Stereocontrol in the Nucleophilic Epoxidation of α-(1-Hydroxyalkyl)-α,β-Unsaturated Sulfones

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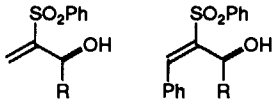
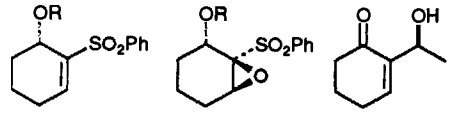
Epoxidation of β-unsubstituted-α-(1-hydroxyalkyl)-α,β-unsaturated sulfones **1** with lithium *tert*-butyl peroxide proceeds with high diastereoselectivity to give the *syn* epoxides **10**. Epoxidation of the triisopropylsilyl ethers **7**, however, leads to the *anti* epoxides **13** with moderate to good selectivity. In contrast to this, epoxidation of (*E*)-α-(1-hydroxyalkyl)-β-phenyl-α,β-unsaturated sulfones **2** proceeds with high diastereoselectivity to give the *anti* epoxides **15**. Epoxidation of the corresponding triisopropylsilyl ethers **9** leads to a reversal in diastereofacial selectivity, giving the *syn* epoxides **16** with moderate selectivity. The sense of diastereoselectivity has been determined by X-ray crystal-structure analyses of compounds **10c**, **13a**, **13b** and **16a** and chemical correlation. Use of potassium *tert*-butyl peroxide as the epoxidising agent for all these epoxidation reactions results in very similar levels of diastereoselectivity to those observed using lithium *tert*-butyl peroxide. A rationalisation for these results, based on the influences of 1,2- and 1,3-allylic strain, is proposed.

We have recently described in preliminary form the results of an investigation into the nucleophilic epoxidation of both β-unsubstituted-α-(1-hydroxyalkyl)-α,β-unsaturated sulfones **1** and (*E*)-α-(1-hydroxyalkyl)-β-phenyl-α,β-unsaturated sulfones **2** using lithium *tert*-butyl peroxide, as well as the corresponding compounds in which the hydroxy group has been protected as a silyl ether.[1] We now present a full account of our work in this area, including the results obtained using potassium *tert*-butyl peroxide as the oxidant, which allows us to refine slightly the model which we have already presented.



1 **2**

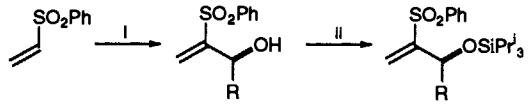
Following the publication of our preliminary communication, a report appeared on the nucleophilic epoxidation of analogous cyclic vinyl sulfones **3**, in which the hydroxy group was either unprotected or protected as a silyl ether.[2] Use of either lithium *tert*-butyl peroxide or of more classical Weitz–Scheffer conditions resulted in the formation principally of the *anti*-oxirane **4**, which suggested that any interaction between the lithium *tert*-butyl peroxide and the hydroxy group was not a major controlling influence on the stereoselectivity. Related reports on the epoxidation of α-(1-hydroxyalkyl)-α,β-enones (*e.g.*, **5**) using nucleophilic epoxidation conditions imply that, at least under Weitz–Scheffer conditions, there is no significant hydrogen-bond interaction between a hydroxy group of the substrate and the nucleophilic hydroperoxide ion.[3]



3 **4** **5**

Results

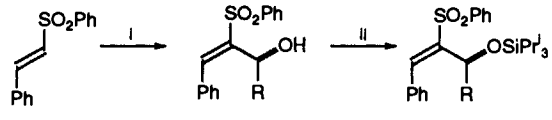
The required β-unsubstituted-α-(1-hydroxyalkyl)-α,β-unsaturated sulfones **1a–c** were obtained by treatment of phenyl vinyl sulfone **6** with the appropriate aldehyde using either 1,4-diazabicyclo[2.2.2]octane (DABCO) or quinuclidin-3-ol as catalyst.[4] Treatment of the free alcohols **1a–c** with triisopropylsilyltrifluoromethanesulfonate–2,6-dimethylpyridine(lutidine)[5] gave the silyl ethers **7a–c** (Scheme 1).



6 **1** **7**

Scheme 1 *Reagents and conditions:* i, quinuclidin-3-ol or DABCO (catalytic), RCHO (4 mol equiv.), THF, room temp.; ii, $Pr^i_3SiOSO_2CF_3$, 2,6-lutidine, CH_2Cl_2

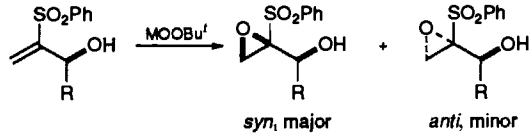
The α-(1-hydroxyalkyl)-β-phenyl-α,β-unsaturated sulfones **2a–c** were prepared by lithiation of phenyl styryl sulfone **8** with MeLi followed by treatment with $MgBr_2{\cdot}Et_2O$ and then an aldehyde, according to the procedure of Eisch.[6] The alcohols **2a–c** were then converted into the corresponding triisopropylsilyl ethers **9a–c** (Scheme 2).



8 **2** **9**

Scheme 2 *Reagents and conditions:* i, MeLi, −95 °C, $MgBr_2{\cdot}Et_2O$, RCHO; ii, $Pr^i_3SiOSO_2CF_3$, 2,6-lutidine, CH_2Cl_2

Treatment of the free alcohols **1a–c** with lithium *tert*-butyl peroxide in tetrahydrofuran (THF) at −20 °C proceeded smoothly to give the corresponding *syn* and *anti* epoxides **10a–c** and **11a–c**. The stereoselectivity of these reactions was uniformly excellent, with large diastereoselectivity in favour of the *syn* epoxides **10a–c** (*vide infra*).



1 **10** **11**

Table 1 Epoxidation of vinyl sulfones **1** and **7** with metal *tert*-butyl peroxides

Vinyl sulfone	R	Products	Lithium *tert*-butyl peroxide		Potassium *tert*-butyl peroxide	
			syn:*anti* Ratio[a]	Yield (%)	*syn*:*anti* Ratio[a]	Yield (%)
1a	Me	**10a/11a**	25:1	62	25:1	71
1b	Pr	**10b/11b**	25:1	65		
1c	Pr^i	**10c/11c**	25:1	62	25:1	54
7a	Me	**12a/13a**	1:12	73	1:25	74
7b	Pr	**12b/13b**	1:25	61		
7c	Pr^i	**12c/13c**	1:4	79	1:3	86

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixtures.

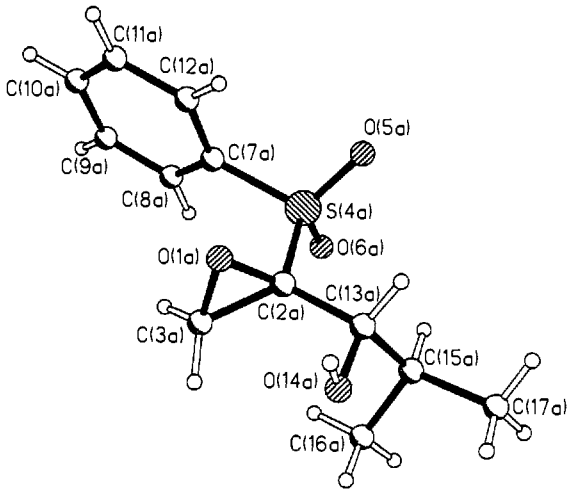
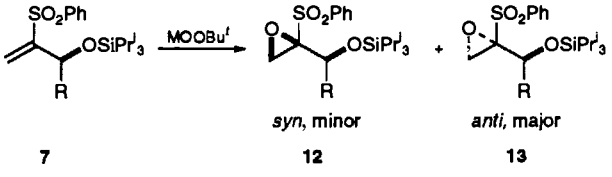


Fig. 1 Molecular structure of compound **10c**. There are two crystallographically independent molecules. Molecule *a* is shown; molecule *b* is labelled analogously and shows no significant differences.

Epoxidation of the silyl ethers **7a–c** was very slow at −20 °C and the reaction was therefore carried out at room temperature to give the *syn* and *anti* epoxides **12a–c** and **13a–c**. Epoxidation of the free alcohols **1a** and **1c**, and of the silyl ethers **7a** and **7c**, was also carried out using potassium *tert*-butyl peroxide in THF at 0 °C. The diastereoisomeric ratios were determined by ^{1}H NMR spectroscopy of the crude reaction products, and the results are summarised in Table 1.



