Tetrahedron Vol. 48, No. 20, pp. 4087-4098, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

[2,3]Wittig Rearrangement-Peterson Olefination Sequence: A Stereocontrolled Entry to Terminal Conjugated Trienes

Naoyuki Kishi, Toshihiko Maeda, Koichi Mikami, and Takeshi Nakai*

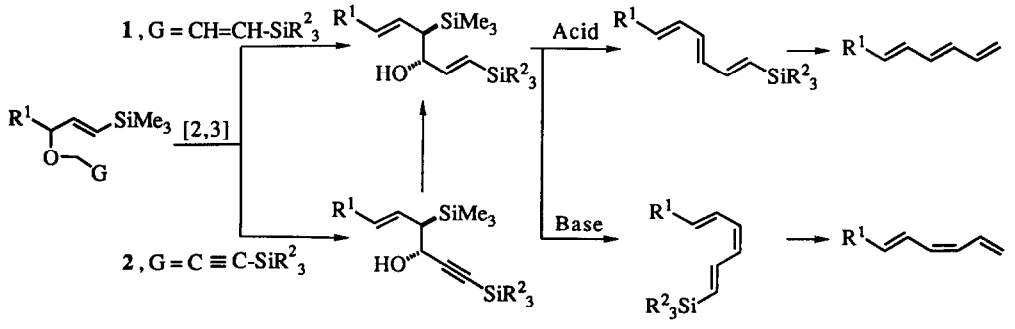
Department of Chemical Technology, Tokyo Institute of Technology,
Meguro-ku, Tokyo 152, Japan

(*Received in Japan* 24 *February* 1992)

Key Words: [2,3]Wittig rearrangement; Peterson olefination; γ-(silyl)allylic ethers; conjugated triene; sarohornene B and C

Abstract: *A new and highly stereocontrolled entry to terminal conjugated trienes is described which relies upon the diastereoselective [2,3]Wittig rearrangement of γ-(silyl)allylic propargyl ethers followed by Peterson olefination. The synthetic utility of this method is demonstrated by the stereocontrolled synthesis of sarohornene B and C (marine natural products).*

A terminal conjugated triene moiety is often found in natural products of biological interest.[1] However, only a few methods have been reported for stereocontrolled synthesis of such trienes.[2] In an attempt to enhance the synthetic utility of the [2,3]Wittig rearrangement,[3] we were interested in the [2,3]Wittig process of the γ-(silyl)allylic ethers (**1** and **2**)[4] which could eventually afford the terminal conjugated trienes via the Peterson olefination[5] (Scheme 1). Reported herein is a new and fully stereocontrolled entry to terminal



Scheme 1

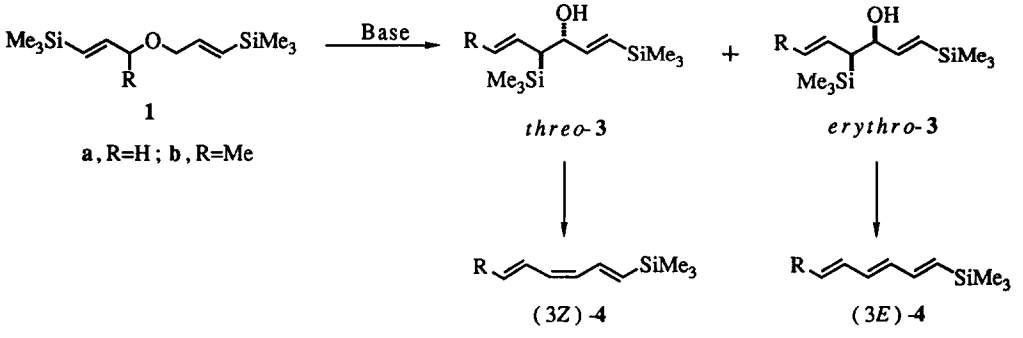
conjugated trienes which relies upon the highly (*E*)- and *threo*-selective [2,3]Wittig variant of the γ-(silyl)allylic propargyl ethers (**2**).[6] The synthetic utility of the [2,3]Wittig-Peterson olefination is demonstrated in the context of the stereocontrolled synthesis of (3*E*, 5*E*)-1, 3, 5-octatriene (sarohornene B) and its (3*Z*)-isomer (sarohornene C) which are the components of male-attractant pheromones isolated from a dioecious marine brown alga, *Sargassum horneri*.[7]

Sarohornene B

Sarohornene C

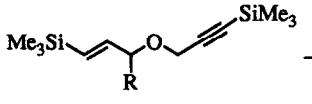
RESULTS AND DISCUSSION

First we examined the diastereoselection in the [2,3]Wittig rearrangement of bis-allylic ethers (**1**) which would directly lead to the formation of trienes (Scheme 2). The substrates (**1**) were easily prepared via etherification of (*E*)-γ-(silyl)allylic alcohols with the (*E*)-γ-(silyl)allyl bromide or mesylate. We found that the treatment of **1a** (R=H) with lithium dicyclohexylamide (LDCA)[8,9] at -40 °C resulted in the formation of a 63 : 37 mixture of the (3*Z*)- and (3*E*)-triene **4a** (R=H)[10] in 79% yield. The low *Z*/*E* ratio apparently suggests the low diastereoselectivity in the [2,3]Wittig rearrangement concerned. Furthermore, the rearrangement of **1b** (R=Me) with butyllithium at -85 °C[11] was found to produce a diastereomeric mixture of the β-silyl alcohol **3b** (*threo* / *erythro*=90 : 10)[12] in 59% yield, along with a geometrical mixture of the triene **4b** [(3*Z*, 5*E*) / (3*E*, 5*E*)=18 : 82][10] in 22% yield. A similar rearrangement of the (*Z*)-counterpart of **1b**, derived from (*Z*)-1-trimethylsilyl-1-buten-3-ol, gave essentially the same results: *threo* / *erythro* =85 : 15[12] (50% yield) and (3*Z*, 5*E*) / (3*E*, 5*E*) =17 : 83[10] (31% yield). Thus, the [2,3]Wittig rearrangement of the bis-allylic ethers (**1**) was found to proceed with a relatively low *threo*-selectivity (60 - 70%), while an extremely high (*E*)-selectivity[13] was observed in the newly formed olefinic bond at the 5-position.

