Control of Diastereofacial Selectivity in the Nucleophilic Epoxidation of γ-Oxygenated α,β-Unsaturated Sulfones

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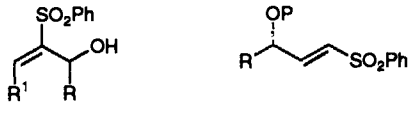
Epoxidation of γ-oxygenated-α,β-unsaturated sulfones **6–10** with either lithium or potassium *tert*-butyl peroxide proceeds with moderate to high diastereoselectivity to give mixtures of the *syn*-2-(phenylsulfonyl)oxiranes **11–15** and the corresponding *anti*-2-(phenylsulfonyl)oxiranes **16–20**. In all cases examined, the presence of a free hydroxy group leads to the *syn*-oxirane with moderate to excellent stereoselectivity. For relatively unbulky substituents at the γ-position (methyl and propyl), the presence of a silyl protecting group leads to the formation of *syn*-oxiranes as the major product, while a methoxyethoxymethyl protecting group leads to the *anti*-oxirane in excess. However, when the γ-substituent is large (isopropyl), the *anti*-products are obtained with both silyl and methoxyethoxymethyl protection. Transition states are proposed to account for these results. X-Ray crystallographic results for compounds **12a**, **19c** and **22** are also reported.

As part of our studies to extend the synthetic utility of 2-(phenylsulfonyl)oxiranes,[1] we have been investigating methods for the stereoselective synthesis of these compounds. We have recently reported on the rôle of an allylic stereocentre in the nucleophilic epoxidation of α-(1′-hydroxyalkyl)-α,β-unsaturated sulfones **1**,[2] and we have also reported in preliminary form our results on the nucleophilic epoxidation of γ-oxygenated-α,β-unsaturated sulfones **2** when using lithium *tert*-butyl peroxide.[3] In this paper, we provide a full account of our work in this area, including the effects of both epoxidation reagent and alkoxy substituent on the sense and extent of diastereofacial selectivity. These further investigations have allowed us to refine significantly the models which we had originally proposed.[3]



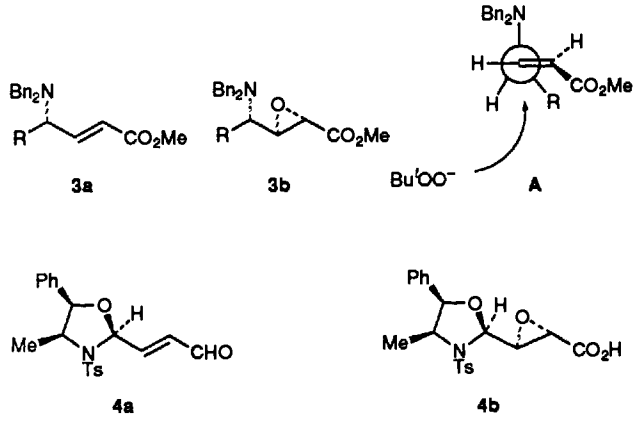
1 **2**

P = protecting group

A substantial body of work has addressed the question of stereochemical control by allylic stereocentres in conjugate additions.[4–6] For example, the stereochemical outcome of the addition of organometallic reagents to both cyclic[7] and acyclic vinyl sulfones[8,9] has been extensively explored, and the results exploited in stereoselective synthesis. Recent investigations, principally based on the application of variable-temperature NMR studies, have sought to address the issue of the influence of ground-state conformation on the stereochemical outcome of such reactions.[10] For example, the favoured conformation of simple protected γ-hydroxy-α,β-unsaturated esters has been shown to be altered simply by replacement of a *tert*-butyldimethylsilyl group by a methyl group (Fig. 1).[10d]

Fig. 1 Favoured conformations of protected γ-hydroxy-α,β-unsaturated esters

Despite all this general interest in the stereochemical aspects of conjugate additions, reports on analogous stereochemical



control in nucleophilic epoxidation processes have been much more limited. Reetz has reported on the high *syn* diastereofacial selectivity in the formation of the epoxides **3b** which are obtained upon epoxidation of γ-amino-α,β-unsaturated esters **3a** with a reagent derived from potassium *tert*-butoxide and *tert*-butyl hydroperoxide in tetrahydrofuran (THF)–ammonia.[11] A rationalisation for these results, based on the attack of the nucleophilic peroxide anion along a modified Bürgi–Dunitz trajectory involving conformation **A**, was suggested. The most important feature of this model is the inside-position of the R-substituent, which removes it from the trajectory of the attacking nucleophile. In a related way, Scolastico has reported on the highly stereoselective epoxidation of the unsaturated aldehyde **4a** when using potassium hypochlorite, which in this case gives the *anti*-epoxy acid **4b**.[12] The different stereochemical outcome in this case was ascribed to the phenyl and methyl substituents on the oxazolidinone disfavouring a conformation in which this group was inside. That is, the conformation represented in structure **4a** is close to the reactive conformation for the conjugate addition.

A final isolated example is the high *anti*-stereoselectivity which was obtained in the epoxidation of the enone **5a** to give the oxirane **5b** by using butylzinc butyl peroxide.[13]

We have therefore sought to establish, systematically, the effects of hydroxy-protecting group and size of γ-substituent on the stereochemical outcome of the nucleophilic epoxidation of γ-oxygenated-α,β-unsaturated sulfones **2**. At the outset of the

present investigation, our aim was to delineate conditions which would allow for the preparation of either of the two possible diastereoisomeric epoxides. The initial investigation centred on the use of lithium *tert*-butyl peroxide as the epoxidising agent,[14] since it was considered that the stereochemical outcome of the epoxidation process could be controlled either by coordination of the lithium reagent to the protecting group, where this was capable of coordination, or by addition from the opposite face when the protecting group was not capable of coordination. Under these latter circumstances, reaction under stereoelectronic control would be likely,[15] leading to products of opposite relative configuration to those obtained under conditions when coordination was possible.

The required precursors, γ-hydroxy-α,β-unsaturated sulfones **6a–c** are readily available in racemic form in a one-step process involving the condensation of phenyl phenylsulfinylmethyl sulfone with aldehydes promoted by piperidine. This process, which involves an initial condensation between the aldehyde and phenyl phenylsulfinylmethyl sulfone, and migration of the double bond to the allylic position, followed by 2,3-sigmatropic rearrangement and hydrolysis, was reported by Carretero[16] and subsequently by Trost.[17] We had also independently discovered this process.[18] Protection of the hydroxy group to give the triphenylsilyl (**7a–c**), *tert*-butyldiphenylsilyl (**8a–c**), triisopropylsilyl (**9a–c**) and methoxyethoxymethyl (MEM) (**10a–c**) derivatives was achieved by using standard procedures. We initially expected that use of the MEM protecting group would allow coordination of the reagent to the substrate, whilst use of the silyl protecting groups would reverse the diastereofacial selectivity. Our results for the nucleophilic epoxidation of the vinylsulfones **6–10** using lithium *tert*-butyl peroxide to give the *syn*-oxiranes **11–15** and the *anti*-oxiranes **16–20**, respectively, are summarised in Table 1.

The stereochemistry of the major isomer **12a**, *syn*-derived from epoxidation of compound **7a**, with R = Me, was established by X-ray crystallography (Fig. 2). Chemical correlation of the products derived from epoxidation of substrates **6a**, **8a**, **9a** and **10a** with this material allowed the stereochemical course of these reactions to be established. The stereochemistry of the major isomer **19c**, *anti*-derived from epoxidation of **9c**, with R = Pr^i, was also established by X-ray crystallography (Fig. 3). This allowed the unambiguous assignment of stereochemistry of the products derived from epoxidation of substrates **6c**, **7c**, **8c** and **10c**, again by correlation.

