(0.095 g) was added to dianion **3** (0.85 mmol), prepared according to the general procedure, in THF (10 mL) at −78 °C. The solution was stirred for 45 min followed by the addition of 5% NH_4Cl (5 mL). Et_2O (100 mL) was added, and the solution was washed with saturated NaCl (3 × 25 mL), dried and evaporated. A crude ^1H NMR analysis (400 MHz, $CDCl_3$) at this point showed a 2.2:1 ratio of diastereoisomers **10** and **11**. Chromatography (60/40 Et_2O/hexanes) yielded **10** and **11** (0.239 g, 64%) in a 1.8:1 ratio of diastereoisomers as a colorless oil: IR (neat) 3140–3700, 2950, 1480, 1120, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9 H), 1.15–2.01 (m, 6 H), 2.10 (t, 1 H, J = 6.8 Hz, minor diastereoisomer), 2.67 (s, 1 H, major diastereoisomer), 2.75 (t, 1 H, J = 6.8 Hz, major diastereoisomer), 2.80 (s, 1 H, minor diastereoisomer), 3.03 (d, 1 H, J = 3.6 Hz, minor diastereoisomer), 3.13 (d, 1 H, J = 4.0 Hz, major diastereoisomer), 3.27 (t, 1 H, J = 4.0 Hz, minor diastereoisomer), 3.41 (m, 1 H, major diastereoisomer), 4.08 (m, 2 H, major diastereoisomer), 4.18 (m, 2 H, minor diastereoisomer), 4.36 (d, 2 H, J = 6.0 Hz, minor diastereoisomer), 4.40 (d, 2 H, J = 6.0 Hz, major diastereoisomer), 5.71 (t, 1 H, J = 6.0 Hz, major diastereoisomer), 6.00 (t, 1 H, J = 6.0 Hz, minor diastereoisomer), 7.37–7.48 (m, 6 H), 7.60–7.81 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 135.7, 133.3, 129.8, 128.8, 127.8, 73.0, 60.4, 58.2, 56.9, 53.4, 31.6, 26.8, 22.6, 19.0, 15.9; mass spectrum (CI), m/e 439 (M^+ + H), 421, 403, 199, 185, 165. Anal. Calcd for $C_{26}H_{34}O_4Si$: C, 71.19; H, 7.81. Found: C, 71.17; H, 8.19.

Preparation of [4a*S*(*R*),7*S*(*R*),7a*R*(*S*)]-3-[3-[(*tert*-Butyldiphenylsilyl)oxy]-(*E*)-propylidene]octahydrobenzofuran-4a,7-diol (12). *p*-Toluenesulfonic acid (0.010 g) was added to a 2.2:1 solution of **10** and **11** (0.120 g) in dichloromethane (20 mL) and stirred for 45 min. Et_2O (75 mL) was added, and the solution was washed with saturated NH_4Cl (3 × 15 mL) and saturated $NaHCO_3$ (3 × 15 mL), dried, and evaporated. Chromatography (60/40 Et_2O/hexanes) yielded **12** (0.069 g, 58%) as a colorless oil: IR (neat) 3120–3700, 2940, 1460, 1125, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9 H), 1.10–1.28 (m, 1 H), 1.34–1.47 (m, 1 H), 1.62–1.71 (m, 2 H), 1.76–1.85 (m, 1 H), 1.92–1.99 (m, 1 H), 2.26 (s, 1 H), 2.44 (d, 1 H, J = 2.8 Hz), 3.38 (m, 1 H), 3.59 (d, 1 H, J = 6.8 Hz), 4.18 (m, 2 H), 4.24, 4.41 (AB q, 2 H, J = 14 Hz), 5.57 (m, 1 H), 7.35–7.47 (m, 6 H), 7.62–7.69 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 135.5, 133.3, 129.8, 127.7, 120.1, 88.4, 77.8, 68.9, 66.9, 61.8, 31.9, 30.0, 26.7, 19.0, 18.6; mass spectrum (CI), m/e 439 (M^+ + H), 421, 403, 199, 165, 147, 121. Anal. Calcd for $C_{26}H_{34}O_4Si$: C, 71.19; H, 7.81. Found: C, 71.08; H, 8.14.

