Phenylsulphonyloxiranes as Functionalised Acyl Anion Equivalents in Organic Synthesis

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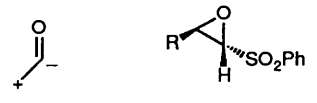
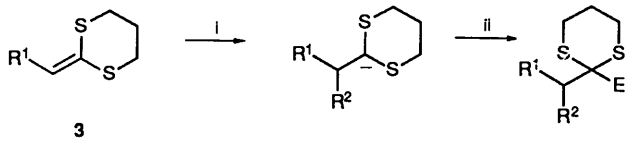
Phenylsulphonyloxiranes can be lithiated with butyllithium α to the phenylsulphonyl group at low temperature. The anions formed are unstable, but sufficiently reactive to allow the isolation of adducts in good yield following treatment with a variety of electrophiles. Reaction of functionalised phenylsulphonyloxiranes with magnesium bromide–diethyl ether at room temperature allows the preparation of synthetically useful α-bromo ketones with complete regiocontrol.

Since the initial reports on the development of Umpolung reagents for organic synthesis,[1] an immense amount of effort has been devoted to exploring their potential.[2] Arguably the most important general class of such reagents are those which function as acyl anion equivalents. Particularly useful examples of this class also incorporate additional functionality.[3] One example is an acyl anion equivalent with α-cationic reactivity, which is then equivalent to the dipolar synthon **1**. This synthon has reversed polarity to that in a normal carbonyl compound, and therefore development of effective reagents for synthon **1** and analogues is potentially important in synthesis. We now report in full our initial efforts to use phenylsulphonyloxiranes **2** as synthetic equivalents for the dipolar synthon **1**.[4]

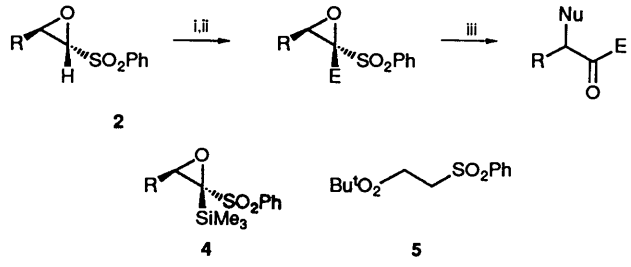
The most widely used approach to synthon **1** has employed ketene thioacetals (especially 2-alkylidene-1,3-dithianes **3**),[5,6] and related compounds in which the sulphur atom has been oxidised.[7] Initial nucleophilic attack of an alkyllithium reagent is then followed by reaction of the lithio anion with an electrophile (Scheme 1).





Scheme 1 *Reagents:* i, R^1Li; ii, electrophile

We wished to develop a complimentary approach, in which anion formation and addition of the electrophile would precede introduction of the nucleophilic reagent. Phenylsulphonyloxiranes **2** appeared to be ideal candidates for this purpose (Scheme 2). An initial report showed that treatment of 3-phenyl-2-phenylsulphonyloxirane with sodium methoxide in MeOD gave clean deuteriation α to the phenylsulphonyl group.[8] In more recent studies, Eisch and Galle have shown that oxiranes substituted with phenylsulphonyl groups could be deprotonated under aprotic conditions, and the anions then quenched with very reactive electrophiles (D_2O, MeI, Me_3SiCl), although only two substrates were examined.[9] The reactivity of phenylsulphonyloxiranes towards nucleophiles has been more extensively studied.[9–16] Generally, attack of the nucleophile at the carbon (C-3) not substituted by the phenylsulphonyl group is observed. Subsequently, the tetrahedral intermediate breaks down leading to formation of a carbonyl compound. Thus the carbonyl group is formed as a result of nucleophilic attack, thereby avoiding the problems associated with the deprotection of a masked carbonyl group. Interestingly, there is one report of opposite regioselectivity when Gassman's nucleophilic hydroxide reagent is used (*i.e.* attack at C-2),[13] and also some indication that amine nucleophiles may be able to attack at C-2.[14] Indeed, we have observed formation of products derived from competing attack at both C-2 and C-3 in reactions of magnesium bromide with 2-phenylsulphonyl-2-trimethylsilyloxiranes **4**.[17]



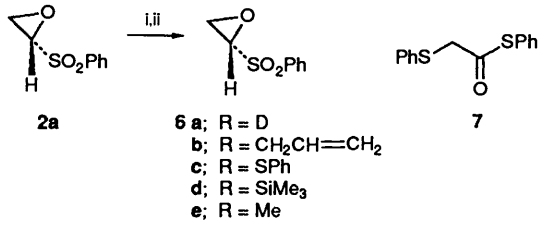
Scheme 2 *Reagents:* i, BuLi; ii, electrophile; iii, nucleophile

There are two useful approaches to the preparation of phenylsulphonyloxiranes. The first involves Darzens reaction between chloromethyl phenyl sulphone and a carbonyl compound.[8,18,19] Subsequently, a modification of this procedure employing phase transfer catalysis was introduced by Makosza,[20] and this is the method of choice when applicable. The second approach involves nucleophilic epoxidation of phenyl vinyl sulphones,[21–23] which can in several cases allow the preparation of compounds not available by the Darzens method. We were particularly interested in the use of phenylsulphonyloxirane **2a** itself, which can be conveniently prepared from phenyl vinyl sulphone using lithium *tert*-butyl hydroperoxide as the nucleophilic oxidant.[23] The use of this reagent appears to be essential since epoxidation using *tert*-butyl hydroperoxide in the presence of Triton-B yields only the peroxide **5**.[24]