The relative stereochemistry of the *syn* epoxide **10c** (Fig. 1), and of the *anti* epoxides **13a** (Fig. 2) and **13b** (Fig. 3) were determined by X-ray crystal-structure analysis, and the relative stereochemistry of the major products from epoxidation of vinyl sulfones **1a**, **1b** and **7c** were determined by chemical correlation as indicated in the Experimental section. The unambiguous assignment of configuration of the epoxides **10a** and **11a** allowed us to establish that compound **10a** is the major product (diastereoisomeric ratio 1.7:1) when 2-(phenylsulfonyl)oxirane is lithiated at low temperature, and then treated successively with magnesium bromide–diethyl ether and ethanal.[7]

Our attention then turned to epoxidation of the α-(1-hydroxyalkyl)-β-phenyl-α,β-unsaturated sulfones **2a–c**, as examples of substrates in which there was a substituent *syn* to the hydroxyalkyl group. Treatment of the free alcohols **2a–c** with lithium *tert*-butyl peroxide in THF at −20 °C proceeded

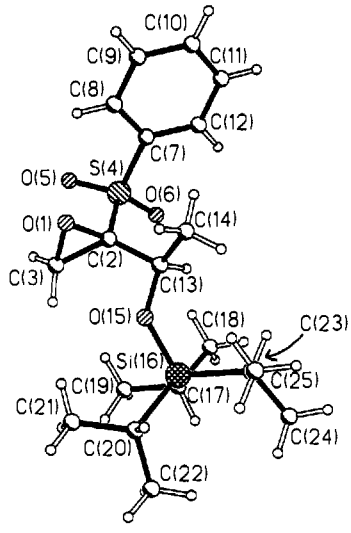


Fig. 2 Molecular structure of compound **13a**

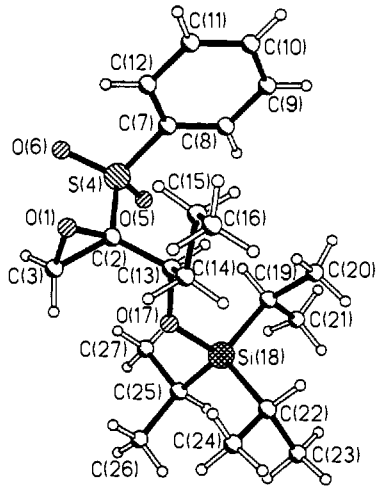


Fig. 3 Molecular structure of compound **13b**

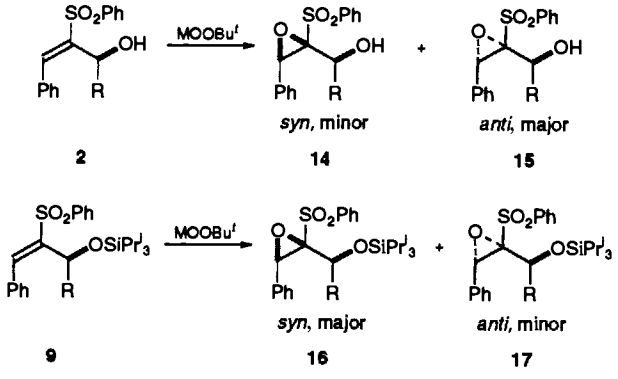
smoothly to give the corresponding *syn* and *anti* epoxides **14a–c** and **15a–c**. In sharp contrast to epoxidation of the unsubstituted vinyl sulfones **1**, the *anti* epoxides **15a–c** were the major stereoisomers. Epoxidation of the silyl ethers **9a–c** requires the reaction to be conducted at room temperature and gave the *syn* and *anti* epoxides **16a–c** and **17a–c**. In this case, again in contrast to epoxidation of the unsubstituted vinyl sulfones **7**, the *syn* epoxides **16a–c** were now the major stereoisomers. Epoxidations of styryl sulfones **2a** and **2c** and **9a** and **9c** were also carried out using potassium *tert*-butyl peroxide for comparison. The results are summarised in Table 2.

The relative stereochemistry of the *syn* epoxide **16a** was

Table 2 Epoxidation of vinyl sulfones **2** and **9** with metal *tert*-butyl peroxides

Vinyl sulfone	R	Products	Lithium *tert*-butyl peroxide		Potassium *tert*-butyl peroxide	
			syn:*anti* Ratio[a]	Yield (%)	*syn*:*anti* Ratio[a]	Yield (%)
2a	Me	**14a/15a**	1:12	72	1:12	72
2b	Pr	**14b/15b**	1:20	63		
2c	Pr^i	**14c/15c**	1:25	53	1:25	56
9a	Me	**16a/17a**	5:1	90	3:1	90
9b	Pr	**16b/17b**	4:1	91		
9c	Pr^i	**16c/17c**	2:1[b]	80	3:1	77

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixtures. [b] Incorrectly reported as 4:1 in the preliminary communication.[1]



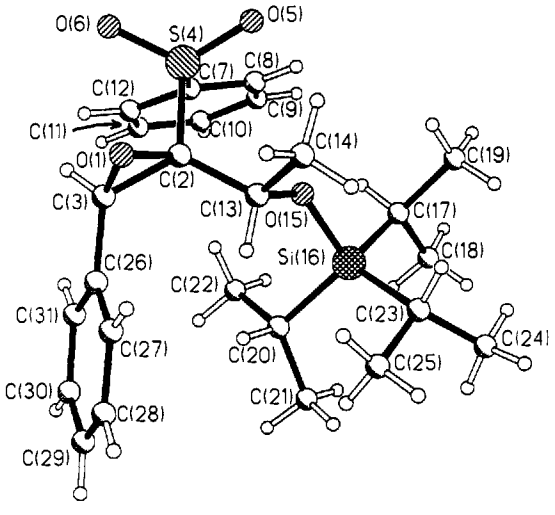


Fig. 4 Molecular structure of compound **16a**

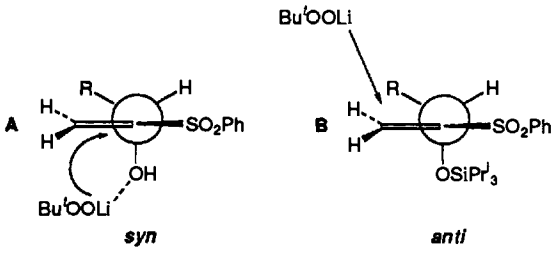
determined by X-ray crystal-structure analysis (Fig. 4),[7] and the relative stereochemistry of the *anti* epoxide **15a** was established by its conversion into the *anti* epoxide **17a**, of opposite relative configuration to compound **16a**. Although we have no unambiguous proof of stereochemistry of the other examples, silylation of the mixture of stereoisomers derived from epoxidation of the free alcohol **2b** established that the major isomer from this reaction was of opposite relative configuration to the major isomer derived from direct epoxidation of the silyl ether **9b**. Similarly, the major isomers derived from epoxidation of the free alcohol **2c** and from the silyl ether **9c** were again established to possess opposite relative stereochemistry. Analysis of the ^{1}H NMR data for all these compounds indicated that the epoxide methine proton for the *anti*-diastereoisomers resonated in all cases at lower field than the corresponding proton in the *syn*-diastereoisomers.

