A Facile Method for the Stereoselective Preparation of (1*Z*,3*E*)-Dienyl Ethers via 1,4-Elimination of 1,4-Dialkoxy-(2*Z*)-alkenes with *n*-Butyllithium

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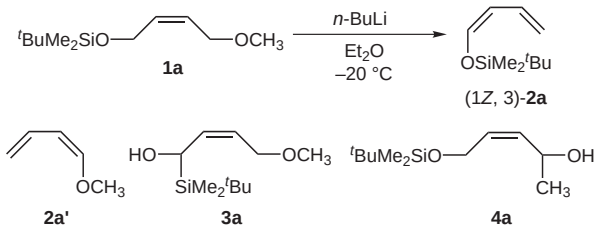
Abstract: Treatment of 1-alkoxy-4-methoxy-(2*Z*)-alkenes or 1-siloxy-4-methoxy-(2*Z*)-alkenes with *n*-butyllithium in diethyl ether is shown to afford the corresponding (1*Z*,3*E*)-dienyl, alkyl or silyl ethers, respectively, in high stereoselectivity via a facile 1,4-elimination. The scope and the regio- and stereochemical features of the synthetic method are described.

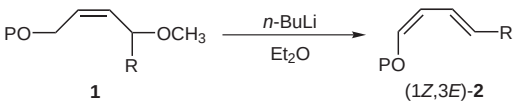
Key words: 1,4-eliminations, dienyl ethers, dienyl acetals, stereoselective synthesis, precoordinations

In the course of studies on the Wittig[1] and retro-Brook[1a] rearrangement of allylic ether systems, it occurred to us that when 4-methoxy-(2*Z*)-butenyl *tert*-butyldimethylsilyl ether (**1a**) was treated with *n*-butyllithium (1.5 equiv) in diethyl ether, the (1*Z*,3)-butadienyl silyl ether (**2a**) was formed in 70% yield as a single stereoisomer without any concomitant formation of possible by-products such as the other dienyl ether **2a′**, the [1,2] retro-Brook product **3a**, and the [1,2] Wittig product **4a** (Scheme 1).



Scheme 1

Prompted by this rather unexpected observation, we decided to investigate the scope and limitation of this type of 1,3-dienyl ether forming reaction in view of the synthetic potentiality of 1,3-dienyl ethers, e.g., as dienolate equivalents for aldol-type[2] and Ferrier-type reactions[3] or as diene components for the Diels–Alder reactions.[4] While several 1,3-dienyl ethers have been prepared via O-silylation or O-alkylation of the dienolates derived from α,β-unsaturated carbonyl compounds, the stereoselectivities of this conventional method are generally unsatisfactory and its scope remains limited in terms of the kind of introducible *O*-alkyl substituents.[5–7] Described herein are a facile and stereoselective synthetic method for various types of (1*Z*,3*E*)-dienyl ethers via 1,4-elimination[8] of 1-siloxy-4-methoxy- and 1,4-dialkoxy-(2*Z*)-alkenes with *n*-butyllithium and the scope and stereochemical feature thereof (Scheme 2).