Electrophilic Substitution Reactions of Phenylsulphonyloxiranes.—In practice, treatment of phenylsulphonyloxirane **2a** in THF (tetrahydrofuran) at −102 °C with butyllithium gave a pale yellow solution of the corresponding lithio anion. Immediate quenching of the anion with D_2O (5 equiv. in THF) at −102 °C led to good recovery of the corresponding deuteriated oxirane **6a** (83%). However, it rapidly became apparent that the anion was unstable, even at this temperature, and that only highly reactive electrophiles could be efficiently employed. For example, addition of allyl bromide gave the

corresponding substituted oxirane **6b** in an optimised yield of 33%. Attempts to improve this by use of extended reaction times and higher temperatures were unsuccessful. However, use of diphenyl disulphide as the electrophile resulted in formation of *S*-phenyl (phenylthio)thioacetate **7** (71%). Presumably this arose *via* attack of thiophenolate on the oxirane **6c**, which would have been expected to be formed initially. In support of this pathway, we have isolated 3-isopropyl-2-phenylsulphonyl-2-phenylthiooxirane by treatment of the lithio anion derived from 3-isopropyl-2-phenylsulphonyloxirane with diphenyl disulphide,[25] and also the phenylthiooxirane **16e** from the lithio anion of **10b** (*vide infra*). Presumably subsequent ring opening with benzenethiolate is much slower in these cases.

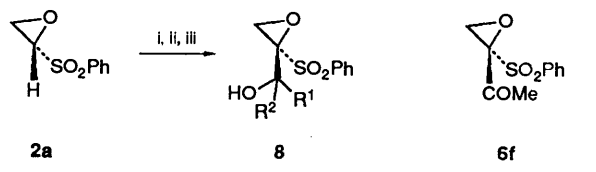
Reaction of the lithio anion of **2a** with chlorotrimethylsilane and iodomethane could be carried out efficiently by *in situ* quenching of the anion. For example, addition of butyllithium to a solution of chlorotrimethylsilane and phenylsulphonyloxirane in THF at −102 °C gave the corresponding trimethylsilyloxirane **6d** in quantitative yield. More surprisingly, use of iodomethane led to the methylated oxirane **6e** (82%) (Scheme 3). Whilst the use of chlorotrimethylsilane as an *in situ* electrophilic quench is well established,[26] the analogous use of methyl iodide appears to be restricted to sulphone anions,[27] which can be formed especially rapidly at low temperatures.



2a **6a**; R = D; **b**; R = $CH_2CH{=}CH_2$; **c**; R = SPh; **d**; R = $SiMe_3$; **e**; R = Me **7**

Scheme 3 *Reagents and conditions:* for **6a–c**, i, BuLi, −102 °C; ii, electrophile; for **6d** and **6e**, i, electrophile; ii, BuLi, −102 °C

Unfortunately, reaction of the lithio anion of **2a** with carbonyl electrophiles was unsatisfactory. For example, addition of benzaldehyde gave the corresponding adduct as a mixture of diastereoisomers in only 25% yield. However, addition of a solution of magnesium bromide in ether–toluene prior to addition of the carbonyl compound[28] allowed the efficient preparation of the corresponding functionalised phenylsulphonyloxiranes **8** (Table 1, Scheme 4). For aldehydes and unsymmetrical ketones a mixture of diastereoisomers is produced. It has not been possible to obtain a pure crystalline sample of a single diastereoisomer for X-ray crystal structure analysis, and it is therefore not possible to assign the relative configurations of the major diastereoisomers. The diastereoisomer ratios (detailed in Table 1) are rather similar to those obtained on reaction of 2-trimethylsilyl substituted oxiranyl anions with aldehydes and non-conjugated or unhindered ketones.[29] Acetylation of **2a** leading to the ketone **6f** (55%)



2a **8** **6f**

Scheme 4 *Reagents and conditions:* i, BuLi, −102 °C; ii, $MgBr_2$, −102 to −90 °C; iii, R^1COR^2, Table 1

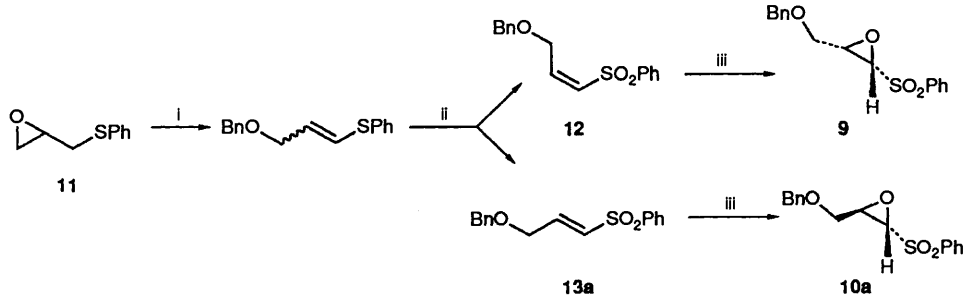
Table 1 Reaction of phenylsulphonyloxirane **2a** with carbonyl compounds

Electrophile	Product	R^1	R^2	Diastereoisomer ratio	Yield (%)
MeCHO	**8a**	Me	H	1.7:1	75
BuCHO	**8b**	Bu	H	1.9:1	75
PhCHO	**8c**	Ph	H	1.5:1	80
MeCOMe	**8d**	Me	Me	—	67
$CH_2[CH_2]_3C{=}O$	**8e**		$[CH_2]_4$	—	77
$CH_2[CH_2]_4C{=}O$	**8f**		$[CH_2]_5$	—	79
MeCOEt	**8g**	Me	Et	1:1	78

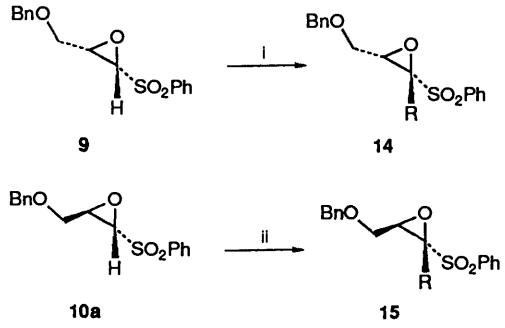
could best be achieved using methyl acetate as electrophile. The role of magnesium bromide in improving the yields of the condensation reaction of the lithio anion of **2a** with carbonyl compounds is debatable. It is conceivable that transmetallation occurs, with formation of the magnesium bromide derivative of phenylsulphonyloxirane. Perhaps more likely, the magnesium bromide functions as a Lewis acid, activating the carbonyl compound towards nucleophilic attack.