We have not been able to confirm unambiguously the stereochemical outcome of the reactions for epoxidation of the examples with R = Pr. However, chemical correlation allowed the relative senses of stereoselectivity for all the examples to be established. Comparison of ^{1}H and ^{13}C NMR spectral data with those obtained in the methyl series allowed a reasonably firm assignment to be made. Thus, for example, the ^{13}C chemical shifts for the carbon atoms of the oxirane and the γ-carbon of the major *syn*-isomers for all the silyl-protected compounds **12a**, **13a** and **14a** were at lower field than the corresponding signals for the minor *anti*-isomers **17a**, **18a** and **19a**. This situation is mirrored in the ^{13}C NMR spectra obtained in the propyl series.

To explore the effect of metal cation and size of epoxidising nucleophile, we have also investigated the epoxidation of some representative examples by using potassium *tert*-butyl peroxide and the classical reagent, basic hydrogen peroxide. While the

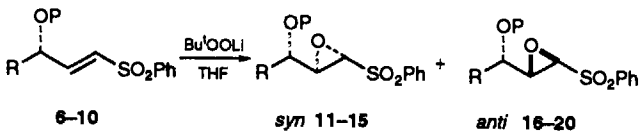


Table 1 Epoxidation of vinyl sulfones **6–10** with lithium *tert*-butyl peroxide

Vinyl sulfone	R	P	Oxirane	*syn*:*anti* ratio	Yield (%)
6a	Me	H	**11a/16a**	3:1	73
7a	Me	$SiPh_3$	**12a/17a**	3:1	77
8a	Me	Bu^tPh_2Si	**13a/18a**	4:1	64
9a	Me	$SiPr^i_3$	**14a/19a**	10:1	94
10a	Me	MEM	**15a/20a**	1:2	63
6b	Pr	H	**11b/16b**	3:1	61
7b	Pr	$SiPh_3$	**12b/17b**	2:1	71
8b	Pr	Bu^tPh_2Si	**13b/18b**	2:1	66
9b	Pr	$SiPr^i_3$	**14b/19b**	4:1	92
10b	Pr	MEM	**15b/20b**	1:5	65
6c	Pr^i	H	**11c/16c**	25:1	23
6c	Pr^i	H[a]	**11c/16c**	25:1[a]	46[a]
7c	Pr^i	$SiPh_3$	**12c/17c**	1:25	79
8c	Pr^i	Bu^tPh_2Si	**13c/18c**	1:25	89
9c	Pr^i	$SiPr^i_3$	**14c/19c**	1:25	96
10c	Pr^i	MEM	**15c/20c**	1:25	55

[a] Reaction carried out using *tert*-butyl hydroperoxide (3.3 mol equiv.) and butyllithium (2.4 mol equiv.).

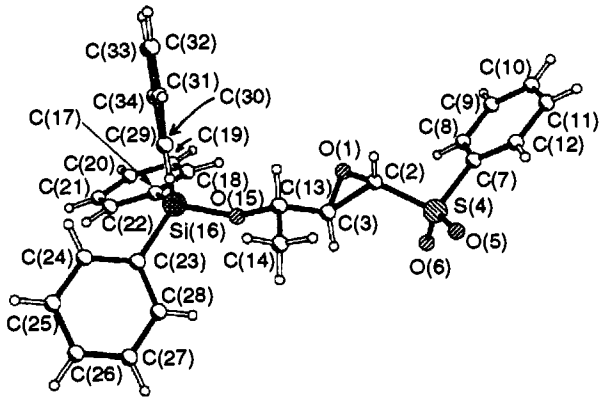


Fig. 2 Molecular structure of compound **12a**

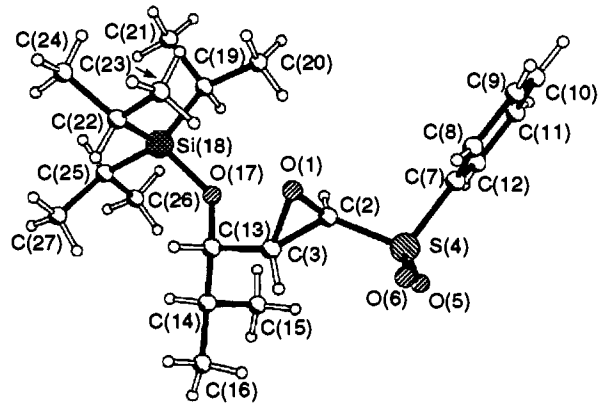


Fig. 3 Molecular structure of compound **19c**

results obtained using potassium *tert*-butyl peroxide closely mirror those obtained using lithium *tert*-butyl peroxide, those using basic hydrogen peroxide were not selective, suggesting that the size of the nucleophile was of great significance. The results for these reactions, together with the corresponding values for the butyllithium–*tert*-butyl hydroperoxide epoxidations for comparison, are given in Table 2.

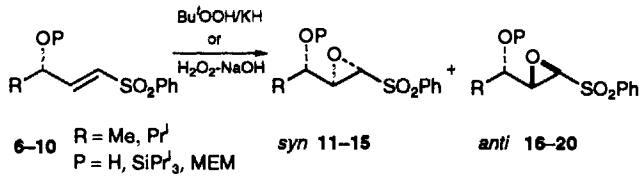


Table 2 Epoxidation of selected vinyl sulfones with potassium *tert*-butyl peroxide and basic hydrogen peroxide

Vinyl sulfone	R	P	Oxirane	*syn*:*anti* Bu'OOLi	*syn*:*anti* Bu'OOK	Yield (%)	*syn*:*anti* H_2O_2–NaOH	Yield (%)
6a	Me	H	**11a/16a**	3:1	1.5:1	75	1:1	53
6c	Pr^i	H	**11c/16c**	25:1	25:1	66	1:1	45
9a	Me	$SiPr^i_3$	**14a/19a**	10:1	7:1	94	1:1	49
9c	Pr^i	$SiPr^i_3$	**14c/19c**	1:25	1:25	79	*a*	*a*
10a	Me	MEM	**15a/20a**	1:2	1:2	84	*b*	*b*
10c	Pr^i	MEM	**15c/20c**	1:25	1:25	67	*b*	*b*

[a] No reaction under these conditions. [b] Not attempted.

Discussion

In our preliminary communcation, we had suggested that the source of *syn*-stereoselectivity in the nucleophilic epoxidation of the free alcohols **6a–c** was attack of the reagent *anti* to the hydroxy group in a conformation in which the alkyl substituent was inside, and the carbon–oxygen bond was parallel to the π-system of the vinyl sulfone. Our recent experience, for example in the epoxidation of α-(1′-hydroxyalkyl)-α,β-unsaturated sulfones **1**,[2] suggests that a free hydroxy group is an excellent directing group for metal *tert*-butyl peroxides. For this reason, we now consider that it is more likely that an interaction between the hydroxy group and the metal *tert*-butyl peroxide, either by coordination of the lithium cation or by hydrogen-bond formation between the alcohol proton and the *tert*-butyl peroxide anion, allows delivery of the reagent from the same face as the hydroxy group. Since we observe good to excellent stereoselectivity in favour of the *syn* isomer, it appears that the alkyl group adopts the sterically less hindered outside position (Fig. 4).

