, 18H), 1.94–2.12 (m, 3H), 2.18–2.27 (br m, 1H), 3.40–3.48 (br, 1H), 5.38–5.44 (m, 1H), 5.51–5.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.06 (2), 14.12, 14.17 (2), 15.3, 22.6 (2), 22.7 (2), 27.25, 27.35, 29.2 (2), 29.66, 29.70, 31.4 (2), 31.9 (2), 32.2, 32.68, 32.70, 33.2, 37.0, 37.7, 37.9, 38.1, 74.1, 74.6, 126.3, 126.4, 134.4, 134.7. Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 80.24; H, 13.25.

3.2.1.15. Heptadeca-6,11-dien-9-ol (4i). Colorless oil; R_f 0.67 (*n*-hexane/EtOAc=3:1); IR (neat) 3398, 2926, 2856, 1466, 1379, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 6H), 1.29–1.40 (m, 12H), 1.77 (br, 1H), 2.02 (q, *J*=6.8 Hz, 4H), 2.07–2.15 (m, 2H), 2.18–2.25 (m, 2H), 3.59 (br m, 1H), 5.41 (dt, *J*=6.8, 15.2 Hz, 2H), 5.53 (dt, *J*=6.8, 15.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 31.4, 32.7, 40.0, 70.5, 125.7, 134.3. Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 80.77; H, 12.67.

3.2.1.16. 8-Chloro-1-phenyloct-4-en-2-ol (5a). Colorless oil; R_f 0.40 (*n*-hexane/EtOAc=3:1); IR (neat) 3562, 3422, 3085, 3062, 3027, 2930, 2870, 2850, 1602, 1496, 1454, 1442, 1387, 972, 744, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (quint, *J*=6.8 Hz, 2H), 2.14–2.33 (m, 4H), 2.71 (dd, *J*=8.0, 13.6 Hz, 1H), 2.82 (dd, *J*=4.8, 13.6 Hz, 1H), 3.54 (t, *J*=6.4 Hz, 2H), 3.85 (m, 1H), 5.53 (m, 2H), 7.20–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8, 32.1, 40.0, 43.3, 44.4, 72.0, 126.4, 127.4, 128.5, 129.3, 132.1, 138.3. HRMS (EI) *m/z* calcd for $C_{14}H_{19}OCl$ 238.1124. Found 238.1160.

3.2.1.17. 8-Chloro-1,1-diphenyloct-4-en-2-ol (5b). A mixture of *E*- and *Z*-isomers; colorless oil; R_f 0.50 (*n*-hexane/EtOAc=3:1); IR (neat) 3566, 3447, 3060, 3027, 2908, 2847, 1598, 1494, 1451, 1387, 973, 757, 746, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.7–1.85 (m, 3H), 1.98–2.20 (m, ca. 1H), 2.15 (q, *J*=6.8 Hz, ca. 2H), 2.2–2.3 (m, 1H), 3.43 and 3.49 (each t, *J*=6.4 Hz, ca. 0.3 and 1.7H, resp.), 3.90 and 3.91 (d, *J*=8.8 Hz, ca. 0.84 and 0.16H, resp.), 4.34–4.39 (m, 1H), 5.35–5.58 (m, 2H), 7.15–7.38 (m, 10H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 29.7, 32.1, 38.3, 44.4, 57.9, 73.1, 126.5, 126.7, 127.4, 128.2, 128.5, 128.6, 128.7, 131.8, 141.2; ^{13}C NMR (*Z*-isomer) (100 MHz, $CDCl_3$) δ 24.5, 32.2, 32.9, 44.4, 58.0, 73.5, 126.5, 126.7, 127.4, 128.2 (2), 128.5 (2), 128.6 (2), 128.7 (2), 131.8, 141.2, 142.1. Anal. Calcd for $C_{20}H_{23}ClO$: C, 76.30; H, 7.36. Found: C, 76.26; H, 7.20.