Discussion

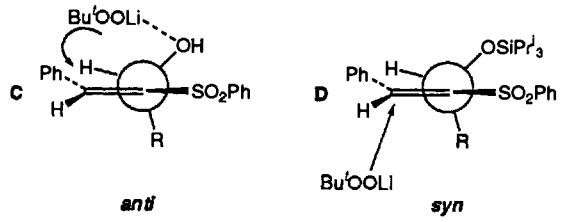
The two examples which have been examined were chosen to probe the effects of various influences on the reactive conformers of the substrates. The major controlling features appear to be the destabilising interaction of the alkyl substituent at the hydroxy group and the phenylsulfonyl group ($A_{1,2}$ strain), which tends to favour conformers with the alkyl group inside, and the effect of $A_{1,3}$ strain which favours conformers with the alkyl group outside.[8] Thus, for the unsubstituted vinyl sulfones **1** and **7**, the stereochemical outcome of the epoxidations can be rationalised on the basis of a reactive conformation in which the alkyl substituent R occupies the inside position and the carbon–oxygen bond is parallel to the π-bond thus activating the double bond towards nucleophilic attack.[9]

During epoxidation of the free alcohols **1a–c**, interaction between the hydroxy group and the reagent, either by co-ordination of the lithium atom (in lithium *tert*-butyl peroxide) or by hydrogen-bond formation from the alcohol proton to the *tert*-butyl peroxide anion (for the potassium reagent), allows delivery of the reagent from the same face (**A**). Such an interaction may also explain the faster relative rates for epoxidation of the free alcohols when compared with the corresponding silyl ethers (*vide supra*). The possibility that the controlling influence in this reaction also has a significant steric component (on the basis that the hydroxy group is smaller than any of the alkyl substituents examined) cannot be excluded.

In the case of the triisopropylsilyl ethers **7a–c**, a similar reactive conformation to that suggested above for the free alcohols **1**, combined with nucleophilic attack of lithium *tert*-butyl peroxide from the opposite face (**B**), yields the observed stereoisomer. Support for this hypothesis is provided by the observation that the lowest diastereoselectivity is found when the alkyl substituent is largest (Pr^i), when a destabilising interaction might be expected between this substituent and the incoming nucleophile.



The reversed stereoselectivity observed for epoxidation of compounds **2a–c** and **9a–c** when compared with the β-unsubstituted examples **1a–c** and **7a–c** is easily rationalised by assuming that the presence of the phenyl substituent *syn* to the allylic stereocentre destabilises the conformation in which the



alkyl group is inside. It is very likely that the effectiveness of this destabilisation is a reflection of the coplanarity of the aromatic ring and the double bond enforced by conjugation. Thus, 1,3-allylic strain becomes the main influence,[8] and overrides the interaction between the alkyl group and the sulfone. The observed stereochemical outcome can now be rationalised by direction of lithium *tert*-butyl peroxide by the free hydroxy group (**C**), or by attack *anti* to the triisopropylsiloxy group, possibly under stereoelectronic control (**D**). In this case too, the possibility that steric effects are important in the epoxidation of the free alcohols *via* transition state **C** cannot be excluded.

In conclusion, the stereochemical course of these epoxidations can be controlled merely by an appropriate choice of protecting group.

Experimental

General experimental procedures have been described previously.[7] NMR spectra were recorded in $CDCl_3$ as solvent, referenced to Me_4Si as the standard; coupling constants (J) are given in Hertz.

β-*Unsubstituted*-α-(1-*hydroxyalkyl*)-α,β-*unsaturated Sulfones* **1**: *General Procedure*.—An aldehyde (~ 100 mmol) was added to a solution of phenyl vinyl sulfone **6** (4.01 g, 23.8 mmol) and the appropriate tertiary amine in THF (20 cm^3) under nitrogen, and the resulting solution was stirred at room temp. for the time indicated. Ethyl acetate (40 cm^3) was added to the solution and the organic phase was washed with hydrochloric acid (3 × 15 cm^3; 1 mol dm^{-3}), dried ($MgSO_4$), and concentrated under reduced pressure.

3-(*Phenylsulfonyl*)*but*-3-*en*-2-*ol* **1a**.[4] The aldehyde used was ethanal (9.00 cm^3, 150 mmol), the base was quinuclidin-3-ol (0.5 g, 3.9 mmol), and the reaction time was 10 days. The crude product was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate to yield phenyl vinyl sulfone (1.40 g, 8.33 mmol recovery) and the *product* **1a** as a yellow solid (1.95 g, 60%), m.p. 41–43 °C (lit.,[4b] 34–36 °C) (Found: C, 56.6; H, 5.8. $C_{10}H_{12}O_3S$ requires C, 56.6; H, 5.7%); ν_{max}(KBr)/cm^{-1} 3495, 3067, 2980, 2934, 2885, 1632, 1304, 964 and 752; δ_H(200 MHz) 1.34 (3 H, d, J 6.5), 2.47 (1 H, br), 4.54 (1 H, q, J 6.5), 6.13 (1 H, d, J 1), 6.43 (1 H, d, J 1), 7.52–7.70 (3 H, m) and 7.88–7.93 (2 H, m); m/z (EI) 213 (MH^+, 90%), 195 (100), 125 (90) and 77 (90).

2-(*Phenylsulfonyl*)*hex*-1-*en*-3-*ol* **1b**.[4] The aldehyde used was butanal (7.00 cm^3, 77.9 mmol), the base was quinuclidin-3-ol (0.5 g, 3.9 mmol), and the reaction time was 28 days. The crude product was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate to yield phenyl vinyl sulfone (1.64 g, 9.76 mmol recovery) and the *product* **1b** as a yellow oil (2.02 g, 60%) (Found: M^+, 240.0822. $C_{12}H_{16}O_3S$ requires M, 240.0820); ν_{max}(film)/cm^{-1} 3501, 3067, 2963, 2936, 2874, 1632, 1304, 970 and 754; δ_H(200 MHz) 0.82 (3 H, t, J 7.3), 1.20–1.69 (4 H, m), 2.33 (1 H, br), 4.36 (1 H, t, J 6.8), 6.09 (1 H, d, J 1), 6.44 (1 H, d, J 1), 7.52–7.76 (3 H, m) and 7.88–7.94 (2 H, m); m/z (EI) 241 (MH^+, 2%), 240 (M^+, 0.1), 223 (20), 197 (100), 125 (40) and 77 (60).

4-*Methyl*-2-(*phenylsulfonyl*)*pent*-1-*en*-3-*ol* **1c**. The aldehyde used in this reaction was 2-methylpropanal (9.00 cm^3, 80.5 mmol), the base was DABCO (0.27 g, 2.38 mmol), and the reaction time was 50 days. The crude product was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate to yield phenyl vinyl sulfone (2.25 g, 13.4 mmol recovery) and the product **1c** as a yellow oil (0.61 g, 24%) (Found: $M^+ - C_3H_7$, 197.0248. $C_9H_9O_3S$ requires m/z, 197.0272); ν_{max}(film)/cm^{-1} 3500, 3067, 2968, 2935, 2876, 1306, 1142 and 754; δ_H(200 MHz) 0.76 (3 H, d, J 6.6), 0.88 (3 H, d, J 6.6), 1.85 (1 H, sep, J 6.6), 2.35 (1 H, br), 4.08 (1 H, br), 6.07 (1 H, d, J 1), 6.46 (1 H, d, J 1), 7.50–7.76 (3 H, m) and 7.85–7.93 (2 H, m); m/z (EI) 197 ($M^+ - C_3H_7$, 60%), 143 (90), 125 (70) and 77 (100).

β-*Unsubstituted*-α-(1-*triisopropylsiloxyalkyl*)-α,β-*unsaturated Sulfones* **7**: *General Procedure*.—2,6-Lutidine (2.6 mol equiv.) and triisopropylsilyl trifluoromethanesulfonate (1.38 mol equiv.) were added to a solution of the substrate **1** (1 mol equiv.) in dichloromethane (10 cm^3 per mmol **1**) at −78 °C under nitrogen. The flask was left at −78 °C for 2 h, and then was warmed to the temperature indicated until all the starting material had reacted. The organic phase was washed successively with aq. citric acid (2 × 15 cm^3; 0.1 mol dm^{-3}) and aq. sodium hydrogen carbonate (2 × 15 cm^3; 0.1 mol dm^{-3}), dried ($MgSO_4$), and concentrated under reduced pressure.

3-(*Phenylsulfonyl*)*but*-3-*en*-2-*yl triisopropylsilyl ether* **7a**. Initial mass of starting material **1a** (0.30 g, 1.42 mmol). The reaction mixture was warmed to 0 °C and was stirred for 4 h before work-up. The crude product was purified by flash chromatography and elution with (50:1) toluene–ethyl acetate to yield *product* **7a** as a solid (0.47 g, 90%), m.p. 36–38 °C (Found: C, 62.1; H, 8.9. $C_{19}H_{32}O_3SSi$ requires C, 61.9; H, 8.8%); ν_{max}(KBr)/cm^{-1} 3067, 2965, 2945, 2893, 2863, 1585, 1306 and 752; δ_H(200 MHz) 0.86 (21 H, br s), 1.39 (3 H, d, J 6.2), 4.57 (1 H, q, J 6.2), 6.25 (1 H, d, J 1), 6.40 (1 H, d, J 1), 7.49–7.68 (3 H, m) and 7.86–7.92 (2 H, m); m/z (EI) 367 (M^+ − H, 5%), 325 (50), 133 (21), 85 (76) and 49 (100).