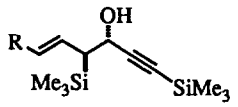


Scheme 2

Next, we examined the diastereoselection in the [2,3]Wittig rearrangement of the allylic propargylic ethers (**2**) (Scheme 3). The substrates (**2**) were easily prepared via etherification of (*E*)-γ-(silyl)allylic alcohols with propargyl bromide followed by silylation. We found that the rearrangement of **2** with butyllithium at -85 °C[11] gave the β-silyl alcohol (5*E*)-**5** as the sole product (without the formation of the conjugated dienyne). Of special interest is that **2a** (R=H) shows a high *erythro*-selectivity,[14] whereas both **2b** (R=Me) and **2c** (R=Et) exhibits a high *threo*-selectivity.[12]



n-BuLi / THF
-85 °C



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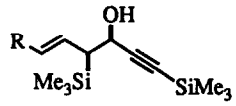


2	*threo*-**5**		*erythro*-**5**	
a, R=H	3	:	97	(90 %)
b, R=Me	96	:	4	(60 %)
c, R=Et	97	:	3	(65 %)

Scheme 3

The stereochemical changeover is explained as follows. Among the two possible transition states T_1 and T_2 (G=C≡C-TMS), the diastereoselectivity should be determined by the relative magnitude of the gauche repulsion of G ⟷ TMS in T_1 *vs.* the 1, 3-repulsion of G ⟷ R in T_2 (Fig. 1). In the case of **2a** (R=H), T_2 should be sterically more favorable, thus leading to a high *erythro*-selection as actually observed. In the case of **2b** (R=Me) and **2c** (R=Et), by contrast, the 1, 3-repulsion prevails over the gauche repulsion, thus leading to a high *threo*-selection as actually observed. A similar argument can be extended to explain the low diastereoselectivity observed in the rearrangement of the bis-allylic ethers (**1**) (G=CH=CH-TMS), wherein the energy difference between T_1 and T_2 would be much smaller.

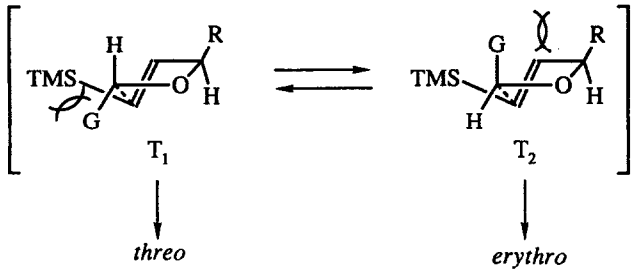
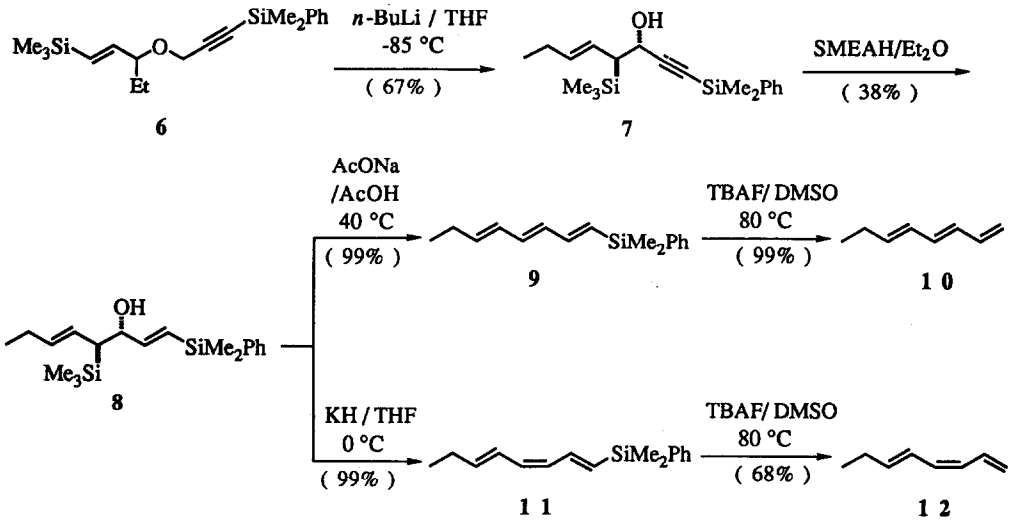


Fig.1

Taking full advantage of the highly *threo*-selective [2,3]Wittig rearrangement of allylic propargylic ethers (**2**), we carried out the stereoselective syntheses of (3*E*, 5*E*)- and (3*Z*, 5*E*)-1, 3, 5-octatriene (**10** and **12**) (Scheme 4). In the synthetic scheme, we chose $PhMe_2Si$ instead of Me_3Si as the silyl group on the

acetylenic terminus in view of the previous observation[15] that conjugated ω-(trimethylsilyl)dienes are not capable of undergoing protiodesilylation with fluoride ion.[16] Thus, the standard rearrangement[11] of ether **6** was found to proceed with an extremely high (*E*)- and *threo*-selectivity (*E* >99%[13], *threo*/*erythro*=99 : 1[12]) to give the β-silyl alcohol **7**, which was then reduced with sodium bis(2-methoxyethoxy)aluminum hydride (SMEAH)[17] to yield the (1*E*, 5*E*)-diene **8**. Olefination of **8** under acidic condition[18] afforded the (3*E*)-triene **9** with 98.0% of stereo-purity,[10] which was subjected to the protiodesilylation with fluoride ion[15] to give sarohornene B (**10**)[19] with 98.0% of stereo-purity[10] without isomerization or cyclization. On the other hand, olefination of **8** under basic condition[18] afforded the (3*Z*)-triene **11** with 98.3% of stereo-purity,[10] followed by protiodesilylation to give sarohornene C (**12**)[19] with 97.5% of stereo-purity.[10]



Scheme 4

In conclusion, this work demonstrates that the [2,3]Wittig rearrangement of γ-(silyl)allylic propargyl ethers, coupled with Peterson olefination, is quite useful for the fully stereocontrolled synthesis of terminal conjugated trienes.

