which contained 0.17 g (29%) of the 5/6-fused acetoxy ketone **14**: ^{1}H NMR (360 MHz) δ 1.10 (s, 9 H), 1.18 (s, 3 H), 1.49 (m, 1 H), 1.73 (s, 3 H), 1.78 (m, 1 H), 2.47 (m, 3 H), 2.67 (m, 1 H), 3.78 (d, J = 6 Hz, 1 H), 4.90 (s, 1 H), 5.93 (s, 1 H), 7.42 (m, 6 H), 7.68 (m, 4 H); ^{13}C NMR (360 MHz) δ 17.23, 19.46, 22.17, 24.10, 27.02, 28.96, 36.48, 45.49, 71.44, 85.51, 127.49, 129.11, 129.71, 129.96, 133.16, 133.44, 135.97, 169.90, 180.00, 208.93; IR ($CHCl_3$) 3080, 2960, 2900, 2870, 1740, 1710, 1675, 1625, 1470, 1000 cm^{-1}; HRMS m/z calcd for $C_{24}H_{25}O_4Si$ (M – C_4H_9 (*tert*-butyl)) 405.1522, obsd 405.1512.

Irradiation of (1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (4a) in Aqueous Acetic Acid. A solution of 0.85 g (11.25 mmol) of dienone **4a** containing 9% of the unoxidized 6/5-fused enone **6f** in 120 mL of THF was placed in a 250-mL capacity cylindrical glass vessel and agitated with a stream of prepurified N_2 while 120 mL of water was added slowly. To the turbid mixture was added 15 mL of glacial acetic acid. The resulting clear solution was irradiated for 1.0 h with a 450-W high-pressure mercury lamp housed in a Pyrex probe. The reaction mixture was then poured into 50 mL of ether, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 25 mL). The combined ethereal extracts were washed with saturated $NaHCO_3$ (5 × 25 mL) and 50 mL of brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give 5.83 g of a mixture of photoproducts. Subjection of the mixture to flash column chromatography (20–30% ethyl acetate in hexane) gave as an initial fraction 0.31 g of *tert*-butyldiphenylsilanol. Further elution of the column gave a second fraction which contained 0.09 g of unoxidized 6/5-fused enone **6f**, a third fraction which contained 0.09 g (11%, based on unrecovered starting material) of the hemiacetal acetate **18**, a fourth fraction which contained 0.19 g (62% based on unrecovered starting material) of 3-(2-methyl-5-hydroxyphenyl)propanal (**20**), and a fifth fraction which contained 0.07 g (8%, based on unrecovered starting material) of 5/6-fused acetoxy ketone **14**.

Irradiation of (1*S*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (1a) in Aqueous Acetic Acid. A solution of 4.52 g (11.25 mmol) of dienone **1a** containing 27% of the unoxidized 6/5-fused enone **5g** in 225 mL of THF was placed in a 600-mL capacity cylindrical glass vessel and agitated with a stream of prepurified N_2 while 225 mL of water was added slowly. To the turbid mixture was added 30 mL of glacial acetic acid. The resulting clear solution was irradiated with a 450-W high-pressure mercury lamp housed in a Pyrex probe for 2.0 h. After this period, the starting material had disappeared as evidenced by TLC analysis (25% ethyl acetate in hexane) of an aliquot of the solution. The reaction mixture was then poured into 100 mL of ether, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (5 × 50 mL) and then with 75 mL of brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give 5.83 g of a mixture of photoproducts. Subjection of the mixture to flash column chromatography (20–30% ethyl acetate in hexane) gave as an initial fraction 1.24 g of unoxidized 6/5-fused enone **5g**. Further elution of the column gave a second fraction which contained 0.06 g (4%) of (2-methyl-5-hydroxyphenyl)-propanal (**20**), a third fraction which contained 0.16 g (5%, based on unrecovered starting material) of 5/6-fused acetoxy ketone **2a**, a fourth fraction which contained 1.50 g (47% based on unrecovered starting material) of 5/6-fused hydroxy ketone **21** [^{1}H NMR (360 MHz) δ 1.07 (s, 3 H), 1.09 (s, 9 H), 1.49 (m, 1 H), 1.78 (m, 1 H), 2.07 (m, 1 H), 2.40 (m, 3 H), 2.60 (m, 1 H), 2.74 (d, J = 6 Hz, 1 H), 3.83 (dd, J = 4.6, 11.7 Hz, 1 H), 5.82 (s, 1 H), 7.42 (m, 6 H), 7.71 (m, 4 H); ^{13}C NMR (360 MHz) δ 14.52, 19.38, 26.99, 27.16, 27.69, 30.45, 36.39, 50.05, 78.51, 127.61, 127.68, 128.66, 129.92, 133.69, 135.82, 179.04, 209.50; IR ($CDCl_3$) 3560, 2950, 2930, 2860, 1705, 1630 cm^{-1}; HRMS m/z calcd for $C_{22}H_{23}O_3Si$ (M – C_4H_9 (*tert*-butyl)) 363.1417, obsd 363.1397], and a fifth fraction which contained 0.50 g (15% based on unrecovered starting material) of the cyclopropyl ketone **22**: ^{1}H NMR (360 MHz) δ 1.00 (s, 3 H), 1.04 (s, 9 H), 1.18 (m, 2 H), 1.52 (m, 2 H), 1.71 (m, 1 H), 1.90 (d, J = 5.5 Hz, 1 H), 2.12 (d, J = 5.5 Hz, 1 H), 2.51 (d, J = 17 Hz, 1 H), 2.77 (d, J = 17 Hz, 1 H), 4.07 (dd, J = 7.5, 10 Hz, 1 H), 7.40 (m, 6 H), 7.72 (m, 4 H); ^{13}C NMR (360 MHz) δ 19.34, 25.68, 26.87, 29.69, 35.79, 36.34, 43.05, 45.39, 58.33, 72.48, 73.00, 127.46, 127.55, 129.59, 129.63, 133.70, 134.02, 135.90, 209.10; IR ($CDCl_3$) 3590, 2960, 2940, 2860, 1720 cm^{-1}; HRMS m/z calcd for $C_{22}H_{23}O_3Si$ (M – C_4H_9 (*tert*-butyl)), 363.1417, obsd 363.1418.

Acknowledgment. Helpful discussions with Professors Gilbert Stork and Marie E. Kraft on the Mitsunobu reaction of hydroxy enone **5a** are gratefully acknowledged, as is the assistance of Mr. Ley Hathcock and Dr. Russell Timkovich with mass spectral analyses and Dr. Ken Belmore with NMR analyses. Grants from the National Institutes of Health and the National Science Foundation for the purchase of high-resolution NMR instrumentation and from the National Institutes of Health for the purchase of a high-resolution mass spectrometer are gratefully acknowledged. P.L.K. wishes to thank The University of Alabama for a Graduate Council Research Fellowship.

Supplementary Material Available: ^{1}H and in some cases ^{13}C NMR spectra for all relevant compounds (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis of Four Stereoisomeric Tetrose Derivatives from Propargyl Alcohol. One-Carbon Homologation of Vinylsilanes via α,β-Epoxy Silanes

Barbara Achmatowicz, Piotr Raubo, and Jerzy Wicha*

Institute of Organic Chemistry, the Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warsaw, Poland

Received May 6, 1992

Silicon-mediated synthesis of stereoisomeric tetroses **1**, **2**, **3**, and **4**, from propargyl alcohol, is described. An allylic alcohol bearing the trimethylsilyl group in the γ-position, *rac*-**9b**, was subjected to the Sharpless kinetic resolution to give (2*S*)-**9b** and the (2*S*,3*S*,4*S*)-epoxide **10a** of very high enantiomeric purity (≥97% ee). Compound (2*S*)-**9b** was epoxidized with *tert*-butyl hydroperoxide and vanadyl acetylacetonate to give epoxide **14a** as the major product. Epoxy silanes **10a** and **14a** were treated with benzenethiol in the presence of silica gel to give the corresponding sulfides (**11a** and **16a**). Sulfides **11b** and **16b** were oxidized to sulfoxides which, without isolation, were subjected to the Pummerer rearrangement followed by hydrolysis. Intermediate vinylsilane **9a** was prepared from vinylsilane **6** via epoxy silane **7** using a novel homologation method.