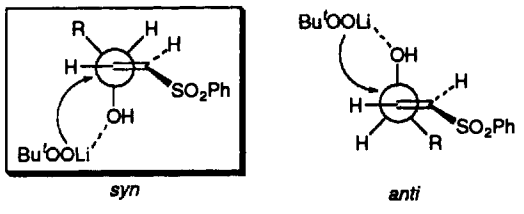


Fig. 4 Possible transition states for the epoxidation of the free alcohols **6**

In the transition state leading to the *anti*-diastereoisomer, the steric hindrance between the alkyl group and the hydrogen would become greater as the size of the alkyl group increases. Hence we would expect the *syn*:*anti* ratio to be larger as the size of the alkyl group increases, as is indeed observed (Table 1). It is important to note that Carretero has established that the addition of organocopper reagents to γ-hydroxy-α,β-unsaturated sulfones proceeds with *anti*-stereoselectivity,[9b] and has rationalised this observation by proposing a transition state in which the hydroxy group occupies the inside position. This arrangement is evidently not important in reactions of these substrates with either lithium or potassium *tert*-butyl peroxide.

In all substrates in which there is silyl-protection, the situation is slightly more complex, since the size of the alkyl substituent influences the sense of diastereofacial selectivity in the epoxidation step. Some possible transition states leading to each diastereoisomer are shown in Fig. 5.

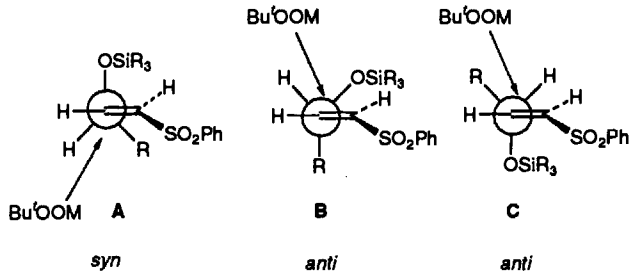


Fig. 5 Possible transition states for the epoxidation of silyl ethers **7–9**

In the propyl and methyl series, the reaction appears to be under stereoelectronic control, so that the alkyl group prefers to occupy the inside position and the metal *tert*-butyl peroxide attacks *anti* to the siloxy group (transition state **A**).[15] This is consistent with the greater *syn* stereoselectivity observed for the methyl substituent compared with the propyl substituent in all the silyl-protected compounds, since the smaller methyl group can occupy the inside position more easily.

In the isopropyl series, with all protecting groups, the *anti*-diastereoisomer is observed exclusively. Of the three transition states, only transition state **B** is compatible with our results since transition state **C** is not viable for bulky R groups. In this case, the isopropyl group appears to be too large to occupy the inside position, and the siloxy group occupies this position instead, perhaps reflecting that this conformation may be close to the ground state (*cf.* Fig. 1). Moreover, this transition state has also been proposed by Yamamoto[4a] in the context of conjugate addition of cuprates to γ-alkoxy-α,β-unsaturated esters.

When the allylic hydroxy group is protected as a MEM group, the major stereoisomer is in all cases the *anti*-isomer, and the extent of stereoselectivity increases with the size of the

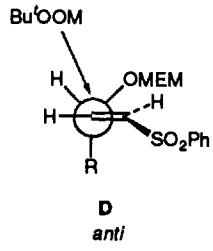


Fig. 6 Possible transition state for the epoxidation of the MEM ether **10**

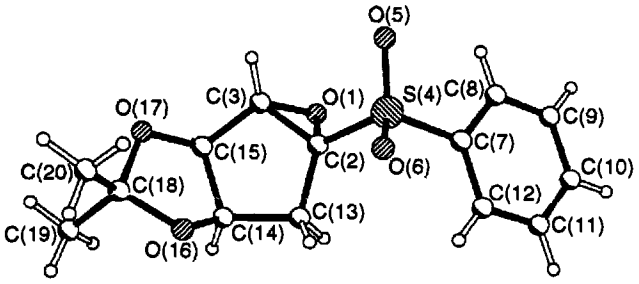


Fig. 7 Molecular structure of compound **22**

21 **22**

alkyl substituent. The only transition state which accommodates these results is **D** (Fig. 6) analogous to **B**. In this situation, the possibility for coordination of lithium *tert*-butyl peroxide by the protecting group exists, although the identical results obtained using potassium *tert*-butyl peroxide suggests that this is not the main influence.

As a final example of the facial selectivity in nucleophilic epoxidation, we have investigated the reaction of the cyclic vinyl sulfone **21**[19] with lithium *tert*-butyl peroxide. The reaction proceeded with high diastereoselectivity, and only a single stereoisomer was isolated. The structure was established as the *anti*-epoxide **22** by an X-ray crystal-structure determination (Fig. 7). In this case, it appears that nucleophilic attack on a *cis*-fused bicyclic system has followed its usual course from the *exo* face, and that there is no significant interaction between the oxygen atoms of the isopropylidene ketal and the lithium reagent.

Experimental

General experimental procedures and instrumentation are as previously described.[1] Phenyl phenylsulfenylmethyl sulfone was prepared by the literature procedure.[20] Full experimental procedures for the preparation of the protected γ-hydroxy-α,β-unsaturated sulfones **7a–c**, **8a–c**, **9a–c** and **10a–c**, as well as the correlation experiments which establish the sense of epoxidation of the different substrates, are provided as supplementary material [Supp. no. 57052 (18 pp.)].*

Phenyl Phenylsulfinylmethyl Sulfone.—A solution of phenyl phenylsulfenyl methyl sulfone (5.07 g, 18.8 mmol) in dichloromethane (60 cm^3) under nitrogen was cooled to −20 °C. *m*-Chloroperbenzoic acid (4.36 g, 25.1 mmol) was added in amounts of ~1 g, whilst, at the same time, dichloromethane (15 cm^3) was added to the reaction mixture. The reaction mixture was then stirred at −20 °C for 3 h. The organic phase was washed successively with saturated aq. sodium sulfite (2 × 15 cm^3) and saturated aq. sodium hydrogen carbonate (2 × 15 cm^3). The organic phase was dried ($MgSO_4$), and concentrated under reduced pressure. The crude material was purified by flash chromatography and elution with (3:1) toluene–ethyl acetate, and the resulting oil was crystallised from a dichloromethane–diethyl ether mixture to yield *title compound* as a solid (4.55 g, 88%), m.p. 95–98 °C (Found: C, 55.6; H, 4.2. $C_{13}H_{12}O_3S_2$ requires C, 55.7; H, 4.3%); ν_{max}(KBr)/cm^{-1} 3065, 1478, 1446, 1329, 1022 and 752; δ_H(200 MHz; $CDCl_3$; standard Me_4Si) 4.30 (1 H, d, *J* 13.8), 4.42 (1 H, d, *J* 13.8) and 7.27–8.05 (10 H, m); *m/z* (EI) 280 (M^+, 30%), 218 (20), 125 (100) and 77 (85).

(E)-1-(*Phenylsulfonyl*)*hex*-1-*en*-3-*ol* **6b**.—Phenyl phenylsulfinylmethyl sulfone (3.07 g, 0.9 mmol) was dissolved in a mixture of toluene (20 cm^3) and acetonitrile (5 cm^3) under nitrogen. Piperidine (1.20 cm^3, 12.1 mmol), followed by pentanal (1.40 cm^3, 13.1 mmol) were added and the resulting solution was stirred at room temperature overnight. Ethyl acetate (40 cm^3) was then added and the organic phase was separated, washed with hydrochloric acid (3 × 15 cm^3; 1 mol dm^{-3}), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate to yield *compound* **6b** as a yellow solid (2.10 g, 80%), m.p. 56–59 °C (Found: C, 60.1; H, 6.8. $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7%); ν_{max}(KBr)/cm^{-1} 3505, 2961, 2934, 2874, 1628, 1306, 1146, 972 and 754; δ_H(200 MHz) 0.91 (3 H, t, *J* 7.1), 1.33–1.61 (4 H, m), 2.62 (1 H, br), 4.38 (1 H, br), 6.59 (1 H, dd, *J* 1.8 and 14.9), 6.99 (1 H, dd, *J* 3.7 and 14.9), 7.48–7.84 (3 H, m) and 7.77–7.90 (2 H, m); *m/z* (EI) 241 (MH^+, 10%), 221 (20), 169 (100), 125 (90) and 77 (50).