P = SiR_3, MOM, EE, THP, etc.
R = H, *n*-Bu, OCH_3

Scheme 2

As already mentioned, we found that silyl ether **1a** was treated with *n*-BuLi in diethyl ether at –20 °C for two hours gave the (1*Z*,3)-dienyl silyl ether **2a** as a single stereoisomer in 70% yield (Table 1, entry 1). The *Z*-geometry was assigned by ^{1}H NMR assay ($J_{1H,2H}$ = 5.9 Hz). Apparently, this reaction can be considered as a 1,4- (or vinylogous 1,2-) elimination process. Of special interest is that the initial deprotonation occurs on the siloxy-bearing methylene in preference to the methoxy-bearing methylene to liberate methanol. To examine the stereoselectivity on the olefinic bond formed at the 3-position, 4-butyl-substituted substrate (**1b**, R = *n*-Bu)[9] was reacted with *n*-BuLi under the same conditions. Interestingly enough, the dienyl silyl ether **2b** was obtained almost exclusively as the 1*Z*,3*E* isomer in 88% yield (entry 2).[10] The stereochemistry was determined by ^{1}H NMR assay ($J_{1H,2H}$ = 5.9 Hz and $J_{3H,4H}$ = 15.6 Hz). Equally high stereoselectivities were observed in similar reactions of 4-methoxy-substituted substrate (**1c**, entry 3). To further expand the scope of the present 1,3-dienyl ether forming reaction, we prepared a series of O-protected ethers **1d**–**h**[11] and carried out their reactions with *n*-butyllithium under the same conditions (entries 4–8). Significantly, the reaction of the EE-protected substrate **1d** gave the (1*Z*,3*E*)-dienyl ether **2d** in a high stereoselectivity, while the reactions of other O-protected substrates also showed a high 1*Z*-stereoselectivity. Thus, these O-protected 1,3-dienyl ethers might find unique synthetic applications, since easy deprotection after synthetic transformations should impart a hydroxyl functionality to the products. Interestingly, this reaction is applicable to the preparation of the 1,3,5-trienyl ether. For instance, a similar reaction of **1i** afforded the (1*Z*,3*E*,5)-trienyl ether **2i** in 53% yield as depicted in Scheme 3.

One remarkable feature of the present dienyl ether forming reaction is that various types of (1*Z*,3)- and (1*Z*,3*E*)-dienyl ethers can be obtained in high stereoselectivities.

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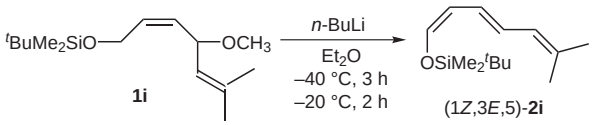
Table 1 The Reactions of Ether **1** with *n*-BuLi[12]

Entry	Substrate[a]	Temp (°C)	Time (h)	Product	Yield (%)[b]	(1*Z*,3*E*)/other isomers[c]
1	**1a** (P = $SiMe_2t$-Bu, R = H)	–20	2	**2a**	70[d]	>98:2
2	**1b** (P = $SiMe_2t$-Bu, R = *n*-Bu)	–20	4	**2b**	88	>98:2
3	**1c** (P = $SiMe_2t$-Bu, R = OCH_3)	–40	2	**2c**	96[d]	>98:2
4	**1d** (P = EE, R = *n*-Bu)	–20	2.5	**2d**	89	93:7
5	**1e** (P = MOM, R = *n*-Bu)	0	3.5	**2e**	66	94:6
6	**1f** (P = BOM, R = *n*-Bu)	–20	3	**2f**	74	97:3
7	**1g** (P = MIP, R = *n*-Bu)	0	3	**2g**	83	>98:2
8	**1h** (P = THP, R = *n*-Bu)	0	4	**2h**	73	90:10

[a] EE = 1-ethoxyethyl; MOM = methoxymethyl; BOM = benzyloxymethyl; MIP = methoxyisopropyl; THP = 2-tetrahydropyranyl.
[b] Isolated yield of the stereoisomeric mixture.
[c] Determined by ^{1}H NMR analysis.
[d] Determined by ^{1}H NMR assay using mesitylene as an internal standard.