EXPERIMENTAL

Boiling points are uncorrected. IR spectra were recorded on JASCO A-102 and JASCO FT/ IR-5000 spectrometers. ^{1}H NMR spectra were recorded on Varian EM-390 (90 MHz), Varian Gemini-200 (200 MHz), Varian Gemini-300 (300 MHz), JEOL GSX-500 (500 MHz) spectrometers and ^{13}C NMR spectra were recorded on Varian Gemini-300 spectrometer, and chemical shifts were reported in ppm using TMS or $CHCl_3$ as internal standard. High resolution mass spectra were performed on JEOL JMS-505H mass spectrometer. GLC analyses were run on Shimazu GC-8A chromatograph equipped with OV-1 or PEG-20M

capillary column (0.25 mm x 50 m) by using N_2 as the carrier gas (1 kg cm^{-2}) at the indicated temperature. Ether and THF were dried by distillation over $LiAlH_4$ and redistillation from sodium benzophenone ketyl prior to use. CH_2Cl_2 was dried by distillation over P_2O_5 and redistillation from CaH_2 before use. Butyllithium was used as a solution in hexane (1.6M) purchased from Aldrich Chemical Company, Inc.. The term "usual workup" is used in the following product isolation procedure: dilution of the reaction mixture with ether and H_2O, successive extraction with ether and brine; treatment of the organic extracts with anhydrous $MgSO_4$; and solvent removal under reduced pressure.

Preparation of γ-(trimethylsilyl)allylic alcohols

(*E*)-1-Trimethylsilyl-1-propen-3-ol.

This alcohol was prepared from 2-propyn-1-ol (8.40 g, 0.15 mol) via silylation followed by reduction according to the literature procedure[17] (16.7 g, 86%; *E* / *Z*=99 : 1 by GLC): b. p. 86-88 °/ 30 mmHg; IR (neat) 3350, 2962, 1620, 1250, 995, 865, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 1.74 (br. s, 1H), 4.16 (dd, J=1.71, 4.35 Hz, 2H), 5.91 (dt, J=1.71, 18.81 Hz, 1H), 6.17 (dt, J=4.35, 18.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.38, 65.46, 129.45, 144.74; GLC (OV-1, 80 °C) t_R (*E*-isomer) =4.9 min, t_R (*Z*-isomer) =4.4 min.

(*E*)-1-Trimethylsilyl-1-buten-3-ol.

This alcohol was prepared from 1-butyn-3-ol (10.5 g, 0.15 mol) by the same manner as described above (16.3 g, 76%; *E* / *Z*=98 : 2 by GLC): b. p. 82-83 °/ 23 mmHg; IR (neat) 3292, 2960, 1624, 1249, 1131, 1062, 990, 940, 868 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9H), 1.24 (d, J=7.44 Hz, 3H), 1.79 (br. s, 1H), 4.26 (ddq, J=1.35, 4.95, 7.44 Hz, 1H), 5.81 (dd, J=1.35, 18.78 Hz, 1H), 6.06 (dd, J=4.95, 18.78 Hz, 1H);^{13}C NMR ($CDCl_3$) δ 1.34, 22.90, 70.44, 128.14, 149.55; GLC (OV-1, 60 °C) t_R (*E*-isomer) =11.2 min, t_R (*Z*-isomer) =9.1 min.

(*Z*)-1-Trimethylsilyl-1-buten-3-ol.

To a stirred solution of nickel acetate (0.97 g, 3.9 mmol) in 30 ml of 95% ethanol was added a solution of $NaBH_4$ (0.15 g, 3.9 mmol) in 4 ml of 95% ethanol and ethylenediamine (0.47 g, 7.8 mmol) at room temperature under N_2 atmosphere. After stirring for 5 min, 1-trimethylsilyl-1-butyn-3-ol (5.32 g, 37 mmol), which was obtained via silylation of 1-butyn-3-ol according to the literature procedure,[17] was added and the flask was purged with hydrogen. Hydrogen uptake was quantative with vigorous stirring at room temperature overnight. The catalyst was filtered off with celite, and usual workup followed by distillation afforded (*Z*)-1-trimethylsilyl-1-buten-3-ol (4.44 g, 83%; *E* / *Z*=7 : 93 by GLC): b. p. 53-54 °/ 9.5 mmHg; IR (neat) 3350, 2962, 1717, 1249, 1052, 839, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.24 (d, J=6.3 Hz, 3H), 2.15 (br. s, 1H), 4.44 (ddq, J=0.8, 6.3, 8.8 Hz, 1H), 5.59 (dd, J=0.8, 14.5 Hz, 1H), 6.25 (dd, J=8.8, 14.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.63, 23.49, 68.84, 130.82, 151.34; GLC (OV-1, 60 °C) t_R (*E*-isomer) =11.2 min, t_R (*Z*-isomer) =9.1 min.

(*E*)-1-Trimethylsilyl-1-penten-3-ol.