Reactions of 3-Hydroxymethyl-2-phenylsulphonyloxirane Derivatives.—In order to use phenylsulphonyloxiranes more generally in synthesis, it is important that other functionality present in the molecule should be compatible with the conditions employed. We have therefore explored the synthesis of oxiranes bearing a hydroxymethyl substituent, since these were the most easily accessible functionalised phenylsulphonyl oxiranes. Both *cis* and *trans* 3-benzyloxymethyl-2-phenylsulphonyloxiranes **9** and **10a** were prepared by the route shown in Scheme 5, starting from 2-(phenylthiomethyl)oxirane **11**.[30] Separation of *cis* and *trans* 3-benzyloxyprop-1-enyl phenyl sulphone **12** and **13a** was effected by careful flash chromatography. Epoxidation of **12** and **13a** using lithium *tert*-butyl hydroperoxide was stereospecific, leading to oxiranes **9** and **10a**, respectively, with none of the other isomer detectable by highfield proton NMR.

Anions derived from **9** and **10a** showed markedly different stability and reactivity (Schemes 6 and 7). Deprotonation of diastereoisomerically pure *cis*-3-benzyloxymethyl-2-phenylsulphonyloxirane **9** with butyllithium at −102 °C in tetrahydrofuran was extremely rapid, occurring within 30 s. Immediate



Scheme 5 *Reagents and conditions:* i, NaH, tetrahydrofuran, reflux, then benzyl bromide, room temp.; ii, *m*-chloroperbenzoic acid, CH_2Cl_2, 0–20 °C, 2 h; ii, Bu^tO_2H, BuLi, −20 °C, 1 h



Scheme 6 *Reagents and conditions:* i, BuLi, tetrahydrofuran, −102 °C, 30 s, then electrophile; ii, BuLi, tetrahydrofuran, −95 °C, 8 min, then electrophile, Table 2

addition of D_2O gave the corresponding *cis* adduct **14a** together with the *trans* adduct **15a** in an approximate ratio of 12 to 1 (Scheme 6, Table 2). However, if addition of the D_2O was delayed (−102 °C, 3 min), the overall yield was reduced and the ratio of *cis* to *trans* adduct decreased to 7 to 1. Immediate addition of other electrophiles gave the corresponding *cis* adducts **14**, together with small amounts of the corresponding *trans* adducts **15**. These results imply that the anion derived from **9** is not configurationally stable even at −102 °C.[31] This is in sharp contrast to anions derived from *cis* trimethylsilyl oxiranes, which are, in almost all cases, configurationally stable.[9,29]

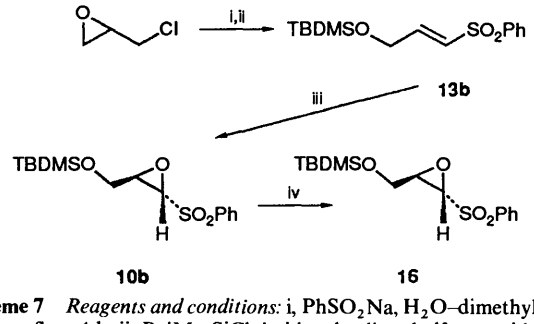
By contrast, efficient anion formation of *trans* 3-benzyloxymethyl-2-phenylsulphonyloxirane **10a** required addition of butyllithium at −95 °C, followed by stirring at the same temperature for 8 min. It is known that deprotonation of *trans*-trialkylsilyloxiranes is also slower than deprotonation of the corresponding *cis* isomers.[9,29] The anion derived from **2a** was configurationally stable, and reacted smoothly on addition of electrophiles to give the *trans* adducts **15** (Scheme 6, Table 2). It is tempting to ascribe the configurational stability of the anion derived from **10a** to internal coordination of the lithium cation by the benzyloxy group, although this may not be the only contributing factor (*vide infra*). It is also possible that the benzyloxy group facilitates epimerisation of the anion derived from **9**.[32]

For synthetic purposes, where ease of removal of the hydroxyl protecting group is a consideration, we chose to prepare *trans*-3-(*tert*-butyldimethylsiloxymethyl)-2-phenylsulphonyloxirane **10b**. Compound **10b** was prepared in three steps, *via* the vinyl sulphone **13b**,[28,33] by the route outlined in Scheme 7, in 68% overall yield. The lithio anion derived from compound **10b** was also configurationally stable, and reacted efficiently with a wide range of electrophiles to give the substituted products **16** in high yield (Table 3). Although methyl iodide reacted efficiently without the addition of a co-solvent, the other alkyl halides (EtI, BuI and $PhCH_2Br$) required the addition of small amounts (4 equiv.) of hexamethylphosphoric triamide (HMPA). This should be contrasted with the behaviour of the lithio anion derived from phenylsulphonyloxirane **2a**, which required addition of magnesium bromide for reaction with carbonyl compounds, and could only be efficiently alkylated with iodomethane. It therefore appears that the *tert*-butyldimethylsiloxymethyl group confers sufficient stability on the lithio anion **10b** that it is a generally useful nucleophile. Since silyl ethers are generally regarded as poorer co-ordinating groups than the corresponding benzyl ethers,[34] the origin of the greater

Table 2 Reactions of the oxiranes **9** and **10a** with electrophiles

Starting material	Electrophile	Product	R	Yield (%)
9	D_2O	**14a**	D	85[a]
9	Me_3SiCl	**14b**	Me_3SiCl	63
9	MeI	**14c**	Me	71
9	MeCHO	**14d**	MeCH(OH)	63[b]
10a	D_2O	**15a**	D	80
10a	Me_3SiCl	**15b**	Me_3SiCl	80
10a	MeI	**15c**	Me	87
10a	MeCHO	**15d**	MeCH(OH)	87[c]

[a] Solvent used was THF–pentane 2:1. [b] Isolated as a 1.5:1 mixture of diastereoisomers. [c] Isolated as a 1.4:1 mixture of diastereoisomers.



