Chiral Ketone-Catalyzed Asymmetric Epoxidation of 2,2-Disubstituted Vinylsilanes

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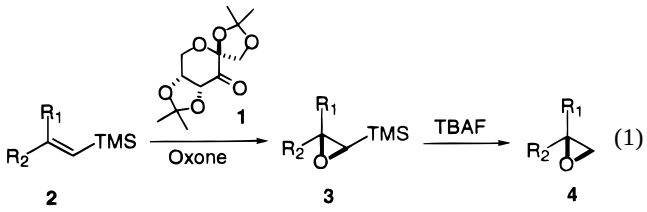
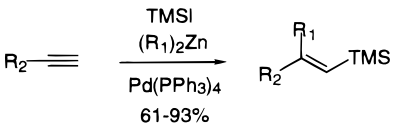
α,β-Epoxysilanes are very useful synthetic intermediates.[1] New epoxides can be obtained from α,β-epoxysilanes by alkylation[2] or desilylation.[3] The silicon group also provides a controlling group for regioselective opening of the epoxide, generating a number of other useful intermediates.[4] Asymmetric epoxidation of vinylsilanes can provide, in principle, an effective approach to prepare chiral α,β-epoxysilanes. Recently we reported a highly enantioselective epoxidation method for trans- and trisubstituted olefins using the fructose-derived ketone **1** as catalyst and Oxone as oxidant.[5] In our efforts to expand the scope of this epoxidation method, we found that 2,2-disubstituted vinylsilanes were quite complimentary substrates, producing 2,2-disubstituted α,β-epoxysilanes with high enantioselectivity (eq 1). Upon desilylation, 1,1-



(1)

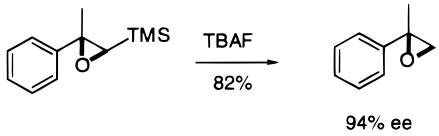
disubstituted terminal epoxides were obtained without loss in enantioselectivity.

The 2,2-disubstituted vinylsilane substrates were readily synthesized by the reported palladium-catalyzed coupling of a terminal alkyne, dialkylzinc, and iodotrimethylsilane (eq 2).[6] Table 1 summarizes the asymmetric epoxidation



(2)

of representative 2,2-disubstituted vinylsilanes. High enantioselectivities were obtained for these substrates. The reactivities of these silanes were somewhat reduced, probably as a result of the steric bulk of the trimethylsilyl group. Although good conversion could be obtained using less ketone (e.g., 0.3 equiv, Table 1, entry 7), higher conversions were obtained when more ketone was used. As shown in eqs 3 and 4, 1,1-disubstituted terminal



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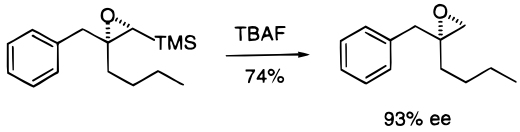

(4)

epoxides were readily obtained with high enantioselectivity from the desilylation of the epoxysilanes using TBAF.[7]

In the dioxirane-mediated epoxidation, the spiro transition state is electronically favored as a result of a stabilizing interaction of an oxygen lone pair of the dioxirane with the π^* orbital of the olefin.[8c,e] Previously, we have shown that the main competing transition state with our epoxidation system is the planar transition state **B** (Scheme 1).[5a] The competition between spiro **A** and planar **B** is affected by the steric bulk of substituents on the olefin. Higher ee can be obtained by decreasing the size of R_2 (favoring spiro **A**) and/or increasing the size of R_3 (disfavoring planar **B**). The sterically demanding silyl group (R_3) certainly disfavors planar **B**, which is an