To a solution of (trimethylsilyl)acetylene (1.47 g, 15.0 mmol) in 20 ml of anhydrous THF was added slowly butyllithium (8.9 ml, 16.5 mmol) at -30 °C under N_2 atmosphere. After stirring for 45 min at room temperature, propionaldehyde (0.95 g, 16.5 mmol) in 5 ml of anhydrous THF was added at -20 °C and stirred for 2 h at room temperature, to give 1-trimethylsilyl-1-pentyn-3-ol (1.75 g, 75%) after usual workup followed by silica gel column chromatography. The obtained alcohol was reduced by the same manner as the literature procedure[17] followed by silica gel column chromatography, to give (*E*)-1-trimethylsilyl-1-penten-3-ol (1.45 g, 83%; *E* / *Z*=97 : 3 by GLC): IR (neat) 3360, 2962, 1624, 1249, 990, 864, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.92 (t, J=7.47 Hz, 3H), 1.55 (dq, J=6.84, 7.47 Hz, 2H), 1.60 (br. s, 1H), 4.01 (dt, J=5.43, 6.84 Hz, 1H), 5.84 (d, J=18.81 Hz, 1H), 6.03 (dd, J=5.43, 18.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.24, 9.67, 29.76, 75.96, 129.44, 148.19; GLC (OV-1, 80 °C) t_R (*E*-isomer) =6.8 min, t_R (*Z*-isomer) =6.0 min; MS m/e 158.1110 (calcd for $C_8H_{18}OSi$, 158.1127).

Preparation of bis-allylic ethers (1)

(*E*)-1-Trimethylsilyl-3-[3-trimethylsilyl-2-(*E*)-propenyloxy]-1-propene (1a).

To a viscous mixture of NaOH (0.71 g, 17.8 mmol), tetrabutylammonium hydrogensulfate (80 mg, 0.24 mmol), and H_2O (0.32 g, 17.8 mmol) was added consecutively (*E*)-1-trimethylsilyl-1-propen-3-ol (0.58 g, 4.4 mmol) and 3-bromo-1-trimethylsilyl-1-propene (0.85 g, 4.4 mmol), which was prepared by bromination of (*E*)-1-trimethylsilyl-1-propen-3-ol with PBr_3, at room temperature and stirred for 10 min. Usual workup followed by silica gel column chromatography gave ether **1a** (0.76 g, 71%): IR (neat) 2960, 1626, 1352, 1249, 1108, 988, 864, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 4.01 (dd, J=1.32, 4.86 Hz, 4H), 5.93 (d, J=18.69 Hz, 2H), 6.10 (dt, J=4.86, 18.69 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -1.37, 73.33, 132.16, 142.13.

(*E*)-1-Trimethylsilyl-3-[3-trimethylsilyl-2-(*E*)-propenyloxy]-1-butene (1b).

To a stirred slurry of KH (0.53 g, 13.1 mmol), naked by anhydrous hexane, in 3.5 ml of anhydrous ether was added slowly a solution of (*E*)-1-trimethylsilyl-1-buten-3-ol (1.74 g, 12.0 mmol) in 7 ml of anhydrous ether at room temperature under N_2 atmosphere. After stirring for 1.5 h at room temperature, a solution of 3-trimethylsilyl-2-propenyl mesylate (2.30 g, 10.9 mmol), which was prepared by mesylation of (*E*)-1-trimethylsilyl-1-propen-3-ol with mesyl chloride and triethylamine in CH_2Cl_2, in 3 ml of anhydrous ether was added and stirred for 1 h at room temperature. Usual workup followed by silica gel column chromatography gave ether **1b** (1.95 g, 69%): IR (neat) 2960, 1624, 1249, 1106, 992, 866, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 18H), 1.24 (d, J=6.33 Hz, 3H), 3.84 (dq, J=6.30, 6.33 Hz, 1H), 3.88 (ddd, J=1.38, 4.59, 13.16 Hz, 1H), 4.02 (ddd, J=1.38, 4.59, 13.16 Hz, 1H), 5.78 (d, J=18.75 Hz, 1H), 5.89 (d, J=18.69 Hz, 1H), 5.91 (dd, J=6.30, 18.75 Hz, 1H), 6.09 (dt, J=4.59, 18.69 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.34, -1.28, 21.05, 71.29, 78.46, 131.31, 131.43, 142.74, 147.60; MS m/e 256.1665 (calcd for $C_{13}H_{28}OSi_2$, 256.1679).

(*Z*)-1-Trimethylsilyl-3-[3-trimethylsilyl-2-(*E*)-propenyloxy]-1-butene.

(*Z*)-Counterpart of the ether **1b** was prepared from (*Z*)-1-trimethylsilyl-1-buten-3-ol (2.0 g, 13.9 mmol) by the same manner for the preparation of ether **1b** (2.0 g, 63%): IR (neat) 2960, 1624, 1369, 1249, 1102, 990, 837, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9H), 0.12 (s, 9H), 1.24 (d, J=6.30 Hz, 3H), 3.88 (dd, J=4.86, 13.40 Hz, 1H), 4.04 (dd, J=4.86, 13.40 Hz, 1H), 3.96- 4.13 (m, 1H), 5.66 (d, J=14.28 Hz, 1H), 5.90 (d, J=18.66 Hz, 1H), 6.09 (dt, J=4.86, 18.66 Hz, 1H), 6.16 (dd, J=9.06, 14.28 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.28, 0.43, 21.58, 71.01, 75.16, 131.24, 131.29, 142.81, 142.91, 150.33.

Preparation of allylic propargylic ethers (2)

(*E*)-1-Trimethylsilyl-3-(3-trimethylsilyl-2-propynyloxy)-1-propene (2a).