The known vinyl sulfones **6a** and **6c** were prepared by an analogous method, and exhibited spectroscopic and m.p. data identical with those reported in the literature.[16]

General Procedure for Epoxidation using Lithium tert-*Butyl Peroxide.*—THF (15 cm^3) and *tert*-butyl hydroperoxide (1.5 mol equiv.; 3.58 mol dm^{-3}) were cooled to −78 °C under nitrogen, and butyllithium (1.1 mol equiv.; 2.38 mol dm^{-3}) was added dropwise to the solution. The reaction mixture was stirred at −78 °C for 10 min, after which a solution of the starting vinyl sulfone in THF (15 cm^3) was added. [The temperature was not allowed to exceed −70 °C during the additions.] The reaction times and temperatures are recorded for each individual substrate. The reaction was quenched using saturated aq. ammonium chloride (~20 cm^3) and was stirred at room temperature for 15 min. The aqueous phase was washed with ethyl acetate (2 × 15 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure.

1-[(trans)-3-(*Phenylsulfonyl*)*oxiran*-2-*yl*]*ethanol* **11a**/**16a**. Initial mass of starting material **6a** (0.23 g, 1.08 mmol). The solution was stirred at −20 °C for 2 h, when all starting material had reacted. The crude product was purified by flash chromatography and elution with (3:1) toluene–ethyl acetate to yield title compounds **11a**/**16b** as a dense oil with the diastereoisomeric ratio 3:1 (0.18 g, 73%) (Found: M^+ − $PhSO_2$, 87.0455. $C_4H_7O_2$ requires *m/z* 87.0446); ν_{max}(film)/cm^{-1} 3507, 3067, 2980, 1448, 1323, 1153 and 754; δ_H(200 MHz) 1.28_{min} and 1.32_{maj} (3 H, 2 d, J_{maj} 6.6, J_{min} 6.5), 2.29 (1 H, br), 3.66–3.69 (1 H, m), 3.95_{maj} and 4.07_{min} (1 H, 2 dq, J_{maj} 3.2 and 6.6, J_{min} 4.0 and 6.5), 4.21–4.23 (1 H, m), 7.52–7.79 (3 H, m) and 7.82–8.02 (2 H, m); δ_C(50 MHz) (major) 136.9, 134.6, 129.5, 128.8, 66.2, 64.6, 60.9 and 20.1; (minor) 136.91, 134.6, 129.5, 128.8, 65.1, 63.4, 60.5 and 18.8; *m/z* (EI) 143 ($PhSO_2H_2^+$, 22%), 125 (PhSO, 50), 87 (M^+ − $PhSO_2$, 24) and 43 (100).

1-[(trans)-3-(*Phenylsulfonyl*)*oxiran*-2-*yl*]*butan*-1-*ol* **11b**/**16b**. Initial mass of starting material **6b** (0.36 g, 1.50 mmol). The solution was stirred at −20 °C for 3 h, whereupon all starting material had reacted. The crude product was purified by flash chromatography and elution with (5:1) toluene–ethyl acetate to yield title compounds **11b**/**16b** as a dense oil with the diastereoisomeric ratio 3:1 (0.24 g, 61%) (Found: M^+ −

* For details of the Supplementary Publications Scheme, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

$PhSO_2$, 115.0755. $C_6H_{11}O_2$ requires *m/z*, 115.0759); ν_{max}(film)/cm^{-1} 3518, 3067, 2961, 2934, 2874, 1448, 1325, 1155 and 754; δ_H(200 MHz) 0.96 (3 H, t, *J* 7.2), 1.39–1.61 (4 H, m), 1.63 (1 H, br), 3.69–3.79 (2 H, m), 4.20_{maj} and 4.22_{min} (1 H, 2 d, J_{maj} 1.7, J_{min} 1.6), 7.49–7.78 (3 H, m) and 7.92–7.96 (2 H, m); δ_C(50 MHz) (major) 137.0, 134.5, 129.4, 128.7, 68.1, 66.1, 60.1, 36.7, 18.4 and 13.9; (minor), 138.1, 134.4, 129.0, 128.2, 66.6, 64.9, 59.8, 35.1, 21.5 and 13.2; *m/z* (EI) 143 ($PhSO_2H_2^+$, 24%), 125 (PhSO, 26), 115 ($M^+ - PhSO_2$, 15), 43 (72) and 32 (100).

2-*Methyl*-1-[(trans)-3-(*phenylsulfonyl*)*oxiran*-2-*yl*]*propan*-1-*ol* **11c**/**16c**. Initial mass of starting material **6c** (0.36 g, 1.51 mmol). The solution was stirred at −20 °C overnight, whereupon all starting material had reacted. The crude product was purified by flash chromatography and elution with (5:1) toluene–ethyl acetate to yield title compounds **11c**/**16c** as a dense oil with the diastereoisomeric ratio 25:1 (0.09 g, 23%) (Found: $M^+ - PhSO_2$, 115.0763. $C_6H_{11}O_2$ requires *m/z* 115.0759); ν_{max}(film)/cm^{-1} 3520, 3067, 2966, 2936, 2878, 1448, 1326, 1155 and 754; δ_H(200 MHz) 1.01 (3 H, d, *J* 6.8), 1.02 (3 H, d, *J* 6.8), 1.89 (1 H, sep, *J* 6.8), 2.01 (1 H, br), 3.49 (1 H, dd, *J* 3.3, and 6.2), 3.76 (1 H, dd, *J* 1.8 and 3.3), 4.17 (1 H, d, *J* 1.8), 7.55–7.76 (3 H, m) and 7.82–8.06 (2 H, m); δ_C(50 MHz) 137.1, 134.5, 129.5, 128.7, 73.2, 66.0, 58.8, 32.8, 18.5 and 17.9; *m/z* (EI) 143 ($PhSO_2H_2^+$, 18%), 125 (PhSO, 40), 115 ($M^+ - PhSO_2$, 17) and 43 (100). The yield of compounds **11c**/**16c** was improved substantially (46%) by the use of excess of reagent [derived from *tert*-butyl hydroperoxide (3.3 mol equiv.) and butyllithium (2.4 mol equiv.)] at −20 °C for 4 h. The ratio of stereoisomers was unchanged.