A general method of carbohydrate synthesis has recently been developed[1] on the basis of titanium-mediated asymmetric epoxidation of allylic alcohols[2] and stereoselective transformations of hydroxy epoxides. Although the success

0022-3263/92/1957-6593$03.00/0

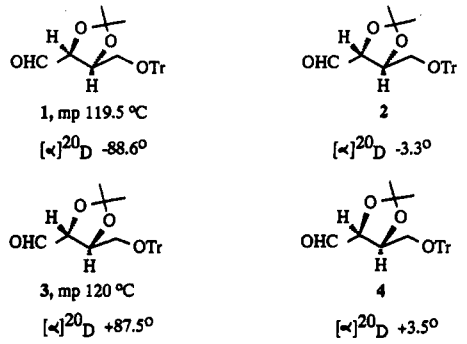
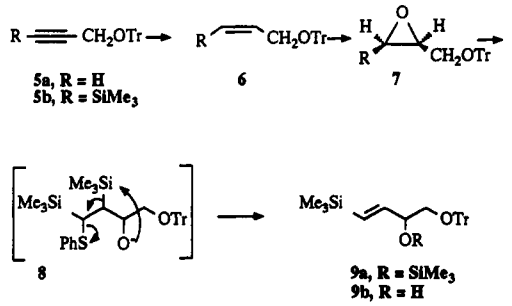


Figure 1.

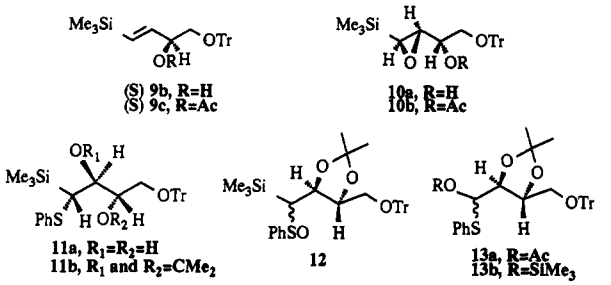
Scheme I



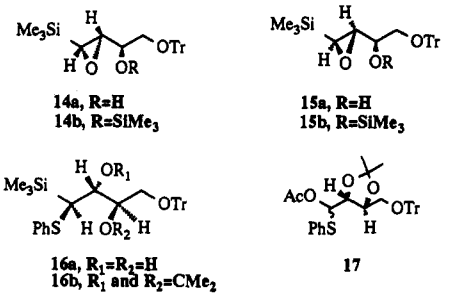
of this method in the synthesis of all classes of saccharides is unquestionable, it appeared to us that use of allylic alcohols bearing a silicon substituent in the γ-position for asymmetric epoxidation would provide some advantages in polyhydroxylated compounds synthesis. In particular, such an approach could benefit from the facts that: (1) kinetic resolution of (*E*)-γ-(trimethylsilyl)allylic alcohols affords both allylic alcohols and α,β-epoxy silanes in extremely high enantiomeric excess,[3] and (2) (α,β-epoxyalkyl) silanes may be transformed stereoselectively into α-hydroxy aldehydes under remarkably mild conditions.[4] As far as extension of the carbon chain is concerned, we envisioned one-carbon homologation of vinylsilanes via epoxy silanes, based upon the reaction of α,β-epoxy silanes with sulfonyl anions.[5] Herein we describe the synthesis of four enantiomeric tetroses **1**–**4** (Figure 1) starting from propargyl alcohol and utilizing a sequence of silicon-assisted reactions.

Acetylene derivative **5b** (Scheme I), prepared from propargyl alcohol via its trityl ether **5a**, was subjected to hydroalumination–protonation reactions[6] to give isomerically pure (*Z*)-vinylsilane **6** (81% yield from propargyl alcohol). Homologation of vinylsilane **6** to four-carbon (*E*)-vinylsilane **9a** was achieved in two steps. Compound **6** was oxidized with *m*-CPBA to epoxide **7** (91% yield) which was then subjected to reaction with the anion generated using phenyl (trimethylsilyl)methyl sulfide and butyllithium.[7] Vinylsilane **9a** was obtained in a 70% yield (after chromatography). This reaction proceeded in an analogous way as reactions involving all-carbon alkyl phenyl sulfones:[5] in the intermediate adduct **8** migration of the trimethylsilyl group from carbon to oxygen took place with simultaneous elimination of the benzenethiolate anion. It is noteworthy that our initial attempts to use phenyl (trimethylsilyl)methyl sulfone as a nucleophilic counterpart of oxirane **7** failed, apparently because of higher steric requirements of this species. Trimethylsilyl ether **9a** was quantitatively hydrolyzed to the corresponding alcohol **9b**.

Scheme II



Scheme III



Kinetic resolution[8] of allylic alcohol **9b** using diisopropyl L-tartrate (L-(+)-DIPT) afforded alcohol (*S*)-**9b** (47% yield) and (2*S*,3*S*,4*S*)-epoxide **10a** (47% yield) (Scheme II). The optical purity of each of these products was ≥97%, as indicated by the ^{1}H NMR spectra of acetates **9c** and **10b**, taken in the presence of tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium [Eu(hfc)$_3$].[9]

Hydroxy epoxide **10a** was treated with an excess of benzenethiol in the presence of silica gel at room temperature for 24 h, according to the methodology developed in our laboratory,[4] to give sulfide **11a** in 98% yield. The hydroxy groups in compound **11a** were protected with the dimethylpropylidene group and the derivative **11b** was oxidized with 1 molar equiv of *m*-CPBA at −78 °C. The crude sulfoxide **12** was treated with acetic anhydride in the presence of sodium acetate at 58 °C to give acetal **13a**

(1) (a) Ko, S. Y.; Lee, A. W. M.; Masamune, S.; Reed, L. A., III; Sharpless, K. B.; Walker, F. J. *Tetrahedron* **1990**, *46*, 245–264. (b) Ko, S. Y.; Lee, A. W. M.; Masamune, S.; Reed, L. A., III; Sharpless, K. B.; Walker, F. J. *Science* **1983**, *220*, 949. (c) Reed, L. A., III; Ito, Y.; Masamune, S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 6468. (d) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. *J. Org. Chem.* **1982**, *47*, 1373–1378.

(2) (a) Katsuki, T.; Sharpless,K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Org. Chem.* **1987**, *52*, 667; (c) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. For recent review, see: Pfenninger, A. *Synthesis* **1986**, 89.

(3) (a) Kitano, Y.; Matsumoto, T.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1323. (b) Kitano, Y.; Matsumoto, T.; Takeda, Y.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1732. (c) Carlier P. R.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 2978.

(4) Raubo, P.; Wicha, J. Unpublished results.

(5) (a) Masnyk, M.; Wicha, J. *Tetrahedron Lett.* **1988**, *29*, 2497. (b) Jankowski, P.; Marczak, S.; Masnyk, M.; Wicha, J. *J. Organomet. Chem.* **1991**, *403*, 49.

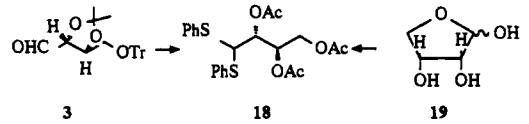
(6) (a) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214–2215. (b) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215–2217.

(7) (a) Kocieński, P. *Tetrahedron Lett.* **1980**, *21*, 1559. (b) Cohen, T.; Sherbine, J. P.; Mendelson, S. A.; Meyers, M. *Tetrahedron Lett.* **1985**, *26*, 2965. (c) Djuric, S. V.; Miyano, M.; Snyder, J. P. *Tetrahedron Lett.* **1986**, *27*, 4403.

(8) (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237–6240. (b) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

(9) Signals of the other enantiomer were not detectable in the spectra (comparison was made to the product derived from racemic material).

Scheme IV



3 18 19

as a mixture of diastereomers in a 91:1 ratio (67% yield after chromatography). It should be noted that the Pummerer rearrangement of sulfoxide **12** occurs under exceptionally mild conditions, as compared to those required for sulfoxides lacking the trimethylsilyl group.