Scheme 7 *Reagents and conditions:* i, $PhSO_2Na$, H_2O–dimethylformamide, reflux, 4 h; ii, Bu^tMe_2SiCl, imidazole, dimethylformamide, room temp., 16 h: iii, Bu^tO_2H, BuLi, tetrahydrofuran, −20 °C, 2 h; iv, BuLi, tetrahydrofuran, −95 °C, 8 min, then electrophile, Table 3

Table 3 Reactions of the oxirane **10b** with electrophiles

Electrophile	Product	R	Yield (%)
D_2O	**16a**	D	85
Me_3SiCl	**16b**	Me_3Si	84
MeI	**16c**	Me	79
MeCO	**16d**	MeCH(OH)	85[a]
PhSSPh	**16e**	PhS	76
EtI	**16f**	Et	68[b]
BuI	**16g**	Bu	75[b]
$PhCH_2Br$	**16h**	$PhCH_2$	60[b]
Pr^iCHO	**16i**	$Pr^iCH(OH)$	83[c]
$CH_2[CH_2]_2$–CH=CH–CO	**16j**	$CH_2[CH_2]_2$–CH=CH–C(OH)	73[d]
MeOCOCl	**16k**	MeO_2C	77
EtO_2CCOCl	**16l**	EtO_2CCO	50
O–$[CH_2]_3$–CO	**16m**	$HO[CH_2]_3CO$	76[e]
O–$[CH_2]_4$–CO	**16n**	$HO[CH_2]_4CO$	87[e]

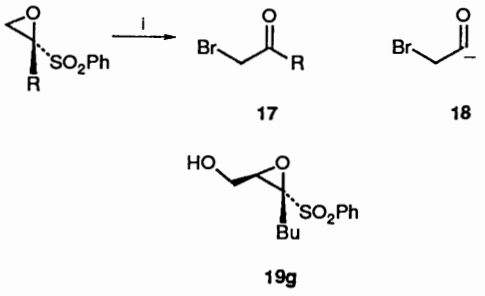
[a] Isolated as a 1.5:1 mixture of diastereoisomers. [b] 4 Equiv. of HMPA were added prior to addition of the electrophile. [c] Chromatographically separable 1.75:1 mixture of diastereoisomers. [d] Chromatographically separable 1.4:1 mixture of diastereoisomers. [e] These compounds exist in solution as mixtures of both possible diastereoisomeric lactols, as well as the open-chain hydroxy ketone.

Table 4 Reaction of substituted phenylsulphonyloxiranes with $MgBr_2$

Substrate	R	Product	Yield (%)
6d	Me_3Si	**17d**	66
6f	COMe	**17f**	64
8a	CH(OH)Me	**17a**	68
8e	$COH(CH_2)_5$	**17e**	80
8g	CMe(OH)Et	**17g**	62

stability of the anions derived from both oxiranes **10a** and **10b** is unclear.

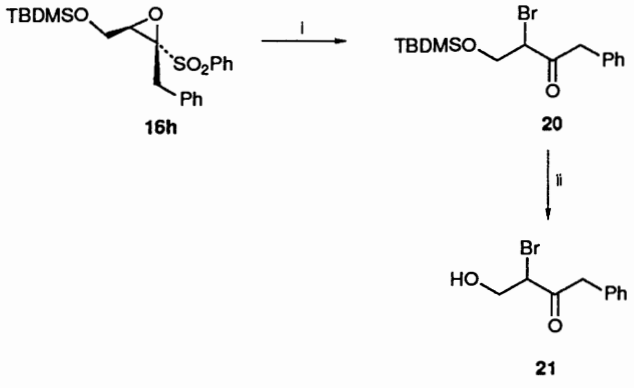
In order to illustrate the potential of the phenylsulphonyloxiranes **6**, **8** and **16** as useful synthetic intermediates, we have employed their reaction with magnesium bromide–diethyl ether in ether to give α-bromo ketones.[10,11] This reaction had previously been applied to phenylsulphonyloxiranes without any additional functionality, although we did not expect any particular difficulty in extending the process to functionalised examples. Indeed, treatment of a selection of the compounds derived from phenylsulphonyloxirane **2a** with magnesium bromide–diethyl ether in diethyl ether gave the corresponding bromomethyl ketones **17** (Scheme 8, Table 4). Thus, phenyl-



Scheme 8 *Reagents and conditions*: $MgBr_2$·Et_2O, ether–toluene, room temp., 2 h, Table 4

sulphonyloxirane **2a** can function as a synthetic equivalent of the α-bromoacetyl anion **18**. Of special note is the reaction of the 2-phenylsulphonyl-2-trimethylsilyloxirane **6d** with $MgBr_2$ to give 2-bromoacetyltrimethylsilane **17d**.[35] We have recently shown that extension of this process to more substituted 2-phenylsulphonyl-2-trimethylsilyloxiranes is possible.[17]

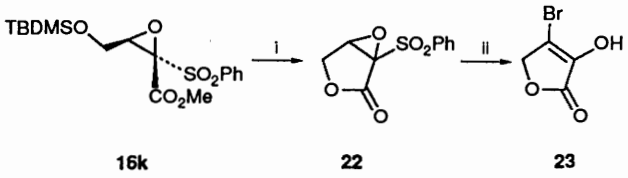
A selection of transformations on the substituted oxiranes **16** has been carried out to demonstrate their utility in synthesis. Removal of the *tert*-butyldimethylsilyl protecting group from the phenylsulphonyloxirane **16g** was cleanly effected by treatment with boron trifluoride–diethyl ether in dichloromethane to give the free alcohol **19g**.[36] It is interesting to note that no competing rearrangement of the phenylsulphonyloxirane to phenylsulphonyl ketone was observed.[37,38] Treat-