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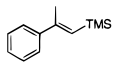
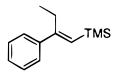
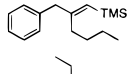
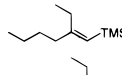
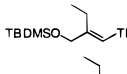
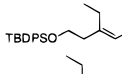
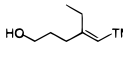
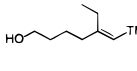
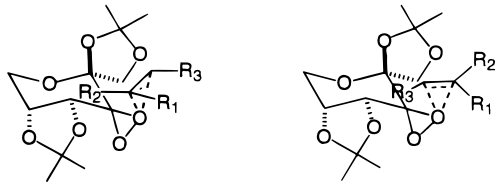
Table 1. Asymmetric Epoxidation of Representative 2,2-Disubstituted Vinylsilanes[a]

entry	substrate	yield (%)[b]	ee (%)	config.
1		74	94[c]	(*R,R*)[g,9]
2		82	92[c]	(*R,R*)[h]
3		66	93[d]	(*R,R*)[h]
4		51	90[e]	(*R,R*)[h]
5		67	84[e]	(*R,R*)[h]
6		67	92[f]	(*R,R*)[h]
7		80 71[i]	90[e] 93[e]	(*R,R*)[h] (*R,R*)[h]
8		75	91[e]	(*R,R*)[h]

[a] All epoxidations were carried out at 0 °C (bath temperature) with substrate (1 equiv), ketone (0.65 equiv), Oxone (1.38 equiv), and K_2CO_3 (5.8 equiv) in CH_3CN−dimethoxymethane−0.05 M $Na_2B_4O_7 \cdot 10H_2O$ aqueous Na_2(EDTA) (4×10^{-4}) solution (1:2:2 v/v); the reactions were stopped after 3 h. [b] The epoxides were purified via flash chromatography and gave satisfactory spectroscopic characterization. [c] Enantioselectivity was determined by chiral HPLC (Chiralcel OD) after desilylation. [d] Enantioselectivity was determined by chiral HPLC (Chiralpak AD) after desilylation. [e] Enantioselectivity was determined by ^{1}H NMR shift analysis of the epoxide directly with Eu(hfc)$_3$. [f] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [g] The absolute configurations were determined by comparing the measured optical rotations with the reported ones after desilylation. [h] The absolute configuration was tentatively assigned by analogy based on the spiro reaction mode. [i] 0.3 equiv of ketone used.

Scheme 1



Spiro (**A**) Planar (**B**)

important contributing factor for the high enantioselectivities observed for the 2,2-disubstituted vinylsilanes.

In summary, we have found that the epoxidation of 2,2-disubstituted vinylsilanes using the fructose-derived chiral ketone **1** as catalyst and Oxone as oxidant is highly enantioselective. The silyl group enhances the enantioselectivity by disfavoring the competing planar transition state through a steric effect. The availability of these enantiomerically enriched 2,2-disubstituted α,*β*-epoxysilanes provides opportunities for potential synthetic applications; for example, chiral 1,1-disubstituted terminal epoxides can be readily obtained from these epoxysilanes by desilylation.

Experimental Section

General Methods. Oxone was purchased from Aldrich (it has been found that the oxidation activity of the purchased Oxone occasionally varies with different batches). All glassware used for the epoxidation was carefully washed to be free of any trace metals that may catalyze the decomposition of Oxone. Dioxane was freshly distilled from CaH_2. THF was distilled from sodium/benzophenone ketyl. Hexane was distilled prior to use. All other solvents were used without further purification. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). Optical rotations were measured on an Autopol III automatic polarimeter in a 10 cm cell. Silica gel 60 (230−400 mesh) from E. Merck Co. was employed for all flash chromatography.

General Epoxidation Procedure. (*E*)-2-Phenyl-1-(trimethylsilyl)-1-butene (0.20 g, 0.97 mmol) was dissolved in CH_3CN−DMM (15 mL, 1:2 v/v). Subsequently were added buffer [10 mL, 0.05 M solution of $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2-(EDTA)], tetrabutylammonium hydrogen sulfate (0.022 g, 0.06 mmol), and ketone **1** (0.167 g, 0.65 mmol). The mixture was cooled to 0 °C (ice bath), and both a solution of Oxone (0.985 g, 1.6 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 7.5 mL) and a solution of K_2CO_3 (0.925 g, 6.7 mmol) in water (7.5 mL) were added via syringe pump such that 6.5 mL of each solution was added over a 2 h period. Upon stirring for an additional 1 h at 0 °C, the reaction mixture was diluted with water (40 mL), extracted with hexane, washed with brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography [silica gel buffered with 1% Et_3N in hexane, hexanes−ethyl acetate (1:0−4:1 v/v) as eluent] to afford (*E*)-2-phenyl-1-(trimethylsilyl)-1-butene oxide as a colorless oil (0.18 g, 82% yield) (Table 1, entry 2).