Scheme 3

The high stereoselectivity, though its exact origin is unclear at present, might be rationalized as a result of the precoordination of the *n*-butyllithium to the both ether oxygens to form complex **A** which should be sterically favored over complex **B**. The complex **A** leads to the 1*Z*,3*E* isomer and the complex **B** leads to the 1*Z*,3*E* or 1*Z*,3*Z* isomers (Figure 1).[13]

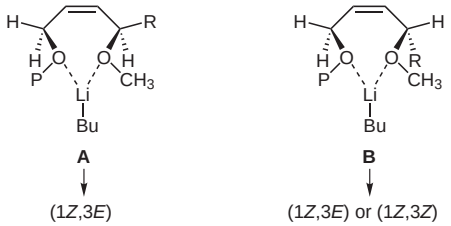
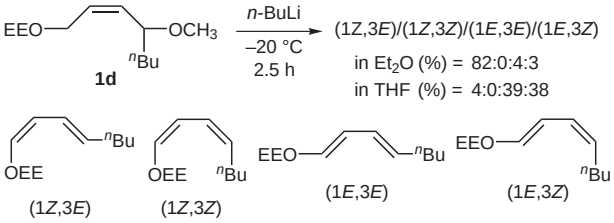
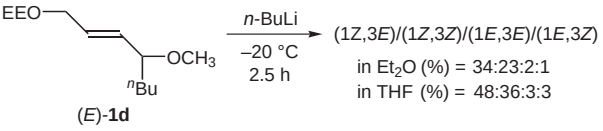


Figure 1

In fact, when a similar reaction of **1d** was carried out in THF which might suppress the aforementioned precoordination, the dienyl ether was obtained as a 1:1 mixture of the 1*E*,3*E* and 1*E*,3*Z* isomer, together with 4% of 1*Z*,3*E* isomer in 81% combined yield, respectively (Scheme 4). The observed 1*Z*-to-1*E* changeover is surprising, while its mechanistic origin is presently unclear.[14] More interestingly, a similar reaction of the 2*E* counterpart of **1d** in diethyl ether, wherein the aforementioned bidentate precoordination is impossible, was found to give a 1.5:1 mixture of the 1*Z*,3*E* and 1*Z*,3*Z* isomer, along with 3% of other isomers in 60% combined yield (Scheme 5). In this *E*-substrate case, switch of the solvent to THF provided nearly identical stereoisomeric ratios.[15]



Scheme 4



Scheme 5

In summary, we have demonstrated that simple treatment of 1-siloxy-4-methoxy- and 1-alkoxy-4-methoxy-(2*Z*)-alkenes with *n*-butyllithium in diethyl ether affords the corresponding 1,3-dienyl ethers as the 1*Z*,3*E*-form in high stereoselectivity. Furthermore, the interesting regio- and stereochemical features of the dienyl ether forming 1,4-elimination reaction are revealed. The synthetic application of the conjugated dienyl ethers thus obtained is underway in our laboratory.