To a solution of 3-(2-propynyloxy)-1-trimethylsilyl-1-propene (0.59 g, 3.5 mmol), which was prepared from (*E*)-1-trimethylsilyl-1-propen-3-ol and propargyl bromide as described for the preparation of **1a** (90%), in 3 ml of anhydrous THF was added dropwise 1.0 M THF solution of ethylmagnesium bromide (4.6 ml, 4.6 mmol) at room temperature under N_2 atmosphere. After stirring for 2 h at room temperature, a solution of chlorotrimethylsilane (0.61 g, 5.6 mmol) in 2 ml of anhydrous THF was added and stirred for 1 h at room temperature to give, after usual workup followed by silica gel column chromatography, ether **2a** (0.80 g, 95%): IR (neat) 2170, 1620, 1250, 1100, 990, 840, 760 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.18 (s, 9H), 4.07 (d, J=4.86 Hz, 2H), 4.10 (s, 2H), 5.94 (d, J=18.72 Hz, 1H), 6.09 (dt, J=4.86, 18.72 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.40, -0.15, 58.18, 72.68, 91.36, 101.41, 133.12, 141.36.

(*E*)-1-Trimethylsilyl-3-(3-trimethylsilyl-2-propynyloxy)-1-butene (2b).

Ether **2b** was prepared from 3-(2-propynyloxy)-1-trimethylsilyl-1-butene (2.41 g, 13.2 mmol) as described for the preparation of **2a** (3.0 g, 89%): IR (neat) 2962, 2178, 1622, 1251, 1079, 992, 847, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.17 (s, 9H), 1.25 (d, J=6.36 Hz, 3H), 3.96-4.01 (m, 1H), 4.01 (d, J=15.75 Hz, 1H), 4.14 (d, J=15.75 Hz, 1H), 5.84-5.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.32, -0.13, 20.89, 56.17, 77.97, 90.54, 102.05, 132.61, 146.45.

(*E*)-1-Trimethylsilyl-3-(3-trimethylsilyl-2-propynyloxy)-1-pentene (2c).

Ether **2c** was prepared from 3-(2-propynyloxy)-1-trimethylsilyl-1-pentene (0.92 g, 4.7 mmol) as described for the preparation of **2a** (0.96 g, 76%): IR (neat) 2964, 2178, 1620, 1334, 1251, 1077, 994, 839, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.18 (s, 9H), 0.89 (t, J=7.41 Hz, 3H), 1.53 (ddq, J=6.24, 7.41, 14.07 Hz, 1H), 1.61 (ddq, J=6.24, 7.41, 14.07 Hz, 1H), 3.72 (dt, J=6.12, 6.24 Hz, 1H), 3.99 (d, J=15.72 Hz, 1H), 4.16 (d, J=15.72 Hz, 1H), 5.78 (dd, J=6.12, 18.45 Hz, 1H), 5.86 (d, J=18.45 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.19, 0.06, 9.86, 27.87, 56.35, 83.78, 90.40, 102.30, 133.79, 145.22; MS m/e 268.1663 (calcd for $C_{14}H_{28}OSi_2$, 268.1679).

[2,3]Wittig rearrangement of bis-allylic ethers (1)

1-Trimethylsilyl-1,3,5-hexatriene (4a).

To a solution of freshly distilled dicyclohexylamine (0.52 g, 2.9 mmol) in 5 ml of anhydrous THF was added dropwise butyllithium (1.65 ml, 2.6 mmol) at 0 °C under N_2 atmosphere and stirred for 1 h at room temperature. This solution was cooled to -40 °C, then a solution of ether **1a** (0.20 g, 0.82 mmol) in 2 ml of anhydrous THF was added and stirred for 1 h at that temperature. To the reaction mixture was added 1.2 g of $NaHSO_4 \cdot H_2O$ and stirred for 1 h at room temperature. The salt was filtered off and the filtrate was diluted with ether and H_2O, and extracted with ether. The ether phase was dried over $MgSO_4$, and evaporation of solvent followed by silica gel column chromatography afforded triene **4a** as a sole product (0.10 g, 79%; 3*Z* / 3*E*=63 : 37 by GLC): IR (neat) 3012, 2960, 1601, 1433, 1249, 1009, 986, 866, 843 cm^{-1}; ^1H NMR ($CDCl_3$) **3*Z*-isomer**, δ 0.11 (s, 5.67H), 5.19 (dd, J=1.77, 10.05 Hz, 0.63H), 5.27 (dd, J=1.77, 16.74 Hz, 0.63H), 5.94 (d, J=18.12 Hz, 0.63H), 5.99 (dd, J=10.00, 10.23 Hz, 0.63H), 6.02 (dd, J=9.69, 10.00 Hz, 0.63H), 6.89 (ddd, J=10.05, 10.23, 16.74 Hz, 0.63H), 6.99 (dd, J=9.69, 18.12 Hz, 0.63H); **3*E*-isomer**, δ 0.09 (s, 3.33H), 5.13 (dd, J=1.77, 9.87 Hz, 0.37H), 5.25 (dd, J=1.77, 16.71 Hz, 0.37H), 5.91 (d, J=18.24 Hz, 0.37H), 6.17-6.31 (m, 0.74H), 6.31-6.44 (m, 0.37H), 6.55 (dd, J=9.63, 18.24 Hz, 0.37H); ^{13}C NMR ($CDCl_3$) δ -1.32, 118.06 (3*E*), 118.60 (3*Z*), 130.13, 132.06, 132.52, 133.64, 135.25, 136.17, 136.85, 138.52 (3*Z*), 143.67 (3*E*); GLC (OV-1, 90 °C) t_R (3*Z*-isomer) =3.8 min, t_R (3*E*-isomer) =4.0 min.

1,4-Bis(trimethylsilyl)-1,5-heptadien-3-ol (3b).