Scheme 9 *Reagents and conditions*: i, $MgBr_2$·Et_2O, Et_2O, room temp., 4.5 h; ii, BF_3·Et_2O, CH_2Cl_2, room temp., 2.5 h

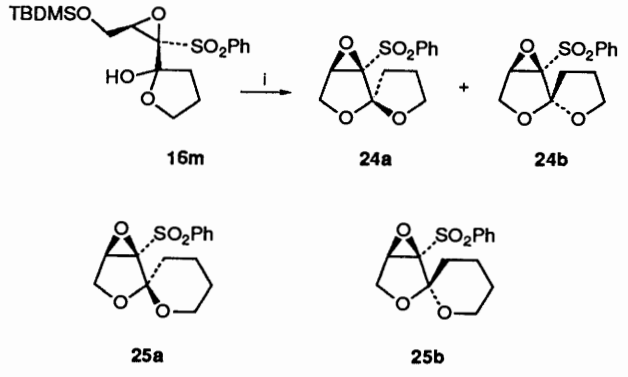
ment of compound **16h** with magnesium bromide in diethyl ether[10] gave the corresponding bromo ketone **20** (85%). Removal of the TBDMS protecting group with boron trifluoride–diethyl ether in dichloromethane gave the bromohydrin **21** (70%), without affecting the α-bromo ketone functionality (Scheme 9).

Reaction of the adduct **16k**, derived from methyl chloroformate, with catalytic trifluoromethanesulphonic acid in dichloromethane gave the lactone **22** (90%). Treatment of this lactone with magnesium bromide in ether gave the 4-bromodihydrofurandione **23**, which existed exclusively as the enolised tautomer in deuteriochloroform (Scheme 10).



Scheme 10 *Reagents and conditions*: i, CF_3SO_3H, CH_2Cl_2, room temp.; ii, $MgBr_2$·Et_2O, tetrahydrofuran, room temp., 4 h

Treatment of the adduct **16m**, which appeared in deuteriochloroform solution to exist as a mixture of both possible diastereoisomeric lactols as well as the open-chain hydroxy ketone, with catalytic perchloric acid in acetone led to the spiroacetal **24a**[39] (56% from **10b**), together with the diastereoisomer **24b** (6% from **10b**) (Scheme 11). The structure of



Scheme 11 *Reagents and conditions*: i, $HClO_4$, acetone, room temp., 3 h

the major diastereoisomer **24a** was established by a single crystal X-ray structure determination (Fig. 1). The ^1H NMR spectra of the two diastereoisomers were quite distinct. In the major diastereoisomer **24a**, the two protons at C-7 (crystallographic numbering) each appear as doublets with $\Delta\delta = 0.34$. This difference in chemical shift is presumably due to deshielding of one of the protons by both the oxirane oxygen and the oxygen in the other half of the spiroacetal. In contrast, the corresponding protons in the minor diastereoisomer appear as an AB system with $\Delta\delta$ *ca.* 0.05. Here each proton at C-7 can be deshielded by only one of the oxygen atoms.

Analogous treatment of the δ-valerolactone adduct **16n**, which also existed in solution as a mixture of two lactols and the open-chain hydroxy ketone, gave the spiroacetals **25a** and **25b** (58% from **10b**), as an inseparable 2.2:1 mixture of diastereoisomers. The relative stereochemistry of the two diastereoisomers was established beyond reasonable doubt by examination of the signals corresponding to those described above for the [5.5] spiroacetals. The major sets of signals exhibited $\Delta\delta = 0.33$, while the minor signals appeared as an AB system with $\Delta\delta$ *ca.* 0.06. By analogy with **24a** and **24b**, we assign the structure of the major diastereoisomer as **25a**, and the minor isomer **25b**.

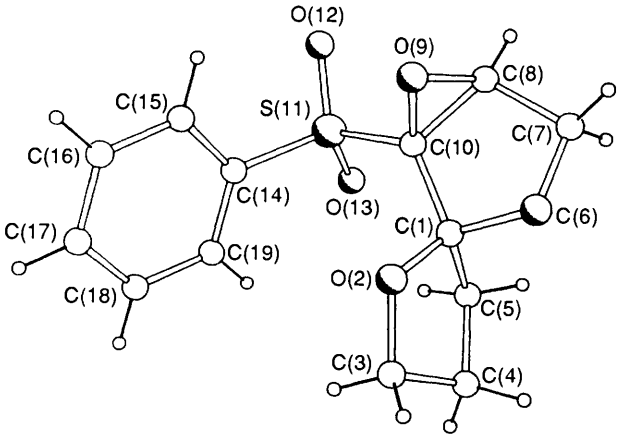


Fig. 1 The molecular structure of **24a**. Selected distances and bond angles: C(1)–O(2) 1.397(3), C(1)–O(6) 1.435(4), C(8)–O(9) 1.430(4), C(10)–O(9) 1.418(4), C(8)–C(10) 1.449(4) Å, C(8)–O(9)–C(10) 61.2(2), O(9)–C(8)–C(10) 59.0(2), O(9)–C(10)–C(8) 59.8(2)°

In conclusion, we have shown that phenylsulphonyloxiranes are potentially useful reagents for the straightforward preparation of a wide range of selectively functionalised small molecules. The starting phenylsulphonyloxiranes are easily accessible, and subsequent transformations can be carried out under very mild conditions. We are at present exploring applications of these and similar systems for asymmetric synthesis.