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(9) Prepared in three steps: (i) *t*-BuMe$_2$SiOCH$_2$C≡CH, *n*-BuLi, THF, –78 °C then *n*-BuCHO, –78 °C to r.t.; (ii) NaH, MeI, THF, 0 °C to r.t.; (iii) H_2 (1 atm), 5% Lindlar cat., quinoline, MeOH, r.t.
(10) All stereoisomers were identified by ^{1}H NMR comparisons of the authentic samples prepared from (EtO)$_2$P(O)CH$_2$OP via the literature procedure (ref. 7d).
(11) Prepared from POCH$_2$C≡CH according to the same three-step procedure as described for **1b** (ref. 9).
(12) **Typical Procedure for the Preparation of 1,3-Dienyl Ethers 2**
To a solution of **1** (1.0 equiv, 0.25 M) in Et$_2$O was added a 1.6 M *n*-BuLi solution in *n*-hexane (1.5 equiv) at –40 °C to 0 °C and the mixture was stirred for 2–4 h at the same temperature. The resulting mixture was quenched with H_2O and extracted with Et$_2$O. The combined extract was washed with brine, dried over $NaSO_4$ and concentrated. The residue was purified by chromatography on silica gel to afford the corresponding 1,3-dienyl ether **2**.
Selected Spectroscopic Data
(2*Z*)-1-(*tert*-Butyldimethylsilyloxy)-4-methoxy-2-butene (1a)
Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.70 (1 H, dtt, *J* = 11.1, 5.9, 1.4 Hz, 2- or 3-H), 5.57 (1 H, dtt, *J* = 11.1, 5.9, 1.4 Hz, 2- or 3-H), 4.24 (1 H, dd, *J* = 5.9, 1.4 Hz, 1-H), 3.99 (1 H, dd, *J* = 5.9, 1.4 Hz, 4-H), 3.33 (3 H, s, OCH_3), 0.90 [9 H, s, $SiC(CH_3)_3$], 0.07 [6 H, s, $Si(CH_3)_2$]. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 132.6, 126.7, 68.3, 59.5, 58.0, 26.0, 18.4, –5.0. IR (film): 3020, 2948, 2924, 2884, 2852, 1475, 1470, 1406, 1362, 1334, 1254, 1190, 1092, 1006, 956, 912, 838, 776 cm^{-1}. Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.05; H, 11.18. Found: C, 61.17; H, 11.48.
(2*Z*)-1-(Benzyloxymethoxy)-4-methoxy-2-octene (1f)
Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.40–7.27 (5 H, m, Ph), 5.82–5.72 (1 H, m, 2-H), 5.49–5.39 (1 H, m, 3-H), 4.78 (2 H, s, OCH_2O), 4.62 (2 H, s, OCH_2Ph), 4.27 (1 H, ddd, *J* = 12.4, 7.3, 1.4 Hz, 1-CH_2), 4.15 (1 H, ddd, *J* = 12.4, 6.1, 1.4 Hz, 1-CH_2), 3.94–3.85 (1 H, m, 4-H), 3.25 (3 H, s, OCH_3), 1.68–1.52 (1 H, m, 5-CH_2), 1.47–1.18 (5 H, m, 5-, 6-, and 7-CH_2), 0.88 (3 H, t, *J* = 6.8 Hz, 8-CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 137.6, 134.2, 128.7, 128.3, 127.7, 127.6, 93.8, 76.6, 69.3, 63.2, 56.1, 35.2, 27.4, 22.7, 14.1. IR (film): 3060, 3024, 2928, 2872, 2816, 1496, 1454, 1402, 1380, 1206, 1190, 1168, 1102, 1048, 962, 958, 736, 698 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.42; H, 9.63.
(1*Z*)-1-(*tert*-Butyldimethylsilyloxy)-1,3-butadiene (2a)[16]