To a solution of **1b** (1.0 g, 3.9 mmol) in 2.9 ml of anhydrous THF was added slowly butyllithium (3.6 ml, 5.8 mmol) at -85 °C under N_2 atmosphere. After stirring for 4 h at -85 °C, the reaction mixture was poured into cold water, and extracted with ether. The ether phase was dried over $MgSO_4$, and evaporation of solvent afforded alcohol **3b** as a major product (0.59 g, 59%; *threo* / *erythro*=90 : 10 by GLC of the resultant triene) along with triene **4b** (0.14g, 22%; 3*Z* / 3*E*=18 : 82 by GLC), after isolation by silica gel column chromatography: IR (neat) 2960, 1615, 1249, 1056, 973, 839, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.06 (s, 9H), 1.70 (d, J=5.76 Hz, 3H), 1.75-1.82 (m, 1H), 1.83 (br. s, 1H), 4.11 (dd, J=6.27, 8.22 Hz, 0.90H), 4.24 (dd, J=5.07, 6.27 Hz, 0.10H), 5.32 (dd, J=10.17, 15.23 Hz, 1H), 5.42 (dq, J=5.76, 15.23 Hz, 1H), 5.86 (d, J=18.69 Hz, 1H), 5.99 (dd, J=6.27, 18.69 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.60, -1.45, 18.17, 42.09, 75.30, 127.12, 128.36, 130.58, 148.02; GLC (OV-1, 120 °C) t_R (3*Z*-triene derived from *threo*-isomer) =6.4 min, t_R (3*E*-triene derived from *erythro*-isomer) =7.0 min. MS m/e 256.1663 (calcd for $C_{13}H_{28}OSi_2$, 256.1679). [The rearrangement of the (*Z*)-counterpart (0.77g, 3.0mmol) was carried out by the same manner to give alcohol **3b** (0.32 g, 50%; *threo* / *erythro*=85 : 15 by GLC of resultant triene) and triene **4b** (0.16 g, 31%; 3*Z* / 3*E*=17 : 83 by GLC).]

1-Trimethylsilyl-1,3,5-heptatriene (4b).

Triene **4b** was obtained as a minor product in the rearrangement of ether **1b** as described above: IR (neat) 2960, 1613, 1568, 1249, 1004, 973, 864, 839, 729 cm^{-1}; ^1H NMR ($CDCl_3$) **3*Z*-isomer**, δ 0.00 (s, 1.62H), 1.83 (d, J=6.78 Hz, 0.54H), 5.77(dq, J=6.78, 14.82 Hz, 0.18H), 5.86 (d, J=18.18 Hz, 0.18H), 5.87 (dd, J=9.90, 10.71 Hz, 0.18H), 5.95 (dd, J=10.47, 10.71 Hz, 0.18H), 6.59 (dd, J=10.47, 14.82 Hz, 0.18H), 6.98 (dd, J=9.90, 18.18 Hz, 0.18H); **3*E*-isomer**, δ 0.08 (s, 7.38H), 1.78 (d, J=6.78 Hz,

2.46H), 5.75 (dq, J=6.78, 15.03 Hz, 0.82H), 5.83 (d, J=18.27 Hz, 0.82H), 6.07 (dd, J=9.69, 15.36 Hz, 0.82H), 6.10 (dd, J=10.32, 15.36 Hz, 0.82H), 6.22 (dd, J=10.32, 15.03 Hz, 0.82H), 6.53 (dd, J=9.69, 18.27 Hz, 0.82H); ^{13}C NMR ($CDCl_3$) **3*Z*-isomer**, δ -1.20, 18.44, 127.07, 129.73, 130.02, 131.48, 134.50, 138.94; **3*E*-isomer**, δ -1.24, 18.38, 130.82, 131.59, 132.91, 133.22, 133.57, 144.21; GLC (OV-1, 120 °C) t_R (3*Z*-isomer) =6.4 min, t_R (3*E*-isomer) =7.0 min.

[2,3]Wittig rearrangement of allylic propargylic ethers (2)

1,4-Bis(trimethylsilyl)-5-hexen-1-yn-3-ol (5a).

To a solution of ether **2a** (0.40 g, 1.7 mmol) in 2 ml of anhydrous THF was added slowly butyllithium (1.1 ml, 1.8 mmol) at -85 °C under N_2 atmosphere. After stirring for 0.5 h at -85 °C, the reaction mixture was poured into cold water, and extracted with ether. The ethe phase was dried over $MgSO_4$, and evaporation of solvent followed by silica gel column chromatography afforded alcohol **5a** (0.36 g, 90%; *threo / erythro*=3 : 97 by GLC): IR (neat) 3400, 2170, 1625, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.17 (s, 9H), 1.94 (dd, J=7.5, 9.7 Hz, 1H), 2.01 (br. s, 1H), 4.45 (d, J=7.5 Hz, 1H), 4.93 (dd, J=2.0, 16.5 Hz, 1H), 5.03 (dd, J=2.0, 10.8 Hz, 1H), 5.71 (ddd, J=9.7, 10.8, 16.5 Hz, 1H). The $J_{3,4}$-value of the (3*Z*)-dienyne obtained via olefination with BF_3•OEt_2 was 10.2 Hz; ^{13}C NMR ($CDCl_3$) δ -1.85, -0.22, 43.92, 63.00, 84.22, 106.54, 115.67, 135.65; GLC (PEG-20M, 130 °C) t_R (*threo*-isomer) =61.6 min, t_R (*erythro*-isomer) =77.5 min.

1,4-Bis(trimethylsilyl)-5-hepten-1-yn-3-ol (5b).

The rearrangement of **2b** (0.50 g, 2.0 mmol) by the same manner as the rearrangement of **2a** afforded alcohol **5b** (0.30 g, 60%; *threo / erythro*=96 : 4 by GLC of the resultant triene): IR (neat) 3450, 2960, 2170, 1250, 1020, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.15 (s, 9H), 1.71 (d, J=6.18 Hz, 3H), 1.75-1.81 (m, 1H), 2.00 (br. s, 1H), 4.39 (d, J=8.52 Hz, 1H), 5.29 (dd, J=10.17, 15.06 Hz, 1H), 5.44 (dq, J=6.18, 15.06 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.74, -0.22, 18.20, 42.42, 63.19, 90.13, 106.68, 127.42, 127.69; GLC (OV-1, 120 °C) t_R (3*Z*-triene derived from *threo*-isomer) =6.4 min, t_R (3*E*-triene derived from *erythro*-isomer) =7.0 min.

