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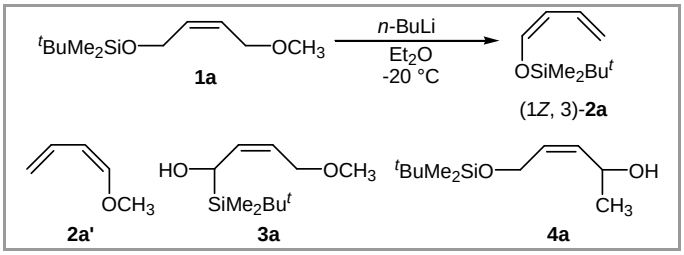
Abstract: Treatment of 1-alkoxy-4-methoxy- or 1-siloxy-4-methoxy-(2*Z*)-alkenes with *n*-butyllithium in ether is shown to afford the corresponding (1*Z*, 3*E*)-dienyl alkyl or silyl ethers, respectively, in high stereoselectivity via a facile 1,4-elimination. The scope and the regio- and stereochemical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

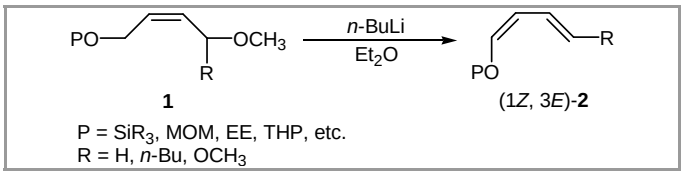
Key words: 1,4-eliminations, dienyl ethers, dienyl acetals, stereoselective synthesis, precoordinations

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 *t*-butyldimethylsilyl ether (**1a**) was treated with *n*-butyllithium (1.5 equiv) in ether, the (1*Z*, 3)-butadienyl silyl ether (**2a**) was formed in 70% yield as a single stereoisomer without any concomitant formations of possible byproducts such as the other dienyl ether **2a'**, the [1,2] retro-Brook product **3a**, and the [1,2] Wittig product **4a** (Equation 1).



Equation 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 -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 (Equation 2).



Equation 2

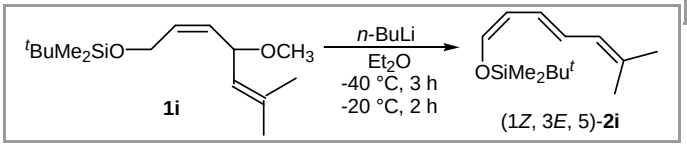
As already mentioned, we found that silyl ether **1a** was treated with *n*-BuLi in ether at -20 °C for 2 h gave the (1*Z*, 3)-dienyl silyl ether **2a** as a single stereoisomer in 70% yield (Table 1, Entry 1). The (*Z*)-geometry was assigned by ^{1}H NMR assay ($J_{1H, 2H}$ = 5.9 Hz). Apparently, this 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 $J_{3H, 4H}$ = 15.4 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*-protec-

Table 1 The reactions of ether **1** with *n*-BuLi

Entry	Substrate[a]	Temp (°C)	Time (h)	Product	Yield (%)[b]	(1*Z*, 3*E*)/other isomers[c]
1	**1a** (P = SiMe$_2$Bu^t, R = H)	-20	2	**2a**	70[d]	>98:2
2	**1b** (P = SiMe$_2$Bu^t, R = *n*-Bu)	-20	4	**2b**	88	>98:2
3	**1c** (P = SiMe$_2$Bu^t, 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.

-ted ethers **1d-1h**[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 Equation 3.



Equation 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. 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).[12]

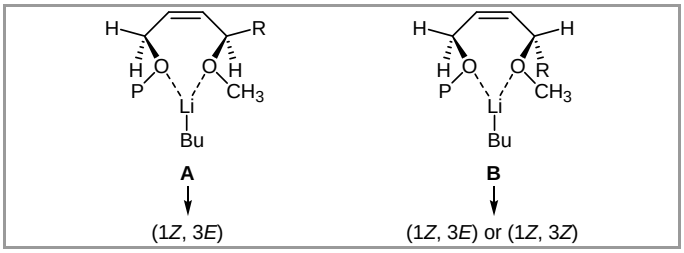
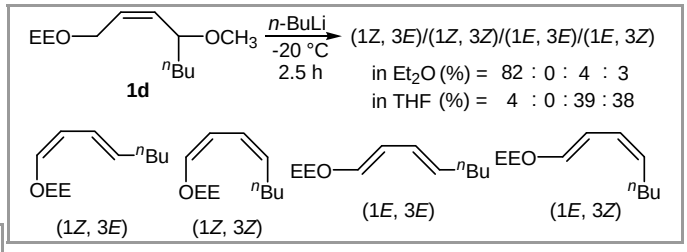