2-(*Phenylsulfonyl*)*hex*-1-*en*-3-*yl triisopropylsilyl ether* **7b**. Initial mass of starting material **1b** (0.40 g, 1.67 mmol). The reaction mixture was warmed to room temp. and was stirred for 16 h before work-up. The crude product was purified by flash chromatography and elution with (50:1) toluene–ethyl acetate to yield the product **7b** as an oil (0.55 g, 83%) (Found: $M^+ - C_3H_7$, 353.1472. $C_{18}H_{29}O_3SSi$ requires m/z 353.1607); ν_{max}(film)/cm^{-1} 3067, 2961, 2945, 2893, 2868, 1586, 1308 and 752; δ_H(200 MHz) 0.78 (3 H, t, J 7.3), 0.88 (21 H, br s), 1.19–1.69 (4 H, m), 4.36 (1 H, t, J 3.8), 6.16 (1 H, d, J 1), 6.47 (1 H, d, J 1), 7.50–7.67 (3 H, m) and 7.86–7.92 (2 H, m); m/z (EI) 353 ($M^+ - C_3H_7$, 100%), 311 (5), 149 (40), 121 (45) and 77 (60).

4-*Methyl*-2-(*phenylsulfonyl*)*pent*-1-*en*-3-*yl triisopropylsilyl ether* **7c**. Initial mass of starting material **1c** (0.30 g, 1.25 mmol). The reaction mixture was warmed to 50 °C and stirred for 5 h before work-up. The crude product was purified by flash chromatography and elution with (50:1) toluene–ethyl acetate to yield the product **7c** as an oil (0.32 g, 61%) (Found: $M^+ - C_3H_7$, 353.1532); ν_{max}(film)/cm^{-1} 3065, 2963, 2945, 2893, 2868, 1585, 1306 and 752; δ_H(200 MHz) 0.76 (3 H, d, J 6.7), 0.91 (21 H, br s), 1.02 (3 H, d, J 6.7), 1.96 (1 H, dsep, J 2.1 and 6.7), 4.54 (1 H, d, J 2.1), 6.10 (1 H, d, J 1), 6.47 (1 H, d, J 1), 7.50–7.68 (3 H, m) and 7.86–7.92 (2 H, m); m/z (EI) 353 ($M^+ - C_3H_7$, 100%), 311 (20), 149 (45), 125 (45) and 77 (25).

(E)-β-*Substituted*-α-(1-*hydroxyalkyl*)-α,β-*unsaturated Sulfones* **2**: *General Procedure*.—Methyllithium (1.2 mol equiv.; 1.40 mol dm^{-3} in diethyl ether) was added dropwise to a solution of (*E*)-phenyl styryl sulfone **8** (1.4 mmol) in THF (10 cm^3) at −95 °C. The resulting yellow solution was stirred for 30 min, by which time the temperature had risen to −65 °C. The flask was then re-cooled to −80 °C, and a solution of

magnesium bromide in diethyl ether–toluene (3:1) (1.5 mol equiv.; 1 mol equiv.) was added. The resulting yellow solution was stirred for a further 30 min, after which the temperature had risen to −45 °C, and the appropriate aldehyde (1.2 mol equiv.; 1.68 mmol) was added. The reaction mixture was allowed to warm to room temp. and was stirred until all starting material had reacted. The solution was quenched using saturated aq. ammonium chloride (~20 cm^3), and was stirred at room temp. for a further 15 min. The aqueous phase was extracted with ethyl acetate (2 × 15 cm^3), and the combined organic extracts were dried ($MgSO_4$), and concentrated under reduced pressure.

(E)-4-*Phenyl*-3-(*phenylsulfonyl*)*but*-3-*en*-2-*ol* **2a**. Initial mass of starting material **8** (0.27 g, 1.11 mmol) and the aldehyde used was ethanal (0.15 cm^3, 2.74 mmol). The crude product was purified by flash chromatography and elution with (15:1) toluene–ethyl acetate to yield the *product* **2a** as a solid (0.22 g, 70%), m.p. 104–106 °C (Found: C, 66.5; H, 5.6. $C_{16}H_{16}O_3S$ requires C, 66.6; H, 5.6%); ν_{max}(KBr)/cm^{-1} 3510, 2974, 2932, 1617, 1447, 1332, 1146 and 758; δ_H(200 MHz) 1.39 (3 H, d, *J* 6.8), 3.03 (1 H, d, *J* 7.8), 4.98 (1 H, dq, *J* 6.8 and 7.8), 7.37–7.83 (8 H, m), 7.84 (1 H, s) and 7.93–7.97 (2 H, m); *m/z* (EI) 288 (M^+, 55%), 273 (80), 163 (80), 131 (100) and 77 (90).

(E)-1-*Phenyl*-2-(*phenylsulfonyl*)*hex*-1-*en*-3-*ol* **2b**. Initial mass of starting material **8** (1.70 g, 6.96 mmol) and the aldehyde used was butanal (0.76 cm^3, 8.41 mmol). The crude product was purified by flash chromatography and elution with (15:1) toluene–ethyl acetate to yield *compound* **2b** as a solid (1.38 g, 63%), m.p. 94–95 °C (Found: C, 68.0; H, 6.3. $C_{18}H_{20}O_3S$ requires C, 68.3; H, 6.4%); ν_{max}(KBr)/cm^{-1} 3501, 2959, 2930, 2870, 1618, 1331 and 758; δ_H(200 MHz) 0.69 (3 H, t, *J* 7.2), 1.22–1.60 (2 H, m), 1.76–1.94 (2 H, m), 2.96 (1 H, br), 4.78 (1 H, m), 7.38–7.84 (8 H, m), 7.85 (1 H, s) and 7.94–7.99 (2 H, m); *m/z* (EI) 316 (M^+, 20%), 273 (100), 195 (30), 175 (20), 131 (60), 125 (20) and 77 (100).

(E)-4-*Methyl*-1-*phenyl*-2-(*phenylsulfonyl*)*pent*-1-*en*-3-*ol* **2c**. Initial mass of starting material **8** (2.01 g, 8.23 mmol) and the aldehyde used was 2-methylpropanal (0.91 cm^3, 9.83 mmol). The crude product was purified by flash chromatography and elution with (15:1) toluene–ethyl acetate to yield *compound* **2c** as a solid (1.09 g, 42%), m.p. 105–107 °C (Found: C, 68.1; H, 6.4%); ν_{max}(KBr)/cm^{-1} 3501, 2960, 2920, 2850, 1635, 1440, 1335, 1140 and 756; δ_H(200 MHz) 0.38 (3 H, d, *J* 6.6), 0.96 (3 H, d, *J* 6.6), 2.11 (1 H, dsep, *J* 6.6 and 10.3), 2.55 (1 H, br), 4.31 (1 H, d, *J* 10.3), 7.35–7.68 (8 H, m), 7.88 (1 H, s) and 7.95–8.02 (2 H, m); *m/z* (EI) 299 (M^+ − OH, 12%), 273 (80), 195 (40), 125 (40) and 77 (100).

(E)-β-*Substituted*-α-(1-*triisopropylsiloxyalkyl*)-α,β-*unsaturated Sulfones* **9**.—General procedure as described for the β-unsubstituted compounds **7a**–**7c**.

(E)-4-*Phenyl*-3-(*phenylsulfonyl*)*but*-3-*en*-2-*yl triisopropylsilyl ether* **9a**. Initial mass of starting material **2a** (1.50 g, 5.21 mmol). The reaction mixture was warmed to room temp. and stirred for 3 h. The crude product was purified by flash chromatography and elution with (40:1) toluene–ethyl acetate to yield the *product* **9a** as a solid (2.21 g, 96%), m.p. 120–122 °C (Found: C, 67.4; H, 8.1. $C_{25}H_{36}O_3SSi$ requires C, 67.5; H, 8.15%); ν_{max}(KBr)/cm^{-1} 2961, 2941, 2866, 1617, 1464, 1310, 1148 and 750; δ_H(200 MHz) 0.82 (21 H, br s), 1.49 (3 H, d, *J* 6.6), 4.98 (1 H, q, *J* 6.6), 7.35–7.91 (8 H, m), 7.92 (1 H, s) and 7.93–7.97 (2 H, m); *m/z* (EI) 443 (M^+ − H, 1%), 429 (1), 401 (100) and 191 (40).

