A New Method for the Stereocontrolled Synthesis of Silyl Dienol Ethers Using (Naphthalene)chromium Tricarbonyl Catalyzed Isomerization

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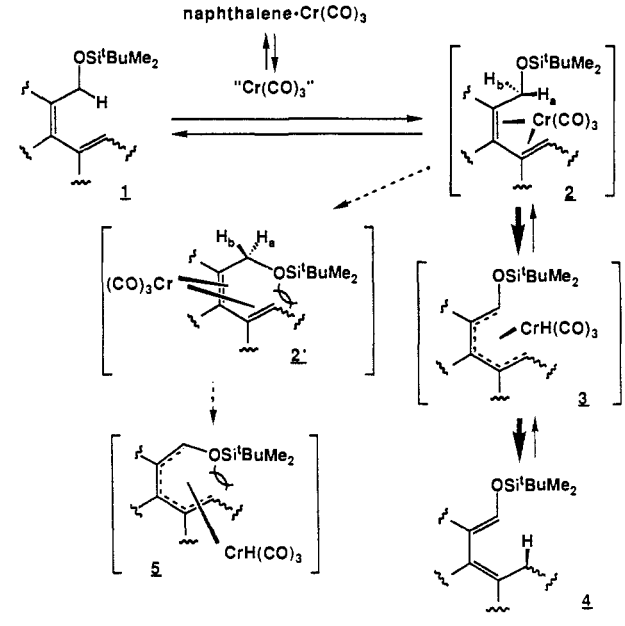
Abstract: Various *tert*-butyldimethylsilyl dienol ethers of type **4** were synthesized in a highly stereoselective manner for the first time. Treatment of (1*Z*)-1-[[(*tert*-butyldimethylsilyl)oxy]methyl]butadiene derivatives **1** with 20 mol % of (naphthalene)$Cr(CO)_3$ in degassed acetone at 20 °C provided silyl dienol ethers **4** exclusively in nearly quantitative yields. In order to demonstrate synthetic utility of silyl dienol ethers of this type, the intermolecular Diels–Alder reaction of **7** with *N*-phenylmaleimide in the presence of a small amount of K_2CO_3 was carried out to give the endo Diels–Alder adduct **20** as the sole product. Furthermore, application to the intramolecular Diels–Alder reaction was also undertaken, giving the endo Diels–Alder adduct (the *cis*-hydrindan derivative) **25**, exclusively.

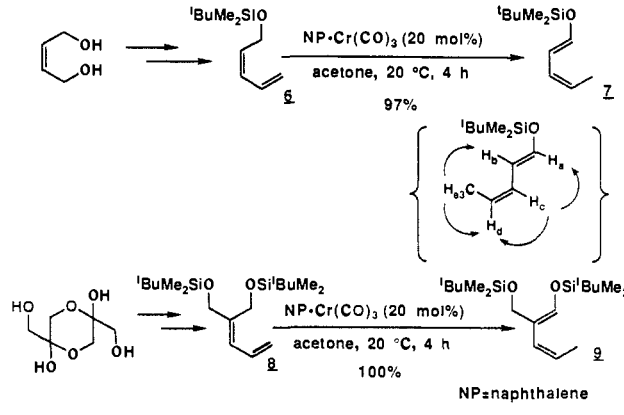
Silyl dienol ethers are frequently utilized in organic synthesis such as Diels–Alder reaction.[1] Unfortunately, stereocontrolled synthesis of silyl dienol ethers has never been reported.[2,3] Herein we report the stereocontrolled synthesis of silyl dienol ethers of type **4** starting with (1*Z*)-1-[(silyloxy)methyl]butadiene derivatives **1** and their application in the Diels–Alder reaction.

Many transition-metal-catalyzed isomerizations of allyl ethers to the corresponding vinyl ethers have been reported,[4] including the ruthenium hydride complex catalyzed isomerization of allyl silyl ethers to silyl enol ethers.[2e] Although this isomerization had poor stereoselectivity, the thermodynamic equilibrium lay far to the silyl enol ether side, suggesting that 1-[(silyloxy)methyl]butadiene derivatives would be isomerized to silyl dienol ethers by some transition-metal catalyst. Recently we have found that the (naphthalene)$Cr(CO)_3$-catalyzed isomerization of conjugated dienes proceeds at room temperature and that the stereochemistry of isomerized products is completely controlled.[5] Thus, it was envisioned that by the use of this catalyst (1*Z*)-1-[(silyloxy)-methyl]butadiene derivatives **1** would be converted to silyl dienol ethers of type **4** in a highly stereoselective manner under mild and neutral conditions. Namely, **1** would coordinate in the cisoid form to "$Cr(CO)_3$" generated in situ, and then rearrange into the U-shaped η^5-intermediates **3** by abstraction of the hydrogen H_a. The intermediate **3** would be formed exclusively because of severe steric repulsion in both the conformational isomer **2'** and the stereoisomer **5** formed by abstraction of the hydrogen H_b (Scheme I).

Scheme I



Scheme II



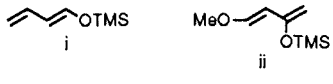
Results and Discussion

To examine the possibility of the above plan, the isomerization of the simple butadiene derivative **6**, which was easily prepared with commercially available *cis*-2-butene-1,4-diol as the starting material, was attempted. Treatment of **6** with 20 mol % of (naphthalene)$Cr(CO)_3$ in degassed acetone at 20 °C for 4 h

(1) (a) Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. (b) Brownbridge, P. *Ibid.* **1983**, 85.

(2) For the synthesis of silyl dienol ethers, see: (a) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, 3209. (b) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2089. (c) Kozikowski, A. P.; Jung, S. H. *Tetrahedron Lett.* **1986**, *27*, 3227. (d) Idem. *J. Org. Chem.* **1986**, *51*, 3400. (e) Suzuki, H.; Koyama, Y.; Morooka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, 1415.

(3) Only two silyl dienol ethers i and ii can be prepared stereospecifically. See ref 2b.



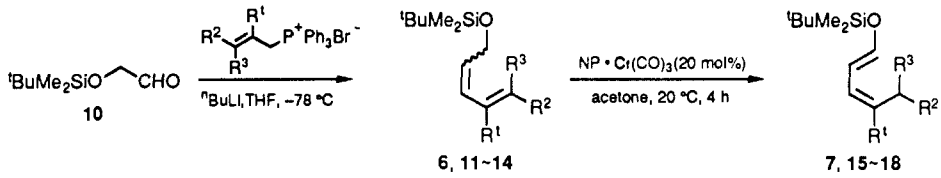
i ii

(4) (a) Jolly, P. W.; Stone, F. G. A.; Mackenzie, K. *J. Chem. Soc.* **1965**, 6416. (b) Golborn, P.; Scheinmann, F. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2870. (c) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 1566. (d) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem.* Commun. **1978**, 694.

(5) (a) Sodeoka, M.; Satoh, S.; Shibasaki, M. *J. Am. Chem. Soc.* **1988**, *110*, 4823. (b) Shibasaki, M.; Sodeoka, M.; Ogawa, Y. *J. Org. Chem.* **1984**, *49*, 4096. (c) Shibasaki, M.; Sodeoka, M. *J. Synth. Org. Chem., Jpn.* **1985**, *43*, 877.