Figure 1

Experimental Section

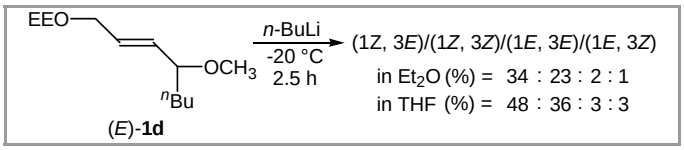
Typical procedure for the preparation of 1,3-dienyl ethers 2 : To a solution of **1** (1.0 equiv, 0.25 M) in Et_2O was added a 1.6 M *n*-butyllithium solution in *n*-hexane (1.5 equiv) at -40-0 °C and the mixture was stirred for 2-4 h at the same temperature. The resulting mixture was quenched with H_2O and extracted with Et_2O. The combined extract was washed with brine, dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel to afford the corresponding 1,3-dienyl ether **2**.

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 (Equation 4). The observed (1*Z*)-to-(1*E*) changeover is



Equation 4

surprising, while its mechanistic origin is presently unclear.[13] More interestingly, a similar reaction of the (2*E*)-counterpart of **1d** in 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 (Equation 5). In this (*E*)-substrate case, switch of the solvent to THF provided nearly identical stereoisomeric ratios.[14]



Equation 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 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.