(trans)-2-*Phenylsulfonyl*-3-[1′-(*triphenylsiloxy*)*ethyl*]*oxirane* **12a**/**17a**. Initial mass of starting material **7a** (0.44 g, 0.94 mmol). The flask was warmed to 0 °C and left for 30 min, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (10:1) toluene–ethyl acetate, to yield *title compounds* **12a**/**17a** as a solid with the diastereoisomeric ratio 3:1 (0.35 g, 77%), m.p. 91–93 °C (Found: C, 69.2; H, 5.4. $C_{28}H_{26}O_4SSi$ requires C, 69.1; H, 5.4%); ν_{max}(KBr)/cm^{-1} 3069, 2963, 2936, 2879, 1448, 1312, 1148 and 739; δ_H(200 MHz) 1.22_{maj} and 1.24_{min} (3 H, 2 d, J_{maj} 6.4, J_{min} 6.5), 3.64_{min} and 3.73_{maj} (1 H, 2 dd, J_{maj} 1.7 and 4.2, J_{min} 1.6 and 3.2), 4.01–4.09 (1 H, m), 4.00_{min} and 4.10_{maj} (1 H, 2 d, J_{maj} 1.7, J_{min} 1.6) and 7.29–8.11 (20 H, m); δ_C(50 MHz) (major) 138.0, 135.6, 133.7, 130.4, 129.1, 128.4, 128.1, 127.9, 67.6, 66.6, 61.3 and 20.3; (minor) 137.1, 135.3, 133.7, 129.5, 128.8, 128.2, 128.1, 125.5, 66.2, 65.8, 60.6 and 20.5; *m/z* (EI) 409 ($M^+ - C_6H_5$, 90%), 365 (100), 323 (90), 267 (100), 259 (100), 125 (60) and 77 (90).

(trans)-2-*Phenylsulfonyl*-3-[1′-(*triphenylsiloxy*)*butyl*]*oxirane* **12b**/**17b**. Initial mass of starting material **7b** (0.71 g, 1.42 mmol). The flask was warmed to 0 °C and left for 1 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (10:1) toluene–ethyl acetate, to yield an oil (0.52 g, 71%), which solidified to compounds **12b**/**17b** as a waxy solid with time, m.p. 51–86 °C, with the diastereoisomeric ratio 2:1; ν_{max}(film)/cm^{-1} 3069, 2961, 2934, 2879, 1448, 1312, 1148 and 743; δ_H(200 MHz) 0.74_{maj} and 0.78_{min} (3 H, 2 t, J_{maj} and J_{min} 7.2), 1.22–1.79 (4 H, m), 3.67_{min} and 3.77_{maj} (1 H, 2 dd, J_{maj} 1.5 and 3.2, J_{min} 1.8 and 3.2), 3.78–3.84 (1 H, m), 4.00_{min} and 4.03_{maj} (1 H, 2 d, J_{maj} 1.5, J_{min} 1.8) and 7.29–8.04 (20 H, m); δ_C(50 MHz) (major) 137.0, 135.7, 135.0, 134.3, 130.3, 129.3, 128.6, 127.9, 71.5, 66.7, 60.2, 36.8, 18.1 and 13.9; (minor) 137.1, 135.5, 134.4, 133.7, 130.1, 129.3, 128.8, 127.7, 69.3, 65.5, 59.7, 36.7, 17.4 and 14.0; *m/z* (EI) 437 ($M^+ - C_6H_5$, 2), 365 (10), 295 (100), 259 (90), 125 (30) and 77 (40).

(trans)-2-(2′-*Methyl*-1′-(*triphenylsiloxy*)*propyl*]-3-(*phenylsulfonyl*)*oxirane* **12c**/**17c**. Initial mass of starting material **7c** (0.61 g, 1.22 mmol). The flask was warmed to room temperature for 1 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (6:1) toluene–ethyl acetate, to yield an oil (0.50 g, 79%) which solidified with time to give the *title compounds* **12c**/**17c**, m.p. 119–124 °C, with the diastereoisomeric ratio 1:25 (Found: C, 70.3; H, 5.8. $C_{39}H_{30}O_4SSi$ requires C, 70.0; H, 5.9%); ν_{max}(film)/cm^{-1} 3071, 2966, 2932, 2878, 1448, 1327, 1155 and 743; δ_H(200 MHz) 0.96 (3 H, d, *J* 7.0), 0.99 (3 H, d, *J* 7.0), 1.86 (1 H, dsep, *J* 1.7 and 7.0), 3.68 (1 H, dd, *J* 1.7 and 3.0), 3.87 (1 H, dd, *J* 1.7 and 3.0), 3.96 (1 H, d, *J* 1.7) and 7.29–7.86 (20 H, m); δ_C(50 MHz) 137.3, 135.6, 135.1, 134.1, 133.6, 129.3, 128.6, 127.8, 73.7, 65.4, 58.1, 32.5, 17.8 and 17.2; *m/z* (EI) 515 (MH^+, 10%), 437 (20), 365 (30), 295 (60), 259 (100), 125 (50) and 77 (30).

(trans)-2-[1′-(tert-*Butyldiphenylsiloxy*)*ethyl*]-3-(*phenylsulfonyl*)*oxirane* **13a**/**18a**. Initial mass of starting material **8a** (0.18 g, 0.41 mmol). The flask was warmed to room temperature for 1 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield title compounds **13a**/**18a** as a dense oil with the diastereoisomeric ratio 4:1 (0.12 g, 64%); ν_{max}(film)/cm^{-1} 3067, 2961, 2934, 2895, 1430, 1329, 1153 and 743; δ_H(200 MHz) 1.02_{min} and 1.04_{maj} (9 H, 2 s), 1.11_{maj} and 1.14_{min} (3 H, 2 d, J_{maj} 6.4, J_{min} 6.5), 3.56_{min} and 3.70_{maj} (1 H, 2 dd, J_{maj} 1.7 and 4.6, J_{min} 1.6 and 3.7), 3.80–3.90 (1 H, m), 3.93_{min} and 4.07_{maj} (1 H, 2 d, J_{maj} 1.7, J_{min} 1.6) and 7.31–7.94 (15 H, m); δ_C(50 MHz) (major) 136.1, 135.9, 135.3, 134.5, 132.6, 129.7, 129.5, 127.8, 66.6, 66.1, 60.6, 27.0, 20.8 and 20.0; *m/z* (EI) 409 ($M^+ - C_4H_9$, 20%), 365 (25), 267 (100), 227 (15), 125 (50) and 77 (25).

(trans)-2-[1′-(tert-*Butyldiphenylsiloxy*)*butyl*]-3-(*phenylsulfonyl*)*oxirane* **13b**/**18b**. Initial mass of starting material **8b** (0.51 g, 1.07 mmol). The flask was warmed to room temperature for 4 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (25:1) toluene–ethyl acetate, to yield title compounds **13b**/**18b** as a dense oil with the diastereoisomeric ratio 2:1 (0.35 g, 66%) (Found: $M^+ - C_4H_9$, 437.1272. $C_{24}H_{25}O_4SSi$ requires *m/z*, 437.1243); ν_{max}(film)/cm^{-1} 3071, 2959, 2932, 2858, 1448, 1329, 1155, 999 and 743; δ_H(200 MHz) 0.69_{maj} and 0.75_{min} (3 H, 2 t, J_{maj} 7.0, J_{min} 7.1), 1.02_{min} and 1.05_{maj} (9 H, 2 s), 1.16–1.60 (4 H, m), 3.55–3.64 (1 H, m), 3.75_{maj} and 3.81_{min} (1 H, 2 dd, J_{maj} 1.7 and 5.8, J_{min} 1.5 and 4.4), 3.92_{min} and 4.01_{maj} (1 H, 2 d, J_{maj} 1.7, J_{min} 1.5) and 7.31–7.92 (15 H, m); δ_C(50 MHz) (major) 137.1, 135.8, 134.4, 133.4, 129.4, 128.8, 127.7, 127.7, 71.7, 66.7, 60.3, 36.8, 26.9, 19.4, 17.9 and 13.9; (minor) 136.0, 135.0, 133.0, 129.9, 129.8, 129.3, 128.7, 127.3, 69.1, 66.0, 59.5, 36.7, 26.4, 19.0, 16.9 and 14.1; *m/z* (EI) 494 (M^+, 1%), 437 (5), 365 (20), 295 (100), 199 (40), 125 (20) and 77 (20).