3.2.1.18. 10-Chloro-3-methyl-1-phenyldec-6-en-4-ol (5d). A mixture of *syn* and *anti*, and *E*- and *Z*-isomers; colorless oil; R_f 0.50 (*n*-hexane/EtOAc=3:1); IR (neat) 3420, 3085, 3062, 3026, 2932, 2873, 1603, 1496, 1455, 1378, 973, 748, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96

and 0.98 (each d, J=6.8, 6.4 Hz, resp., 3H), 1.40–1.60 (m, 3H), 1.83 (quint, J=6.8 Hz, 3H), 2.0–2.3 (m, 4H), 2.50–2.64 (m, 1H), 2.65–2.80 (m, 1H), 3.41–3.58 (m, 1H), 3.52 (t, J=6.8 Hz, 2H), 5.49 (m, 2H), 7.15–7.21 (m, 3H), 7.24–7.30 (m, 2H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 13.9 and 15.3, 29.7 (2), 32.1 (2), 33.6 and 34.0, 35.1 and 37.0, 37.3 and 37.8, 44.4 (2), 74.0 and 74.7, 125.6 (2), 127.9 and 128.0, 128.2 (4), 128.3 (4), 131.9 and 132.1, 142.5 and 142.6. Anal. Calcd for $C_{17}H_{25}ClO$: C, 72.71; H, 8.97. Found: C, 72.67; H, 8.73.

3.2.1.19. 9-Chloro-2-methylnon-5-en-3-ol (5f). A mixture of *E*- and *Z*-isomers; colorless oil; R_f 0.53 (*n*-hexane/EtOAc=3:1); IR (neat) 3413, 2946, 2936, 2876, 1471, 1446, 1387, 972 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, J=6.4 Hz, 3H), 0.93 (d, J=6.4 Hz, 3H), 1.51 (br, 1H), 1.67 (oct, J=6.4 Hz, 1H), 1.85 (quint, J=6.8 Hz, 2H), 2.06 (br m, 1H), 2.12–2.30 (br m, 3H), 3.35 (br, 1H), 3.54 (t, J=6.4 Hz, 2H), 5.50 (br, 2H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 17.5, 18.76, 29.7, 32.1, 33.0, 37.5, 44.3, 75.6, 128.0, 131.8; ^{13}C NMR (*Z*-isomer) (100 MHz, $CDCl_3$) δ 18.84, 24.5, 32.2, 32.3, 33.2, 37.5, 44.4, 76.2, 127.5, 130.6. Anal. Calcd for $C_{10}H_{19}ClO$: C, 62.98; H, 10.04. Found: C, 62.86; H, 10.02.

3.2.1.20. 1-Chloro-8-methyltetradec-4-en-7-ol (5h). A mixture of *syn* and *anti*, and *E*- and *Z*-isomers; colorless oil; R_f 0.67 (*n*-hexane/EtOAc=3:1); IR (neat) 3393, 2928, 2856, 1458, 1378, 972 cm^{-1}; ^{1}H NMR (*E*-isomer) (400 MHz, $CDCl_3$) δ 0.85–0.92 (m, 6H), 1.10–1.65 (m, 12H), 1.85 (quint, J=6.8 Hz, 2H), 2.00–2.28 (m, 4H), 3.43 (m, 1H), 3.49 (m, 1H), 3.54 (t, J=6.4 Hz, 2H), 5.50 (m, 2H); ^{13}C NMR (*E*-isomer) (100 MHz, $CDCl_3$) δ 13.9 and 15.2, 14.2 (2), 22.7 (2), 27.2 and 27.3, 29.6 and 29.7, 29.75 and 29.77, 31.9 (2), 32.1 (2), 33.2 (2), 36.9 and 37.78, 37.85 and 38.2, 44.4 (2), 74.2 and 74.8, 128.2 and 128.3, 131.7 and 132.0. Anal. Calcd for $C_{15}H_{29}ClO$: C, 69.07; H, 11.21. Found: C, 69.10; H, 11.15.

3.2.1.21. 1-Chloropentadeca-4,9-dien-7-ol (5i). Colorless oil; R_f 0.53 (*n*-hexane/EtOAc=3:1); IR (neat) 3405, 2927, 2872, 1441, 1379, 971 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 3H), 1.15–1.40 (m, 7H), 1.73 (br, 1H), 1.84 (quint, J=6.8 Hz, 2H), 2.02 (q, J=6.8 Hz, 2H), 2.05–2.27 (m, 5H), 3.54 (t, J=6.4 Hz, 2H), 3.61 (br m, 1H), 5.40 (dt, J=6.8, 15.2 Hz, 1H), 5.47–5.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 29.8, 31.4, 32.2, 32.7, 39.9, 40.1, 44.4, 70.4, 125.5, 127.5, 131.7, 134.6. HRMS (EI) *m/z* calcd for $C_{15}H_{27}O$ 258.1750. Found 258.1733.