Acetal **13a** was further processed by applying the Masamune–Sharpless methodology. Reduction with DIBAH in methylene chloride at −78 °C gave the 2*S*,3*S* derivative **1** (79% yield). Treatment of **13a** with potassium carbonate in methanol resulted in saponification of the acetate group and epimerization at C_2 to afford (2*R*,3*S*)-threose **2** in 69% yield.

Alternatively, the crude trimethylsilyl sulfoxide **12** was heated in toluene at 60 °C for 2 h to promote the sila-Pummerer rearrangement.[10] The trimethylsilyl acetal **13b** thus formed was hydrolyzed with methanol containing a trace of perchloric acid to give erythrose **1** (82%). Mild alkaline hydrolysis of **13b** (methanolic potassium carbonate at room temperature for 16 h), combined with epimerization, afforded threose **2** in 85% yield.

To explore chirality transfer in epoxidation of allylic alcohols, alcohol (*S*)-**9b** was treated with tetrabutyl hydroperoxide (TBHP) in the presence of vanadyl acetylacetonate [$VO(acac)_2$].[11] Erythro (2*R*,3*R*,4*R*)-**14a** and threo (2*R*,3*S*,4*S*)-**15a** epoxides were obtained in 57 and 13% yields (4.4:1 ratio), respectively (Scheme III). Interestingly, oxidation of allylic alcohol **9b** with *m*-CPBA in methylene chloride at −20 to −10 °C proved to be virtually unselective, affording epoxides **14a** and **15a** in a 1:1.2 ratio. Likewise, epoxidation of silyl ether **9a** with *m*-CPBA under buffered conditions yielded diastereomers **14b** and **15b** in a 1:1.4 ratio. Epoxide (2*R*,3*R*,4*R*)-**14a** was further transformed, as described above for its enantiomer **10a**. Thus, epoxide ring opening with benzenethiol and silica gel afforded sulfide **16a** in 91% yield. The latter compound was quantitatively converted to acetonide **16b** which was subjected to the Pummerer rearrangement to give acetal **17** (67% yield, 9:1 diastereomer ratio). Finally, DIBAH removal of the acetate group in **17** afforded erythrose **3** (67% yield) whereas alkaline hydrolysis of **17** yielded threose **4** (85%).

To confirm the stereochemical assignments, erythrose **3** was treated first with hydrochloric acid and benzenethiol and then with acetic anhydride, pyridine, and DMAP to yield the derivatives **18** ($[\alpha]^{19}_D$ +63.1°). Similar treatment of authentic D-(−)-erythrose gave the same compound **18** ($[\alpha]^{19}_D$ +58.5°).

Experimental Section

Melting points were determined on a hot-stage apparatus. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, in $CDCl_3$ unless specified otherwise. MS were obtained at 70 eV ionizing potential. All reactions involving organometallic reagents were carried out under argon with stirring. Organic solutions were dried over anhyd Na_2SO_4, and solvents were evaporated on a rotary evaporator. Column chromatography was performed on Merck silica gel 60, 230–400 mesh, and TLC on Merck slica gel G. Ligroin fraction boiling at 75–90 °C was used. Optical rotations were measured using a 8-mL-capacity cell (10-cm path length) in $CHCl_3$.

3-*O*-(Triphenylmethyl)prop-1-yn-3-ol (5a). A mixture of TrCl (2.7 g, 9.7 mmol), DMAP (26 mg, 0.21 mmol), pyridine (0.75 mL, 9.8 mmol), propargyl alcohol (0.57 mL, 9.7 mmol), and CH_2Cl_2 (4 mL) was stirred for 6 h. Workup and chromatography of the crude product (SiO_2, ligroin–toluene) gave crystalline trityl ether **5a** (2.58 g, 89%). A sample was crystallized from ether–heptane to give the pure product: mp 112–112.5 °C; NMR δ_H (60 MHz) 2.34 (t, 1, J = 2 Hz, C_1 H), 3.82 (d, 2, J = 2 Hz, C_3 H), 7.0–7.7 (m, 15, arom H); δ_C 52.8 (C_3), 73.4 (C_1), 80.4 (C_2), 87.6 (CPh_3), 127.3 (C_p), 128.1 (C_o), 128.7 (C_m), 143.6 (C_{ipso}). Anal. Calcd for $C_{22}H_{18}O$ (298.36): C, 88.56; H, 6.08. Found: C, 88.53; H, 6.06.

3-*O*-(Triphenylmethyl)-1-(trimethylsilyl)prop-1-yn-3-ol (5b). To a solution of alkyne **5a** (1.58 g, 5.53 mmol) in anhyd THF (6 mL) at −70 °C was added BuLi (1.6 M in hexane, 3.4 mL, 5.4 mmol) followed, after 30 min, by Me_3SiCl (0.8 mL, 6.4 mmol) in THF (7 mL). Stirring at −70 to −60 °C was continued for 1.5 h, the mixture was allowed to warm to 0 °C, and the reaction was quenched with saturated aqueous NH_4Cl (1 mL). Workup and chromatography of the crude product (SiO_2, 10 g, ligroin–toluene) gave crystalline compound **5b** (1.89 g, 96%). A sample was recrystallized from pentane to give **5b**: mp 93–94 °C; NMR δ_H (60 MHz) 0.17 (s, 9, TMS H), 3.8 (s, 2, C_3 H), 7.0–7.7 (m, 15, arom H); δ_C −0.4 (TMS C), 53.6 (C_3), 87.6 (CPh_3), 90.2 (C_1), 102.3 (C_2), 127.3 (C_p), 128.0 (C_o), 128.8 (C_m), 143.7 (C_{ipso}). Anal. Calcd for $C_{25}H_{26}OSi$ (370.55): C, 80.96; H, 7.05. Found: C, 81.03; H, 7.07.

(*Z*)-3-*O*-(Triphenylmethyl)-1-(trimethylsilyl)prop-1-en-3-ol (6). To a mixture of acetylene **5b** (0.721 g, 1.95 mmol), *N*-methylmorpholine (0.22 mL), and toluene (3 mL) was added DIBALH (1.2 M in toluene) at 58 °C in four portions (0.5 mL each) at 30-min intervals. After an additional 75 min, DIBALH (0.5 mL) was added, and stirring was continued for 1 h. The mixture was cooled to rt and was treated successively with MeOH (0.5 mL), saturated aqueous Na_2SO_4 (0.5 mL), and toluene (10 mL). After 30 min the precipitate was filtered off, and the filtrate was washed with saturated aqueous sodium potassium tartrate. Workup and chromatography of the crude product (SiO_2, ligroin) gave olefin **6** (691 mg, 95%). A sample was crystallized to give pure **6**: mp 33–34 °C ($MeOH–H_2O$); NMR δ_H 0.12 (s, 9, TMS H), 3.63 (dd, 2, J = 1.4, 6.2 Hz, C_3 H), 5.66 (dt, 1, J = 1.4, 14.4 Hz, C_1 H), 6.67 (dt, 1, J = 6.2, 14.4 Hz, C_2 H), 7.2–7.5 (m, 15, arom H); δ_C −0.5 (TMS C), 64.8 (C_3), 86.8 (CPh_3), 127.1 (C_p), 127.9 (C_o), 128.8 (C_m), 131.7 (C_1), 144.3 (C_{ipso}), 144.7 (C_2). Anal. Calcd for $C_{25}H_{28}OSi$ (372.56): C, 80.59; H, 7.57. Found: C, 80.54; H, 7.43.