0002-7863/90/1512-4906$02.50/0

Table I. Synthesis and Isomerization of the Various [(Silyloxy)methyl]butadiene Derivatives



R^1	R^2	R^3	diene	yield (%)	isomer ratio (*Z*:*E*)	silyl dienol ethers	yield (%)	yield based on *Z* isomer (%)	recovery of *E* isomer (%)
H	H	H	**6**	70	87:13	**7**	86	99	87
^{n}Bu	H	H	**11**	61[a]	71:29	**15**	70	99	100
H	Me	H	**12**	82	83:17	**16**	80	98	98
Me	Me	H	**13**	53	82:18	**17**	82	100	97
H	Me	Me	**14**	88	81:19	**18**	58[b]	72	24[c]

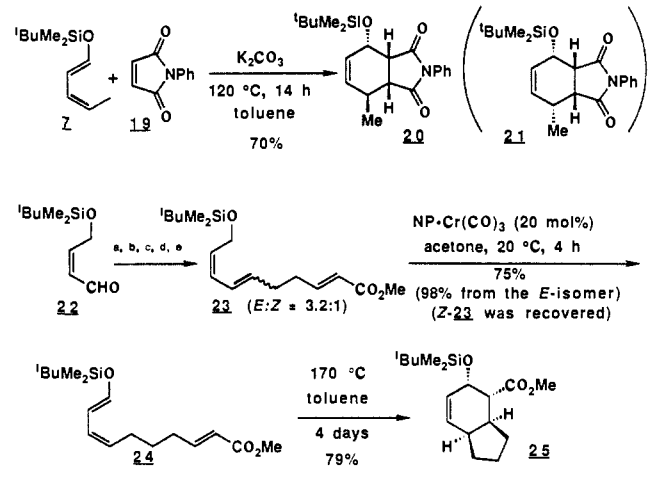
[a] The ylide was generated by LDA, and the Wittig reaction was carried out at 0 °C. [b] Reaction was carried out at 120 °C in hexane–THF (20:1) with 20 mol % of (methyl benzoate)$Cr(CO)_3$. [c] The *E* isomer was recovered with a small amoutn of the *Z* isomer (*Z*:*E* = 27:73).

provided the silyl dienol ether **7** as the sole product in 97% yield. The stereochemistry and isomeric purity were unequivocally determined from the ^{1}H NMR spectra (NOE). The coupling constant between H_a and H_b was 11.0 Hz and J_{cd} was 10.2 Hz, in accord with those of silyl dienol ethers having *E*,*Z* configurations.[2b] Furthermore, irradiation of H_c showed an enhancement of H_a and H_d, and irradiation of H_e showed an enhancement of H_b and H_d. Likewise, **8** was also transformed into **9**[6] exclusively in quantitative yield (Scheme II). Various (1*Z*)-1-[(silyloxy)-methyl]butadiene derivatives were prepared stereoselectively, in a ratio of ca. 4(*Z*):1(*E*), from the (silyloxy) acetaldehyde **10**[7] by the use of Wittig reaction (Table I). Although the undesired (1*E*)-1-[(silyloxy)methyl]butadiene derivatives were formed in the above reactions, it was expected that the (1*E*)-1-[(silyloxy)-methyl]butadiene derivatives would remain unchanged under the isomerization conditions because of the absence of a readily abstractable hydrogen. Indeed, in every case only the (1*Z*)-1-[(silyloxy)methyl]butadiene derivatives were converted to the silyl dienol ethers[6] in a highly stereoselective manner (quantitative yields based on the 1*Z* isomers), while the (1*E*)-1-[(silyloxy)-methyl]butadiene derivatives were completely recovered. Since the silyl dienol ethers were readily separable from the (1*E*)-1-[(silyloxy)methyl]butadiene derivatives by silica gel column chromatography (e.g., R_f value 0.63 for **7**, 0.28 for **6** (*E* isomer), silica gel plate, ether–hexane (1:30)), a simple method for the highly stereocontrolled synthesis of various silyl dienol ethers has been established for the first time. In the case of dienes having a cis substituent ($R^3 \neq H$) such as **14**, no isomerization was observed under the standard conditions probably owing to the difficulty of adopting the cisoid conformation, suggesting that higher reaction temperature is necessary for the isomerization reaction of **14**. (Naphthalene)$Cr(CO)_3$ in acetone, however, was found to be readily decomposed at 120 °C, and also the thermally more stable (methyl benzoate)$Cr(CO)_3$ complex was gradually decomposed in acetone or THF at 120 °C, indicating that solvated $Cr(CO)_3$ complex is fairly unstable at 120 °C. This drawback has been overcome by the use of (methyl benzoate)$Cr(CO)_3$ complex in hexane–THF (20:1) at 120 °C (1 week) to afford **18**[6] in 72% yield based on the 1*Z* isomer of **14**.

The results described above show clearly that the isomerization reaction of acyclic dienes of type **1** probably proceeds via formation of U-shaped η^5-pentadienyl hydride intermediates, demonstrating the generality of stereocontrolled isomerization of conjugated dienes by (arene)$Cr(CO)_3$.[5]

Next the thermal stability of U-shaped η^5-intermediates was examined. ^{1}H NMR spectra of a mixture of **6** and 2 equiv of (naphthalene)$Cr(CO)_3$ in acetone-d^6 were taken at various temperatures. However, the proton (Cr-H), which was expected to show the highfield absorption, could not be detected in any case,

Scheme III[a]



[a] (a) $Ts(CH_2)_3CH_2OH$, ^{n}BuLi, THF, −78 °C, 79%, (b) Ac_2O, Et_3N, CH_2Cl_2, 99%, (c) 5% Na–Hg, MeOH–EtOAc, 88%, (d) PCC, MS4A, AcONa, CH_2Cl_2, 71%, (e) Ph_3P = $CHCO_2Me$, benzene, room temperature, 90%.

indicating that U-shaped η^5-intermediates are fairly unstable in contrast to the isolable (cyclopentadienyl)$CrH(CO)_3$.[8]

In order to demonstrate synthetic utility of silyl dienol ethers of type **4**, their use in Diels–Alder reactions was undertaken. The Diels–Alder reaction of **7** with *N*-phenylmaleimide was attempted and proceeded smoothly at 120 °C in toluene containing a catalytic amount of K_2CO_3 to give the endo Diels–Alder adduct **20**,[6] exclusively, in 70% yield. The Diels–Alder reaction in the absence of K_2CO_3 provided **21**, which appeared to be formed from the *E*,*E* isomer of **7** generated in situ, together with **20**. Next, the intramolecular Diels–Alder reaction of **24** was investigated. The requisite triene **24**[6] was efficiently obtained from the unsaturated aldehyde **22** by the use of (naphthalene)$Cr(CO)_3$ catalyzed isomerization as a key step. Heating of **24** in toluene at 170 °C for 4 days provided the endo Diels–Alder adduct **25**[6] as the sole product in 79% yield (Scheme III). The ^{1}H NMR data (*J* value and NOE) for this compound was in accord with that of the most stable conformer suggested by Allinger's MM2 (85) calculations of the steric energy. Moreover, direct transformation of **23** into **25** was also attempted. Treatment of **23** with 20 mol % of (methyl benzoate)$Cr(CO)_3$ in hexane–THF (20:1) at 170 °C for 168 h afforded the desired product **25** in one pot (36%) together with **24** (11%) and **23** (16%).[9]

In summary, we have developed the method for the stereocontrolled synthesis of silyl dienol ethers of type **4** and shown their synthetic utility by using them in Diels–Alder reactions. We believe that the combination of the present methodology with

(6) The stereochemistry and isomeric purity were unequivocally determined from ^{1}H NMR spectra (NOE and NOESY). See also Experimental Section and ref 2b.

(7) Fray, M. J.; Jones, R. H.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2753. See also Experimental Section.

(8) Fischer, E. O. *Inorg. Synth.* **1963**, *7*, 136.

(9) Mainly the *Z* isomer was recovered.

high-pressure techniques in Diels–Alder reactions[10] should prove valuable for the construction of a variety of natural products possessing a functionalized six-membered ring.

Experimental Section

In general, reactions were carried out in dry solvents under an argon atmosphere unless otherwise mentioned. Solvents were distilled before use as follows: acetone from $KMnO_4$; tetrahydrofuran (THF) from sodium benzophenone ketyl; dichloromethane (CH_2Cl_2), benzene, toluene, dimethylformamide (DMF) from calcium hydride. Flash chromatography was performed by the use of silica gel (Merck Kieselgel 60, 230–400 mesh).

Satisfactory IR, ^1H NMR, and MS data were obtained on all intermediates described herein with use of chromatographically homogeneous samples.