Colorless oil; purified by chromatography on silica gel (hexane–Et$_2$O = 100:1 to 20:1 as eluent). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.76 (1 H, dddd, *J* = 17.3, 10.7, 10.3, 1.1 Hz, 3-H), 6.19 (1 H, ddd, *J* = 5.9, 1.1, 1.1 Hz, 1-H), 5.20 (1 H, dd, *J* = 10.7, 5.9 Hz, 2-H), 5.07 (1 H, m, *J* = 17.3, 2.0 Hz, 4_{cis}-H), 4.89 (1 H, ddd, *J* = 10.3, 2.0, 1.1 Hz, 4_{trans}-H), 0.94 [9 H, s, $SiC(CH_3)_3$], 0.16 [6 H, s, $Si(CH_3)_2$]. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.4, 129.8, 112.9, 111.1, 25.7, 18.4, –5.3. IR (film): 3080, 2952, 2928, 2884, 2856, 1642, 1594, 1472, 1438, 1392, 1362, 1254, 1174, 1080, 998, 928, 890, 840, 784 cm^{-1}.
(1*Z*,3*E*)-1-(*tert*-Butyldimethylsilyloxy)-1,3-octadiene (2b)
Colorless oil; purified by chromatography on silica gel (hexane–EtOAc = 100:1 as eluent). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.40 (1 H, ddd, *J* = 15.6, 10.8, 1.1 Hz, 3-H), 6.09 (1 H, d, *J* = 5.9 Hz, 1-H), 5.55 (1 H, dt, *J* = 15.6, 6.8 Hz, 4-H), 5.13 (1 H, dd, *J* = 10.8, 5.9 Hz, 2-H), 2.14–2.02 (2 H, dt, *J* = 6.8, 6.8 Hz, 5-CH_2), 1.44–1.24 (4 H, m, 6-CH_2 and 7-CH_2), 0.94 [9 H, s, $SiC(CH_3)_3$], 0.89 (3 H, t, *J* = 7.0 Hz, 8-CH_3), 0.15 [6 H, s, $Si(CH_3)_2$]. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.2, 130.9, 122.8, 110.8, 32.7, 31.8, 25.7, 22.4, 18.4, 14.1, –5.2. IR (film): 3028, 2952, 2924, 2852, 1654, 1612, 1470, 1410, 1362, 1254, 1156, 1112, 1050, 1006, 972, 838, 780 cm^{-1}. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.70; H, 12.03.
(1*Z*,3*E*)-1-(*tert*-Butyldimethylsilyloxy)-4-methoxy-1,3-butadiene (2c)
Pale yellow oil; purified by chromatography on silica gel (hexane–Et$_2$O = 30:1 as eluent). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.55 (1 H, d, *J* = 13.0 Hz, 4-H), 6.06 (1 H, d, *J* = 5.9 Hz, 1-H), 5.84 (1 H, dd, *J* = 13.0, 10.8 Hz, 3-H), 5.05 (1 H, dd, *J* = 10.8, 5.9 Hz, 2-H), 3.59 (3 H, s, OCH_3), 0.94 [9 H, s, $SiC(CH_3)_3$], 0.15 [6 H, s, $Si(CH_3)_2$]. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 148.2, 136.6, 106.5, 98.9, 56.2, 25.7, 18.4, –5.2. IR (film): 2948, 2928, 2892, 2852, 1656, 1608, 1470, 1406, 1362, 1332, 1256, 1208, 1166, 1136, 1124, 1064, 938, 838, 780 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34. Found: C, 61.58; H, 10.61.
(1*Z*,3*E*)-1-(1-Ethoxyethoxy)-1,3-octadiene (2d)
Pale yellow oil; purified by chromatography on silica gel (hexane–EtOAc = 70:1 to 40:1 as eluent). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.39 (1 H, ddd, *J* = 15.4, 10.8, 1.4 Hz, 3-H), 6.12 (1 H, d, *J* = 5.9 Hz, 1-H), 5.57 (1 H, dt, *J* = 15.4, 7.0 Hz, 4-H), 5.12 (1 H, dd, *J* = 10.8, 5.9 Hz, 2-H), 4.94 (1 H, q, *J* = 5.4 Hz, OCHO), 3.74 (1 H, dq, *J* = 9.5, 7.2 Hz, OCH_2CH_3), 3.49 (1 H, dq, *J* = 9.5, 7.2 Hz, OCH_2CH_3), 2.12–2.04 (2 H, dt, *J* = 7.0, 6.8 Hz, 5-CH_2), 1.43–1.25 (4 H, m, 6-CH_2 and 7-CH_2), 1.39 [3 H, d, *J* = 5.4 Hz, $OCH(CH_3)O$], 1.21 (3 H, t, *J* = 7.2 Hz, OCH_2CH_3), 0.89 (3 H, t, *J* = 7.0 Hz,