Experimental

Unless otherwise stated all new compounds were homogeneous by TLC; NMR spectra were run in $CDCl_3$ and recorded for ^1H at 200 or 300 MHz on Bruker instruments. *J* values are given in Hz. Where spectra for inseparable diastereoisomeric mixtures are reported, the signals due to the major isomer are indicated †. IR spectra were obtained on a Nicolet 20SX as capillary films (for oils) or KBr disks (for solids), and mass spectra were measured on either an AEI MS9 or a Kratos MS80 using the EI method, or on a Kratos MS80 using the FAB method with MNBA as the matrix. Peaks due to ^{79}Br only are recorded. Temperatures of reaction mixtures were determined directly using a Cole-Palmer P.I. 8013 digital thermometer fitted with a type K 1.5 mm hyperdermic probe. All reactions were conducted under a positive pressure of dry nitrogen in oven-dried glassware, except when using water as a solvent. Cooling baths for reactions at −102 °C were prepared using liquid nitrogen and either methanol or ethanol. All solvents were distilled: light petroleum refers to that fraction with boiling point 40–60 °C; dry CH_2Cl_2 was distilled from P_2O_5; dry THF (tetrahydrofuran) was distilled from potassium benzophenone ketyl; dry diethyl ether was distilled from sodium benzophenone ketyl; dry hexamethylphosphoric triamide (HMPA) was distilled from calcium hydride. All aldehydes were distilled prior to use. Anhydrous solutions of *tert*-butyl hydroperoxide in toluene were obtained by azeotropic drying, and concentrations were determined by ^1H NMR.[40] Butyllithium was obtained from Aldrich as nominal 2.5 or 1.6 mol dm^{-3} solutions in hexanes, and the true concentration determined by titration using diphenylacetic acid as indicator.[41] Solutions of magnesium bromide–diethyl ether in toluene–diethyl ether were prepared by the literature method.[42] Phenylsulphonyloxirane was prepared by the literature procedure.[23] Organic extracts were dried using $MgSO_4$, and then concentrated using a rotary evaporator. Flash chromatography was performed using either Merck 9385 or Fluka 60738 silica.

General Procedure for Reactions of Phenylsulphonyloxirane **2a**.—A solution of phenylsulphonyloxirane **2a** (1 mmol) in a mixture of dry THF (9 cm^3) and dry pentane (3 cm^3) was cooled to −105 °C. Butyllithium (1.8 mmol) was added slowly so that the temperature did not rise above −100 °C, and then immediately a solution of the electrophile in dry THF (1 cm^3) was added. The reaction mixture was stirred for 5 min, aqueous NH_4Cl (10% solution; 5 cm^3) was added, and the mixture then allowed to warm to room temp. The reaction mixture was then extracted with light petroleum (2 × 20 cm^3) and the combined extracts dried ($MgSO_4$) and concentrated under reduced pressure.

2-Deuterio-2-phenylsulphonyloxirane **6a**. Electrophile was D_2O (5.5 equiv.). The residue was purified by flash chromatography using 3:1 light petroleum–ethyl acetate as the eluent to yield the *oxirane* **6a** (83%) as a white crystalline solid, m.p. 42–43 °C (Found: C, 51.85; H, 4.2. $C_8H_7DO_3S$ requires C, 51.9; H, 3.8%); ν_{max}(KBr)/cm^{-1} 2260, 1446, 1313 and 1159; δ_H(300 MHz) 3.11 (1 H, d, *J* 5.3), 3.38 (1 H, d, *J* 5.3), 7.57–7.62 (2 H, m), 7.68–7.73 (1 H, m) and 7.91–7.94 (2 H, m); *m/z* (FAB) 371 (M_2H^+, 7%), 339 (38), 321 (14), 186 (95, MH^+), 137 (80) and 125 (100).

2-Phenylsulphonyl-2-(prop-2′-en-1′-yl)oxirane **6b**. Electrophile was allyl bromide (4 equiv.). The residue was purified by flash chromatography using 3:1 light petroleum–ethyl acetate as the eluent to yield the *oxirane* **6b** as an oil (33%); ν_{max}(film)/cm^{-1} 1643, 1584, 1447, 1322 and 1167; δ_H(300 MHz) 2.58 (1 H, dd, *J* 6.4 and 15.2), 2.96 (1 H, d, *J* 4.7), 2.97 (1 H, dd, *J* 7.7 and 15.2), 3.45 (1 H, d, *J* 4.8), 5.08–5.15 (2 H, m), 5.43–5.57 (1 H, m), 7.57–7.62 (2 H, m), 7.68–7.74 (1 H, m) and 7.91–7.95 (2 H, m); *m/z* (FAB) 449 (M_2H^+, 5%), 307 (6), 225 (35, MH^+), 137 (43) and 125 (100).

S-Phenyl (phenylthio)thioacetate **7**. Electrophile was diphenyl disulphide (1.6 equiv.). The residue was purified by flash chromatography using 20:1 light petroleum–ethyl acetate as the eluent to yield the *thioester* **7** as a white crystalline solid (71%), m.p. 62–63 °C (Found: M^+, 260.0372. $C_{14}H_{12}OS_2$ requires M, 260.0330); ν_{max}(KBr)/cm^{-1} 1684, 1478, 1438 and 1046; δ_H(300 MHz) 3.90 (2 H, s) and 7.23–7.46 (10 H, m); *m/z* (EI) 260 (M^+, 19%) and 123 (100).

2-Phenylsulphonyl-2-trimethylsilyloxirane **6d**. Electrophile was chlorotrimethylsilane (2.5 equiv.), which was added prior to addition of the butyllithium. The residue was purified by Kugelrohr distillation (oven temp. 200 °C, 0.7 mmHg) to give the *silyl oxirane* **6d** as an oil (100%), which solidified to a waxy low-melting solid on cooling, m.p. 25–26 °C; ν_{max}(film)/cm^{-1} 3067, 2961, 1585, 1447, 1308, 1253, 1157 and 851; δ_H(300 MHz) 0.20 (9 H, s), 2.93 (1 H, d, *J* 5.1), 3.29 (1 H, d, *J* 5.1), 7.62–7.67 (2 H, m), 7.73–7.78 (1 H, m) and 7.98–8.02 (2 H, m); *m/z* (FAB) 513 (M_2H^+, 100%), 371 (28), 329 (40), 287 (36), 257 (MH^+, 78), 241 (96), 215 (95), 198 (87) and 125 (100).