(*Z*)-4-[(*tert*-Butyldimethylsilyl)oxy]-2-buten-1-ol. To a stirred solution of *cis*-2-butene-1,4-diol (3.03 g, 34.4 mmol) in DMF (18 mL) were added imidazole (492 mg, 7.24 mmol) and *tert*-butyldimethylsilyl chloride (1.09 g, 7.23 mmol) at −10 °C. The mixture was stirred at 23 °C for 1 h, and then water was added at 0 °C. The reaction mixture was extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography (ether–hexane, 2:3) to give (*Z*)-4-[(*tert*-butyldimethylsilyl)oxy]-2-buten-1-ol (1.22 g 84%) as a colorless oil: ^1H NMR (100 MHz, $CDCl_3$) δ 0.05 (s, 6 H), 0.87 (s, 9 H), 1.86 (s, 1 H), 4.15–4.27 (m, 4 H), 5.52–5.84 (m, 2 H), IR (neat) 3350 cm^{-1}; MS *m/z* 187 (M^+ − Me), 171, 145 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+ − C_4H_9) calcd for $C_6H_{13}O_2Si$ 145.0685, found 145.0660.

(*Z*)-4-[(*tert*-Butyldimethylsilyl)oxy]-2-butenal (22). To a stirred solution of (*Z*)-4-[(*tert*-butyldimethylsilyl)oxy]-2-buten-1-ol (151 mg, 0.75 mmol) in pentane (9 mL) was added activated MnO_2 (1.30 g, 15.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h and then diluted with ether. After filtration through a Celite pad, the filtrate was concentrated. The residue was purified by silica gel flash chromatography (ether–hexane, 1:10) to give (*Z*)-4-[(*tert*-butyldimethylsilyl)oxy]-2-butenal (**22**) (94 mg, 63%) as a colorless oil; ^1H NMR (100 MHz, $CDCl_3$) δ 0.09 (s, 6 H), 0.91 (s, 9 H), 4.68 (dd, *J* = 5.0, 2.1 Hz, 2 H), 5.98 (ddt, *J* = 12.8, 6.9, 2.1 Hz, 1 H), 6.57 (dt, *J* = 12.8, 5.0 Hz, 1 H), 10.22 (d, *J* = 6.9 Hz, 1 H); IR (neat) 2750, 1690, 1610 cm^{-1}; MS *m/z* 200 (M^+), 143 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{10}H_{20}O_2Si$ 200.1232, found 200.1216.

(*Z*)-5-[(*tert*-Butyldimethylsilyl)oxy]-1,3-pentadiene (6). To a stirred suspension of methyltriphenylphosphonium bromide (118 mg, 0.33 mmol) in THF (1 mL) was added potassium *tert*-butoxide (36 mg, 0.32 mmol) at 0 °C. After the solution was stirred for 15 min, (*Z*)-4-[(*tert*-butyldimethylsilyl)oxy]-2-butenal (21 mg, 0.11 mmol) in THF (2 mL) was added at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and then quenched with saturated aqueous NH_4Cl, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel flash chromatography (ether–hexane, 1:40) to give the diene **6** (21 mg, 100%) as a colorless oil: ^1H NMR (270 MHz, C_6D_6) δ 0.08 (s, 6 H), 0.91 (s, 9 H), 4.36 (dd, *J* = 4.8, 1.0 Hz, 2 H), 5.14 (d, *J* = 10.0 Hz, 1 H), 5.23 (d, *J* = 17.0 Hz, 1 H), 5.55 (dt, *J* = 11.0, 4.8 Hz, 1 H), 6.01 (ddt, *J* = 11.0, 11.0, 1.0 Hz, 1 H), 6.59 (ddd, *J* = 17.0, 11.0, 10.0 Hz, 1 H); IR (neat) 3110, 1595 cm^{-1}; MS *m/z* 199 (M^+ + H), 183 (M^+ − Me), 141 (M^+ − ^{t}Bu), 75 (base peak); HR-Ms (M^+ − C_4H_9) calcd for $C_7H_{13}OSi$ 141.0736, found 141.0739.

1,3-Bis[(*tert*-butyldimethylsilyl)oxy]-2-propanone. To a stirred solution of dihydroxyacetone dimer (504 mg, 2.80 mmol) in DMF (4 mL) were added imidazole (958 mg, 14.1 mmol) and *tert*-butyldimethylsilyl chloride (2.11 g, 14.0 mmol) at 0 °C. The mixture was stirred at 23 °C for 1 h, and then water was added at 0 °C. The reaction mixture was extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane, 1:25) to give 1,3-bis[(*tert*-butyldimethylsilyl)-oxy]-2-propanone (1.67 g, 94%) as a colorless oil: ^1H NMR (100 MHz, $CDCl_3$) δ 0.09 (s, 12 H), 0.92 (s, 18 H), 4.42 (s, 4 H); IR (neat) 1745 cm^{-1}; MS *m/z* 319 (M^+ + H), 303 (M^+ − Me), 261 (M^+ − ^{t}Bu), 73 (base peak); HR-MS (M^+ − C_4H_9) calcd for $C_{11}H_{25}O_3Si_2$ 261.1342, found 261.1339.

5-[(*tert*-Butyldimethylsilyl)oxy]-4-[[(*tert*-butyldimethylsilyl)oxy]-methyl]-1,3-pentadiene (8). To a stirred solution of allyl *p*-tolyl sulfone (75 mg, 0.38 mmol) in THF (2 mL) was added ^{n}BuLi (1.59 M in hexane, 0.24 mL, 0.38 mmol) at −78 °C. After the mixture was stirred for 15 min, a solution of 1,3-bis[(*tert*-butyldimethylsilyl)oxy]-2-propanone (101 mg, 0.32 mmol) in THF (2.5 mL) was added. The mixture was stirred at −78 °C for 1 h, and then acetic anhydride (39 μL, 0.41 mmol) was added. After the mixture was stirred at −78 °C for 30 min and 23 °C for 1 h, methanol and saturated aqueous $NaHCO_3$ were added at 0 °C. The whole mixture was stirred at 23 °C for 30 min, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel flash chromatography (ethyl acetate–hexane, 1:12) to give the coupling products (162 mg) as a mixture of the acetate and the alcohol (ca. 2:1). To a stirred solution of this coupling products (88 mg) in methanol (3 mL) were added NaH_2PO_4 (879 mg) and sodium amalgam (5%, 1.3 g) at −30 °C. After being stirred at −30 °C for 2 h, the reaction mixture was quenched with water, allowed to warm to 23 °C, extracted with ether, washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel flash chromatography (ether–hexane, 1:200) to give the diene **8** (38 mg, 64%) as a colorless oil: ^1H NMR (100 MHz, C_6D_6) δ 0.10 (s, 6 H), 0.14 (s, 6 H), 1.00 (s, 9 H), 1.04 (s, 9 H), 4.35 (s, 2 H), 4.39 (s, 2 H), 5.09 (bd, *J* = 10.0 Hz, 1 H), 5.35 (bd, *J* = 16.5 Hz, 1 H), 6.36 (bd, *J* = 11.0 Hz, 1 H), 6.74 (ddd, *J* = 16.5, 11.0, 10.0 Hz, 1 H); IR (neat) 3100, 1600 cm^{-1}; MS *m/z* 342 (M^+), 327 (M^+ − Me), 285 (M^+ − ^{t}Bu), 147 (base peak); HR-MS (M^+ − C_4H_9) calcd for $C_{14}H_{29}O_2Si_2$ 285.1706, found 285.1705.