(E)-1-*Phenyl*-2-(*phenylsulfonyl*)*hex*-1-*en*-3-*yl triisopropylsilyl ether* **9b**. Initial mass of starting material **2b** (0.32 g, 1.01 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (40:1) toluene–ethyl acetate to yield the product **9b** as an oil (0.45 g, 94%) (Found: M^+ − C_3H_7, 429.1846. $C_{24}H_{33}O_3SSi$ requires *m/z*, 429.1920); ν_{max}(film)/cm^{-1} 2940, 2920, 2860, 1460, 1320, 1145 and 750; δ_H(200 MHz) 0.73 (3 H, t, *J* 7.1), 0.89 (21 H, br s), 1.12–1.35 (2 H, m), 1.70–1.88 (2 H, m), 4.85 (1 H, t, *J* 6.7), 7.35–7.61 (8 H, m), 7.91 (1 H, s) and 7.92–7.96 (2 H, m); *m/z* (EI) 429 (M^+ − C_3H_7, 60%), 287 (15), 125 (25), 91 (100) and 77 (50).

(E)-4-*Methyl*-1-*phenyl*-2-(*phenylsulfonyl*)*pent*-1-*en*-3-*yl triisopropylsilyl ether* **9c**. Initial mass of starting material **2c** (0.32 g, 1.01 mmol). The flask was warmed to room temp. and was left overnight. The crude product was purified by flash chromatography and elution with (40:1) toluene–ethyl acetate to yield the *product* **9c** as a solid (0.44 g, 92%), m.p. 133–135 °C (Found: C, 68.7; H, 8.6. $C_{27}H_{40}O_3SSi$ requires C, 68.6; H, 8.5%); ν_{max}(KBr)/cm^{-1} 2960, 2930, 2860, 1620, 1460, 1305, 1140 and 750; δ_H(200 MHz) 0.97 (6 H, d, *J* 7.5), 1.04 (21 H, br s), 2.17 (1 H, dsep, *J* 7.5 and 8.1), 4.53 (1 H, d, *J* 8.1), 7.35–7.65 (8 H, m), 7.92 (1 H, s) and 7.95–8.01 (2 H, m); *m/z* (EI) 429 (M^+ − C_3H_7, 100%), 251 (30), 229 (20), 115 (100) and 77 (100).

2-(1′-*Hydroxyalkyl*)-2-(*phenylsulfonyl*)*oxiranes* **10**/**11**: *General Procedure.*—Butyllithium (2.4 mol equiv.) was added dropwise to a solution of *tert*-butyl hydroperoxide (3.3 mol equiv.) in THF (15 cm^3) at −78 °C under nitrogen. The reaction mixture was stirred at −78 °C for 10 min, and then a solution of the appropriate vinyl sulfone in (1 mol equiv.) THF (15 cm^3) was added so that the temperature did not exceed −70 °C during the addition. The reaction mixture was then allowed to warm to −20 °C, and stirred for *ca.* 3 h. If TLC of the reaction mixture after this time showed starting material still to be present, the flask was warmed to 0 °C and left for a further 2 h. If there was still starting material present, then the flask was warmed to room temp. until all starting material had reacted. The solution was quenched using saturated aq. ammonium chloride (~20 cm^3) and stirred at room temp. for 15 min. The aqueous phase was extracted with ethyl acetate (2 × 15 cm^3), and the combined extracts were dried ($MgSO_4$), and concentrated under reduced pressure.

1-[2-(*Phenylsulfonyloxiranyl*]*ethanol* **10a**/**11a**. Initial mass of starting material **1a** (0.38 g, 1.79 mmol). The solution was stirred at −20 °C for 2 h. The crude product was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate to yield the *products* **10a**/**11a** as an oil with the diastereoisomeric ratio 25:1 (0.25 g, 62%) (Found: MH^+, 229.0500. $C_{10}H_{13}O_4S$ requires *m/z* 229.0534); ν_{max}(film)/cm^{-1} 3500, 3067, 2984, 2937, 1586, 1310, 1167 and 765; δ_H(200 MHz) 1.40 (3 H, d, *J* 6.4), 2.25 (1 H, br), 3.12 (1 H, d, *J* 4.8), 3.42 (1 H, d, *J* 4.8), 4.33 (1 H, q, *J* 6.4), 7.54–7.75 (3 H, m) and 7.90–7.96 (2 H, m); δ_C(50 MHz) 136.2, 134.6, 129.6, 129.2, 74.3, 63.1, 48.0 and 17.3; *m/z* (EI) 229 (MH^+, 6%), 156 (70), 125 (90), 91 (80), 77 (95) and 51 (100).

1-[2-(*Phenylsulfonyloxiranyl*]*butan*-1-*ol* **10b**/**11b**. Initial mass of starting material **1b** (0.36 g, 1.50 mmol). The solution was stirred at −20 °C for 3 h. The crude product was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate to yield the *products* **10b**/**11b** as an oil with the diastereoisomeric ratio 25:1 (0.25 g, 65%) (Found: MH^+, 257.0959. $C_{12}H_{17}O_4S$ requires *m/z*, 257.0847); ν_{max}(film)/cm^{-1} 3410, 3069, 2964, 2876. 1586, 1310, 1190 and 756; δ_H(200 MHz) 0.91 (3 H, t, *J* 7.1), 1.22–1.70 (2 H, m), 1.72–1.94 (2 H, m), 2.34 (1 H, br), 3.12 (1 H, d, *J* 4.8), 3.41 (1 H, d, *J* 4.8), 4.12 (1 H, t, *J* 8.7), 7.53–7.78 (3 H, m) and 7.87–7.95 (2 H, m); δ_C(50 MHz) 136.2, 134.5, 129.5, 129.2, 73.7, 66.7, 48.2, 35.2, 18.6 and 13.7; *m/z* (EI) 257 (MH^+, 40%), 227 (55), 125 (100) and 77 (90).

2-*Methyl*-1-[2-(*phenylsulfonyl*)*oxiranyl*]*propan*-1-*ol* **10c**/**11c**. Initial mass of starting material **1c** (0.43 g, 1.79 mmol). The solution was stirred at −20 °C for 4 h. The crude product was purified by flash chromatography and elution with (5:1) toluene–ethyl acetate to yield the *products* **10c**/**11c** as a solid

with the diastereoisomeric ratio 25:1 (0.29 g, 62%), m.p. 61–63 °C (Found: C, 55.9; H, 6.1. $C_{12}H_{16}O_4S$ requires C, 56.2; H, 6.3%); ν_{max}(KBr)/cm^{-1} 3520, 3067, 2970, 2936, 2878, 1586, 1308, 1168 and 760; δ_H(200 MHz) 0.92 (3 H, d, *J* 6.8), 0.94 (3 H, d, *J* 6.8), 2.25 (1 H, br), 2.34 (1 H, dsep, *J* 4.5 and 6.8), 3.18 (1 H, d, *J* 4.9), 3.40 (1 H, d, *J* 4.9), 3.84 (1 H, d, *J* 4.5), 7.53–7.74 (3 H, m) and 7.88–7.99 (2 H, m); δ_C(50 MHz) 136.0, 134.5, 129.5, 129.2, 72.6, 71.4, 48.4, 30.4, 20.0 and 16.0; *m*/*z* (EI) 256 (M^+, 10%), 213 (100), 195 (20), 125 (100) and 77 (100).

2-Phenylsulfonyl-2-[1′-(triisopropylsiloxy)alkyl]oxiranes.—General procedure was as described above for epoxidation of the free alcohols, but using *tert*-butyl hydroperoxide (1.5 mol equiv.) and butyllithium (1.1 mol equiv.).