General Desilylation Procedure. To a solution of (*E*)-2-phenyl-1-(trimethylsilyl)-1-propene oxide (0.050 g, 0.24 mmol) in THF (2.5 mL) was added tetrabutylammonium fluoride (1 M in THF, 0.5 mL, 0.5 mmol) dropwise under N_2. Upon stirring under N_2 for 2 h, the reaction mixture was diluted with diethyl ether (10 mL), washed with water, dried ($MgSO_4$), filtered, concentrated, and purified via flash chromatography (hexanes−ethyl acetate, 9:1 v/v) to yield α-methylstyrene oxide as a colorless oil (0.027 g, 84%).

(*R,R*)-2-Phenyl-1-(trimethylsilyl)-1-propene Oxide (Table 1, entry 1). Colorless oil. IR (KBr) 1603, 1493, 1447, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) *δ* 7.45−7.25 (m, 5H), 2.25 (s, 1H), 1.75 (s, 3H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$) *δ* 144.6, 128.6, 127.3, 125.1, 63.0, 61.0, 21.3, −1.4.

α-Methylstyrene Oxide.[9] Colorless oil. $[\alpha]^{25}_D = +2.5$ (*c* 0.18, acetone).

(*R,R*)-2-Phenyl-1-(trimethylsilyl)-1-butene Oxide (Table 1, entry 2).[10] IR (KBr) 1448, 1250, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) *δ* 7.30−7.20 (m, 5H), 2.21 (dq, *J* = 14.1, 7.4 Hz, 1H), 2.16 (s, 1H), 1.58 (dq, *J* = 14.1, 7.4 Hz, 1H), 0.89 (t, J = 7.4 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$) *δ* 142.5, 128.5, 127.2, 126.1, 66.0, 62.7, 28.0, 10.2, −1.4.

α-Ethylstyrene Oxide.[7c] Colorless oil. $[\alpha]^{25}_D = -25.2$ (*c* 0.64, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 7.32−7.16 (m, 5H), 2.9 (d, *J* = 5.5 Hz, 1H), 2.67 (d, *J* = 5.5 Hz, 1H), 2.12 (dq, *J* = 14.6, 7.5 Hz, 1H), 1.74 (dq, *J* = 14.6, 7.5 Hz, 1H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) *δ* 140.4, 128.5, 127.7, 126.4, 61.3, 55.7, 28.6, 9.4.

(*R,R*)-2-Benzyl-1-(trimethylsilyl)-1-hexene Oxide (Table 1, entry 3).

Vinylsilane. Colorless oil. IR (KBr) 1612, 1494, 1247 cm^{-1}; ^{1}H NMR ($CDCl_3$) *δ* 7.37−7.18 (m, 5H), 5.25 (t, *J* = 1.0 Hz, 1H), 3.46 (s, 2H), 2.16−2.06 (m, 2H), 1.53−1.27 (m, 4H), 0.947 (t, *J* = 7.2 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$) *δ* 158.9, 140.5, 129.4, 128.6, 126.3, 46.3, 35.5, 31.7, 23.3, 14.5, 0.7.

α,*β*-Epoxysilane. Colorless oil. IR (KBr) 1604, 1454, 1249, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) *δ* 7.34−7.20 (m, 5H), 2.97 (d, *J* = 14.2 Hz, 1H), 2.85 (d, *J* = 14.2 Hz, 1H), 2.14 (s, 1H), 1.58−1.24 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$) *δ* 138.0, 129.8, 128.6, 126.7, 64.9, 58.1, 43.1, 33.0, 28.4, 23.3, 14.4, −1.4.