8-CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.9, 131.5, 122.8, 108.1, 100.9, 62.5, 32.7, 31.8, 22.4, 20.6, 15.2, 14.0. IR (film): 3036, 2956, 2924, 2872, 1656, 1618, 1444, 1382, 1342, 1276, 1226, 1150, 1134, 1112, 1080, 1052, 974, 880, 830, 748 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.52; H, 11.47.

(1*Z*,3*E*)-1-(Methoxymethoxy)-1,3-octadiene (2e)

Colorless oil; purified by chromatography on silica gel (hexane–EtOAc = 70:1 to 40:1 as eluent). ^1H NMR (270 MHz, $CDCl_3$): δ = 6.39 (1 H, ddd, *J* = 15.5, 10.9, 1.1 Hz, 3-H), 6.03 (1 H, d, *J* = 6.2 Hz, 1-H), 5.60 (1 H, dt, *J* = 15.5, 7.0 Hz, 4-H), 5.17 (1 H, dd, *J* = 10.9, 6.2 Hz, 2-H), 4.83 (2 H, s, OCH_2O), 3.42 (3 H, s, OCH_3), 2.16–2.02 (2 H, dt, *J* = 7.0, 6.8 Hz, 5-CH_2), 1.45–1.23 (4 H, m, 6-CH_2 and 7-CH_2), 0.90 (3 H, t, *J* = 7.0 Hz, 8-CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 141.2, 132.2, 122.4, 108.9, 96.4, 55.8, 32.7, 31.7, 22.4, 14.1. IR (film): 3036, 2952, 2920, 1658, 1618, 1464, 1386, 1306, 1242, 1160, 1114, 1042, 974, 924, 830, 750 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.38; H, 10.75.

(1*Z*,3*E*)-1-(Benzyloxymethoxy)-1,3-octadiene (2f)

Colorless oil; purified by chromatography on silica gel (hexane–EtOAc = 80:1 to 50:1 as eluent). ^1H NMR (270 MHz, $CDCl_3$): δ = 7.37–7.27 (5 H, m, Ph), 6.40 (1 H, ddd, *J* = 15.4, 10.8, 1.1 Hz, 3-H), 6.10 (1 H, d, *J* = 6.2 Hz, 1-H), 5.61 (1 H, dt, *J* = 15.4, 7.0 Hz, 4-H), 5.19 (1 H, dd, *J* = 10.8, 6.2 Hz, 2-H), 4.95 (2 H, s, OCH_2O), 4.65 (2 H, s, OCH_2Ph), 2.16–2.06 (2 H, dt, *J* = 7.0, 6.8 Hz, 5-CH_2), 1.45–1.25 (4 H, m, 6-CH_2 and 7-CH_2), 0.90 (3 H, t, *J* = 7.0 Hz, 8-CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 141.2, 137.0, 132.2, 128.3, 128.0, 127.8, 122.4, 109.0, 94.3, 69.8, 32.7, 31.7, 22.4, 14.1. IR (film): 3032, 2952, 2924, 2868, 1658, 1618, 1496, 1454, 1380, 1300, 1226, 1172, 1116, 1042, 974, 904, 832, 744, 696 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.16; H, 9.21.

(1*Z*,3*E*)-1-(1-Methoxy-1-methylethoxy)-1,3-octadiene (2g)

Pale yellow oil; purified by chromatography on silica gel (hexane–EtOAc = 80:1 to 60:1 as eluent). ^1H NMR (270 MHz, C_6D_6): δ = 6.83 (1 H, ddd, *J* = 15.5, 10.7, 1.1 Hz, 3-H), 6.32 (1 H, d, *J* = 6.2 Hz, 1-H), 5.61 (1 H, dt, *J* = 15.5, 7.0 Hz, 4-H), 5.30 (1 H, dd, *J* = 10.7, 6.2 Hz, 2-H), 3.01 (3 H, s, OCH_3), 2.13–2.01 (2 H, dt, *J* = 7.0, 6.5 Hz, 5-CH_2), 1.38–1.15 [10 H, m, $OC(CH_3)_2O$ and 6, 7-CH_2], 0.81 (3 H, t, *J* = 7.0 Hz, 8-CH_3). ^{13}C NMR (68 MHz, C_6D_6): δ = 137.0, 131.0, 124.2, 108.9, 101.9, 48.9, 33.2, 32.3, 25.0, 22.8, 14.3. IR (film): 3032, 2988, 2952, 2924, 2852, 1656, 1616, 1464, 1402, 1374, 1264, 1218, 1184, 1138, 1106, 1072, 1032, 974, 868, 782, 750 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.55; H, 11.44.