2-Phenylsulfonyl-2-[1′-(triisopropylsiloxy)ethyl]oxirane **12a**/**13a**. Initial mass of starting material **7a** (0.44 g, 1.19 mmol). The reaction mixture was warmed to room temp. and was stirred for 1 h. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield the *product* **12a**/**13a** as an oil with the diastereoisomeric ratio 1:12 (0.34 g, 74%), m.p. 58–61 °C (Found: C, 59.4; H, 8.6. $C_{19}H_{32}O_4SSi$ requires C, 59.3; H, 8.4%); ν_{max}(KBr)/cm^{-1} 3067, 2965, 2945, 2894, 2868, 1310, 1118 and 760; δ_H(200 MHz) (major) 1.00 (21 H, br s), 1.14 (3 H, d, *J* 6.4), 3.25 (1 H, d, J_{maj} 5.8), 3.37 (1 H, d, J_{maj} 5.8), 4.67 (1 H, q, J_{maj} 6.4), 7.53–7.73 (3 H, m) and 7.90–7.96 (2 H, m); δ_C(50 MHz) (major) 136.9, 134.3, 129.6, 129.1, 76.6, 64.8, 49.9, 20.5, 17.9 and 12.2; *m*/*z* (EI) 341 ($M^+ - C_3H_7$, 25%), 198 (50), 125 (100) and 77 (55).

2-Phenylsulfonyl-2-[1′-(triisopropylsiloxy)butyl]oxirane **12b**/**13b**. Initial mass of starting material **7b** (0.50 g, 1.26 mmol). The reaction mixture was warmed to room temp. and stirred for 3 h. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield the *product* **12b**/**13b** as an oil with the diastereoisomeric ratio 1:25 (0.32 g, 61%), m.p. 54–56 °C (Found: C, 61.1; H, 8.9. $C_{21}H_{36}O_4SSi$ requires C, 61.1; H, 8.8%); ν_{max}(KBr)/cm^{-1} 3067, 2963, 2945, 2868, 1310, 1118 and 756; δ_H(200 MHz) 0.26 (3 H, t, *J* 7.3), 1.00 (21 H, br s), 1.21–1.66 (4 H, m), 3.11 (1 H, d, *J* 5.6), 3.46 (1 H, d, *J* 5.6), 4.39 (1 H, t, *J* 5.6), 7.51–7.72 (3 H, m) and 7.90–7.96 (2 H, m); δ_C(50 MHz) 137.2, 134.2, 129.7, 129.0, 75.3, 70.3, 49.4, 37.3, 18.2, 18.0, 14.2 and 12.5; *m*/*z* (EI) 369 ($M^+ - C_3H_7$, 20%), 227 (45), 125 (100) and 77 (25).

2-Phenylsulfonyl-2-[2′-methyl-1′-(triisopropylsiloxy)propyl]oxirane **12c**/**13c**. Initial mass of starting material **7c** (0.30 g, 0.75 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield the *product* **12c**/**13c** as a solid with the diastereoisomeric ratio 1:4 (0.26 g, 79%), m.p. 54–56 °C (Found: C, 61.2; H, 8.8. $C_{21}H_{36}O_4SSi$ requires C, 61.1; H, 8.8%); ν_{max}(KBr)/cm^{-1} 3069, 2965, 2945, 2893, 2868, 1310, 1120 and 754; δ_H(200 MHz) 0.72 (6 H, m), 1.06_{min} and 1.09_{maj} (21 H, 2 br s), 1.32–1.67 (1 H, m), 3.08_{min} and 3.12_{maj} (1 H, 2 d, J_{maj} = J_{min} = 5.6), 3.34_{maj} and 3.39_{min} (1 H, 2 d, J_{maj} and J_{min} 5.6), 4.18_{min} and 4.47_{maj} (1 H, 2 d, J_{maj} 5.3, J_{min} 6.0), 7.52–7.73 (3 H, m) and 7.88–7.93 (2 H, m); δ_C(50 MHz) (major) 134.4, 129.8, 129.1, 128.3, 72.7, 49.5, 33.1, 19.0, 18.3, 17.1, 14.3 and 12.8; (minor) 136.2, 129.8, 129.1, 128.3, 74.1, 49.7, 33.7, 19.3, 18.8, 17.8, 14.2 and 13.0; *m*/*z* (EI) 413 (MH^+, 25%), 369 (100), 255 (20), 227 (35), 125 (100) and 77 (20).

Correlation Experiments.—*2-Phenylsulfonyl-2-[1′-(triisopropylsiloxy)alkyl]oxiranes.* The free alcohols **10**/**11** were converted into the silyl ethers **12**/**13** according to the general procedure used for the preparation of the silyl ethers **7**.

2-Phenylsulfonyl-2-[1′-(triisopropylsiloxy)ethyl]oxirane **12a**/**13a**. Initial mass of starting material **10a**/**11a** (0.17 g, 0.75 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield an oil with the diastereoisomeric ratio 25:1 **12a**/**13a** (0.16 g, 55%); δ_H(200 MHz) 0.87 (21 H, br s), 1.59 (3 H, d, *J* 6.1), 3.10 (1 H, d, *J* 5.6), 3.30 (1 H, d, *J* 5.6), 4.32 (1 H, q, *J* 6.1), 7.53–7.73 (3 H, m) and 7.90–7.96 (2 H, m); δ_C(50 MHz) 136.1, 134.4, 129.7, 129.1, 74.6, 63.3, 45.5, 22.4, 17.9 and 12.1.

2-Phenylsulfonyl-2-[1′-(triisopropylsiloxy)butyl]oxirane **12b**/**13b**. Initial mass of starting material **10b**/**11b** (0.24 g, 0.94 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield an oil with the diastereoisomeric ratio 25:1 **12b**/**13b** (0.28 g, 72%); δ_H(200 MHz) 0.90 (21 H, br s), 0.96 (3 H, t, *J* 7.2), 1.51–1.95 (4 H, m), 3.12 (1 H, d, *J* 5.7), 3.27 (1 H, d, *J* 5.7), 4.31 (1 H, t, *J* 4.1), 7.52–7.72 (3 H, m) and 7.89–7.94 (2 H, m); δ_C(50 MHz) 137.0, 134.3, 129.7, 128.9, 72.6, 66.6, 45.8, 37.6, 18.2, 18.1, 14.4 and 12.4.

2-Methyl-1-[2-(phenylsulfonyl)oxiranyl]propan-1-ol **10c**/**11c**. The silyl ethers **12c**/**13c** (1:4 diastereoisomeric mixture) (0.1 g, 0.25 mmol) were dissolved in dichloromethane (5 cm^3), and boron trifluoride–diethyl ether (0.06 cm^3, 0.50 mmol, 2 mol equiv.) was added. The solution was stirred at room temp. for 3 h and then diluted with ethyl acetate (15 cm^3), filtered through Celite®, and concentrated under reduced pressure. The crude product was purified by flash chromatography and elution with (5:1) toluene–ethyl acetate to yield an oil (0.05 g, 80%) which was diastereoisomerically pure according to ^{1}H NMR spectroscopy and identified as compound **11c**; δ_H(200 MHz) 0.72 (3 H, d, *J* 6.6), 0.89 (3 H, d, *J* 6.6), 1.85 (1 H, dsep, *J* 6.6 and 8.5), 2.42 (1 H, br), 3.09 (1 H, d, *J* 5.0), 3.45 (1 H, d, *J* 5.0), 3.74 (1 H, d, *J* 8.5), 7.54–7.74 (3 H, m) and 7.89–7.98 (2 H, m). The minor isomer was not isolated.

(trans)-3-*Substituted* 2-(1′-*hydroxyalkyl*)-2-(*phenylsulfonyl*)-*oxiranes* **14**/**15**.—General procedure was as described above for epoxidation of the unsubstituted compounds **1**.