(1*R,2*S**)-1,2-Epoxy-3-*O*-(triphenylmethyl)-1-(trimethylsilyl)propan-3-ol (7).** To a stirred solution of olefin **6** (300 mg, 0.8 mmol) in CH_2Cl_2 (1 mL), were added dry Na_2HPO_4 (155 mg, 1.09 mmol) and m-CPBA (90%, 200 mg, 1.04 mmol). After 20 h the mixture was diluted with CH_2Cl_2 (20 mL) and washed with saturated aqueous Na_2SO_3. The crude product (recovered in the usual way) was chromatographed (SiO_2, 2.5 g, ligroin–acetone) to give epoxide **7** (285 mg, 91%): mp 75–75.5 °C (pentane); NMR δ_H (500 MHz) −0.10 (s, 9, TMS H), 2.25 (d, 1, J = 5.4 Hz, C_1 H), 3.06 (dd, 1, J = 7.2, 10.3 Hz, C_3 Ha), 3.11 (dd, 1, J = 3.8, 10.3 Hz, C_3 Hb), 3.45 (ddd, 1, J = 3.8, 7.2 Hz, C_2 H), 7.2–7.5 (m, 15, arom H); δ_C −2.3 (TMS C), 49.0 (C_1), 55.7 (C_2), 65.5 (C_3), 86.8 (CPh_3), 127.2 (C_p), 128.0 (C_o), 128.9 (C_m), 144.1 (C_{ipso}). Anal. Calcd for $C_{25}H_{28}O_2Si$ (388.56): C, 77.27; H, 7.26. Found: C, 77.21; H, 7.32.

(*E*)-1-*O*-(Triphenylmethyl)-2-*O*,4-bis(trimethylsilyl)-but-3-ene-1,2-diol (9a). To a solution of phenyl (trimethylsilyl)methyl sulfide (942 mg, 4.8 mmol) in anhyd THF (15 mL) was added *n*-butyllithium (1.6 M in hexane, 3 mL, 4.8 mmol) at −5 °C. After 30 min at 0 °C the mixture was cooled to −40 °C, and epoxide **7** (630 mg, 1.63 mmol) in THF (5 mL) was added during 15 min. The mixture was stirred at −40 to −35 °C for 1.5 h and then allowed to warm to rt. Saturated aqueous NH_4Cl (10

(10) (a) Ager, D. J.; Cookson, R. C. *Tetrahedron Lett.* **1980**, *21*, 1677. (b) Ager, D. J. *J. Chem. Soc., Perkin Trans 1* **1983**, 1135.

(11) Sharpless, K. B.; Verhoeven, T. R. *Aldrichemica Acta* **1979**, *12*, 63–73 and references quoted therein.

(12) After manuscript of this paper was submitted for publication, we became cognizant of two very recent communications related to our work. Yoshida et al.[13] have described transformation of (α,β-epoxyalkyl)silanes to α-hydroxy aldehydes, utilizing electrochemical oxidation of α-alkoxysilanes. Kobayashi et al.[14] have reported on homologation of vinylsilanes via epoxy silanes.

(13) Yoshida, J.-i.; Tsuyoshi, M.; Yuko, M.; Sachihiko, I. *J. Org. Chem.* **1992**, *57*, 1321–1322.

(14) Kobayashi, Y.; Ito, T.; Yamakawa, I.; Urabe, H.; Sato, F. *Synlett.* **1991**, 813–815.

mL) and toluene (40 mL) were added. Workup and chromatography of the crude product (SiO_2, 17 g, ligroin–toluene) gave vinylsilane **9a** (542 mg, 70%) as a colorless oil: NMR δ_H (500 MHz) 0.06 (s, 9, TMS H), 0.11 (s, 9, TMSO H), 3.00 (dd, 1, J = 5.5, 9.1 Hz, C_1 Ha), 3.11 (dd, 1, J = 6.5, 9.1 Hz, C_1 Hb), 4.25 (m, 1, C_2 H), 5.91 (dd, 1, J = 1.2, 18.7 Hz, C_2 H), 6.02 (dd, 1, J = 5.1, 18.7 Hz, C_1 H), 7.20–7.50 (m, 15, arom H); δ_C (125 MHz) –1.4 (TMS C), 0.3 (TMSO C), 68.0 (C_1), 74.7 (C_2), 86.4 (CPh_3), 126.9 (C_p), 127.7 (C_o), 128.8 (C_m), 130.4 (C_4), 144.2 (C_{ipso}), 146.1 (C_3). Anal. Calcd for $C_{29}H_{38}O_2Si_2$ (474.77): C, 73.36; H, 8.07. Found: C, 73.25; H, 8.26.

(*E*)-1-*O*-(Triphenylmethyl)-4-(trimethylsilyl)but-3-ene-1,2-diol (9b). Silyl ether **9a** (103 mg, 0.22 mmol) in toluene (0.5 mL) was treated with $HClO_4$ [1 mL of a solution prepared from 70% aqueous $HClO_4$ (0.1 mL) and MeOH (100 mL)]. After 1 min the reaction was quenched with aqueous $NaHCO_3$ (0.1 mL). Workup gave alcohol **9b** (87 mg, 100%): IR (film) 3600 and 3460 (OH) cm^{-1}; NMR δ_H (500 MHz) 0.06 (s, 9, TMS H), 2.40 (d, 1, J = 4.3 Hz, OH), 3.13 (dd, 1, J = 7.1, 9.3 Hz, C_1 Ha), 3.22 (dd, 1, J = 3.8, 9.3 Hz, C_1 Hb), 4.26 (m, 1, C_2 H), 5.97 (dd, 1, J = 1.6, 18.8 Hz, C_4 H), 5.99 (dd, 1, J = 5.0, 18.8 Hz, C_3 H), 7.22–7.47 (m, 15, arom H); δ_C (125 MHz) –1.4 (TMS C), 67.2 (C_1), 73.4 (C_2), 86.7 (CPh_3), 127.1 (C_p), 127.9 (C_o), 128.7 (C_m), 131.2 (C_4), 143.8 (C_{ipso}), 144.5 (C_3). Anal. Calcd for $C_{26}H_{30}O_2Si$ (402.59): C, 77.57; H, 7.51. Found: C, 77.34; H, 7.41.

Asymmetric Epoxidation of *rac*-9b To Give (2*S*)-(*E*)-4-(Trimethylsilyl)-1-*O*-(triphenylmethyl)but-3-ene-1,2-diol [(*S*)-9b] and (2*S*,3*S*,4*S*)-3,4-Epoxy-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (the Erythro Isomer) (10a). To a suspension of powdered and freshly activated molecular seives 4A (576 mg) in anhyd CH_2Cl_2 (10 mL), stirred under argon at –20 °C, successively were added $Ti(Oi\text{-}Pr)_4$ (0.49 mL, 1.64 mmol), L-(+)-DIPT (0.42 mL, 1.97 mmol), (after 10 min) allylic alcohol **9b** (644 mg, 1.60 mmol) in CH_2Cl_2 (10 mL), and (after subsequent 10 min) TBHP (3.5 M in toluene, 0.69 mL, 2.4 mmol). The mixture was stirred at –20 °C for additional 1 h and was set aside in a freezer (–22 °C) for 6 h. Saturated aqueous Na_2SO_4 (1.6 mL) and ether (3 mL) were then added, and the mixture was stirred at rt for 30 min. Solid anhydrous Na_2SO_4 (0.5 g) was added, and stirring was continued for 15 min. The precipitate was filtered through a pad of Celite, and the pad was washed with toluene (50 mL). The solvent was removed in vacuo, and the residue was chromatographed (SiO_2, 10 g, toluene–acetone) to give

(1) Allylic alcohol (*S*)-**9b** (301 mg, 47%): $[\alpha]^{18}_D$ –3.1° (*c* 1.59); spectroscopic data as described for **9b**.

(2) Epoxide **10a** (317 mg, 47%): $[\alpha]^{20}_D$ –3.9° (*c* 4.60); IR (film) 3470 (OH) cm^{-1}; NMR δ_H (500 MHz) 0.014 (s, 9, TMS H), 2.22 (d, 1, J = 3.2 Hz, OH), 2.34 (dd, 1, J = 0.4, 3.6 Hz, C_4 H), 2.98 (dd, 1, J = 3.6, 4.2 Hz, C_3 H), 3.26 (dd, 1, J = 4.8, 9.5 Hz, C_1 Ha), 3.30 (dd, 1, J = 5.6, 9.5 Hz, C_1 Hb), 3.88 (m, 1, C_2 H), 7.2–7.5 (m, 15, arom H); δ_C (125 MHz) –3.7 (TMS C), 48.3 (C_4), 56.3 (C_3), 65.2 (C_1), 70.1 (C_2), 86.9 (CPh_3), 127.1 (C_p), 127.9 (C_o), 128.6 (C_m), 143.7 (C_{ipso}). Anal. Calcd for $C_{26}H_{30}O_3Si$ (418.59): C, 74.60; H, 7.22. Found: C, 74.49; H, 7.20.