2-Methyl-2-phenylsulphonyloxirane **6e**. The electrophile was iodomethane (4.6 equiv.), which was added prior to the addition of the butyllithium. The residue was purified by Kugelrohr distillation (oven temp. 200 °C, 1 mmHg) to yield the *oxirane* **6e** as an oil (0.502 g, 83%); ν_{max}(film)/cm^{-1} 3068, 3002, 2935, 1585, 1447, 1318, 1140 and 1080; δ_H(300 MHz) 1.62 (3 H, s), 2.92 (1 H, d, *J* 4.9), 3.53 (1 H, d, *J* 4.9), 7.57–7.63 (2 H, m), 7.68–7.74 (1 H, m) and 7.91–7.96 (2 H, m); *m/z* (FAB) 199 (MH^+, 19), 149 (28) and 125 (100).

Reactions of Phenylsulphonyloxirane **2a** *with Carbonyl Compounds*.—Butyllithium (1.2 mmol) was added over 2 min to a solution of phenylsulphonyloxirane **2a** (1.0 mmol) in dry THF (5 cm^3) at −102 °C. A solution of magnesium bromide in diethyl ether–toluene (1 mol dm^{-3}; 1.3 cm^3, 1.3 mmol) was then added over 2 min, during which time the internal temperature of the reaction mixture rose to −95 °C. The electrophile was added, and the reaction mixture was warmed to the temperature indicated over the time indicated. Aqueous NH_4Cl (10%; 10

cm^3) was added and, after the mixture had warmed to room temp., it was extracted with ethyl acetate (2 × 20 cm^3). The combined organic extracts were dried and evaporated to dryness. The residue was purified by flash chromatography using 3:1 light petroleum–ethyl acetate except where otherwise indicated.

2-*Acetyl*-2-*phenylsulphonyloxirane* **6f**. The electrophile was methyl acetate (3 equiv.), and the reaction mixture was warmed to −50 °C over 5 min before quenching. The *oxirane* **6f** was a white crystalline solid, m.p. 51–52 °C (55%) (Found: C, 53.2; H, 4.40. $C_{10}H_{10}O_4S$ requires C, 53.1; H, 4.45%); ν_{max}(KBr)/cm^{-1} 1724, 1449, 1328 and 1165; δ_H(300 MHz) 2.17 (3 H, s), 3.25 (1 H, d, *J* 5.3), 3.68 (1 H, d, *J* 5.3), 7.56–7.62 (2 H, m), 7.68–7.74 (1 H, m) and 7.95–7.99 (2 H, m); *m/z* (FAB) 227 (MH^+, 50%), 154 (19), 137 (38) and 125 (100).

2-(1′-*Hydroxyethyl*)-2-*phenylsulphonyloxirane* **8a**. The electrophile was ethanal (3.5 equiv.), and the reaction mixture was warmed to −70 °C over 7 min before quenching. The *oxirane* **8a** was an oil (a 1.7:1 mixture of diastereoisomers) (75%); ν_{max}(film)/cm^{-1} 3506, 3064, 2984, 2938, 1584, 1447, 1310 and 1166; δ_H(300 MHz) 1.04 (d, *J* 6.5) and 1.37† (d, *J* 6.4) (together 3 H), 2.73 (1 H, br s), 3.11† (d, *J* 4.8) and 3.17 (d, *J* 4.9) (together 1 H), 3.39† (d, *J* 4.9) and 3.43 (d, *J* 4.9) (together 1 H), 4.33† (q, *J* 6.4) and 4.45 (q, *J* 6.5) (together 1 H), 7.54–7.61 (2 H, m), 7.66–7.73 (1 H, m) and 7.90–7.94 (2 H, m); *m/z* (FAB) (MH^+, 28%), 154 (37), 137 (42) and 125 (100).

2-(1′-*Hydroxypentyl*)-2-*phenylsulphonyloxirane* **8b**. The electrophile was pentanal (2 equiv.), and the reaction mixture was kept at −90 °C for 15 min before quenching. The *oxirane* **8b** was an oil (a 1.9:1 mixture of diastereoisomers) (75%); ν_{max}(film)/cm^{-1} 3515, 2958, 2931, 2869, 1585, 1447, 1311 and 1162; δ_H(300 MHz) 0.81 (t, *J* 7.0) and 0.90† (t, *J* 7.1) (together 3 H), 1.25–1.39 (4 H, m), 1.43–1.59† (m) and 1.84–1.95 (m) (together 2 H), 2.22 (1 H, br s), 3.10–3.15 (1 H, m), 3.40–3.50 (1 H, m), 4.08–4.13† (m) and 4.17–4.22 (m) (together 1 H), 7.56–7.63 (2 H, m), 7.67–7.74 (1 H, m) and 7.89–7.96 (2 H, m); *m/z* (FAB) 271 (MH^+, 10%), 241 (6) and 125 (100).

2-(1′-*Hydroxybenzyl*)-2-*phenylsulphonyloxirane* **8c**. The electrophile was benzaldehyde (1.5 equiv.), and reaction mixture was warmed to −70 °C for 5 min before quenching. The *oxirane* **8c** was a white crystalline solid, m.p. 94–98 °C (a 1.5:1 mixture of diastereoisomers) (80%) (Found: C, 62.0; H, 4.7. $C_{15}H_{14}O_4S$ requires C, 62.0; H, 4.85%); ν_{max}(KBr)/cm^{-1} 3493, 1448, 1309 and 1158; δ_H(300 MHz) 2.63† (d, *J* 5.0) and 2.96 (d, *J* 5.2) (together 1 H), 3.02 (1 H, br s), 3.41† (d, *J* 5.0) and 3.45 (d, *J* 5.2) (together 1 H), 5.38 (s) and 5.43† (s) (together 1 H), 7.08–7.20 (m) and 7.24† (s) (together 5 H), 7.57–7.62 (2 H, m), 7.69–7.78 (1 H, m) and 7.90–7.93 (2 H, m); *m/z* (FAB) 291 (MH^+, 4%), 273 (10), 154 (73), 136 (74) and 125 (100).