(trans)-2-[1′-(tert-*Butyldiphenylsiloxy*)-2′-*methylpropyl*]-3-(*phenylsulfonyl*)*oxirane* **13c**/**18c**. Initial mass of starting material **8c** (0.25 g, 0.52 mmol). The flask was warmed to room temperature for 4 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield *title compounds* **13c**/**18c** as a solid with the diastereoisomeric ratio 1:25 **13c**/**18c** (0.23 g, 89%), m.p. 109–112 °C (Found: C, 67.8; H, 6.9. $C_{28}H_{34}O_4SSi$ requires C, 68.0; H, 6.9%); ν_{max}(KBr)/cm^{-1} 3071, 2966, 2932, 2858, 1448, 1329, 1155 and 743; δ_H(200 MHz) 0.86 (3 H, d, *J* 7.0), 0.97 (3 H, d, *J* 7.0), 1.03 (9 H, s), 1.86 (1 H, dsep, *J* 2.0 and 7.0), 3.29–3.66 (2 H, m), 3.86 (1 H, d, *J* 1.3) and 7.29–7.90 (15 H, m); δ_C(50 MHz) 136.1, 135.2, 134.3, 132.7, 129.9, 129.3, 128.7, 127.6, 73.6, 65.9, 57.5, 32.6, 27.0, 19.4, 17.4 and 16.8; *m/z* (EI) 437 ($M^+ - C_4H_9$, 25%), 365 (20), 295 (100), 256 (40), 199 (100), 125 (30) and 77 (20).

(trans)-2-*Phenylsulfonyl*-3-[1′-(*triisopropylsiloxy*)*ethyl*]*oxirane* **14a**/**19a**. Initial mass of starting material **9a** (0.12 g, 0.32 mmol). The flask was warmed to 0 °C for 2 h, whereupon all

starting material had reacted. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield compounds **14a**/**19a** as a dense oil with the diastereoisomeric ratio 10:1 (0.12 g, 94%) (Found: $M^+ - C_3H_7$, 341.1294. $C_{16}H_{25}O_4SSi$ requires *m/z*, 341.1243); ν_{max}(film)/cm^{-1} 3067, 2962, 2945, 2893, 2868, 1448, 1329, 1155, 745; δ_H(200 MHz) 1.03$_{min}$ and 1.04$_{maj}$ (21 H, 2 br s), 1.29 (3 H, d, *J* 6.4), 3.58$_{min}$ and 3.67$_{maj}$ (1 H, 2 dd, J_{maj} 1.7 and 4.7, J_{min} 1.4 and 2.5), 3.95$_{maj}$ and 3.99$_{min}$ (1 H, 2 dq, J_{maj} 4.7 and 6.4, J_{min} 2.5 and 6.4), 4.08$_{maj}$ and 4.17$_{min}$ (1 H, 2 d, J_{maj}, 1.7, J_{min} 1.4), 7.55–7.71 (3 H, m) and 7.91–7.96 (2 H, m); δ_C(50 MHz) (major) 136.4, 134.4, 129.4, 128.7, 67.0, 66.5, 61.7, 20.5, 18.0 and 12.2; (minor) 136.7, 134.2, 129.4, 128.7, 67.0, 65.4, 60.9, 20.8, 17.9 and 12.2; *m/z* (EI) 341 ($M^+ - C_3H_7$, 2%), 325 (20), 297 (30), 199 (100), 125 (60) and 77 (50).

(trans)-2-*Phenylsulfonyl*-3-[1′-(*triisopropylsiloxy*)*butyl*]-*oxirane* **14b**/**19b**. Initial mass of starting material **9b** (0.44 g, 1.11 mmol). The flask was warmed to room temperature for 1 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield *title compounds* **14b**/**19b** as a solid with the diastereoisomeric ratio 4:1 **14b**/**19b** (0.42 g, 92%), m.p. 47–48 °C (Found: C, 60.9; H, 9.0. $C_{21}H_{36}O_4SSi$ requires C, 61.1; H, 8.8%); ν_{max}(KBr)/cm^{-1} 3067, 2964, 2943, 2868, 1448, 1329, 1155 and 748; δ_H(200 MHz) 0.94 (3 H, t, *J* 7.2), 1.04$_{min}$ and 1.05$_{maj}$ (21 H, 2 br s), 1.35–1.65 (4 H, m), 3.59–3.70 (2 H, m), 4.04$_{maj}$ and 4.17$_{min}$ (1 H, 2 d, J_{maj} 1.4, J_{min} 1.7), 7.55–7.75 (3 H, m) and 7.91–7.96 (2 H, m); δ_C(50 MHz) (major) 134.3, 129.3, 128.8, 128.7, 71.5, 66.9, 60.7, 37.6, 18.0, 17.8, 14.4 and 12.4; (minor) 134.4, 129.4, 128.8, 128.5, 71.6, 67.7, 59.7, 37.4, 18.0, 16.8, 14.3 and 12.6; *m/z* (EI) 413 (MH^+, 10%), 369 (60), 227 (100), 125 (20), and 77 (10).

(trans)-2-[2′-*Methyl*-1′-(*triisopropylsiloxy*)*propyl*]-3-(*phenylsulfonyl*)*oxirane* **14c**/**19c**. Initial mass of starting material **9c** (0.25 g, 0.63 mmol). The flask was warmed to room temperature overnight whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (30:1) toluene–ethyl acetate, to yield *title compounds* **14c**/**19c** as a solid with the diastereoisomeric ratio 1:25 (0.25 g, 96%), m.p. 95–98 °C (Found: C, 60.9; H, 9.0%); ν_{max}(KBr)/cm^{-1} 3067, 2964, 2943, 2868, 1448, 1155 and 999; δ_H(200 MHz) 1.01 (27 H, br s), 1.96 (1 H, dsep, *J* 3.6 and 7.0), 3.58 (1 H, dd, *J* 1.8 and 4.0), 4.00 (1 H, dd, *J* 3.6 and 4.0), 4.19 (1 H, d, *J* 1.8), 7.56–7.71 (3 H, m) and 7.92–7.97 (2 H, m); δ_C(50 MHz) 134.4, 129.4, 128.9, 128.7, 72.0, 65.5, 57.7, 33.3, 18.0, 17.8, 16.5 and 12.6; *m/z* (EI) 413 (M^+, 2%), 369 (2), 227 (80), 125 (50), 77 (60) and 75 (100).

(trans)-2-[1′-(2″-*Methoxyethoxymethoxy*)*ethyl*]-3-(*phenylsulfonyl*)*oxirane* **15a**/**20a**. Initial mass of starting material **10a** (0.50 g, 1.66 mmol). The flask was warmed to 0 °C and left for 1 h, whereupon all starting material had reacted. The crude material was purified and the diastereoisomers were separated by flash chromatography with (10:1) toluene–ethyl acetate as eluent, to yield the major diastereoisomer **20a** as a dense orange oil (0.22 g, 44%) and the *minor diastereoisomer* **15a** also as a dense orange oil (0.11 g, 19%) (Found for **20a**: MH^+, 317.1040. $C_{14}H_{21}O_6S$ requires *m/z*, 317.1059); ν_{max}(film)/cm^{-1} 3067, 2978, 2932, 2891, 1327, 1155 and 754; δ_H(200 MHz) (major) 1.28 (3 H, d, J_{maj} 6.5), 3.40 (3 H, s), 3.51–3.77 (5 H, m), 3.91 (1 H, dq, J_{maj} 2.3 and 6.5), 4.19 (1 H, d, J_{maj} 1.7), 4.67 (2 H, s), 7.58–7.76 (3 H, m) and 7.87–7.97 (2 H, m); (minor) 1.30 (3 H, d, J_{min} 6.4), 3.38 (3 H, s), 3.51–3.76 (5 H, m), 3.81 (1 H, dq, J_{min} 2.5 and 6.4), 4.08 (1 H, d, J_{min} 1.7), 4.73 (1 H, d, J_{min} 6.4), 4.77 (1 H, d, J_{min} 6.4), 7.56–7.75 (3 H, m) and 7.87–7.96 (2 H, m); δ_C(50 MHz) (major) 136.7, 134.5, 129.4, 129.1, 95.8, 71.7, 70.3, 67.3, 66.8, 60.1, 59.3 and 17.6; (minor) 136.6, 134.2, 129.1, 128.4, 93.8, 71.8, 68.8, 67.1, 66.0, 60.9, 59.0 and 17.1; *m/z* (EI) 317 (MH^+, 20%), 241 (20), 145 (30), 125 (70), 77 (55) and 59 (100).