(2*S*,3*S*,4*S*)-2-*O*-Acetyl-3,4-epoxy-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (10b). A mixture of alcohol **10a** (36 mg), pyridine (0.03 mL), Ac_2O (0.03 mL), DMAP (2 mg), and CH_2Cl_2 (0.5 mL) was stirred for 1 h. Workup gave acetate **10b** (36 mg, 91%): $[\alpha]^{20}_D$ –10.8° (*c* 4.39); IR (film) 1750 and 1230 (acetate) cm^{-1}; NMR δ_H 0.03 (s, 9, TMS H), 2.11 (s, 3, CH_3CO), 2.28 (d, 1, J = 3.4 Hz, C_4 H), 2.92 (dd, 1, J = 3.4, 5.2 Hz, C_3 H), 3.28 (dd, 1, J = 3.9, 10.1 Hz, C_1 Ha), 3.33 (dd, 1, J = 5.9, 10.1 Hz, C_1 Hb), 5.01 (m, 1, C_2 H), 7.1–7.5 (m, 15, arom H); δ_C –4.0 (TMS C), 20.8 (CH_3CO), 49.6 (C_4), 53.9 (C_3), 63.2 (C_1), 73.1 (C_2), 86.7 (CPh_3), 127.2 (C_p), 128.0 (C_o), 128.8 (C_m), 143.9 (C_{ipso}), 170.2 (CO). Anal. Calcd for $C_{28}H_{32}O_4Si$ (460.63): C, 73.00; H, 7.00. Found: C, 73.08; H, 7.14. ^1H NMR with (+)-Eu(hfc)$_3$ indicated ≥97% ee.

(2*S*)-(*E*)-2-*O*-Acetyl-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)but-3-ene-1,2-diol [(*S*)-9c]. Alcohol (*S*)-**9b** (41 mg) was acetylated in a similar way as described above to give acetate (*S*)-**9c** (46 mg, 100%): $[\alpha]^{20}_D$ –2.0° (*c* 4.64); IR (film) 1750 and 1240 (acetate) cm^{-1}; NMR δ_H 0.06 (s, 9, TMS H), 2.13 (s, 3, CH_3CO), 3.12 (dd, 1, J = 4.2, 9.7 Hz, C_1 Ha), 3.21 (dd, 1, J = 6.8, 9.7 Hz, C_1 Hb), 5.51 (m, 1, C_2 H), 5.93 (dd, 1, J = 4.1, 18.8 Hz, C_4 H), 5.96 (dd, 1, J = 7.4, 18.8 Hz, C_3 H), 7.2–7.5 (m, 15, aromat. H); δ_C –1.7 (TMS C), 21.0 (CH_3CO), 64.9 (C_1), 74.8 (C_2), 86.4 (CPh_3), 127.1 (C_p), 127.9 (C_o), 128.8 (C_m), 132.9 (C_4), 140.8 (C_3), 144.0 (C_{ipso}), 170.4 (CO). Anal. Calcd for $C_{28}H_{32}O_3Si$ (444.63): C, 75.63; H, 7.26. Found: C, 75.59; H, 7.38. ^1H NMR with (+)-Eu(hfc)$_3$ indicated ≥97% ee.

(1*S*,2*S*,3*S*)-1-(Phenylthio)-1-(trimethylsilyl)-4-*O*-(triphenylmethyl)butane-2,3,4-triol (11a). (a) A mixture of hydroxy epoxide **10a** (46 mg, 0.11 mmol), benzenethiol (0.25 mL), and silica gel (160 mg) was set aside at rt for 24 h. Toluene (10 mL) was added, and the silica gel was filtered off and washed with toluene (10 mL). The combined filtrates were concentrated in vacuo, and the residue was transferred to a silica gel column (0.5 g, ligroin). The column was eluted with ligroin to remove excess of benzenethiol and then with ligroin–toluene to give sulfide **11a** (57 mg, 98%): mp 137–139 °C (acetone–hexane); $[\alpha]^{20}_D$ +28.4° (*c* 3.47); NMR δ_H 0.18 (s, 9, TMS H), 2.45 (d, 1, J = 6.5 Hz, C_3 OH), 2.50 (d, 1, J = 5.3 Hz, C_2 OH), 2.95 (d, 1, J = 3.7 Hz, C_1 H), 3.23 (dd, 1, J = 4.7, 9.8 Hz, C_4 Ha), 3.41 (dd, 1, J = 3.1, 9.8 Hz, C_4 Hb), 3.72 (m, 1, C_3 H), 3.94 (ddd, 1, J = 3.7, 5.3, 8.1 Hz, C_2 H), 7.1–7.4 (m, 20, arom H); δ_C –0.8 (TMS C), 38.7 (C_1), 64.8 (C_4), 71.3 and 75.5 (C_2 and C_3), 87.0 (CPh_3), 126.2 (PhS C_p), 127.3 (Tr C_p), 128.1 (Tr C_o), 128.7 (Tr C_m), 129.1 (PhS C_m), 129.6 (PhS C_o), 137.3 (PhS C_{ipso}), 143.8 (Tr C_{ipso}). Anal. Calcd for $C_{32}H_{36}O_3SSi$ (528.76): C, 72.68; H, 6.86. Found: C, 72.59; H, 6.80.

(b) A mixture of hydroxy epoxide **10a** (151 mg, 0.36 mmol), benzenethiol (0.08 mL, 0.78 mmol), toluene (0.5 mL), and silica gel (380 mg) was set aside at 60 °C for 20 h. Workup as under a gave sulfide **11a** (162 mg, 85% yield). *rac*-**11a**: mp 120–122 °C.

(1*S*,2*S*,3*S*)-1-(Phenylthio)-2,3-*O*-isopropylidene-1-(trimethylsilyl)-4-*O*-(triphenylmethyl)butane-2,3,4-triol (11b). A mixture of diol **11a** (411 mg), 2-methoxypropene (0.2 mL), PPTS (7 mg), and CH_2Cl_2 (5 mL) was stirred under argon for 3.5 h. Workup and chromatography of the crude product (SiO_2, 5 g, ligroin–toluene) gave acetonide **11b** (443 mg, 100%) as colorless oil: $[\alpha]^{20}_D$ –17.3° (*c* 4.81); NMR δ_H 0.03 (s, 9, TMS H), 1.35 and 1.45 (2 s, 3 and 3, CH_3), 2.59 (d, 1, J = 8.3 Hz, C_1 H), 3.06 (dd, 1, J = 5.3, 9.9 Hz, C_4 Ha), 3.16 (dd, 1, J = 4.3, 9.9 Hz, C_4 Hb), 4.19 (ddd, 1, J = 4.8, 4.8, 6.2 Hz, C_3 H), 4.43 (dd, 1, J = 6.2, 8.3 Hz, C_2 H), 7.0–7.5 (m, 20, arom H); δ_C –1.3 (TMS C), 25.0, 27.2 (Me), 32.3 (C_1), 63.3 (C_4), 77.4 and 80.4 (C_2 and C_3), 86.9 (CPh_3), 107.6 (CMe_2), 126.4 (PhS C_p), 127.1 (Tr C_p), 127.9 (Tr C_o), 128.9 (PhS C_m), 129.0 (Tr C_m), 130.8 (PhS C_o), 136.5 (PhS C_{ipso}), 144.1 (Tr C_{ipso}). Anal. Calcd for $C_{35}H_{40}O_3SSi$ (568.82): C, 73.34; H, 7.09. Found: C, 73.49; H, 7.09. *rac*-**11b** (1*R**,2*R**,3*R**): mp 110.5–112 °C (pentane).