Preparation of 3,4-[4-[3-[(*tert*-Butyldiphenylsilyl)oxy]-(*E*)-propylidene]tetrahydrofurano]-5β-cholestane-3β,5-diol (13). 4β,5β-Epoxycholestan-3-one[6] (0.512 g) was added to dianion **3** (1.28 mmol), prepared according to the general procedure, in THF (15 mL) at −78 °C. The solution was stirred for 45 min followed by the addition of 5% NH_4Cl (5 mL). The reaction mixture was diluted with Et_2O (100 mL), washed with 5% NH_4Cl (3 × 20 mL), dried, and evaporated. The crude reaction mixture was diluted with dichloromethane (30 mL), *p*-toluenesulfonic acid (0.010 g) was added, and the solution was stirred for 45 min. Et_2O (100 mL) was added, and the solution was washed with saturated NH_4Cl (3 × 25 mL) and saturated $NaHCO_3$ (3 × 25 mL), dried, and evaporated. Chromatography (60/40 Et_2O/hexanes) yielded **13** (0.325 g, 35%) as a white solid: mp 51–52 °C; IR (KBr disk) 3200–3640, 2980, 1380, 1140, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.69 (s, 3 H), 0.82–2.10 (m, 37 H), 0.98 (s, 3 H), 1.05 (s, 9 H), 2.25 (br s, 1 H), 2.93 (s, 1 H), 2.96 (br s, 1 H), 4.18 (m, 2 H), 4.37 (m, 2 H), 5.86 (t, 1 H, J = 6.4 Hz), 7.37–7.48 (m, 6 H), 7.66–7.71 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 135.7, 135.6, 133.3, 129.8, 128.8, 127.7, 72.9, 67.4, 67.3, 60.5, 58.8, 56.2, 55.9, 48.1, 42.5, 39.7, 39.5, 36.10, 36.07, 35.8, 35.2, 31.3, 30.2, 28.4, 28.3, 28.2, 28.0, 26.8, 24.3, 23.8, 22.8, 22.6, 21.4, 19.1, 18.6, 18.4, 11.9; mass spectrum (CI), m/e 733 (M^+ + Li), 691, 453, 327. Anal. Calcd for $C_{47}H_{70}O_4Si$: C, 77.63; H, 9.70. Found: C, 77.36; H, 9.98.

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Characterization of 2-Siloxyoxiranes Formed by Epoxidation of Silyl Enol Ethers with Dimethyldioxirane

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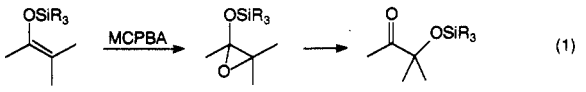
The oxidation of silyl enol ethers by peroxy acids involves the intermediacy of 2-siloxyoxiranes (eq 1).[1] Under the normally acidic reaction conditions, however, these intermediates quickly rearrange to the corresponding α-siloxy carbonyl compounds, and few 2-siloxyoxiranes have been isolated or characterized.[2,3] We have examined dimethyldioxirane as a reagent for the preparation of 2-siloxyoxiranes. Dioxirane reagents[4,5] are efficient yet mild oxidants, react well at low temperatures, and should not promote acid-catalyzed rearrangement of the siloxyoxirane products. Two recent reports of the epoxidation of alkyl enol ethers by dioxirane reagents prompts us to report our results.[6]



(1)

Initial attempts to isolate the epoxides formed by the reaction of dimethyldioxirane with simple *tert*-butyldimethylsilyl enol ethers met with limited success. α-Siloxy and α-hydroxy carbonyl compounds arising from the rearrangement of the siloxyoxirane intermediates[1] were often predominant. To minimize the rearrangement upon workup, we performed the reactions directly in acetone-d_6 using dimethyldioxirane-d_6. Dimethyldioxirane-d_6 was prepared from acetone-d_6 and aqueous potassium caroate and was distilled as a solution in wet acetone-d_6 (see the Experimental Section).[7] The reagent thus prepared could be dried over $MgSO_4$, but was generally used wet since $MgSO_4$ catalyzed some decomposition of the dioxirane.

Silyl enol ethers **1a–g** reacted with 1 equiv of dimethyldioxirane-d_6 in acetone-d_6 at −78 °C (Scheme I). After 2–5 min, each reaction mixture was warmed to room temperature and immediately examined by ^1H NMR and mass spectrometry (EI, low resolution). An aliquot of each product solution was evaporated at 0 °C under reduced pressure and examined by infrared spectroscopy. Thus, the analysis of each product solution was complete within 15–30 min after product formation.

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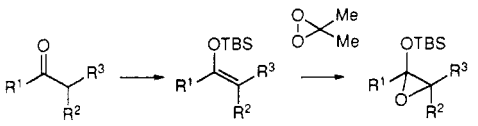
Scheme I



1a-g 2a-g 3a-g

	R^1	R^2	R^3
a	tBu	H	H
b	Ph	H	H
c	Et	H	Me
d	H	$-CH_2CH_2CH_2CH_2CH_2-$	
e	$-CH_2CH_2CH_2CH_2-$		H
f	$-CH_2CH_2CH_2CH_2-$		Me
g	Ph	Me	Me

In all cases, mass spectrometry showed incorporation of one atom of oxygen per molecule. Base peaks corresponded to $M^+ - 57$ (loss of *tert*-butyl radical). With one exception (the reaction of **2b**), NMR spectroscopy indicated quantitative formation of the siloxyoxiranes **3**; IR absorptions at 1250, 935–960, and 840 cm^{-1} were observed with little or no peaks attributable to carbonyl groups.

Reaction of **2b** gave as products a 1:1 mixture of siloxyoxirane **3b** and rearranged compounds (α-siloxy and α-hydroxy ketones), as evidenced by NMR spectroscopy. A carbonyl stretch (1700 cm^{-1}) was present in the product IR. This result was reproducible (two experiments) and presumably resulted from partial rearrangement of the initially formed siloxyoxirane during the time required to obtain the NMR spectrum (approximately 5 min from reaction).