(trans)-2-[1′-(2″-*Methoxyethoxymethoxy*)*butyl*]-3-(*phenylsulfonyl*)*oxirane* **15b**/**20b**. Initial mass of starting material **10b** (0.68 g, 2.07 mmol). The flask was warmed to 0 °C and left for 2 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (10:1) toluene–ethyl acetate, to yield *title compounds* **15b**/**20b** as a dense yellow oil with the diastereoisomeric ratio 1:5 (0.46 g, 65%) (Found: MH^+, 345.1319. $C_{16}H_{25}O_6S$ requires *m/z*, 345.1372); ν_{max}(film)/cm^{-1} 3065, 2934, 2876, 1327, 1157 and 754; δ_H(200 MHz) 0.94$_{maj}$ and 0.96$_{min}$ (3 H, 2 t, J_{maj} and J_{min} 7.2), 1.25–1.71 (4 H, m), 3.37$_{maj}$ and 3.38$_{min}$ (3 H, 2 s), 3.40–3.79 (6 H, m), 4.03$_{min}$ and 4.19$_{maj}$ (1 H, 2 d, J_{maj} 1.5, J_{min} 1.8), 4.62$_{maj}$, 4.69 $_{maj}$ and 4.73$_{min}$ (2 H, 2 d and s, J_{maj} 7.1), 7.51–7.75 (3 H, m) and 7.86–7.96 (2 H, m); δ_C(50 MHz) (major) 137.1, 134.5, 129.4, 128.8, 95.1, 74.6, 71.7, 67.5, 60.1, 58.6, 34.6, 34.1, 18.0 and 13.9; (minor) 137.0, 134.5, 129.3, 127.6, 95.7, 75.7, 72.6, 66.1, 59.4, 59.0, 36.7, 33.4, 18.4 and 14.0; *m/z* (EI) 345 (MH^+, 3%), 325 (1), 289 (2), 252 (8), 125 (80), 77 (80) and 59 (100).

(trans)-2-[1′-(2″-*Methoxyethoxymethoxy*)-2′-*methylpropyl*]-3-(*phenylsulfonyl*)*oxirane* **15c**/**20c**. Initial mass of starting material **10c** (0.32 g, 0.98 mmol). The flask was warmed to room temperature for 2 h, whereupon all starting material had reacted. The crude material was purified by flash chromatography and elution with (10:1) toluene–ethyl acetate, to yield *title compounds* **15c**/**20c** as a dense oil with the diastereoisomeric ratio 1:25 (0.19 g, 55%) (Found: MH^+, 345.1314); ν_{max}(film)/cm^{-1} 3071, 2966, 2932, 2878, 1448, 1327, 1155 and 754; δ_H(200 MHz) 1.00 (3 H, d, *J* 6.9), 1.02 (3 H, d, *J* 6.9), 1.96 (1 H, dsep, *J* 2.3 and 6.9), 3.36 (3 H, s), 3.51–3.70 (6 H, m), 4.22 (1 H, d, *J* 1.6), 4.62 (1 H, d, *J* 7.1), 4.68 (1 H, d, *J* 7.1), 7.57–7.73 (3 H, m) and 7.92–7.96 (2 H, m); δ_C(50 MHz) 137.2, 134.5, 129.4, 128.7, 95.6, 77.1, 71.7, 67.4, 66.0, 59.0, 57.4, 31.3, 19.0 and 18.3; *m/z* (EI) 345 (MH^+, 10%), 327 (2), 289 (12), 125 (60), 89 (100) and 77 (80).

Potassium Hydride Epoxidations. General Procedure.—Potassium hydride (0.15 cm^3, 1.5 mmol; 35% w/v) and THF (10 cm^3) were placed in a flask flushed with nitrogen. The flask was cooled to 0 °C, *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 substrate (1.00 mmol) in THF (10 cm^3) was added (temperature is not allowed to exceed −70 °C). The flask was then allowed to warm to 0 °C, and 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 washed with ethyl acetate (2 × 15 cm^3), and the extract was dried, and concentrated under reduced pressure.

Sodium Hydroxide–Hydrogen Peroxide Epoxidations: General Procedure.—The vinyl sulfone substrate (1.00 mmol) was placed in a flask under nitrogen. Dichloromethane (1 cm^3) and methanol (3 cm^3) were added and the flask was then cooled to 0 °C, when hydrogen peroxide (0.25 cm^3, 3.00 mmol; 30%) and sodium hydroxide (0.50 cm^3, 1.50 mmol; 3 mol dm^{-3}) were also added. The reaction mixture was warmed to room temperature and was stirred until there was no starting material present. The organic phase was quenched with water (~30 cm^3) and extracted with dichloromethane (3 × 15 cm^3), and the extract was dried, and concentrated under reduced pressure.

(1RS,2RS,3SR,4SR)-3,4-*Isopropylidenedioxy*-1-*phenylsulfonyl*-1,2-*epoxycyclopentane* **22**.—A solution of (3RS,4SR)-3,4-isopropylidenedioxy-1-(phenylsulfonyl)cyclopentene **21**[19] (0.646 g, 2.31 mmol) in THF (10 cm^3) was added to a solution of lithium *tert*-butyl peroxide, prepared by addition of butyllithium (1.95 cm^3, 2.54 mmol; 1.3 mol dm^{-3} in hexanes) to

Table 3 Crystallographic data

Compound	**12a**	**19c**	**22**
Formula	$C_{28}H_{26}O_4SSi$	$C_{21}H_{36}O_4SSi$	$C_{14}H_{16}O_5S$
M	486.6	412.7	296.3
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	11.6415(11)	8.192(2)	8.410(2)
b/Å	7.8523(8)	11.734(3)	9.047(2)
c/Å	28.092(3)	13.236(3)	9.915(2)
α/°		109.15(2)	99.552(11)
β/°	91.372(13)	100.832(14)	91.07(2)
γ/°		95.646(14)	106.19(2)
V/Å^3	2567.2(4)	1162.8(5)	712.8(3)
Z	4	2	2
D_c/g cm^{-3}	1.259	1.179	1.381
Radiation, λ/Å	Mo-Kα, 0.710 73	Mo-Kα, 0.710 73	Cu-Kα, 1.541 84
μ/mm^{-1}	0.204	0.213	2.177
F(000)	1024	448	312
Temperature/K	295	240	295
Crystal size/mm	0.52 × 0.48 × 0.20	0.36 × 0.32 × 0.28	0.56 × 0.56 × 0.46
No. reflections for cell	32	32	32
$2\theta_{max}$/°	50	50	130
Maximum indices hkl	13, 9, 33	9, 13, 15	9, 10, 11
Reflections measured	5842	4108	2671
Unique reflections	4523	4108	2373
R_{int}	0.0933	0.0	0.1302
Weighting parameters a, b	0.0628, 1.7974	0.0448, 0.6400	0.1026, 0.4648
Extinction coefficient x	0	0	0.020(2)
No. of refined parameters	308	252	184
$wR2$ (all data)	0.1865	0.1224	0.1943
$R1$ ('observed' data)	0.0539	0.0390	0.0607
Goodness-of-fit	1.080	1.071	1.077
Max., min. electron density: e Å^{-3}	0.634, −0.323	0.302, −0.268	0.652, −0.521