1-[(trans)-3-Phenyl-2-(phenylsulfonyl)oxiranyl]ethanol **14a**/**15a**. Initial mass of starting material **2a** (0.63 g, 2.19 mmol). The solution was stirred at −20 °C for 3 h. The crude product was purified by flash chromatography and elution with (10:1) toluene–ethyl acetate to yield product **14a**/**15a** as an oil with the diastereoisomeric ratio 1:12 (0.48 g, 72%); ν_{max}(film)/cm^{-1} 3518, 3065, 2972, 2950, 2938, 2872, 1617, 1449, 1310, 1148 and 750; δ_H(200 MHz) 1.26 (3 H, d, *J* 7.0), 2.18 (1 H, br), 3.67 (1 H, q, *J* 7.0), 4.60_{min} and 4.88_{maj} (1 H, 2 s), 7.29–7.76 (8 H, m) and 7.92–8.06 (2 H, m); δ_C(50 MHz) (major) 137.8, 134.7, 132.5, 131.3, 129.6, 128.9, 127.2, 126.3, 78.6, 68.0, 61.5 and 18.8; *m*/*z* (EI) 304 (M^+, 5%), 323 (70), 279 (45), 253 (50), 125 (20) and 77 (100).

1-[(trans)-3-Phenyl-2-(phenylsulfonyl)oxiranyl]butan-1-ol **14b**/**15b**. Initial mass of starting material **2b** (0.83 g, 2.62 mmol). The solution was stirred at −20 °C for 4 h. The crude product was purified by flash chromatography and elution with (10:1) toluene–ethyl acetate to yield product **14b**/**15b** as an oil with the diastereoisomeric ratio 1:20 (0.55 g, 63%); ν_{max}(film)/cm^{-1} 3500, 3067, 2950, 2920, 2860, 1645, 1459, 1300, 1140 and 750; δ_H(200 MHz) 0.47 (3 H, t, *J* 7.3), 0.91–1.16 (2 H, m), 1.32–1.49 (2 H, m), 1.91 (1 H, br), 3.38_{maj} and 3.52_{min} (1 H, 2 dt, J_{maj} 3.9 and 9.8, J_{min} 3.7 and 10.0), 4.39_{min} and 4.83_{maj} (1 H, 2 s), 7.26–7.76 (8 H, m) and 7.92–8.04 (2 H, m); δ_C(50 MHz) (major) 137.7, 134.3, 133.2, 132.2, 129.8, 128.9, 128.8, 126.6, 78.6, 71.3, 61.5, 35.0, 18.8 and 13.0; *m*/*z* (EI) 317 ($M^+ - CH_3$, 10%), 275 (90), 256 (20), 247 (50), 229 (10), 125 (80) and 77 (100).

2-Methyl-1-[(trans)-3-phenyl-2-(phenylsulfonyl)oxiranyl]-propan-1-ol **14c**/**15c**. Initial mass of starting material **2c** (0.32 g, 1.01 mmol). The solution was stirred at −20 °C for 5 h. The crude product was purified by flash chromatography and

elution with (10:1) toluene–ethyl acetate to yield compounds **14c**/**15c** as an oil with the diastereoisomeric ratio 1:25 (0.18 g, 53%), ν_{max}(film)/cm^{-1} 3510, 3067, 2925, 2840, 1645, 1320, 1130 and 752; δ_H(200 MHz) 0.59 (3 H, d, *J* 6.5), 0.82 (3 H, d, *J* 6.5), 2.31 (1 H, d, *J* 7.7), 2.44 (1 H, dsep, *J* 6.5 and 10.5), 3.18 (1 H, dd, *J* 7.7 and 10.5), 4.67 (1 H, s), 7.26–7.78 (8 H, m) and 8.01–8.07 (2 H, m); δ_C(50 MHz) 136.9, 134.4, 131.5, 129.9, 129.2, 129.1, 128.5, 126.9, 76.8, 61.5, 31.8, 26.5, 20.0 and 19.0; *m*/*z* (EI) 330 ($M^+ - 2$ H, 25%), 224 (30), 178 (55), 125 (50), 77 (80) and 4 (100).

(trans)-3-*Substituted*-2-*phenylsulfonyl*-2-[1′-(*triisopropylsiloxy*)*alkyl*]*oxiranes*.—General procedure as described above for epoxidation of the free alcohols, but using *tert*-butyl hydroperoxide (1.5 mol equiv.) and butyllithium (1.1 mol equiv.).

(trans)-3-*Phenyl*-2-*phenylsulfonyl*-2-[1′-(*triisopropylsiloxy*)*ethyl*]*oxirane* **16a**/**17a**. Initial mass of starting material **9a** (0.50 g, 1.13 mmol). The mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield *compounds* **16a**/**17a** as an oil with the diastereoisomeric ratio 5:1 (0.47 g, 90%), m.p. 94–96 °C (Found: C, 64.9; H, 7.9. $C_{25}H_{36}O_4SSi$ requires C, 65.2; H, 7.9%); ν_{max}(KBr)/cm^{-1} 3069, 2960, 2940, 2867, 1454, 1308, 1159 and 756; δ_H(200 MHz) 0.78_{maj} and 0.82_{min} (21 H, 2 br s), 1.23_{maj} and 1.33_{min} (3 H, 2 d, J_{maj} 6.5, J_{min} 6.9), 3.70_{min} and 4.06_{maj} (1 H, 2 q, J_{maj} 6.5, J_{min} 6.9), 4.82_{maj} and 5.10_{min} (1 H, 2 s), 7.35–7.77 (8 H, m) and 7.95–8.06 (2 H, m); δ_C(50 MHz) (major) 138.1, 134.2, 131.6, 130.0, 129.0, 128.8, 128.2, 127.1, 126.3, 78.6, 65.0, 61.3, 20.6, 17.8 and 12.4; *m*/*z* (EI) 461 (MH^+, 20%), 418 (20), 401 (60), 275 (100), 256 (80), 125 (100) and 77 (80).

(trans)-3-*Phenyl*-2-(*phenylsulfonyl*)-2-[1′-(*triisopropylsiloxy*)*butyl*]*oxirane* **16b**/**17b**. Initial mass of starting material **9b** (0.28 g, 0.59 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield compound **16b**/**17b** as an oil with the diastereoisomeric ratio 4:1 (0.26 g, 91%) (Found: $M^+ - C_3H_7$, 445.1833. $C_{24}H_{33}O_4SSi$ requires *m*/*z*, 445.1869); ν_{max}(film)/cm^{-1} 3067, 2935, 2915, 2880, 2860, 1440, 1310, 1145 and 750; δ_H(200 MHz) 0.48–0.64 (3 H, m), 0.78_{maj} and 0.82_{min} (21 H, 2 br s), 1.09–1.61 (4 H, m), 3.70_{min} and 3.91_{maj} (1 H, 2 t, J_{maj} 7.9, J_{min} 9.4), 4.71_{maj} and 5.11_{min} (1 H, 2 s), 7.32–7.66 (8 H, m) and 7.89–8.07 (2 H, m); δ_C(50 MHz) (major) 141.3, 138.5, 134.1, 131.6, 130.0, 129.0, 128.5, 127.2, 126.9, 78.8, 69.5, 60.2, 38.0, 19.1, 17.9, 14.1 and 12.3; *m*/*z* (EI) 445 ($M^+ - C_3H_7$, 80%), 429 (100), 373 (10), 303 (90), 256 (60), 125 (60) and 77 (50).

(trans)-2-[2′-*Methyl*-1′-(*triisopropylsiloxy*)*propyl*]-3-*phenyl*-2-(*phenylsulfonyl*)*oxirane* **16c**/**17c**. Initial mass of starting material **9c** (0.36 g, 0.76 mmol). The mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield *compounds* **16c**/**17c** as a solid with the diastereoisomeric ratio 2:1 (0.30 g, 80%), m.p. 133–135 °C (Found: C, 66.3; H, 8.4. $C_{27}H_{40}O_4SSi$ requires C, 66.3; H, 8.3%); ν_{max}(KBr)/cm^{-1} 3067, 2920, 2860, 1460, 1315, 1145 and 756; δ_H(200 MHz) 0.63_{maj} and 0.79_{min} (6 H, 2 d, $J_{maj} = J_{min} = 6.8$), 0.91_{min} and 0.92_{maj} (21 H, 2 br s), 1.61–1.84 (1 H, m), 3.44_{min} and 3.93_{maj} (1H, 2 d, J_{maj} 8.5, J_{min} 9.9), 4.57_{maj} and 5.00_{min} (1 H, 2 s), 7.35–7.72 (8 H, m) and 7.92–8.05 (2 H, m); δ_C(50 MHz) (major) 142.2, 134.2, 133.2, 132.5, 132.2, 130.5, 129.2, 128.2, 74.1, 60.1, 33.2, 29.8, 20.7, 19.3, 18.3 and 12.7; (minor) 142.8, 133.4, 133.1, 131.7, 130.3, 129.6, 128.6, 127.2, 79.9, 62.1, 32.4, 29.4, 20.5, 19.7, 18.5 and 12.3; *m*/*z* (EI) 445 ($M^+ - C_3H_7$, 50%), 429 (100), 331 (10), 261 (40), 125 (50) and 77 (40).