2-Benzyl-1-hexene Oxide. Colorless oil. $[\alpha]^{25}_D = -6.0$ (*c* 0.29, $CHCl_3$); IR (KBr) 1496, 1454, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) *δ* 7.33−7.20 (m, 5H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.85 (d, *J* = 14.4 Hz, 1H), 2.62 (d, *J* = 4.8 Hz, 1H), 2.57 (d, *J* = 4.8 Hz, 1H), 1.64−1.25 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) *δ* 137.4, 130.0, 128.6, 126.8, 60.1, 52.2, 41.0, 34.0, 27.3, 23.1, 14.4. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.88; H, 9.57.

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(R,R)-2-Ethyl-1-(trimethylsilyl)-1-hexene Oxide (Table 1, entry 4).

Vinylsilane. Colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.12 (t, J = 1.5 Hz, 1H), 2.2−2.0 (m, 4H), 1.5−1.2 (m, 4H), 0.99 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 162.1, 122.3, 38.4, 30.7, 29.3, 22.9, 14.4, 14.1, 0.71.

α,β-Epoxysilane. Colorless oil. $[\alpha]^{25}_D$ = +16.5 (*c* 0.96, $CHCl_3$); IR (KBr) 1466, 1250, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 1H), 1.75−1.2 (m, 8H), 0.98 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 6.7 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 65.2, 58.7, 35.8, 27.3, 26.4, 23.2, 14.4, 10.3, −1.4. Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 66.16; H, 11.88.

(*R*,*R*)-2-[(*tert*-Butyldimethylsiloxy)methyl]-1-(trimethylsilyl)-1-butene Oxide (Table 1, entry 5).

Vinylsilane. Colorless oil. IR 1628, 1250, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.49 (t, J = 1.0 Hz, 1H), 4.08 (d, J = 1.0 Hz, 2H), 2.12 (q, J = 7.6 Hz, 2H), 1.00 (t, J = 7.6 Hz, 3H), 0.91 (s, 9H), 0.10 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 159.1, 120.7, 67.1, 26.3, 26.2, 18.8, 14.5, 0.6, −5.0.

α,β-Epoxysilane. Colorless oil. $[\alpha]^{25}_D$ = +11.7 (*c* 2.16, $CHCl_3$); IR (KBr) 1463, 1251, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.68 (d, J = 11.1 Hz, 1H), 3.52 (d, J = 11.1 Hz, 1H), 2.09 (d, J = 0.5 Hz, 1H), 1.81 (dqd, J = 13.9, 7.5, 0.5 Hz, 1H), 1.44 (dq, J = 13.9, 7.5 Hz, 1H), 0.99 (t, J = 7.5 Hz, 3H), 0.87, (s, 9H), 0.11 (s, 9H). 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 66.9, 65.5, 55.7, 26.2, 24.2, 18.6, 10.4, −1.5, −5.0, −5.1. Anal. Calcd for $C_{14}H_{32}O_2Si_2$: C, 58.27; H, 11.18. Found: C, 58.46; H, 11.13.

(*R*,*R*)-4-(*tert*-Butyldiphenylsiloxy)-2-ethyl-1-(trimethylsilyl)-1-butene Oxide (Table 1, entry 6).

Vinylsilane. Colorless oil. IR (KBr) 1613, 1472, 1247, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.71−7.65 (m, 4H), 7.44−7.34 (m, 6H), 5.19, (t, J = 1.0 Hz, 1H), 3.75 (t, J = 7.0 Hz, 2H), 2.34 (dt, J = 7.0, 1.0 Hz, 2H), 2.10 (q, J = 7.5 Hz, 2H), 1.05 (s, 9H), 0.96 (t, J = 7.5 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 158.4, 136.0, 134.4, 129.9, 127.9, 125.2, 63.5, 41.6, 29.6, 27.3, 19.6, 14.0, 0.8.