[(*tert*-Butyldimethylsilyl)oxy]acetoaldehyde (10). To a stirred solution of 3-[(*tert*-butyldimethylsilyl)oxy]propene (5.57 g, 32.4 mmol) in ether (100 mL) was added $NaIO_4$ (20.7 g, 96.8 mmol) in water (100 mL) at 23 °C, and OsO_4 (0.41 g, 1.61 mmol) in ^{t}BuOH (41 mL) at 0 °C. After being stirred at 23 °C for 2 h, the reaction mixture was quenched with Na_2SO_3 at 0 °C, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by careful distillation to give the aldehyde **10** (2.35 g, 42%, 65 °C (17 mmHg) as a colorless oil.[7]

General Procedure for Wittig Reactions. To a stirred suspension of the phosphonium salt (0.87 mmol) in THF (8 mL) was added ^{n}BuLi (1.61 M in hexane, 0.8 mmol) at −78 °C. The mixture was stirred at 0 °C for 3 min and then cooled to −78 °C again. A solution of the aldehyde **10** (0.58 mmol) in THF (2 mL) was then added dropwise to the ylide solution. After being stirred at −78 °C for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl, allowed to warm to 23 °C, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel flash chromatography to give the diene as a colorless oil.

(*Z*)-2-Butyl-5-[(*tert*-butyldimethylsilyl)oxy]-1,3-pentadiene (11): ^1H NMR (100 MHz, C_6D_6) δ 0.09 (s, 6 H), 0.86 (t, *J* = 7.0 Hz, 3 H), 1.01 (s, 9 H), 1.12–1.43 (m, 4 H), 1.94–2.27 (m, 2 H), 4.50 (d, *J* = 3.7 Hz, 2 H), 4.80 (bs, 1 H), 5.01 (bs, 1 H), 5.80–5.91 (m, 2 H); IR (neat) 1630, 1610 cm^{-1}; MS *m/z* 254 (M^+), 239 (M^+ − Me), 211, 197 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{15}H_{30}OSi$ 254.2066, found 254.2055.

(2*Z*,4*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-2,4-hexadiene (12): ^1H NMR (100 MHz, C_6D_6) δ 0.12 (s, 6 H), 1.02 (s, 9 H), 1.60 (dd, *J* = 6.5, 1.5 Hz, 3 H), 4.39 (d, *J* = 6.0 Hz, 2 H), 5.36–5.74 (m, 2 H), 6.00 (ddt, *J* = 10.5, 10.5, 1.5 Hz, 1 H), 6.31 (ddq, *J* = 14.5, 10.5, 1.5 Hz, 1 H); IR (neat) 1660 cm^{-1}; MS *m/z* 212 (M^+), 197 (M^+ − Me), 155 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{12}H_{24}OSi$ 212.1597, found 212.1593.

(2*Z*,4*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-4-methyl-2,4-hexadiene (13): ^1H NMR (100 MHz, C_6D_6) δ 0.10 (s, 6 H), 1.01 (s, 9 H), 1.54 (d, *J* = 7.0 Hz, 3 H), 1.63 (bs, 3 H), 4.51 (d, *J* = 6.5 Hz, 2 H), 5.36 (bq, *J* = 7.0 Hz, 1 H), 5.68 (dt, *J* = 12.0, 6.5 Hz, 1 H), 5.92 (d, *J* = 12.0 Hz, 1 H); IR (neat) 1645 cm^{-1}; MS *m/z* 226 (M^+), 211 (M^+ − Me), 169 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1753.

(*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5-methyl-2,4-hexadiene (14): ^1H NMR (100 MHz, C_6D_6) δ 0.10 (s, 6 H), 1.00 (s, 9 H), 1.74 (s, 3 H), 1.84 (s, 3 H), 4.45 (bd, *J* = 6.5 Hz, 2 H), 5.52–5.79 (m, 1 H), 6.18 (bd, *J* = 11.5 Hz, 1 H), 6.31 (ddt, *J* = 11.5, 11.5, 1.0 Hz, 1 H); IR (neat) 1655 cm^{-1}; MS *m/z* 226 (M^+), 211 (M^+ − Me), 169 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1748.

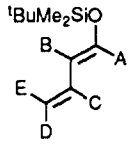
General Procedure for the Isomerization Reactions. The diene (0.1 mmol) and (naphthalene)$Cr(CO)_3$ (0.02 mmol, 20 mol%) were dissolved in acetone (2 mL). After deoxygenation by four freeze–pump–thaw cycles, the solution was stirred under argon atmosphere for 4 h at 23 °C. Removal of the solvent and the purification by silica gel flash chromatography afforded the silyl dienol ether. (See Table II for ^1H NMR data of silyl dienol ethers.)

(1*E*,3*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-1,3-pentadiene (7): IR (neat) 3040, 1655, 1615 cm^{-1}; MS *m/z* 198 (M^+), 183 (M^+ − Me), 141 (M^+ − ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1449.

Recovered (*E*)-6: ^1H NMR (100 MHz, C_6D_6) δ 0.08 (s, 6 H), 1.00 (s, 9 H), 4.10 (d, *J* = 4.8, 2 H), 5.01 (bd, *J* = 10.0 Hz, 1 H), 5.15 (bd,

(10) For the recent review, see: Matsumoto, K.; Sera, A. *Synthesis* **1985**, 999.

Table II. ^{1}H NMR Data of Silyl Dienol Ethers



	^{1}H NMR (C_6D_6): chemical shift (ppm), J value (Hz)						
	A	B	C	D	E	^{t}BuMe$_2$Si	NOE
7 (100 MHz)	H: 6.62 (d), J_{AB} = 11.0	H: 6.30 (dd), J_{BA} = 11.0, J_{BC} = 11.0	H: 6.05 (ddq), J_{CB} = 11.0, J_{CD} = 10.2 J_{CE} = 2.0	H: 5.32 (dq), J_{DC} = 10.2, J_{DE} = 7.0	CH_3: 1.61 (dd), J_{EC} = 2.0, J_{ED} = 7.0	0.05 (s, 6 H), 0.93 (s, 9 H)	$H_C \rightarrow H_A$ (3%), $H_C \rightarrow H_D$ (3%), $CH_{3E} \rightarrow H_D$ (3%), $CH_{3E} \rightarrow H_B$ (3%)
9 (270 MHz)	H: 6.43 (bs)	^{t}BuMe$_2$SiOCH$_2$: 4.64 (s, 2 H)	H: 6.07 (ddq), J_{CA} = 1.3, J_{CD} = 11.7, J_{CE} = 2.1	H: 5.58 (dq), J_{DC} = 11.7, J_{DE} = 6.9	CH_3: 1.93 (dd), J_{EC} = 2.1, J_{ED} = 6.9	0.06 (s, 6 H), 0.21 (s, 6 H), 0.96 (s, 9 H), 1.07 (s, 9 H)	$H_A \leftrightarrow H_C$ ($\rightarrow$4%, $\leftarrow$4%), $H_A \leftrightarrow CH_{3E}$ ($\rightarrow$0.8%, $\leftarrow$2%), $CH_{2B} \rightarrow H_C$ (0.4%), $CH_{2B} \leftrightarrow CH_{3E}$($\rightarrow$2%, $\leftarrow$1%), $H_C \leftrightarrow H_D$ ($\rightarrow$5%, $\leftarrow$5%), $CH_{3E} \rightarrow H_D$ (7%)
15 (100 MHz)	H: 6.64 (d), J_{AB} = 11.5	H: 6.28 (dd), J_{BA} = 11.5, J_{BC} = 11.5	H: 5.90 (dq), J_{CB} = 11.5, J_{CE} = 1.0	$CH_3CH_2CH_2CH_2$: 2.06 (bt, 2 H), J = 7.2, 0.83–0.94 (m, 3 H), 1.18–1.49 (m, 4 H)	CH_3: 1.65 (d), J_{EC} = 1.0	0.10 (s, 6 H), 0.96 (s, 9 H)	$H_C \rightarrow H_A$ (6%), $H_C \rightarrow CH_{2D}$ (3%), $CH_{3E} \rightarrow H_B$ (6%)
16 (100 MHz)	H: 6.63 (d), J_{AB} = 11.0	H: 6.31 (dd), J_{BA} = 11.0, J_{BC} = 11.0	H: 6.02 (ddt), J_{CB} = 11.0, J_{CD} = 10.5, J_{CE} = 1.5	H: 5.32 (dt), J_{DC} = 10.5, J_{DE} = 7.5	CH_3CH_2: 2.11 (ddq, 2 H), J_{EC} = 1.5, J_{ED} = 7.5, J = 7.5, 0.95 (t, 3 H), J = 7.5	0.06 (s, 6 H), 0.94 (s, 9 H)	
17 (100 MHz)	H: 6.60 (d), J_{AB} = 11.0	H: 6.25 (dd), J_{BA} = 11.0, J_{BC} = 11.0	H: 5.79 (bd), J_{CB} = 11.0	CH_3: 1.73 (bs)	CH_3CH_2: 2.06 (q, 2 H), J = 7.5, 0.93(t, 3 H), J = 7.5	0.08, (s, 6 H), 0.95 (s, 9 H)	$H_C \rightarrow H_A$ (4%), $H_C \rightarrow CH_{3D}$ (2%), $CH_{2E} \rightarrow H_B$ (6%)
18 (100 MHz)	H: 6.60 (d), J_{AB} = 11.0	H: 6.29 (dd), J_{BA} = 11.0, J_{BC} = 11.0	H: 5.92 (ddd), J_{CB} = 11.0, J_{CD} = 10.0, J_{CE} = 0.5	H: 5.16 (dd), J_{DC} = 10.0, J_{DE} = 10.0	$(CH_3)_2CH$: 2.47–2.84 (m, 1 H), 1.00 (d, 6 H), J = 8.0	0.04 (s, 6 H), 0.92 (s, 9 H)	$H_A \rightarrow H_C$ (5%), $H_B \rightarrow CH_E$ (6%), $H_B \rightarrow CH_{3E}$ (1.6%)