(1*RS*,2*S*,3*S*)-1-*O*-Acetyl-1-(phenylthio)-2,3-*O*-isopropylidene-4-*O*-(triphenylmethyl)erythritol (13a). To a solution of sulfide **11b** (404 mg, 0.71 mmol) in CH_2Cl_2 (3.5 mL), stirred under argon at –78 °C, was added *m*-CPBA (90%, 144 mg, 0.75 mmol) in CH_2Cl_2 (2.1 mL). After 45 min at –78 °C the mixture was diluted with CH_2Cl_2 (40 mL) and washed with aqueous $NaHCO_3$ and with water. The solvent was evaporated, and the residue was treated with anhyd AcONa (87 mg, 1.04 mmol) and with Ac_2O (4 mL). The mixture was stirred at 58 °C for 2 h, cooled, and diluted with toluene (20 mL). The solvent was removed in vacuo, and the residue was diluted with toluene (20 mL), filtered, and evaporated. The residue was filtered through SiO_2 (10 g, toluene) to give acetate **13a** (257 mg, 65%) as a mixture of diastereomers in a 91:9 ratio (NMR): IR (film) 1755 and 1215 (acetate) cm^{-1}; NMR, major diastereomer, δ_H 1.36 and 1.51 (2 s, 3 and 3, acetonide CH_3), 1.97 (s, 3, CH_3CO), C_{ipso}), (d, 2, J = 5.0 Hz, C_4 H), 4.26 (dd, 1, J = 6.3, 7.1 Hz, C_2 H), 4.38 (dt, 1, J = 5.0, 6.3 Hz, C_3 H), 6.08 (d, 1, J = 7.1 Hz, C_1 H), 7.2–7.5 (m, 20, arom H); minor diastereomer, 1.26 (s), 1.42 (s), 1.82 (s), 6.0 (d, J = 6.1 Hz); δ_C (major diastereomer) 20.8 (CH_3CO), 25.4 and 27.0 (CH_3C), 62.7 (C_4), 76.5 and 77.3 (C_2 and C_3), 87.1 (CPh_3), 109.5 (CMe_2), 127.2 (Tr C_p), 128.0 (Tr C_o), 128.5 (PhS C_p), 129.0 (Tr C_m), 129.1 (PhS C_m), 131.1, 133.9 (C_1, PhS C_{ipso}), 144.0 (Tr C_{ipso}), 169.1 (CO). Anal. Calcd for $C_{34}H_{34}O_5S$ (554.67): C, 73.62; H, 6.18; S, 5.78. Found: C, 73.37; H, 5.99; S, 5.47.

(2*S*,3*S*)-2,3-*O*-Isopropylidene-4-*O*-(triphenylmethyl)-erythrose (1). (a) Via Acetal 13a. To a solution of acetate **13a** (65 mg, 0.162 mmol) in CH_2Cl_2 (1.5 mL) was added DIBALH (1 M in hexane, 0.4 mL) at –78 °C. After 1 h at –78 °C the reaction

was quenched with saturated aqueous Na_2SO_4 (0.2 mL), and the mixture was allowed to warm to rt. Solid anhyd Na_2SO_4 (200 mg) was added, and the mixture was set aside for 30 min and then diluted with toluene (10 mL) and filtered through a pad of Celite. The solvent was removed, and the residue was chromatographed (SiO_2, 1.5 g, 100–200 mesh, toluene) to give aldehyde **1** (37 mg, 79%): mp 119.5–121 °C (acetone–hexane); $[\alpha]^{20}_D$ –88.6° (*c* 2.10); IR (film) 2820 and 2720 (HCO), 1735 (CO) cm^{-1}; NMR δ_H 1.42 and 1.72 (2 s, 3 and 3, acetonide CH_3), 2.97 (dd, 1, J = 3.0, 10.5 Hz, C_4 Ha), 3.44 (dd, 1, J = 3.7, 10.5 Hz, C_4 Hb), 4.42 (dd, 1, J = 1.9, 8.1 Hz, C_2 H), 4.51 (ddd, 1, J = 3.3, 3.3, 8.1 Hz, C_3 H), 7.1–7.5 (m, 15, arom H), 9.66 (d, 1, J = 1.9 Hz, C_1 H); δ_C 24.8 and 26.7 (Me), 61.3 (C_4), 77.8 (C_3), 80.7 (C_2), 87.4 (CPh_3), 110.9 (Me_2C), 127.3 (C_p), 128.0 (C_o), 128.8 (C_m), 143.8 (C_{ipso}), 200.0 (CHO). Anal. Calcd for $C_{26}H_{26}O_4$ (402.57): C, 77.59; H, 6.51. Found: C, 77.58; H, 6.58.

(b) Via Acetal 13b. To a solution of sulfide *rac*-**11b** (182 mg, 0.32 mmol) in CH_2Cl_2 (7 mL), stirred under argon at –78 °C, was added *m*-CPBA (90%, 64 mg, 0.33 mmol) in CH_2Cl_2 (3 mL). After 3 h at –78 °C, anhyd Na_2CO_3 (40 mg) was added, the mixture was allowed to warm to rt, and then it was diluted with CH_2Cl_2 (20 mL) and washed successively with 1 M aqueous NaOH, water, and brine. The solvent was removed in vacuo, and the residue was diluted with toluene (3 mL) and stirred at 60 °C for 2 h. The solution was cooled and treated with $HClO_4$ in MeOH (1 mL of a mixture: 0.1 mL of 70% aqueous $HClO_4$ and 100 mL of MeOH). After 1.5 min, 1 M NaOH (1 mL) was added. The mixture was diluted with toluene (25 mL) and washed successively with 1 M NaOH, water and brine. The solvent was removed, and the crude product was chromatographed (SiO_2, 1g, hexane–toluene) to give aldehyde *rac*-**1** (106 mg, 82%): mp 131–133 °C (acetone–hexane). The IR and NMR spectra of this product are identical with those of the product described under a.

(2*R*,3*S*)-2,3-*O*-Isopropylidene-4-*O*-(triphenylmethyl)-threose (2). (a) Via Acetal 13a. A mixture of acetate **13a** (30 mg, 0.075 mmol), anhyd K_2CO_3 (28 mg, 0.28 mmol), and MeOH (1 mL) was stirred for 21 h and then diluted with toluene (15 mL) and washed with 0.5 N aqueous NaOH. Workup and chromatography of the crude product (SiO_2, 100–200 mesh, 0.5 g, toluene–acetone) gave aldehyde **2** (15 mg, 69%) as colorless oil: $[\alpha]^{20}_D$ –3.3° (*c* 2.09); IR (film) 2800 and 2720 (HCO), 1740 (CO) cm^{-1}; NMR δ_H 1.42 and 1.49 (2 s, 3 and 3, acetonide CH_3), 3.34 (m, 2, C_4 H), 4.26 (m, 2, C_2 and C_3 H), 7.1–7.6 (m, 15, arom H), 9.75 (d, 1, J = 1.4 Hz, C_1 H); δ_C 26.2 and 26.7 (Me), 64.0 (C_4), 76.2 (C_3), 82.6 (C_2), 87.1 (CPh_3), 111.7 (CMe_2), 127.3 (C_p), 128.0 (C_o), 128.8 (C_m), 143.8 (C_{ipso}), 200.5 (CHO). Anal. Calcd for $C_{26}H_{26}O_4$ (402.47): C, 77.59; H, 6.51. Found: C, 77.35; H, 6.55.

(b) Via Acetal 13b. To a solution of sulfide *rac*-**11b** (150 mg, 0.264 mmol) in CH_2Cl_2 (6 mL), stirred under argon at –78 °C, was added *m*-CPBA (90%, 55 mg, 0.29 mmol) in CH_2Cl_2 (1.4 mL). After 1 h at –78 °C, the mixture was diluted with CH_2Cl_2 (20 mL) and was washed successively with 1 M aqueous NaOH, water, and brine. The solvent was removed in vacuo, and the residue was diluted with toluene (5 mL) and stirred at 60 °C for 2 h. After cooling, the solvent was removed in vacuo. The residue was dissolved in MeOH (5 mL), and anhyd K_2CO_3 (41 mg, 0.3 mmol) was added. The mixture was stirred for 16 h, and then it was diluted with toluene (30 mL) and washed successively with 1 M NaOH, water, and brine. The solvent was removed, and the crude product was chromatographed (SiO_2, 1 g, toluene–acetone) to give aldehyde *rac*-**2** (90 mg, 85%) as colorless oil. The IR and NMR spectra of this product are identical with those of the product described under a.