3.2.1.22. 2-(2-Phenylethyl)oxirane (2c). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 3H), 1.78–1.94 (m, 2H), 2.48 (dd, J=2.8, 4.8 Hz, 2H), 2.71–2.87 (m, 3H), 2.92–2.99 (m, 1H), 7.15–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2, 34.3, 47.2, 51.7, 125.9, 128.2, 128.3, 141.1.

3.2.1.23. 2-(2-Phenylethyl)-2-methyloxirane (2d). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 3H), 1.79–1.97 (m, 2H), 2.59 (q, J=5.2 Hz, 2H), 2.66–2.78 (m, 2H), 7.17–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 31.4, 38.5, 53.9, 56.6, 125.8, 128.1, 128.3, 141.4.

3.2.1.24. 2-Hexyloxirane (2g). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=6.8 Hz, 3H), 1.23–1.59 (m, 10H), 2.47 (dd, J=3.2, 5.2 Hz, 1H), 2.75 (t, J=4.6 Hz, 1H), 2.88–2.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 26.0, 29.1, 31.8, 32.5, 47.1, 52.4.

3.2.1.25. 2-Hexyl-2-methyloxirane (2h). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 3H), 1.23–1.63 (m, 10H), 1.31 (s, 3H), 2.59 (dd, J=4.8, 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 20.9, 22.6, 25.2, 29.3, 31.8, 36.7, 53.9, 57.0.

3.2.1.26. 2-(1-Heptenyl)oxirane (2i). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=6.8 Hz, 3H), 1.23–1.45 (m, 6H), 2.07 (q, J=6.8 Hz, 2H), 2.65 (dd, J=2.8, 4.8 Hz, 1H), 2.94 (t, J=4.8 Hz, 1H), 3.32 (dq, J=2.8, 8.4 Hz, 1H), 5.13 (dd, J=8.4, 15.2 Hz, 1H), 5.96 (dt, J=6.8, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 28.6, 31.3, 32.3, 48.8, 52.5, 127.3, 137.2.

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4. (a) Epoxides **2b** and **2f** were commercially available; (b) Epoxides **2d**, **2e**, **2h** and **2j** were prepared according to Corey's method using dimethyloxosulfonium methylide from the corresponding ketones. Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364; (c) Preparation of **2i** was performed according to the method reported by Lautens et al.[2b] via epoxidation of epichlorohydrin, 1-chlorononon-3-en-2-ol, prepared by a nucleophilic chloromethylation (using chloromethyllithium) of 2-octenal;[7] (d) Epoxidation of alkenes was performed with *m*-CPBA to give **2a**, **2c**, and **2g**.
5. 2,2-Diphenylethanal was prepared from stilbene oxide **2b** in 62% isolated yield by treatment with $In(OTf)_3$ (3 mol %) in CH_2Cl_2 at 20 °C for 30 min.
6. In connection with this fact, we would like to add the following separate experimental results. Epoxide **2i** (0.5 mmol) was treated with 3 mol % of $Er(OTf)_3$ in dichloromethane at 20 °C for 1 h to give non-3-enal.[1i] The ^1H NMR spectrum clearly showed that non-3-enal was produced as a single olefinic aldehyde (ca. 50%) together with much of impurities, which may be less polar saturated hydrocarbonic compounds. Treatment of this crude non-3-enal with **1a** (0.5 mmol) in the presence of $In(OTf)_3$ (5 mol %) gave **3i** selectively in 45% isolated yield based on epoxide **2i**. This result clearly shows that allyl-transfer reaction giving **3i** surely occurs also via an intermediate aldehyde, and also that the direct reaction of epoxide **2i** with **1a** is much effective (46% yield; see Table 2, entry 10). It is noteworthy that treatment of **2i** with 3 mol % of $In(OTf)_3$ gave only a trace of non-3-enal, although $Er(OTf)_3$ is ineffective for allyl-transfer reaction. This clearly shows an unstability of non-3-enal and a usefulness of such a tandem reaction.
7. Sadhu, K. M.; Matteson, D. S. *Tetrahedron Lett.* **1986**, *27*, 795–798.
8. Allyl donors **1a–c** were prepared from acetone by allylation with the corresponding Grignard reagents (for **1a**, **1b**) and by Reformatsky reaction with 1-bromo-6-chlorohex-2-ene and zinc (for **1c**), see Ref. 3f.