Correlation Experiments.—(trans)-3-*Phenyl*-2-*phenylsulfonyl*-2-[1′-(*triisopropylsiloxy*)*alkyl*]*oxiranes*. The free alcohols **14**/**15** were converted into the silyl ethers **16**/**17** according to the general procedure used for the preparation of the silyl ethers **7**.

(trans)-3-*Phenyl*-2-*phenylsulfonyl*-2-[1′-(*triisopropylsiloxy*)*ethyl*]*oxirane* **16a**/**17a**. Initial mass of starting material **14a**/**15a** (0.10 g, 0.45 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield compounds **16a**/**17a** as an oil with the diastereoisomeric ratio 1:12 (0.30 g, 86%); δ_H(200 MHz) 0.78_{min} and 0.82_{maj} (21 H, 2 br s), 1.23_{min} and 1.33_{maj} (3 H, 2 d, J_{maj} 6.9, J_{min} 6.5), 3.70_{maj} and 4.06_{min} (1 H, 2 q, J_{maj} 6.9, J_{min} 6.5), 4.82_{min} and 5.10_{maj} (1 H, 2 s), 7.35–7.77 (8 H, m) and 7.95–8.06 (2 H, m); δ_C(50 MHz) (major) 139.6, 133.6, 132.1, 130.0, 129.5, 128.8, 128.5, 126.2, 79.0, 69.6, 61.0, 20.3, 18.1 and 12.1.

(trans)-3-*Phenyl*-2-*phenylsulfonyl*-2-[1′-(*triisopropylsiloxy*)*butyl*]*oxirane* **16b**/**17b**. Initial mass of starting material **14b**/**15b** (0.37 g, 1.11 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield compounds **16b**/**17b** as an oil with the diastereoisomeric ratio 1:20 (0.54 g, 99%); δ_H(200 MHz) 0.64 (3 H, t, *J* 7.1), 0.78_{min} and 0.82_{maj} (21 H, 2 br s), 1.09–1.61 (4 H, m), 3.70_{maj} and 3.91_{min} (1 H, 2 t, J_{maj} 9.4, J_{min} 7.9), 4.71_{min} and 5.11_{maj} (1 H, 2 s), 7.32–7.66 (8 H, m) and 7.89–8.07 (2 H, m); δ_C(50 MHz) (major) 139.5, 133.6, 132.2, 130.0, 128.8, 128.6, 128.3, 126.8, 79.0, 72.4, 61.6, 38.3, 18.2, 18.0, 14.1 and 12.4.

(trans)-2-[2′-*Methyl*-1′-(*triisopropylsiloxy*)*propyl*]-3-*phenyl*-2-(*phenylsulfonyl*)*oxirane* **16c**/**17c**. Initial mass of starting material **14c**/**15c** (0.10 g, 0.30 mmol). The reaction mixture was warmed to room temp. and stirred overnight. The crude product was purified by flash chromatography and elution with (100:1) toluene–ethyl acetate to yield products **16c**/**17c** as an oil with the diastereoisomeric ratio 1:25 (0.14 g, 95%); δ_H(200 MHz) 0.79 (6 H, d, *J* 6.8), 0.91 (21 H, br s), 1.61–1.84 (1 H, m), 3.44 (1 H, d, *J* 9.9), 5.00 (1 H, s), 7.35–7.72 (8 H, m) and 7.92–8.05 (2 H, m); δ_C(50 MHz) 142.8, 133.4, 133.1, 131.7, 130.3, 129.6, 128.6, 127.2, 79.9, 62.1, 32.4, 29.4, 20.5, 19.7, 18.5 and 12.3.

Epoxidations using Potassium tert-*Butyl Peroxide: General Procedure*.—Potassium hydride (0.15 cm^3, 1.5 mmol; 35% w/v) was washed with light petroleum under nitrogen, and THF (10 cm^3) was then added. The flask was cooled to 0 °C, and *tert*-butyl hydroperoxide (0.60 cm^3, 2.22 mmol; 3.74 mol dm^{-3}) was added dropwise and the resulting solution was stirred at 0 °C for 10 min. The flask was then cooled to −78 °C after which a solution of the vinyl sulfone (1.00 mmol) in THF (10 cm^3) was added (the temperature was not allowed to exceed −70 °C). The mixture was then allowed to warm to 0 °C, and it was stirred until all starting material had reacted. The flask was then recooled to −78 °C and the solution was quenched with saturated aq. ammonium chloride (~20 cm^3). The aqueous phase was extracted with ethyl acetate (2 × 15 cm^3), and the combined extracts were dried ($MgSO_4$), and concentrated under reduced pressure. The diastereoisomeric ratios were determined by ^{1}H NMR spectroscopy of the crude reaction mixtures, which were then purified by flash chromatography using the same solvent systems as used previously.

X-Ray Crystallography.—Crystal data for compounds **10c**, **13a**, **13b** and **16a** are given in Table 3, together with information on procedures for data collection and structure determination. Instrumentation, methods and definitions are as previously described,[10] with refinement on F^2. All measurements were made with Mo-Kα radiation (λ 0.710 73 Å); cell parameters were refined from 2θ-values in the range 20–25° for selected reflections. All four structures are centrosymmetric and hence racemic; for consistency of presentation, all molecular structures are shown in the Figures with the same absolute configuration,

Table 3 Crystallographic data

	10c	**13a**	**13b**	**16a**
Formula	$C_{12}H_{16}O_4S$	$C_{19}H_{32}O_4SSi$	$C_{21}H_{36}O_4SSi$	$C_{25}H_{36}O_4SSi$
M	256.3	384.6	412.7	460.7
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/n$	*Pbca*	$P\bar{1}$	$P\bar{1}$
a/Å	8.538(6)	17.213(8)	8.556(3)	9.0816(8)
b/Å	20.829(14)	11.605(6)	11.412(4)	9.4779(8)
c/Å	14.621(8)	20.932(8)	12.528(4)	15.650(2)
α/°			96.65(2)	86.947(9)
β/°	106.16(6)		105.63(2)	88.644(9)
γ/°			97.94(2)	73.596(6)
V/Å^3	2497(3)	4181(3)	1151.6(7)	1290.3(2)
Z	8	8	2	2
D_c/g cm^{-3}	1.363	1.222	1.190	1.186
μ/mm^{-1}	0.259	0.232	0.215	0.199
F(000)	1088	1664	448	496
Temperature/K	180	200	150	295
Crystal size/mm	0.64 × 0.60 × 0.56	0.70 × 0.60 × 0.28	0.50 × 0.50 × 0.15	0.54 × 0.46 × 0.42
No. reflections for cell	30	32	32	32
$2\theta_{max}$/°	45	50	50	50
Maximum indices *hkl*	9, 22, 15	20, 13, 24	10, 13, 14	10, 11, 18
Reflections measured	5048	4862	5899	5880
Unique reflections	3269	3677	4048	4535
R_{int}	0.0340	0.0247	0.0598	0.0351
Weighting parameters a, b	0.0296, 3.6221	0.0389, 1.9472	0.0322, 0.9865	0.0927, 0.4538
Extinction coefficient x	0.0013(3)	0.0009(2)	0.007(3)	0
No. of refined parameters	314	234	252	288
$wR2$ (all data)	0.1251	0.1010	0.1655	0.1504
$R1$ ('observed' data)	0.0527	0.0337	0.0435	0.0500
Goodness-of-fit	1.132	1.079	1.215	1.032
Max., min. el. density/e Å^{-3}	0.317, −0.385	0.363, −0.262	0.388, −0.307	0.661, −0.403

although these are the opposite hand to the refined coordinates for compounds **13a** and **16a**. Refined coordinates, other parameters, together with full lists of bond lengths and angles, are available as supplementary material from the CCDC.*

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* For details of the crystallographic deposition scheme, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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