J = 16.0 Hz, 1 H), 5.71 (dt, J = 14.2, 4.8 Hz, 1 H), 6.17–6.49 (m, 2 H); IR (neat) 3100, 1600 cm^{-1}; MS m/z 198 (M^+), 197 (M^+ – H), 141 (M^+ – ^{t}Bu), 73 (base peak); HR-MS (M^+) calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1449.

(1*Z*,3*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-2-[[(*tert*-butyldimethylsilyl)oxy]methyl]-1,3-pentadiene (9): IR (neat 3300, 1645, 1615 cm^{-1}; MS m/z 342 (M^+), 285 (M^+ – ^{t}Bu), 73 (base peak); HR-MS (M^+) calcd for $C_{18}H_{38}O_2Si_2$ 342.2410, found 242.2388.

(1*E*,3*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-4-methyl-1,3-octadiene (15): IR (neat) 1665, 1620 cm^{-1}; MS m/z 254 (M^+), 211, 197 (M^+ – ^{t}Bu), 73 (base peak); HR-MS (M^+) calcd for $C_{15}H_{30}OSi$ 254.2066, found 254.2058.

Recovered (*E*)-11: ^{1}H NMR (100 MHz, C_6D_6) δ 0.11 (s, 6 H), 0.89–1.79 (m, 7 H), 1.02 (s, 9 H), 2.22 (t, J = 7.3 Hz, 2 H), 4.23 (bd, J = 5.0 Hz, 2 H), 4.99 (bs, 1 H), 5.06 (bs, 1 H), 5.84 (dt, J = 16.0, 5.0 Hz, 1 H), 6.44 (d, J = 16.0 Hz, 1 H); IR (neat) 1610 cm^{-1}; MS m/z 254 (M^+), 253, 239 (M^+ – Me), 211, 197 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{15}H_{30}OSi$ 254.2066, found 254.2082.

(1*E*,3*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-1,3-hexadiene (16): IR (neat) 1650, 1610 cm^{-1}; MS m/z 212 (M^+), 155 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{12}H_{24}OSi$ 212.1597, found 212.1615.

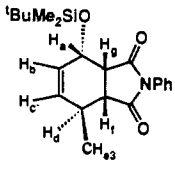
Recovered (*E*)-12: ^{1}H NMR (100 MHz, C_6D_6) δ 0.09 (s, 6 H), 1.01 (s, 9 H), 1.59 (d, J = 7.6 Hz, 3 H), 4.15 (d, J = 5.1 Hz, 2 H), 5.38–5.77 (m, 2 H), 5.93–6.43 (m, 2 H); IR (neat) 3050, 1650 cm^{-1}; MS m/z 212 (M^+), 197 (M^+ – Me), 155 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{12}H_{24}OSi$ 212.1597, found 212.1576.

(1*E*,3*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-4-methyl-1,3-hexadiene (17): IR (neat) 1655, 1620 cm^{-1}; MS m/z 226 (M^+), 211 (M^+ – Me), 169 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1738.

Recovered (*E*)-13: ^{1}H NMR (100 MHz, C_6D_6) δ 0.12 (s, 6 H), 1.03 (s, 9 H), 1.58 (d, J = 7.0 Hz, 3 H), 1.68 (bs, 3 H), 4.24 (d, J = 5.0 Hz, 2 H), 5.52 (bq, J = 7.0 Hz, 1 H), 5.69 (dt, J = 15.5, 5.0 Hz, 1 H), 6.42 (d, J = 15.5 Hz, 1 H); IR (neat) 1650, 1630 cm^{-1}; MS m/z 226 (M^+), 211 (M^+ – Me), 169 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1760.

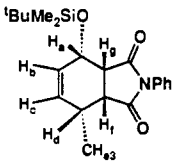
(1*E*,3*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5-methyl-1,3-hexadiene (18): IR (neat) 1650, 1610 cm^{-1}; MS m/z 226 (M^+), 211 (M^+ – Me), 169 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1760.

(1*R,2*R**,3*S**,6*S**)-*N*-Phenyl-3-[(*tert*-butyldimethylsilyl)oxy]-6-methylcyclohex-4-ene-1,2-dicarboximide (20)**. A solution of silyl dienol ether **7** (25 mg, 0.13 mmol), *N*-phenylmaleimide (66 mg, 0.38 mmol), and K_2CO_3 (1.0 mg, 0.007 mmol) in toluene (0.3 mL) was stirred at 120 °C for 12 h in Pyrex sealed tube. After cooling to 23 °C, the reaction mixture was diluted with ether, filtered through a silica gel pad, and concentrated. The residue was purified by silica gel flash chromatography (ethyl acetate–hexane, 1:7) to give the adduct **20** (33 mg, 70%) as a colorless solid: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.00 (s, 3 H), 0.03 (s, 3 H), 0.79 (s, 9 H), 1.44 (d, J_{ed} = 7.0 Hz, 3 H, H_e), 2.74 (dd, J_{fg} = 10.0, J_{fd} = 8.0 Hz, 1 H, H_f), 2.88–2.96 (m, 1 H, H_d), 3.04 (dd, J_{gf} = 10.0, J_{ga} = 4.0 Hz, 1 H, H_g), 4.77 (ddd, J_{ab} = 6.0, J_{ag} = 4.0, J_{ac} = 0.5 Hz, 1 H, H_a), 5.86 (dd, J_{cb} = 9.5, J_{cd} = 2.0 Hz, 1 H, H_c), 6.13 (ddd, J_{bc} = 9.5, J_{ba} = 6.0, J_{bd} = 3.5 Hz, 1 H, H_b), 7.32–7.48 (m, 5 H); NOE (NOESY) $H_a \leftrightarrow H_b$, $H_b \leftrightarrow H_c$, $H_c \leftrightarrow H_d$, $H_d \leftrightarrow H_e$, $H_e \leftrightarrow H_f$, $H_f \leftrightarrow H_g$; IR (neat) 1780, 1710, 1600 cm^{-1}; MS m/z 372 (M^+ + H), 356 (M^+ – Me), 314 (M^+ – ^{t}Bu, base peak), 240 (M^+ – ^{t}BuMe$_2$SiO); HR-MS (M^+ – C_4H_9) calcd for $C_{17}H_{20}O_3NSi$ 314.1212, found 314.1205.