1,4-Bis(trimethylsilyl)-5-octen-1-yn-3-ol (5c).

The rearrangement of **2c** (0.60 g, 2.2 mmol) by the same manner as the rearrangement of **2a** afforded alcohol **5c** (0.39 g, 65%; *threo / erythro*=97 : 3 by GLC of the methyl ether): IR (neat) 3440, 2964, 2172, 1251, 1029, 971, 843, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.16 (s, 9H), 0.98 (t, J=7.41 Hz, 3H), 1.87 (dd, J=8.31, 10.29 Hz, 1H), 1.88 (br. s, 1H), 2.06 (dq, J=6.30, 7.41 Hz, 2H), 4.41 (d, J=8.31 Hz, 1H), 5.27 (dd, J=10.29, 15.18 Hz, 1H), 5.48 (dt, J=6.30, 15.18 Hz, 1H). The $J_{3,4}$-value of the (3*Z*)-dienyne obtained via olefination with KH was 10.4 Hz; ^{13}C NMR ($CDCl_3$) δ -1.72, -0.17, 14.23, 25.96, 42.27, 63.22, 90.06, 106.70, 125.46, 134.63; GLC (PEG 20M, 90 °C) t_R (*threo*-isomer) =4.6 min, t_R (*erythro*-isomer) =5.9 min.

Syntheses of sarohornene B (10) and C (12)

(*E*)-3-(3-Dimethylphenylsilyl-2-propynyloxy)-1-trimethylsilyl-1-pentene (6).

Ether **6** was prepared from 3-(2-propynyloxy)-1-trimethylsilyl-1-pentene (0.77 g, 3.9 mmol) as described for the preparation of **2a**, by treatment with chlorodimethylphenysilane instead of chlorotrimethylsilane (1.06 g, 74%): IR (neat) 2960, 2178, 1429, 1251, 1116, 1079, 994, 837, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.44 (s, 6H), 0.91 (t, J=7.41 Hz, 3H), 1.55 (ddq, J=6.30, 7.44, 15.99 Hz, 1H), 1.63 (ddq, J=6.30, 7.44, 15.99 Hz, 1H), 3.79 (dt, J=6.12, 6.30 Hz, 1H), 4.06 (d, J=15.99 Hz, 1H), 4.23 (d, J=15.99 Hz, 1H), 5.80 (dd, J=6.12, 18.63 Hz, 1H), 5.89 (d, J=18.63 Hz, 1H), 7.32-7.70 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -1.26, -1.23, 9.82, 27.87, 56.29, 83.56, 88.44, 104.13, 127.82, 129.39, 133.55, 133.64, 133.94, 145.15; MS m/e 330.1823 (calcd for $C_{19}H_{30}OSi_2$, 330.1836).

1-Dimethylphenylsilyl-4-trimethylsilyl-5-octen-1-yn-3-ol (7).

The rearrangement of **6** (0.18 g, 0.54 mmol) by the same manner as the rearrangement of **2a** afforded alcohol **7** (0.12 g, 67%; *threo* / *erythro*=99 : 1 by GLC of the methyl ether): IR (neat) 3440, 2964, 2172, 1431, 1249, 1118, 1029, 971, 839, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.42 (s, 6H), 0.99 (t, J=7.41 Hz, 3H), 1.90 (dd, J=7.71, 10.23 Hz, 1H), 1.96 (br. s, 1H), 2.07 (dq, J=6.24, 7.41 Hz, 2H), 4.49 (d, J=7.71 Hz, 1H), 5.33 (dd, J=10.23, 15.33 Hz, 1H), 5.50 (dt, J=6.24, 15.33 Hz, 1H), 7.30-7.70 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -1.79, 0.00, 14.20, 25.93, 41.98, 63.39, 88.01, 108.55, 125.25, 127.78, 129.36, 133.68, 134.52, 136.64; GLC (OV-1, 170 °C) t_R (*threo*-isomer) =16.6 min, t_R (*erythro*-isomer) =18.4 min; MS m/e 330.1834 (calcd for $C_{19}H_{30}OSi_2$, 330.1836).

1-Dimethylphenylsilyl-4-trimethylsilyl-1,5-octadien-3-ol (8).

Treatment of alcohol **7** (0.32 g, 1.0 mmol) with 3.6 M toluene solution of sodium bis(2-methoxyethoxy)aluminum hydride (0.34 ml, 1.2 mmol) according to the literature procedure[17] followed by silica gel column chromatography afforded alcohol **8** (0.12 g, 38%): IR (neat) 3420, 2962, 1429, 1249, 1114, 976, 841, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 0.35 (s, 6H), 0.98 (t, J=7.41 Hz, 3H), 1.67 (dd, J=7.20, 10.14 Hz, 1H), 1.87 (br. s, 1H), 2.06 (dq, J=6.03, 7.41 Hz, 2H), 4.21 (dd, J=5.34, 7.20 Hz, 1H), 5.30 (dd, J=10.14, 15.32 Hz, 1H), 5.44 (dt, J=6.03, 15.32 Hz, 1H), 5.98 (d, J=18.67 Hz, 1H), 6.09 (dd, J=5.34, 15.32 Hz, 1H), 7.28-7.62 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -2.62, -1.70, 14.32, 25.95, 41.62, 74.90, 125.82, 127.48, 127.71, 128.94, 133.84, 134.30, 138.37, 150.25; MS m/e 332.1998 (calcd for $C_{19}H_{32}OSi_2$, 332.1993).