(2*R*,3*R*,4*R*)-3,4-Epoxy-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (14a) and (2*R*,3*S*,4*S*)-3,4-Epoxy-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (15a). Epoxidation of (*S*)-9b with TBHP–VO(acac)$_2$. To a solution of allylic alcohol (*S*)-**9b** (666 mg, 1.66 mmol) in toluene (1 mL) were added $VO(acac)_2$ (56 mg, 0.21 mmol) and TBHP (3.5 M in toluene, 1.2 mL, 4.2 mmol). The mixture was stirred for 2 h, and then it was diluted with toluene (50 mL) and washed with saturated aqueous Na_2SO_3 and brine. The solvent was removed in vacuo, and the residue was chromatographed (SiO_2, 10 g, toluene–acetone) to give the following:

1. (2*R*,3*R*,4*R*) (erythro) epoxide **14a** (396.7 mg, 57%): $[\alpha]^{20}_D$ +3.9° (*c* 4.58). NMR spectra of this product are identical with those of **10a**.

2. (2*R*,3*S*,4*S*) (threo) epoxide **15a** (93.3 mg, 13%): $[\alpha]^{20}_D$ –17.6° (*c* 3.62); NMR δ_H (500 MHz) 0.05 (s, 9, TMS H), 2.22 (d, 1, J = 6.3 Hz, OH), 2.67 (d, 1, J = 3.6 Hz, C_4 H), 2.98 (dd, 1, J = 3.6, 4.4 Hz, C_3 H), 3.27 (d, 2, J = 5.4 Hz, C_1 H), 3.65 (ddt, 1, J = 4.4, 5.4, 6.3 Hz, C_2 H), 7.2–7.5 (m, 15, arom H); δ_C –3.9 (TMS C), 48.2 (C_4), 57.0 (C_3), 65.6 (C_1), 71.7 (C_2), 86.9 (CPh_3), 127.3 (C_p), 128.0 (C_o), 128.8 (C_m), 144.0 (C_{ipso}). Anal. Calcd for $C_{28}H_{30}O_3Si$ (418.59): C, 74.60; H, 7.22. Found: C, 74.60; H, 7.49.

(2*R,3*R**,4*R**)-3,4-Epoxy-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (*rac*-14a) and (2*R**,3*S**,4*S**)-3,4-Epoxy-4-(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (*rac*-15a). Epoxidation of 9b with *m*-CPBA.** Olefin *rac*-**9b** (45 mg, 0.11 mmol) in CH_2Cl_2 (0.5 mL) was treated at –20 °C with *m*-CPBA (90%, 32 mg, 1.65 mmol) in CH_2Cl_2 (0.75 mL). The mixture was stirred at –20 to –15 °C for 5 h and left aside at –10 °C for 44 h. Workup and chromatography (SiO_2, 2 g, toluene–acetone) of the crude product gave a mixture of epoxides *rac*-**14a** and *rac*-**15a** (33 mg, 72%) in a 1:1.2 ratio and unreacted olefin *rac*-**9b** (9 mg, 20%).

(2*R,3*R**,4*R**)-3,4-Epoxy-2-*O*,4-bis(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (*rac*-14b) and (2*R**,3*S**,4*S**)-3,4-Epoxy-2-*O*,4-bis(trimethylsilyl)-1-*O*-(triphenylmethyl)butane-1,2-diol (*rac*-15b). Epoxidation of 9a with *m*-CPBA.** A mixture of *m*-CPBA (90%, 105 mg, 0.55 mmol), Na_2HPO_4 (101 mg, 0.7 mmol), and CH_2Cl_2 (0.5 mL) was stirred for 30 min, whereupon it was cooled to 0 °C, and olefin **9a** (183 mg, 0.39 mmol) in CH_2Cl_2 (1.5 mL) was added. The mixture was stirred at 0 °C for 6 h and set aside at 0 °C for 18 h. Workup and chromatography of the crude product (SiO_2, 2 g, ligroin–toluene) gave erythro epoxide **14b** (55 mg, 30%), threo epoxide **15b** (78 mg, 43%), and unreacted olefin **9a** (46 mg, 25%).

14b (erythro): NMR δ_H 0.04 (s, 9, TMS H), 0.14 (s, 9, TMSO H), 2.21 (d, 1, J = 3.4 Hz, C_4 H), 2.89 (dd, 1, J = 3.5, 5.0 Hz, C_3 H), 3.16 (dd, 1, J = 4.7, 9.4 Hz, C_1 Ha), 3.23 (dd, 1, J = 6.0, 9.4 Hz, C_1 Hb), 3.75 (q, 1, J = 5.2 Hz, C_2 H), 7.2–7.6 (m, 15, arom H); δ_C –3.9 (TMS C), 0.04 (TMSO C), 48.7 (C_4), 56.5 (C_3), 66.8 (C_1), 74.2 (C_2), 86.6 (CPh_3), 127.1 (C_p), 127.9 (C_o), 128.9 (C_m), 144.3 (C_{ipso}). Anal. Calcd for $C_{29}H_{38}O_3Si_2$ (490.77): C, 70.97; H, 7.80. Found: C, 71.10; H, 8.02.

15b (threo): NMR δ_H 0.01 (s, 9, TMS H), 0.12 (s, 9, TMSO H), 2.21 (d, 1, J = 3.6 Hz, C_4 H), 2.94 (dd, 1, J = 3.6, 6.5 Hz, C_3 H), 3.11 (dd, 1, J = 5.2, 9.4 Hz, C_1 Ha), 3.15 (dd, 1, J = 5.9, 9.4 Hz, C_1 Hb), 3.40 (q, 1, J = 5.8 Hz, C_2 H), 7.2–7.5 (m, 15, arom H); δ_C –3.8 (TMS C), –0.1 (TMSO C), 48.7 (C_4), 58.3 (C_3), 66.4 (C_1), 75.4 (C_2), 86.8 (CPh_3), 127.2 (C_p), 127.9 (C_o), 128.9 (C_m), 144.2 (C_{ipso}). Anal. Calcd for $C_{29}H_{38}O_3Si_2$ (490.77): C, 70.97; H, 7.80. Found: C, 70.82; H, 8.01.

(1*R*,2*R*,3*R*)-1-(Phenylthio)-1-(trimethylsilyl)-4-*O*-(triphenylmethyl)butane-2,3,4-triol (16a). A mixture of epoxy alcohol **15a** (330 mg), benzenethiol (0.5 mL), and silica gel (515 mg) was set aside for 24 h. Workup as described above for a similar reaction gave adduct **16a** (380 mg, 91%): mp 137–139 °C (acetone–hexane); $[\alpha]^{20}_D$ –28.6° (*c* 2.76). The NMR spectra of this product are identical with those of **11a**.

(1*R*,2*R*,3*R*)-1-(Phenylthio)-2,3-*O*-isopropylidene-1-(trimethylsilyl)-4-*O*-(triphenylmethyl)butane-2,3,4-triol (16b). A mixture of diol **16a** (339 mg), 2-methoxypropene (0.17 mL), PPTS (6 mg), and CH_2Cl_2 (4 mL) was stirred for 3.5 h. Workup gave acetonide **16b** (365 mg, 100%) as colorless oil: $[\alpha]^{20}_D$ +17.4° (*c* 3.63). NMR spectra of this product are identical with those of **11b**.

(1*RS*,2*R*,3*R*)-1-*O*-Acetyl-1-(phenylthio)-2,3-*O*-isopropylidene-4-*O*-(triphenylmethyl)erythritol (17). A solution of **16b** (323 mg, 0.57 mmol) in CH_2Cl_2 (3 mL) was treated with *m*-CPBA (90%, 114 mg, 0.59 mmol) in CH_2Cl_2 (1.7 mL) at –78 °C for 45 min. Workup gave crude sulfoxide which was treated with anhyd AcONa (73 mg) and Ac_2O (3 mL) at 58 °C for 2 h. Workup and chromatography (SiO_2, 7 g, toluene) of the crude product gave acetal **17** (212 mg, 67%) as a mixture of diastereomers in a 9:1 ratio. The NMR spectra of this product are identical with those of **13a**.