α,β-Epoxysilane. Colorless oil. $[\alpha]^{25}_D$ = +6.0 (*c* 0.91, $CHCl_3$); IR (KBr) 1428, 1250, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.68−7.62 (m, 4H), 7.43−7.32 (m, 6H), 3.72 (dd, J = 6.6, 6.3 Hz, 2H), 2.12 (s, 1H), 2.06 (dt, J = 14.1, 6.3 Hz, 1H), 1.69−1.38 (m 3H), 1.03 (s, 9H), 0.96 (t, J = 7.5 Hz, 3H), 0.10 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 135.9, 134.1, 130.0, 128.0, 63.7, 61.2, 58.8, 38.8, 27.3, 27.2, 19.5, 10.2, −1.30. Anal. Calcd for $C_{25}H_{38}O_2Si_2$: C, 70.36; H, 8.98. Found: C, 70.16; H, 8.90.

(*R*,*R*)-4-Ethyl-5-(trimethylsilyl)-4-penten-1-ol Oxide (Table 1, entry 7).

Vinylsilane. The substrate was obtained from the desilylation of (*E*)-5-(*tert*-butyldimethylsiloxy)-2-ethyl-1-(trimethylsilyl)-1-pentene. Colorless oil. IR (KBr) 3319, 1613, 1464, 1248, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.19, (t, J = 1.0 Hz,1H), 3.64 (q, J = 6.0 Hz, 2H), 2.151 (q, J = 7.5 Hz, 2H), 2.15 (td, J = 7.6, 1.0 Hz, 2H), 1.74−1.64 (m, 2H), 1.63−1.55 (m, 1H) 1.01 (t, J = 7.5 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 161.1, 123.2, 63.2, 34.7, 31.3, 29.2, 14.1, 0.6.

α,β-Epoxysilane. Colorless oil. $[\alpha]^{25}_D$ = +21.5 (*c* 1.83, $CHCl_3$); IR 3466, 1457, 1250, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.65 (m, 2H), 2.08 (d, J = 0.8 Hz, 1H), 2.01−1.91 (br s, 1H), 1.81−1.57 (m, 5H), 1.41 (dq, J = 14.6, 7.5 Hz, 1H), 1.00 (dd, J = 7.8, 7.5 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 65.1, 63.1, 58.9, 32.4, 28.2, 26.5, 10.5, −1.4. Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.50; H, 10.72.

(*R*,*R*)-5-Ethyl-6-(trimethylsilyl)-5-hexen-1-ol Oxide (Table 1, entry 8).

Vinylsilane. The substrate was obtained from the desilylation of (*E*)-6-(*tert*-butyldimethylsiloxy)-2-ethyl-1-(trimethylsilyl)-1-hexene. Colorless oil. IR (KBr) 3320, 1613, 1458, 1247, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.15 (s, 1H), 3.63 (qd, J = 6.0, 1.0 Hz, 2H), 2.11 (q, J = 7.5 Hz, 2H), 2.08 (t, J = 6.6 Hz, 2H), 1.61−1.41 (m, 4H), 0.99 (t, J = 7.5 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 161.3, 122.8, 63.2, 38.2, 32.8, 29.2, 24.5, 14.0, 0.7.

α,β-Epoxysilane. Colorless oil. $[\alpha]^{25}_D$ = +18.5 (*c* 1.35, $CHCl_3$); IR 3426, 1459, 1250, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.61 (t, J = 6.5 Hz, 2H), 2.02 (d, J = 0.6 Hz, 1H), 1.95 (br s, 1H), 1.70−1.35 (m, 8H). 0.97 (t, J = 7.5 Hz, 3H), 0.10 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 65.2, 62.9, 58.7, 35.6, 33.0, 26.4, 21.7, 10.3, −1.4. Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.05; H, 11.18. Found: C, 61.00; H, 10.97.

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Supporting Information Available: The NMR spectral and HPLC data for the determination of the enantiomeric excess of the epoxides. This material is available free of charge via the Internet at http://pubs.acs.org.

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