We expected compounds **3b** and **3g** to be labile in comparison to the other siloxyoxiranes due to benzylic assistance to the opening of the epoxide. Indeed, **3b** and **3g** were the least stable of the products (vide infra). Compound **3g**, however, was stable enough to be observed pure by NMR. We presume steric interaction between the phenyl and *cis*-methyl groups obstructs alignment of the phenyl π-system and the σ^* orbital of the breaking C–O ring bond.

Rearrangement of the siloxyoxiranes to the corresponding α-siloxy (or hydroxy) carbonyl compounds in the wet acetone solutions (room temperature) was followed by ^1H NMR spectroscopy. Although no detailed kinetic analysis was performed, approximate half-lives of the siloxyoxiranes were <3 h (**3a**), 5 h (**3c**), 55 h (**3d**), 15 h (**3e**), 20 h (**3f**), and <3 h (**3g**).

We are investigating the possibility of carrying out other chemistry on these now available siloxyoxiranes, and the results will be described in due course.

Experimental Section

Materials and Methods. Organic chemicals from Aldrich were used without further purification. Silyl enol ethers were prepared by reaction of the parent ketones and aldehyde with *tert*-butyldimethylsilyl triflate in the presence of triethylamine[8] and purified by chromatography on silica gel (2–5% ethyl acetate in hexanes). Dimethyldioxirane-d_6 was prepared according to the small-scale procedure of Adam et al.[7] using 10 g of acetone-d_6 and was distilled as a solution in wet acetone-d_6. By ^1H NMR analysis, the reagent contained 4–5 volume % of water. It could be dried over $MgSO_4$ but was usually used wet since $MgSO_4$ catalyzed decomposition of the dioxirane. Solutions of dimethyldioxirane-d_6 in acetone-d_6 thus obtained were assayed by reaction with thioanisole and found to be around 0.1 M.

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Table I. ^1H NMR Data[a]

compd	δ, ppm
3a	0.05 (s, 3 H), 0.11 (s, 3 H), 0.87 (s, 9 H), 0.95 (s, 9 H), 2.70 (d, J = 3.6 Hz, 1 H), 2.81 (d, J = 3.6 Hz, 1 H)
3b	0.06 (s, 3 H), 0.09 (s, 3 H), 0.91 (s, 9 H), 2.85 (d, J = 4.6 Hz, 1 H), 3.20 (d, J = 4.6 Hz, 1 H), 7.34–7.97 (m, 5 H)
3c	0.10 (s, 3 H), 0.17 (s, 3 H), 0.89 (s, 9 H), 0.92 (t, J = 7.5 Hz, 3 H), 1.23 (d, J = 5.2 Hz, 3 H), 1.50 (m, 1 H), 1.97 (m, 1 H), 2.83 (q, J = 5.2 Hz, 1 H)
3d	0.14 (s, 3 H), 0.15 (s, 3 H), 0.90 (s, 9 H), 1.34–1.69 (m, 10 H), 4.61 (s, 1 H)
3e	0.11 (s, 3 H), 0.14 (s, 3 H), 0.88 (s, 9 H), 1.22–2.00 (m, 8 H), 3.17 (d, J = 3.6 Hz, 1 H)
3f	0.10 (s, 3 H), 0.16 (s, 3 H), 0.88 (s, 9 H), 1.24–1.40 (m, 4 H), 1.27 (s, 3 H), 1.69 (m, 2 H), 1.96 (m, 2 H)
3g	−0.23 (s, 3 H), 0.00 (s, 3 H), 0.85 (s, 9 H), 0.92 (s, 3 H), 1.47 (s, 3 H), 7.32–7.45 (m, 5 H).

[a] 250 MHz spectrometer, samples in acetone-d_6, and peaks referenced to acetone-d_5 (δ 2.04 ppm).

Epoxidation of Silyl Enol Ethers. To 10 mg of silyl enol ether in 0.1 mL of acetone-d_6, −78 °C, was added dropwise 1.0 equiv of a chilled (−20 to 0 °C) solution of dimethyldioxirane-d_6 in acetone-d_6. After 2–5 min, the reaction solution was warmed to room temperature and examined by ^1H NMR spectroscopy (Table I) and low-resolution mass spectrometry (EI). A portion of the product was then freed of solvent by rotary evaporation at 0 °C, taken up in chloroform-*d*, and examined by infrared spectroscopy.

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Synthesis of Substituted Vinyl Sulfides by Reaction of [1-(Phenylthio)cyclopropyl]carbinyl Halides and Organocuprates[1]

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The longevity and scope of the work reported for cyclopropane derivatives attests to the interest and importance of these highly reactive molecules. In previous work we prepared cyclopropylcarbinyl halides (1) and showed they reacted with amines[3] in a ring-opening reaction best described as an homoallylic S_N2' reaction. Homoallylic substitution dominated when the halogen-bearing carbon was sterically hindered but direct S_N2' displacement was favored when that carbon was unencumbered. Halides 1 also react with lithium dialkylcuprates[4] to give the homoallylic alkene 2 with excellent selectivity for the *E* isomer.

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