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 (1H, dtt, *J* = 11.1, 5.9, 1.4 Hz, 2- or 3-H), 5.57 (1H, dtt, *J* = 11.1, 5.9, 1.4 Hz, 2- or 3-H), 4.24 (1H, dd, *J* = 5.9, 1.4 Hz, 1-H), 3.99 (1H, dd, *J* = 5.9, 1.4 Hz, 4-H), 3.33 (3H, s, OCH_3), 0.90 (9H, s, $SiC(C\underline{H}_3)_3$), 0.07 (6H, s, $Si(C\underline{H}_3)_2$); ^{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 (5H, m, Ph), 5.82-5.72 (1H, m, 2-H), 5.49-5.39 (1H, m, 3-H), 4.78 (2H, s, OCH_2O), 4.62 (2H, s, $OC\underline{H}_2Ph$), 4.27 (1H, ddd, *J* = 12.4, 7.3, 1.4 Hz, 1-CH_2), 4.15 (1H, ddd, *J* = 12.4, 6.1, 1.4 Hz, 1-CH_2), 3.94-3.85 (1H, m, 4-H), 3.25 (3H, s, OCH_3), 1.68-1.52 (1H, m, 5-CH_2), 1.47-1.18 (5H, m, 5-, 6-, and 7-CH_2), 0.88 (3H, 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)[15]: colorless oil; purified by chromatography on silica gel (hexane/Et_2O = 100:1 to 20:1 as eluent); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.76 (1H, dddd, *J* = 17.3, 10.7, 10.3, 1.1 Hz, 3-H), 6.19 (1H, ddd, *J* = 5.9, 1.1, 1.1 Hz, 1-H), 5.20 (1H, dd, *J* = 10.7, 5.9 Hz, 2-H), 5.07 (1H, m, *J* = 17.3, 2.0 Hz, 4_{cis}-H), 4.89 (1H, ddd, *J* = 10.3, 2.0, 1.1 Hz, 4_{trans}-H), 0.94 (9H, s, $SiC(C\underline{H}_3)_3$), 0.16 (6H, s, $Si(C\underline{H}_3)_2$); ^{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 (1H, ddd, *J* = 15.6, 10.8, 1.1 Hz, 3-H), 6.09 (1H, d, *J* = 5.9 Hz, 1-H), 5.55 (1H, dt, *J* = 15.6, 6.8 Hz, 4-H), 5.13 (1H, dd, *J* = 10.8, 5.9 Hz, 2-H), 2.14-2.02 (2H, dt, *J* = 6.8, 6.8 Hz, 5-CH_2), 1.44-1.24 (4H, m, 6-CH_2 and 7-CH_2), 0.94 (9H, s, $SiC(C\underline{H}_3)_3$), 0.89 (3H, t, *J* = 7.0 Hz, 8-CH_3), 0.15 (6H, s, $Si(C\underline{H}_3)_2$); ^{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_2O = 30:1 as eluent); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.55 (1H, d, *J* = 13.0 Hz, 4-H), 6.06 (1H, d, *J* = 5.9 Hz, 1-H), 5.84 (1H, dd, *J* = 13.0, 10.8 Hz, 3-H), 5.05 (1H, dd, *J* = 10.8, 5.9 Hz, 2-H), 3.59 (3H, s, OCH_3), 0.94 (9H, s, $SiC(C\underline{H}_3)_3$), 0.15 (6H, s, $Si(C\underline{H}_3)_2$); ^{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 (1H, ddd, *J* = 15.4, 10.8, 1.4 Hz, 3-H), 6.12 (1H, d, *J* = 5.9 Hz, 1-H), 5.57 (1H, dt, *J* = 15.4, 7.0 Hz, 4-H), 5.12 (1H, dd, *J* = 10.8, 5.9 Hz, 2-H), 4.94 (1H, q, *J* = 5.4 Hz, OCHO), 3.74 (1H, dq, *J* = 9.5, 7.2 Hz, $OC\underline{H}_2CH_3$), 3.49 (1H, dq, *J* = 9.5, 7.2 Hz, $OC\underline{H}_2CH_3$), 2.12-2.04 (2H, dt, *J* = 7.0, 6.8 Hz, 5-CH_2), 1.43-1.25 (4H, m, 6-CH_2 and 7-CH_2), 1.39 (3H, d, *J* = 5.4 Hz, $OCH(C\underline{H}_3)O$), 1.21 (3H, t, *J* = 7.2 Hz, $OCH_2C\underline{H}_3$), 0.89 (3H, 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); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.39 (1H, ddd, *J* = 15.5, 10.9, 1.1 Hz, 3-H), 6.03 (1H, d, *J* = 6.2 Hz, 1-H), 5.60 (1H, dt, *J* = 15.5, 7.0 Hz, 4-H), 5.17 (1H, dd, *J* = 10.9, 6.2 Hz, 2-H), 4.83 (2H, s, OCH_2O), 3.42 (3H, s, OCH_3), 2.16-2.02 (2H, dt, *J* = 7.0, 6.8 Hz, 5-CH_2), 1.45-1.23 (4H, m, 6-CH_2 and 7-CH_2), 0.90 (3H, 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); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.37-7.27 (5H, m, Ph), 6.40 (1H, ddd, *J* = 15.4, 10.8, 1.1 Hz, 3-H), 6.10 (1H, d, *J* = 6.2 Hz, 1-H), 5.61 (1H, dt, *J* = 15.4, 7.0 Hz, 4-H), 5.19 (1H, dd, *J* = 10.8, 6.2 Hz, 2-H), 4.95 (2H, s, OCH_2O), 4.65 (2H, s, $OC\underline{H}_2Ph$), 2.16-2.06 (2H, dt, *J* = 7.0, 6.8 Hz, 5-CH_2), 1.45-1.25 (4H, m, 6-CH_2 and 7-CH_2), 0.90 (3H, 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); ^{1}H NMR (270 MHz, C_6D_6) δ 6.83 (1H, ddd, *J* = 15.5, 10.7, 1.1 Hz, 3-H), 6.32 (1H, d, *J* = 6.2 Hz, 1-H), 5.61 (1H, dt, *J* = 15.5, 7.0 Hz, 4-H), 5.30 (1H, dd, *J* = 10.7, 6.2 Hz, 2-H), 3.01 (3H, s, OCH_3), 2.13-2.01 (2H, dt, *J* = 7.0, 6.5 Hz, 5-CH_2), 1.38-1.15 (10H, m, $OC(CH_3)_2O$ and 6, 7-CH_2), 0.81 (3H, 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); ^{1}H

NMR (270 MHz, $CDCl_3$) δ 6.42 (1H, ddd, *J* = 15.5, 10.9, 0.8 Hz, 3-H), 6.10 (1H, d, *J* = 5.9 Hz, 1-H), 5.59 (1H, dt, *J* = 15.5, 7.3 Hz, 4-H), 5.16 (1H, dd, *J* = 10.9, 5.9 Hz, 2-H), 4.94 (1H, t, *J* = 3.1 Hz, OCHO), 3.85 (1H, ddd, *J* = 11.2, 9.5, 3.5 Hz, THP-6-CH_2), 3.62-3.52 (1H, m, THP-6-CH_2), 2.16-2.04 (2H, dt, *J* = 7.3, 6.8 Hz, 5-CH_2), 1.99-1.11 (10H, m, THP-3,4,5-CH_2 and 6, 7-CH_2), 0.90 (3H, 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 (1H, dd, *J* = 15.1, 10.5 Hz, 3-H), 6.30 (1H, dd, *J* = 15.1, 10.8 Hz, 4-H), 6.17 (1H, d, *J* = 5.7 Hz, 1-H), 5.93-5.86 (1H, m, 5-H), 5.24 (1H, dd, *J* = 10.5, 5.7 Hz, 2-H), 1.79 (3H, s, $C(CH_3)_2$), 1.76 (3H, s, $C(CH_3)_2$), 0.94 (9H, s, $SiC(C\underline{H}_3)_3$), 0.16 (6H, s, $Si(C\underline{H}_3)_2$); ^{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.