(1*R,2*R**,3*S**,6*R**)-*N*-Phenyl-3-[(*tert*-butyldimethylsilyl)oxy]-6-methylcyclohex-4-ene-1,2-dicarboximide (21)**. Diels–Alder reaction in the absence of K_2CO_3 afforded the stereoisomer **21** (16%) along with **20** (28%): ^{1}H NMR (270 MHz, C_6D_6) δ 0.10 (s, 3 H), 0.17 (s, 3 H), 0.97 (s, 9 H), 1.49 (d, J_{ed} = 7.3 Hz, 3 H, H_e), 2.28–2.36 (m, 1 H, H_d), 2.49 (dd, J_{fg} = 10.0, J_{fd} = 8.0 Hz, 1 H, H_f), 2.64 (dd, J_{gf} = 10.0, J_{ga} = 6.0 Hz, 1 H, H_g), 4.41 (dd, J_{ag} = 6.0, J_{ab} = 5.0 Hz, 1 H, H_a), 5.68 (dd, J_{cb} = 9.5, J_{cd} = 5.0 Hz, 1 H, H_c), 5.79 (ddd, J_{bc} = 9.5, J_{ba} = 5.0, J_{bd} = 1.0 Hz, 1 H, H_b), 7.00–7.26 (m, 3 H), 7.50–7.54 (m, 2 H); NOE (NOESY) $H_a \leftrightarrow H_g$, $H_b \leftrightarrow H_c$, $H_d \leftrightarrow H_f$, $H_f \leftrightarrow H_g$; IR (neat) 1780, 1720, 1600 cm^{-1}; MS m/z 372 (M^+ + H), 356 (M^+ – Me), 314 (M^+ – ^{t}Bu, base peak), 240 (M^+ – ^{t}BuMe$_2$SiO); HR-MS (M^+ – C_4H_9) calcd for $C_{17}H_{20}O_3NSi$ 314.1212, found 314.1223.

1-[(*tert*-Butyldimethylsilyl)oxy]-4-iodobutane. To a stirred suspension of $CaCO_3$ (400 mg, 4.0 mmol) and NaI (6.00 g, 40.0 mmol) in THF (25 mL) was added *tert*-butyldimethylsilyl chloride (6.00 g, 39.8 mmol). The mixture was refluxed for 48 h, and then 6% aqueous $Na_2S_2O_3$ was added at 23 °C. The whole mixture was extracted with ether, washed with



brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane, 1:100–1:50) to give 1-[(*tert*-butyldimethylsilyl)oxy]-4-iodobutane (11.4 g, 91%) as a colorless oil: ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.05 (s, 6 H), 0.89 (s, 9 H), 1.57–2.07 (m, 4 H), 3.23 (t, J = 7.0 Hz, 2 H), 3.64 (t, J = 5.9 Hz, 2 H); IR (neat) 1390, 1360, 1180 cm^{-1}; MS m/z 257 (M^+ – ^{t}Bu), 215 (base peak), 187 (M^+ – I); HR-MS (M^+ – C_4H_9) calcd for $C_6H_{14}OISi$ 256.9859, found 256.9857.

4-[(*tert*-Butyldimethylsilyl)oxy]-1-(*p*-tolylsulfonyl)butane. To a stirred solution of 1-[(*tert*-butyldimethylsilyl)oxy]-4-iodobutane (3.01 g, 9.59 mmol) in DMF (10 mL) was added sodium *p*-toluenesulfinate (2.04 g, 11.5 mmol). The mixture was stirred at 60 °C for 3 h, and then water was added at 23 °C. The reaction mixture was extracted with ether, washed with water, 6% aqueous $Na_2S_2O_3$, water, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography (ether–hexane, 1:6–1:4) to give 4-[(*tert*-butyldimethylsilyl)oxy]-1-(*p*-tolylsulfonyl)butane (2.99 g, 91%) as a colorless oil: ^{1}H NMR (100 MHz, $CDCl_3$) δ –0.01 (s, 6 H), 0.83 (s, 9 H), 1.44–1.93 (m, 4 H), 2.45 (s, 3 H), 3.01–3.17 (m, 2 H), 3.57 (t, J = 5.6 Hz, 2 H), 7.34 (d, J = 8.3 Hz, 2 H), 7.78 (d, J = 8.3 Hz, 2 H); IR (neat) 1600, 1320, 1140 cm^{-1}; MS m/z 327 (M^+ – Me), 285 (M^+ – ^{t}Bu, base peak); HR-MS (M^+ – C_4H_9) calcd for $C_{13}H_{21}O_3SSi$ 285.0981, found 285.0964.

4-(*p*-Tolylsulfonyl)-1-butanol. To a stirred solution of 4-[(*tert*-butyldimethylsilyl)oxy]-1-(*p*-tolylsulfonyl)butane (1.51 g, 4.42 mmol) in THF (15 mL) was added tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 5.3 mmol) at 0 °C. The mixture was stirred at 23 °C for 30 min, and then water was added. The reaction mixture was extracted with ether, washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane, 3:1) to give 4-(*p*-tolylsulfonyl)-1-butanol (994 mg, 99%) as a colorless oil: ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.42–1.99 (m, 5 H), 2.45 (s, 3 H), 3.05–3.20 (m, 2 H), 3.63 (dt, J = 5.6, 5.6 Hz, 2 H), 7.35 (d, J = 8.1 Hz, 2 H), 7.78 (d, J = 8.1 Hz, 2 H); IR (neat) 3500, 1600 cm^{-1}; MS m/z 229 (M^+ + H), 228 (M^+), 210 (M^+ – H_2O), 73 (M^+ – Ts), 55 (base peak); HR-MS (M^+) calcd for $C_{11}H_{16}O_3S$ 228.0820, found 228.0838.

(*Z*)-8-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfonyl)-6-octene-1,5-diol. To a stirred solution of 4-(*p*-tolylsulfonyl)-1-butanol (1.20 g, 5.26 mmol) in THF (40 mL) was added ^{n}BuLi (1.64 M in hexane, 6.40 mL, 10.5 mmol) at –78 °C, and the mixture was stirred at –78 °C for 15 min. Then to this solution was added dropwise a solution of the aldehyde **22** (967 mg, 4.84 mmol) in THF (30 mL) at –78 °C. After being stirred at –78 °C for 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel flash chromatography (ethyl acetate–hexane, 1:1) to give (*Z*)-8-[(*tert*-butyldimethylsilyl)oxy]-4-(*p*-tolylsulfonyl)-6-octene-1,5-diol (1.64 g, 79%, diastereomeric mixture) as a pale yellow oil: ^{1}H NMR (100 MHz, $CDCl_3$) δ –0.01, 0.05 (s and s, together 6 H), 0.85, 0.86 (s and s, together 9 H), 1.57–2.19 (m, 6 H), 2.47 (s, 3 H), 2.98–3.27 (m, 1 H), 3.48–3.67 (m, 2 H), 3.91, 4.21 (d and d, J = 5.9 and 5.5 Hz, together 2 H), 4.76–4.90 (m, 1 H), 5.39–5.86 (m, 2 H), 7.39 (d, J = 8.3 Hz, 2 H), 7.81 (d, J = 8.3 Hz, 2 H); IR (neat) 3500, 3040, 1600 cm^{-1}; MS m/z 371 (M^+ – ^{t}Bu), 353 (M^+ – ^{t}Bu, H_2O), 123 (base peak); HR-MS (M^+ – C_4H_9) calcd for $C_{17}H_{27}O_5SSi$ 371.1349, found 371.1321.