(2*S*,3*R*)-2,3-*O*-Isopropylidene-4-*O*-(triphenylmethyl)-threose (4). A mixture of thioacetal **17** (55 mg, 0.10 mmol), anhyd

K_2CO_3 (35 mg, 0.25 mmol), and MeOH (1.5 mL) was stirred for 19 h. The product was isolated in the usual way and chromatographed (SiO_2, 1.5 g, 100–200 mesh, toluene–acetone) to give aldehyde 4 (34 mg, 85%) as colorless oil: $[\alpha]^{19}_D$ +3.5° (c 2.14). NMR spectra of this product are identical with those of 2.

(2*R*,3*R*)-2,3-*O*-Isopropylidene-4-*O*-(triphenylmethyl)-erythrose (3). A solution of thioacetal 17 (152 mg, 0.274 mmol) in CH_2Cl_2 (2 mL) was treated with DIBALH (1 M in hexane, 0.9 mL) at −78 °C for 1 h. Workup and chromatography of the crude product (SiO_2, 2 g, toluene) gave aldehyde 3 (74 mg, 67%): mp 120–122 °C (acetone–hexane); $[\alpha]^{19}_D$ +87.5° (c 2.08). The NMR spectra of this product are identical with those of 1.

(2*R*,3*R*)-1,1-Bis(phenylthio)butane-2,3,4-triol Triacetate (18). (a) From D-(−)-Erythrose (19). A mixture of D-(−)-erythrose (88 mg), benzenethiol (0.5 mL), and concd HCl (0.5 mL) was stirred for 18 h. Solid $CaCO_3$ was added, and the mixture was diluted with MeOH (10 mL) and filtered. The filtrate was evaporated in vacuo. The residue was washed with hexane and dried whereupon it was treated wit pyridine (1 mL), Ac_2O (1 mL), and DMAP (10 mg) for 30 min. Workup and chromatography (SiO_2, 5 g, toluene–acetone) gave the derivative 18 (76 mg) as colorless oil: $[\alpha]^{19}_D$ +58.5° (c 1.91); IR (film) 1755 and 1220 (acetate) cm^{-1}; NMR δ_H 1.93, 2.00, and 2.01 (3 s, 3 each, CH_3), 4.16 (dd, 1, J = 4.8, 12.5 Hz, C_4 Ha), 4.34 (dd, 1, J = 2.7, 12.5 Hz, C_4 Hb), 4.50 (d, 1, J = 3.4, C_1 H), 5.50 (dd, 1, J = 3.4, 7.6 Hz, C_2 H), 5.59 (ddd, 1, J = 2.7, 4.8, 7.6 Hz, C_3 H), 7.2–7.6 (m, 10, arom H); δ_C 20.25, 20.36, 20.46 (Me), 61.3, 61.8 (C_1, C_4), 70.5, 72.4 (C_2, C_3), 128.3, 128.5 (C_p), 129.2 (C_m), 132.8, 133.7 (C_o), 133.8, 134.5 (C_{ipso}), 169.7, 170.7 (CO). Anal. Calcd for $C_{22}H_{24}O_6S_2$ (448.53): C, 58.91; H, 5.39; S, 14.30. Found: C, 59.13; H, 5.47; S, 14.16.

(b) From Compound 3. A mixture of aldehyde 3 (47 mg), benzenethiol (0.25 mL), and concd HCl (0.25 mL) was stirred for 14 h and worked up as described above. The crude product was treated with pyridine (0.2 mL), Ac_2O (0.2 mL), and DMAP (3 mg) for 2 h. Workup and chromatography (SiO_2, 1 g) of the crude product gave acetal 18 (40 mg, 76%) as colorless oil: $[\alpha]^{19}_D$ + 63.1° (c 2.06), showing the same spectral properties as the product described under a.

Reactions of Carbonyl Compounds with [(Trimethylsilyl)propargyl]diisobutyltelluronium Bromide Mediated by Different Strong Bases: Highly Regioselective Synthesis of (Trimethylsilyl)propargyl Alcohol and Highly Stereoselective Synthesis of *cis*-(Trimethylsilyl)alkynyl Epoxides†

Zhang-Lin Zhou, Yao-Zeng Huang,* Li-Lan Shi, and Jiong Hu

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

Received January 14, 1992

[(Trimethylsilyl)propargyl)]diisobutyltelluronium bromide (1), after being treated with alkyl- or aryllithium reagent, undergoes a lithium–tellurium exchange reaction via an unstable transient tetraorganyltellurium intermediate, and the in situ generated lithium species reacts with carbonyl compounds to give (trimethylsilyl)-propargyl alcohols 2 in high yields with high regioselectivity. However, when the telluronium salt 1 was treated with nonnucleophilic bases such as LDA or lithium 2,2,6,6-tetramethylpiperidide, the moderately stabilized silylated telluronium ylide formed. The silylated telluronium ylide reacted with carbonyl compounds to afford (trimethylsilyl)alkynyl epoxides 11 in good to excellent yields with high cis stereoselectivity.

Recently there has been a remarkable interest in the synthetic application of organotellurium reagents.[1] With the development of sulfonium, sulfoxonium, and selenonium ylides,[2] the application of several stabilized and moderately stabilized telluronium ylides in organic synthesis has been described.[3] In our previous paper, we found that diphenyltelluronium methylide—the first nonstabilized telluronium ylide generated from methyldiphenyltelluronium tetraphenylborate—reacted with aldehydes or ketones to form substituted oxiranes.[4] However, the reactions of trimethyl- and methyldiphenyltelluronium salts (precursors of nonstabilized telluronium ylides) with aromatic aldehydes gave secondary alcohols with the use of alkyl- or aryllithium reagent.[5] Later, we reported that the reactions of carbonyl compounds with benzyldibutyltelluronium bromide (precursor of semistabilized telluronium ylide) and dibutyl(cyanomethyl)-telluronium chloride (precursor of stabilized telluronium ylide) afforded homobenzylic alcohols and β-hydroxy nitriles respectively promoted by alkyl- or aryllithium reagent.[6] However, no report concerning the synthesis and reactions of a silylated telluronium ylide has appeared in the literature. We wish to report herein that reactions of carbonyl compounds with [(trimethylsilyl)propargyl]di-

† This paper is the 100th report on the application of elementoorganic compounds of 15th and 16th groups in organic synthesis. For the 99th report and preliminary communication, see: Zhou, Z. L.; Huang, Y. Z.; Shi, L. L. *J. Chem. Soc., Chem. Commun.* **1992**, 986.

(1) (a) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordin and Breach Science: New York, 1974. (b) Uemura, S. *Kagaku* **1981**, *36*, 381. (c) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274. (d) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1. (e) Back, T. G. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; p 2. (f) Engman, L. *Phosphorus Sulfur* **1988**, *38*, 105. (g) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, *793*, 897.

(2) (a) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides*; Academic: New York, 1975. (b) Dumont, W.; Bayet, P.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 274. (c) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (d) Takaki, K.; Yasumura, M.; Negoro, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 671.

(3) (a) Osuka, A.; Mori, Y.; Shimizu, H.; Suzuki, H. *Tetrahedron Lett.* **1983**, *24*, 2599. (b) Osuka, A.; Suzuki, H. *Tetrahedron Lett.* **1983**, *24*, 5109. (c) Osuka, A.; Hanasaki, Y.; Suzuki, H. *Nippon Kagaku Kaishi* **1987**, 1505. (d) Huang, X.; Xie, L. H.; Wu, H. *J. Org. Chem.* **1988**, *53*, 4862. (e) Zhou, Z. L.; Sun, Y. S.; Shi, L. L.; Huang, Y. Z. *J. Chem. Soc., Chem. Commun.* **1990**, 1439. (f) Zhou, Z. L.; Shi, L. L.; Huang, Y. Z. *Tetrahedron Lett.* **1990**, *31*, 7657.

(4) Shi, L. L.; Zhou, Z. L.; Huang, Y. Z. *Tetrahedron Lett.* **1990**, *31*, 4173.

(5) Shi, L. L.; Zhou, Z. L.; Huang, Y. Z. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2847.

(6) (a) Li, S. W.; Zhou, Z. L.; Huang, Y. Z.; Shi, L. L. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1099. (b) Zhou, Z. L.; Shi, L. L.; Huang, Y. Z. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1931.

0022-3263/92/1957-6598$03.00/0