References and Notes

(1) For reviews: (a) Tomooka, K. In *The Chemistry of Organolithium Compounds*, ed. by Rappoport, Z.; Marek, I. John Wiley & Sons Ltd., Chichester, **2004**, Vol. 2, pp 749-828. (b) Clayden, J. In *Organolithiums: Selectivity for Synthesis*, ed. by Baldwin, J. E.; Williams, R. M. Pergamon, Manchester, **2002**, Chap. 8. (c) Tomooka, K.; Yamamoto, H.; Nakai, T. *Liebigs Ann./Recueil* **1997**, 1275. (d) Nakai, T.; Mikami, K. *Org. React.* **1994**, *46*, 105. (e) Brückner, R. In *Comprehensive Organic Synthesis*, ed. by Trost, B. M.; Fleming, I. Pergamon, Oxford, **1991**, Vol. 6, Chap. 4.6.

(2) (a) Casiraghi, G.; Zanardi, F.; Appendino, G.; Rassu, G. *Chem. Rev.* **2000**, *100*, 1929. (b) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161.

(3) (a) Inui, M.; Hosokawa, S.; Nakazaki, A.; Kobayashi, S. *Tetrahedron Lett.* **2005**, *46*, 3245. (b) Suzuki, T.; Inui, M.; Hosokawa, S.; Kobayashi, S. *Tetrahedron Lett.* **2003**, *44*, 3713.

(4) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.

(5) For a review of 1,3-dienyl silyl ethers (silyl dienol ethers): Brownbridge, P. *Synthesis* **1983**, 85.

(6) Previous preparation of 1,3-dienyl silyl ethers: (a) Choi, J.; Imai, E.; Mihara, M.; Oderaotoshi, Y.; Minakata, S.; Komatsu, M. *J. Org. Chem.* **2003**, *68*, 6164. (b) Janey, J. M.; Iwama, T.; Kozmin, S. A.; Rawal, V. H. *J. Org. Chem.* **2000**, *65*, 9059. (c) Moreno, M. J. S. M.; Martins, R. M. L. M.; Melo, M. L. S.; Neves, A. S. C. *Chem. Lett.* **1997**, 529. (d) Tominaga, Y.; Kamio, C.; Hosomi, A. *Chem. Lett.* **1989**, 1761. (e) Iqbal, J.; Khan, M. A. *Synth. Commun.* **1989**, *19*, 515. (f) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2089. (g) Colvin, E. W.; Thom, I. G. *Tetrahedron* **1986**, *42*, 3137. (h) Casey, C. P.; Jones, C. R.; Tukada, H. *J. Org. Chem.* **1981**, *46*, 2089. (i) Hirai, K.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 3413. (j) Miller, R. D.; McKean, D. R. *Synthesis* **1979**, 730. (k) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(7) Previous preparation of alkyl 1,3-dienyl ethers: (a) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 448. (b) Hiranuma, H.; Miller, S. I. *J. Org. Chem.* **1982**, *47*, 5083. (c) Dowd, P.; Weber, W. *J. Org. Chem.* **1982**, *47*, 4774. (d) Kluge, A. F.; Cloudsdale, I. S. *J. Org. Chem.* **1979**, *44*, 4847. (e) Earnshaw, C.; Wallis, C. J.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3099.

(8) A similar type of 1,4-elimination reaction has been reported using allylic acetals: Canepa, C.; Prandi, C.; Sacchi, L.; Venturello, P. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1875.

(9) Prepared in the three steps: (i) $^tBuMe_2SiOCH_2C{\equiv}CH$, *n*-BuLi, THF, -78 °C then *n*-BuCHO, -78 °C to rt. (ii) NaH, MeI, THF, 0 °C to rt. (iii) H_2 (1 atm), 5% Lindlar cat, quinoline, MeOH, rt.

(10) All stereoisomers were identified by ^1H NMR comparisons of the authentic samples prepared from $(EtO)_2P(O)CH_2OP$ via the literature procedure (ref. 7d).

(11) Prepared from $POCH_2C{\equiv}CH$ according to the same three step procedure as described for **1b** (ref. 9).

(12) 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.

(13) 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).

(14) Use of TMEDA-Et_2O instead of THF gave almost the same results.

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