(1*E*, 3*E*, 5*E*)-1-Dimethylphenylsilyl-1,3,5-octatriene (9).

Alcohol **8** (30 mg, 0.09 mmol) and sodium acetate (88 mg, 1.1 mmol) were dissolved in 0.4 ml of acetic acid and the mixture was heated at 40 °C for 1 h to give, after usual workup, triene **9** (22 mg, 99%; stereopurity 98.0% by GLC): IR (neat) 2966, 1736, 1688, 1429, 1257, 1116, 1006, 820, 789 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 6H), 1.02 (t, J=7.44 Hz, 3H), 2.13 (dq, J=6.66, 7.44 Hz, 2H), 5.80 (dt, J=6.66, 15.06 Hz, 1H), 5.93 (d, J=18.35 Hz, 1H), 6.07 (dd, J=9.63, 15.06 Hz, 1H), 6.16 (dd, J=9.27, 14.84 Hz, 1H), 6.24 (dd, J=9.63, 14.84 Hz, 1H), 6.59 (dd, J=9.27, 18.35 Hz, 1H), 7.28-7.58 (m, 5H); ^{13}C NMR

($CDCl_3$) δ 1.02, 13.44, 25.89, 127.73, 127.78, 128.90, 129.15, 130.52, 132.94, 133.84, 134.32, 138.35, 145.86; GLC (OV-1, 140 °C) t_R (1*E*, 3*E*, 5*E*) =16.0 min; MS m/e 242.1492 (calcd for $C_{16}H_{22}Si$, 242.1492).

(3*E*, 5*E*)-1,3,5-Octatriene (sarohornene B) (10).

To a solution of triene **9** (32 mg, 0.13 mmol) in 1.4 ml of DMSO was added a 1.0 M THF solution of tetrabutylammonium fluoride (0.70 ml, 0.70 mmol) and the mixture was heated at 80 °C for 0.5 h. The reaction mixture was diluted with ether and H_2O, extracted with ether, washed with H_2O several times, dried over $MgSO_4$ and removal of solvent under atmospheric pressure to give triene **10**[19a] (18 mg, 99%; stereo-purity 98.0% by GLC): IR (neat) 2964, 1464, 1261, 1077, 899, 808 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (t, J=7.38 Hz, 3H), 2.10 (dq, J=7.17, 7.38 Hz, 2H), 5.01 (dd, J=1.59, 10.71 Hz, 1H), 5.14 (dd, J=1.59, 16.71 Hz, 1H), 5.75 (dt, J=7.17, 14.85 Hz, 1H), 6.04 (dd, J=9.84, 14.85 Hz, 1H), 6.10 (dd, J=9.87, 14.97 Hz, 1H), 6.19 (dd, J=9.84, 14.97 Hz, 1H), 6.33 (ddd, J=9.87, 10.71, 16.71 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.53, 29.80, 116.24, 129.28, 131.13, 133.70, 137.29, 137.57; GLC (OV-1, 60 °C) t_R (3*E*, 5*E*) =4.5 min.

(1*E*, 3*Z*, 5*E*)-1-Dimethylphenylsilyl-1,3,5-octatriene (11).

To a stirred solution of KH (24 mg, 0.60 mmol), naked by anhydrous hexane, in 1 ml of anhydrous THF was added slowly a solution of alcohol **8** (90 mg, 0.27 mmol) in 1.5 ml of anhydrous THF at 0 °C under N_2 atmosphere, and the mixture was stirred for 0.5 h at 0 °C to give, after usual workup, triene **11** (66 mg, 99%; stereo-purity 98.3% by GLC): IR (neat) 2964, 1638, 1605, 1429, 1249, 1116, 975, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.04 (t, J=7.41 Hz, 3H), 2.18 (dq, J=7.29, 7.41 Hz, 2H), 5.82 (dt, J=7.29, 15.03 Hz, 1H), 5.94 (dd, J=9.94, 10.12 Hz, 1H), 5.98 (d, J=18.15 Hz, 1H), 6.01 (dd, J=10.12, 10.38 Hz, 1H), 6.54 (dd, J=10.38, 15.03 Hz, 1H), 7.07 (dd, J=9.94, 18.15 Hz, 1H), 7.30-7.64 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 2.50, 13.55, 26.04, 124.69, 127.76, 128.96, 129.83, 130.71, 131.87, 133.86, 138.93, 140.55; GLC (OV-1, 140 °C) t_R (1*E*, 3*Z*, 5*E*) =12.1 min; MS m/e 242.1483 (calcd for $C_{16}H_{22}Si$, 242.1492).

(3*Z*, 5*E*)-1,3,5-Octatriene (sarohornene C) (12).

Protiodesilylation of triene **11** (60 mg, 0.25 mmol) by the same manner as the protiodesilylation of **9** afforded triene **12**[19a] (34 mg, 68%; stereo-purity 97.5% by GLC): IR (neat) 2962, 1458, 1379, 1263, 1081, 897, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J=7.44 Hz, 3H), 2.15 (dq, J=7.28, 7.44 Hz, 2H), 5.11 (dd, J=1.65, 10.11 Hz, 1H), 5.19 (dd, J=1.65, 16.71 Hz, 1H), 5.78 (dt, J=7.28, 15.06 Hz, 1H), 5.88 (dd, J=10.77, 10.85 Hz, 1H), 5.96 (dd, J=10.50, 10.77 Hz, 1H), 6.49 (dd, J=10.50, 15.06 Hz, 1H), 6.80 (ddd, J=10.11, 10.85, 16.71 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.06, 28.90, 117.09, 124.55, 127.77, 130.26, 132.20, 138.16; GLC (OV-1, 60 °C) t_R (3*Z*, 5*E*) =4.7 min.

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