tert-butyl hydroperoxide (0.95 cm^3, 3.47 mmol; 3.6 mol dm^{-3} in toluene) in THF (20 cm^3). The reaction mixture was allowed to react at −15 °C for 16 h, and then worked up by extraction with diethyl ether in the usual way. Removal of solvent gave the oxirane **22** (0.61 g, 90%) as a crystalline solid, m.p. 120–122 °C (from diethyl ether–light petroleum); ν_{max}(KBr disk)/cm^{-1} 2987, 2936, 1378, 1324, 1219, 1166 and 1092; δ_H(300 MHz) 1.29 (3 H, s), 1.47 (3 H, s), 2.24 (1 H, dd, J 6.0 and 15.1), 2.55 (1 H, d, J 15.1), 4.09 (1 H, s), 4.53 (1 H, d, J 5.5), 4.59 (1 H, dd, J 5.5 and 6.0), 7.57–7.62 (2 H, m), 7.68–7.73 (1 H, m), 7.90–7.94 (2 H, m); m/z (FAB) 297 (MH^+, 35%), 281 (M^+ − Me, 32) and 125 (100).

X-Ray Crystallography.—Crystal data for compounds **12a**, **19c** and **22** are given in Table 3, together with information on procedures for data collection and structure determination. Instrumentation, methods and definitions were as previously described,[21] with refinement on F^2. Absorption corrections were not applied, and extinction effects were significant only for compound **22**. Atomic scattering factors were taken from ref. 22. 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.

References

1 M. Ashwell, W. Clegg and R. F. W. Jackson, *J. Chem. Soc., Perkin Trans. 1*, 1991, 897; S. F. C. Dunn and R. F. W. Jackson, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2863.
2 R. F. W. Jackson, S. P. Standen, W. Clegg and A. McCamley, preceding paper.
3 R. F. W. Jackson, S. P. Standen and W. Clegg, *Tetrahedron Lett.*, 1991, **32**, 5393.
4 For some representative experimental work, see: (*a*) Y. Yamamoto, Y. Chounan, S. Nishii, T. Ibuka and H. Kitahara, *J. Am. Chem. Soc.*, 1992, **114**, 7652; (*b*) M. Larchevêque, G. Tamagnan and Y. Petit, *J. Chem. Soc., Chem. Commun.*, 1989, 31; M. T. Reetz and D. Röhrig, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1706; A. Bernardi, S. Cardani, C. Scolastico and R. Villa, *Tetrahedron*, 1990, **46**, 1987; J. Leonard, S. Mohialdin, D. Reed and M. F. Jones, *Synlett*, 1992, 741; A. G. M. Barrett and S. A. Lebold, *J. Org. Chem.*, 1990, **55**, 3853; C. A. Ibarra, M. S. A. Pérez, I. de Castro and M. J. Fernandez, *J. Chem. Soc., Perkin Trans. 2*, 1991, 467; I. Jako, P. Uiber, A. Mann, C.-G. Wermuth, T. Boulanger, B. Norberg, G. Evrard and F. Durant, *J. Org. Chem.*, 1991, **56**, 5729; K. A. Swiss, W. Hinkley, C. A. Maryanoff and D. C. Liotta, *Synthesis*, 1992, 127; V. L. Patrucinio, P. R. R. Costa and C. R. D. Correia, *Synthesis*, 1994, 474; A. Dondoni, A. Marra and P. Merino, *J. Am. Chem. Soc.*, 1994, **116**, 3324. For earlier references, see those cited in refs. 6(*a*) and 6(*b*) below.
5 For a recent general discussion, see: P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press, Oxford, 1992, p. 20.
6 For theoretical discussions, see: A. E. Dorigo and K. Morokuma, *J. Am. Chem. Soc.*, 1989, **111**, 6524; A. Bernardi, A. M. Capelli, C. Gennari and C. Scolastico, *Tetrahedron: Asymmetry*, 1990, **1**, 21.
7 P. L. Fuchs and T. F. Braish, *Chem. Rev.*, 1986, **86**, 903.
8 M. Kitamura, M. Isobe, Y. Ichikawa and T. Goto, *J. Org. Chem.*, 1984, **49**, 3517; M. Isobe, Y. Ichikawa, Y. Funabashi, S. Mio and T. Goto, *Tetrahedron*, 1986, **42**, 2863; Y. Ichikawa, M. Isobe, D. Bai and T. Goto, *Tetrahedron*, 1987, **43**, 4737.
9 (*a*) C. Alcaraz, J. C. Carretero and E. Domínguez, *Tetrahedron Lett.*, 1991, **32**, 1385; (*b*) E. Domínguez and J. C. Carretero, *Tetrahedron Lett.*, 1993, **34**, 5803.

10 (*a*) B. W. Gung, M. A. Wolf, K. Ohm and A. J. Peat, *Tetrahedron Lett.*, 1993, **34**, 1417; (*b*) B. W. Gung, M. A. Wolf and Z. Zhu, *J. Org. Chem.*, 1993, **58**, 3350; (*c*) B. W. Gung and M. B. Francis, *J. Org. Chem.*, 1993, **58**, 6177; (*d*) B. W. Gung and M. A. Wolf, *J. Org. Chem.*, 1993, **58**, 7038.
11 M. T. Reetz and E. H. Lauterbach, *Tetrahedron Lett.*, 1991, **32**, 4477.
12 S. Cardani, A. Bernardi, L. Colombo, C. Gennari, C. Scolastico and I. Venturini, *Tetrahedron*, 1988, **44**, 5563.
13 K. Yamamoto and N. Yamamoto, *Chem. Lett.*, 1989, 1149.
14 O. Meth-Cohn, C. Moore and H. C. Taljaard, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2663.
15 M. Chérest, H. Felkin and N. Prudent, *Tetrahedron Lett.*, 1968, 2199; M. Chérest and H. Felkin, *Tetrahedron Lett.*, 1968, 2205; N. T. Anh, *Top. Curr. Chem.*, 1980, **88**, 145.
16 E. Domínguez and J. C. Carretero, *Tetrahedron*, 1990, **46**, 7197.
17 B. M. Trost and T. A. Grese, *J. Org. Chem.*, 1991, **56**, 3189.
18 N. J. Hindley and R. F. W. Jackson, paper presented at the symposium in honour of Prof. R. A. Raphael, Cambridge, 22nd July, 1988.
19 M. H. Nantz, X. Radisson and P. L. Fuchs, *Synth. Commun.*, 1987, **17**, 55.
20 C. T. Hewkin, R. F. W. Jackson and W. Clegg, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3091.
21 P. L. Bailey, C. T. Hewkin, W. Clegg and R. F. W. Jackson, *J. Chem. Soc., Perkin Trans. 1*, 1993, 577.
22 *International Tables for Crystallography*, ed. A. J. C. Wilson, vol C, Tables 4.2.6.8 and 6.1.1.4, Kluwer Academic, Dordrecht, 1992.

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