(1*Z*,3*E*)-1-(2-Tetrahydropyranyloxy)-1,3-octadiene (2h)

Pale yellow oil; purified by chromatography on silica gel (hexane–EtOAc = 70:1 to 40:1 as eluent). ^1H NMR (270 MHz, $CDCl_3$): δ = 6.42 (1 H, ddd, *J* = 15.5, 10.9, 0.8 Hz, 3-H), 6.10 (1 H, d, *J* = 5.9 Hz, 1-H), 5.59 (1 H, dt, *J* = 15.5, 7.3 Hz, 4-H), 5.16 (1 H, dd, *J* = 10.9, 5.9 Hz, 2-H), 4.94 (1 H, t, *J* = 3.1 Hz, OCHO), 3.85 (1 H, ddd, *J* = 11.2, 9.5, 3.5 Hz, THP-6-CH_2), 3.62–3.52 (1 H, m, THP-6-CH_2), 2.16–2.04 (2 H, dt, *J* = 7.3, 6.8 Hz, 5-CH_2), 1.99–1.11 (10 H, m, THP-3,4,5-CH_2 and 6,7-CH_2), 0.90 (3 H, t, *J* = 7.3 Hz, 8-CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.8, 131.8, 122.6, 108.4, 98.5, 61.9, 32.7, 31.8, 29.7, 25.2, 22.4, 18.7, 14.1. IR (film): 3032, 2946, 2924, 2868, 1658, 1618, 1454, 1356, 1242, 1202, 1124, 1028, 970, 904, 872, 816, 750 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.25; H, 10.78.

(1*Z*,3*E*)-1-(*tert*-Butyldimethylsilyloxy)-6-methyl-1,3,5-heptatriene (2i)

Colorless oil; purified by chromatography on silica gel (hexane–Et_2O = 50:1 to 20:1 as eluent). ^1H NMR (270 MHz, $CDCl_3$): δ = 6.48 (1 H, dd, *J* = 15.1, 10.5 Hz, 3-H), 6.30 (1 H, dd, *J* = 15.1, 10.8 Hz, 4-H), 6.17 (1 H, d, *J* = 5.7 Hz, 1-H), 5.93–5.86 (1 H, m, 5-H), 5.24 (1 H, dd, *J* = 10.5, 5.7 Hz, 2-H), 1.79 [3 H, s, $C(CH_3)_2$], 1.76 [3 H, s, $C(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 0.16 [6 H, s, $Si(CH_3)_2$]. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 139.5, 134.0, 125.9, 125.6, 123.2, 111.3, 26.2, 25.7, 18.4, –5.2. IR (film): 3028, 2952, 2924, 2856, 1646, 1628, 1584, 1470, 1408, 1274, 1256, 1236, 1140, 1066, 1032, 1006, 986, 964, 838, 780 cm^{-1}. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.78; H, 11.23.

(13) Use of *s*-BuLi or *t*-BuLi in Et_2O instead of *n*-BuLi gave the same results, which suggests that the aggregation states of *n*-BuLi under our reaction conditions are monomer or dimer, since *t*-BuLi becomes dimeric in Et_2O without substrates.

(14) The complete 1*Z*-to-1*E* changeover was observed in the case of **1d**. The reaction of silyl derivative **1b** in THF under the same conditions gave a mixture of stereoisomers without any detectable retro-Brook rearrangement product: (1*Z*,3*E*)/(1*Z*,3*Z*)/(1*E*,3*E*)/(1*E*,3*Z*) = 42:1:16:21 (yield, %).

(15) Use of TMEDA–Et_2O instead of THF gave almost the same results.

(16) Hartung, J.; Kneuer, R. *Eur. J. Org. Chem.* **2000**, 1677.