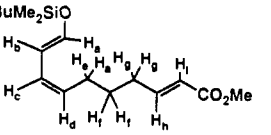
(*Z*)-4,8-Diacetoxy-1-[(*tert*-butyldimethylsilyl)oxy]-5-(*p*-tolylsulfonyl)-2-octene. To a stirred solution of (*Z*)-8-[(*tert*-butyldimethylsilyl)oxy]-4-(*p*-tolylsulfonyl)-6-octene-1,5-diol (101 mg, 0.24 mmol) in triethylamine (1.0 mL) were added acetic anhydride (86 μL, 0.91 mmol) and a catalytic amount of DMAP at 0 °C, and the mixture was stirred at 23 °C for 1 h. The reaction mixture was quenched with methanol at 0 °C, stirred at 23 °C for 30 min, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane, 1:3) to give (*Z*)-4,8-diacetoxy-1-[(*tert*-butyldimethylsilyl)oxy]-5-(*p*-tolylsulfonyl)-2-octene (120 mg, 99%, diastereomeric mixture) as a pale yellow oil: ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.03, 0.07 (s and s, together 6 H), 0.87, 0.89 (s and s, together 9 H), 1.76–2.11 (m, 4 H), 1.79, 1.87 (s and s, together 3 H), 2.01, 2.05 (s and s, together 3 H), 2.46 (s, 3 H), 3.02–3.16, 3.26–3.43 (m and m, together 1 H), 3.93–4.36 (m, 4 H), 5.26–5.97 (m, 3 H), 7.37 (d, J = 8.3 Hz, 2 H), 7.77 (d, J = 8.3 Hz, 2 H); IR (neat) 3040, 1740, 1600 cm^{-1}; MS m/z 455 (M^+ – ^{t}Bu), 395 (M^+ – ^{t}Bu, AcOH), 335 (M^+ – ^{t}Bu, 2 AcOH), 300, 139 (base peak), 43; HR-MS (M^+ – C_4H_9) calcd for $C_{21}H_{31}O_7SSi$ 455.1560, found 455.1552.

(4*E*,6*Z*)-8-[(*tert*-Butyldimethylsilyl)oxy]-4,6-octadien-1-ol. To a stirred solution of (*Z*)-4,8-diacetoxy-1-[(*tert*-butyldimethylsilyl)oxy]-5-(*p*-tolylsulfonyl)-2-octene (302 mg, 0.59 mmol) in methanol–ethyl acetate (4–2 mL) was added sodium amalgam (5%, 5.43 g, 11.8 mmol) at –20 °C, and the mixture was stirred at –20 °C for 2 h. The reaction mixture was quenched with water and allowed to warm to 23 °C, and the organic solvents were removed. To the residue was added methanol at 0 °C, and the reaction mixture was stirred at 23 °C for 15 min. After removal of methanol, the residue was extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel flash chromatography (ether–hexane, 1:1) to give (4*E*,6*Z*)-8-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1-ol (133 mg, 88%, mixture of isomers, 4*E*:4*Z* = 3.2:1) as a colorless oil: ^{1}H NMR (270 MHz, C_6D_6) δ 0.12 (s, 6 H), 0.49 (bt, J = 5.4 Hz, 1 H), 1.02 (s, 9 H), 1.36–1.47 (m, 2 H), 2.01–2.17 (m, 2 H), 3.31 (dt, J = 5.4, 5.4 Hz, 2 H), 4.39 (d, J = 6.6 Hz, 2 H), 5.38–5.75 (m, 2 H), 6.03, 6.26–6.45 (dd and m, J = 11.2, 11.2 Hz, together 2 H); IR (neat) 3360, 3040, 1650 cm^{-1}; MS m/z 256 (M^+), 239 (M^+ – H_2O), 199 (M^+ – ^{t}Bu), 57 (base peak); HR-MS (M^+) calcd for $C_{14}H_{28}O_2Si$ 256.1858, found 256.1879.

(4*E*,6*Z*)-8-[(*tert*-Butyldimethylsilyl)oxy]-4,6-octadienal. To a stirred solution of (4*E*,6*Z*)-8-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1-ol (127 mg, 0.50 mmol) in CH_2Cl_2 (8 mL) were added molecular sieves 4A (powder, 965 mg), sodium acetate (20 mg, 0.24 mmol), and pyridinium chlorochromate (322 mg, 1.49 mmol) at 0 °C. After being stirred at 0 °C for 1 h, the reaction mixture was diluted with ether, filtered through a Florisil column, and concentrated. The residue was purified by silica gel flash chromatography (ether–hexane, 1:8) to give (4*E*,6*Z*)-8-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadienal (90 mg, 71%, 4*E*:4*Z* = 3.2:1) as a colorless oil: ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.08 (s, 6 H), 0.91 (s, 9 H), 1.21–1.62 (m, 4 H), 4.34 (d, J = 6.1 Hz, 2 H), 5.31–6.42 (m, 4 H), 9.78 (t, J = 1.5 Hz, 1 H); IR (neat) 2730, 1730, 1650 cm^{-1}; MS m/z 255 (M^+ + H), 254 (M^+), 197 (M^+ – ^{t}Bu), 75 (base peak); HR-MS (M^+) calcd for $C_{14}H_{26}O_2Si$ 254.1702, found 254.1704.

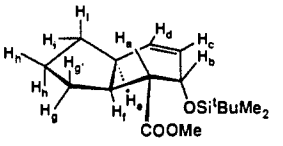
Methyl (2*E*,6*E*,8*Z*)-10-[(*tert*-Butyldimethylsilyl)oxy]-2,6,8-decatrienoate (23). To a stirred solution of (4*E*,6*Z*)-8-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadienal (82 mg, 0.32 mmol) in benzene (0.7 mL) was added [(methoxycarbonyl)methylene]triphenylphosphorane (430 mg, 1.29 mmol) at 0 °C. After being stirred at 23 °C for 4 h, the reaction mixture was diluted with ether, filtered through a Florisil column, and concentrated. The residue was purified by silica-gel flash chromatography (ether–hexane, 1:25) to give the triene **23** (90 mg, 90%, 4*E*:4*Z* = 3.2:1) as a colorless oil and its 2*Z* isomer (5 mg, 5%). The spectral data of **23** were as follows: ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.08 (s, 6 H), 0.90 (s, 9 H), 2.26–2.33 (m, 4 H), 3.73 (s, 3 H), 4.34 (dd, J = 6.4, 1.5 Hz, 2 H), 5.31–6.43 (m, 5 H), 6.96 (dt, J = 15.6, 6.7 Hz, 1 H); IR (neat) 1730, 1660 cm^{-1}; MS m/z 310 (M^+), 253 (M^+ – ^{t}Bu), 89 (base peak); HR-MS (M^+) calcd for $C_{17}H_{30}O_3Si$ 310.1964, found 310.1937. The spectral data of the 2*Z* isomer were as follows: ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.08 (s, 6 H), 0.90 (s, 9 H), 2.16–2.44 (m, 2 H), 2.66–2.88 (m, 2 H), 3.71 (s, 3 H), 4.33 (dd, J = 6.6, 1.3 Hz, 2 H), 5.30–6.43 (m, 5 H), 5.78 (dt, J = 11.6, 1.5 Hz, 1 H); IR (neat) 1730, 1650 cm^{-1}; MS m/z 310 (M^+), 309, 279, 253 (M^+ – ^{t}Bu), 89 (base peak); HR-MS (M^+) calcd for $C_{17}H_{30}O_3Si$ 310.1964, found 310.1945.

Methyl (2*E*,7*Z*,9*E*)-10-[(*tert*-Butyldimethylsilyl)oxy]-2,7,9-decatrienoate (24): ^{1}H NMR (270 MHz, C_6D_6) δ 0.08 (s, 6 H), 0.95 (s, 9 H), 1.23–1.31 (m, 2 H, H_f), 1.83 (ddt, J_{gh} = 7.0, J_{gi} = 2.0, J_{gf} = 7.0 Hz, 2 H, H_g), 1.97 (ddt, J_{cd} = 7.4, J_{ce} = 1.5, J_{ef} = 7.4 Hz, 2 H, H_e), 3.48 (s, 3 H), 5.15 (dt, J_{dc} = 10.8, J_{de} = 7.4 Hz, 1 H, H_d), 5.85 (dt, J_{ih} = 15.6, J_{ig} = 2.0 Hz, 1 H, H_i), 6.02 (ddt, J_{cb} = 11.5 J_{cd} = 10.8, J_{ce} = 1.5 Hz, 1 H, H_c), 6.23 (ddd, J_{ba} = 11.5, J_{bc} = 11.5, J_{bd} = 1.0 Hz, 1 H, H_b), 6.61 (d, J_{ab} = 11.5 Hz, 1 H, H_a), 7.01 (dt, J_{hi} = 15.6, J_{hg} = 7.0 Hz, 1 H, H_h); NOE $H_c \rightarrow H_a$: 6%, $H_c \rightarrow H_d$: 7%, $H_e \rightarrow H_b$: 8%; IR (neat) 1730, 1650, 1610 cm^{-1}; MS m/z 310 (M^+), 279, 253 (M^+ – ^{t}Bu), 89 (base peak); HR-MS (M^+) calcd for $C_{17}H_{30}O_3Si$ 310.1964, found 310.1961. The spectral data of the recovered 6*Z* isomer of **23** were as follows: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 6 H), 0.90 (s, 9 H), 2.26–2.38 (m, 4 H), 3.72 (s 3 H), 4.35 (d, J = 5.8 Hz, 2 H), 5.43–5.50 (m, 1 H), 5.58 (ddt, J = 6.2, 1.5, 8.8 Hz, 1 H), 5.84 (dt, J = 15.5, 1.8 Hz, 1 H), 6.18–6.29 (m, 2 H), 6.96 (dt, J = 15.5, 6.8 Hz, 1 H); IR (neat) 1730, 1660 cm^{-1}; MS m/z 310 (M^+), 309, 253 (M^+ – ^{t}Bu), 89 (base peak); HR-MS (M^+) calcd for $C_{17}H_{30}O_3Si$ 310.1964, found 310.1970.



(1*S,2*R**,3*S**,6*S**)-2-[(*tert*-Butyldimethylsilyl)oxy]-1-carbometh-**

oxybicyclo[4.3.0]non-4-ene (25). A solution of the triene **24** (13 mg, 0.042 mmol) in toluene (1 mL) was stirred at 170 °C for 4 days in Pyrex sealed tube. After the solution was cooled to 23 °C, the solvent was removed. The residue was purified by silica gel flash chromatography (ether–hexane, 1:80) to give the adduct **25** (10.3 mg, 79%) as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.00 (s, 3 H), 0.02 (s, 3 H), 0.83 (s, 9 H), 1.06–1.25 (m, 1 H, H_i), 1.30 (dddd, $J_{g'g}$ = 14.0, $J_{g'f}$ = 4.0, $J_{g'h}$ = 6.9, $J_{g'h}$ = 6.9 Hz, 1 H, $H_{g'}$), 1.42–1.73 (m, 2 H, H_h), 1.82–1.92 (m, 1 H, H_i), 2.08 (dddd, $J_{gg'}$ = 14.0, J_{gf} = 8.1, J_{gh} = 8.1, J_{gh} = 4.8 Hz, 1 H, H_g), 2.37 (dd, J_{af} = 11.5, J_{ab} = 3.7 Hz, 1 H, H_a), 2.42–2.54 (m, 1 H, H_e), 2.67 (dddd, J_{fa} = 11.5, J_{fg} = 8.1, J_{fe} = 8.1, $J_{fg'}$ = 4.0 Hz, 1 H, H_f), 3.67 (s, 3 H), 4.38 (dd, J_{bc} = 5.1, J_{ba} = 3.7 Hz, 1 H, H_b), 5.73 (ddd, J_{cd} = 9.9, J_{cb} = 5.1, J_{ce} = 1.8 Hz, 1 H, H_c), 5.88 (dd, J_{dc} = 9.9, J_{de} = 4.0 Hz, 1 H, H_d); NOE $H_a \rightarrow H_i$ (3%), $H_a \rightarrow H_b$ (7%), $H_a \rightarrow H_g$ (3%), $H_f \rightarrow H_e$ (2%), $H_f \rightarrow H_g$ (4%); IR (neat) 1750, 1730, 1650 cm^{-1}; MS m/z 310 (M^+), 309, 295, 279, 253 ($M^+ - {}^t$Bu, base beak), 89; HR-MS ($M^+ - H$) calcd for $C_{17}H_{29}O_3Si$ 309.1886, found 309.1904. The most stable conformer suggested by Allinger's MM_2 (85) calculations is as follows.



Enantioselective Hydrogenation of Olefins with Homogeneous Ziegler–Natta Catalysts†

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Abstract: Styrene, 2-methyl-1-pentene, 2-phenyl-1-butene, and *cis*- and *trans*-2-hexene have been hydrogenated in the presence of catalysts derived from $[Al(CH_3)\text{-}O]_n$ and (−)-[ethylenebis(4,5,6,7-tetrahydro-1(*R*)-indenyl)]zirconium derivatives. α-Olefins are readily polymerized with this catalytic system; in the presence of hydrogen, hydrogenated monomers can be obtained depending on the hydrogen pressure. Terminal olefins substituted in the 2- or 3-positions and internal olefins are not polymerized but undergo hydrogenation. Styrene is hydrogenated at 12 turnovers/min at 20 atm of H_2 at 25 °C with this catalytic system. The catalytic deuteriation of styrene with [(−)-(EBTHI)ZrX, X = (*R*)-1,1′-bi-2-naphtholate] **2** yields (−)-(*R*)-1,2-dideuterioethylbenzene in 93% yield with an optical purity of 65%, indicating that the (Re) enantioface of styrene is deuterated preferentially. This is the opposite enantioface selectivity as observed in propylene oligomerization with the same catalytic system. In the presence of **2**, 2-phenyl-1-butene is hydrogenated to give (−)-(*R*)-2-phenylbutane in 95% yield with an optical purity of 36%. These results are discussed on the basis of a simple stereochemical model for the transition state of the olefin insertion step.

Although olefin hydrogenation in the presence of homogeneous Ziegler–Natta catalysts has been known since the early sixties,[3] up to now no reports have appeared on the use of these catalysts in enantioselective hydrogenation reactions,[4] primarily due to the lack of chiral transition metal species, which show the appropriate stereoselectivity and catalytic activity. A key breakthrough was the development by Brintzinger and co-workers of chiral group 4 metallocenes,[5,6] which were shown to be important components of homogeneous stereospecific polymerization catalysts.[7,8,9]

We became interested in olefin hydrogenation with these catalyst systems during our investigations on the asymmetric hydrooligomerization of propylene in the presence of the chiral homogeneous Ziegler–Natta system ethylenebis(tetrahydro-1-indenyl)zirconocene/aluminoxane.[9] In view of both large substrate selectivity and remarkably high stereospecificities of these catalysts in polymerization reactions of α-olefins, we investigated the activity of these systems for enantioselective hydrogenation reactions.

In this paper, we report our investigations on the chemoselectivity of these catalysts in the hydrogenation of olefins and the enantioselectivity in the hydrogenation of 1,1-disubstituted olefins and in the deuteriation of α-olefins. Besides the potential synthetic significance, these studies have provided key information on the origin of stereocontrol in hydrogenation and polymerization reactions with these catalyst systems.

Results

Dependence on Catalyst Precursor. We had previously observed that catalysts derived from zirconocene dichloride precursors exhibit a different response to hydrogen than catalysts derived from zirconocene dimethyl precursors.[9b] Therefore, we investigated the hydrogenation activity of these catalysts as a function of the

Table I. Hydrogenation of Styrene as a Function of the Zirconium Catalyst Precursor

catalyst precursor[a]	[cat], $\times 10^3$ M	Al/Zr	[olefin], M	gas	P_0, atm	yield, %
1	1.5	112	1.39	H_2	20	93
2	1.5	172	1.47	D_2	17.5	89
3	1.5	119	1.38	H_2	20	0

[a] [Ethylenebis(tetrahydro-1-indenyl)dimethylzirconium (**1**); (−)-[ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconium (*R*)-binaphtholate (**2**), $[\alpha]^{25}_{436}$ 1761 (c = 1.1 mg/mL in $CHCl_3$); [ethylenebis(tetrahydro-1-indenyl)]zirconium dichloride (**3**).

† This paper is dedicated to the memory of Professor Piero Pino.

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