2-(1′-*Hydroxy*-1′-*methylethyl*)-2-*phenylsulphonyloxirane* **8d**. The electrophile was propanone (2.5 equiv.), and the reaction mixture was warmed to −65 °C over 7 min before quenching. The *oxirane* **8d** was an oil (67%) (Found: C, 54.0; H, 5.8. $C_{11}H_{14}O_4S$ requires C, 54.5; H, 5.8%); ν_{max}(film)/cm^{-1} 3509, 2982, 1585, 1448, 1308 and 1161; δ_H(300 MHz) 1.44 (3 H, s), 1.47 (3 H, s), 3.14 (1 H, d, *J* 4.8), 3.21 (1 H, d, *J* 4.8), 7.53–7.59 (2 H, m), 7.65–7.71 (1 H, m) and 7.93–7.96 (2 H, m); *m/z* (FAB) 243 (MH^+, 62%), 225 (100) and 137 (69).

2-(1′-*Hydroxycyclopentyl*)-2-*phenylsulphonyloxirane* **8e**. The electrophile was cyclopentanone (2.8 equiv.), and the reaction mixture was warmed to −55 °C over 7 min before quenching. The residue was purified by flash chromatography using 100:1 dichloromethane–ethanol as eluent to yield the *oxirane* **8e** as an oil which eventually crystallised, m.p. 57–61 °C (77%) (Found: C, 57.85; H, 5.9. $C_{13}H_{16}O_4S$ requires C, 58.2; H, 6.0%); ν_{max}(KBr)/cm^{-1} 3518, 2961, 1448, 1307, 1159 and 754; δ_H(300 MHz) 1.34–1.90 (8 H, m), 2.90 (1 H, br s), 3.06 (1 H, d, *J* 4.7), 3.41 (1 H, d, *J* 4.7), 7.53–7.59 (2 H, m), 7.65–7.71 (1 H, m) and 7.94–7.97 (2 H, m); *m/z* (FAB) 269 (MH^+, 3%), 251 (25), 154 (20), 137 (30) and 125 (100).

2-(1′-*Hydroxycyclohexyl*)-2-*phenylsulphonyloxirane* **8f**. The electrophile was cyclohexanone (1.5 equiv.), and the reaction mixture was warmed to −60 °C over 7 min before quenching. The *oxirane* **8f** was an oil (79%) (Found: C, 59.5; H, 6.5. $C_{14}H_{18}O_4S$ requires C, 59.55; H, 6.45%); ν_{max}(KBr)/cm^{-1} 3514, 2935, 2861, 1448, 1307 and 1159; δ_H(300 MHz) 1.14–1.93 (10 H, m), 3.13 (1 H, d, *J* 4.7), 3.20 (1 H, d, *J* 4.7), 7.52–7.61 (2 H, m), 7.64–7.75 (1 H, m) and 7.92–7.96 (2 H, m); *m/z* (FAB) 283 (MH^+, 4%), 265 (25), 154 (18), 137 (34) and 125 (100).

2-(1′-*Hydroxy*-1′-*methylpropyl*)-2-*phenylsulphonyloxirane* **8g**. The electrophile was butanone (2 equiv.), and the reaction mixture was warmed to −58 °C over 7 min before being quenched. The *oxirane* **8g** was an oil (78%); ν_{max}(film)/cm^{-1} 3510, 2979, 1585, 1448, 1309, 1160 and 755; δ_H(300 MHz) 0.85† (t, *J* 7.5) and 0.90 (t, *J* 7.5) (together 3 H), 1.34 (3 H, s), 1.78–1.95 (2 H, m), 2.40 (1 H, br s), AB system (δ_A 3.06, δ_B 3.08, J_{AB} 4.8), 3.10 (d, *J* 4.9), 3.18 (d, *J* 4.9) (together 2 H), 7.49–7.55 (2 H, m), 7.62–7.68 (1 H, m) and 7.89–7.92 (2 H, m); *m/z* (FAB) 256 (MH^+, 22%), 239 (55), 154 (59), 137 (71) and 125 (100).

2-(*Phenylthiomethyl*)*oxirane* **11**.[30]—A mixture of thiophenol (7 cm^3, 68.2 mmol), 2-chloromethyloxirane (5.33 cm^3, 68.1 mmol) in water (70 cm^3) was stirred at room temp. Solid NaOH pellets (2.73 g, 68.2 mmol) were added carefully. The mixture was stirred at room temp. for 10 min, and then warmed to 50 °C for 1.5 h. After cooling, the reaction mixture was extracted twice with diethyl ether (50 cm^3 and 20 cm^3). The combined ether extracts were dried and concentrated. Distillation of the residue gave the *oxirane* **11** (9.44 g, 83%) as an oil (b.p. 100 °C, 0.8 mmHg) (lit.,[30] 111–113 °C, 4 mmHg; ν_{max}(film)/cm^{-1} 3056, 2994, 2920, 1584, 1480, 1440 and 742; δ_H(300 MHz) 2.49 (1 H, dd, *J* 2.4 and 4.7), 2.74 (1 H, t, *J* 4.7); 2.92 (1 H, *J*, 7.2 and 15.3), 3.10–3.18 (2 H, m), 7.17–7.30 (3 H, m) and 7.39–7.43 (2 H, m); *m/z* (FAB) 167 (MH^+, 100%) and 123 (66).

(Z) *and* (E)-3-*Benzyloxyprop*-1-*enyl Phenyl Sulphone* **12** *and* **13a**.—2-(Phenylthiomethyl)oxirane **11** (18.3 g, 110 mmol) was dissolved in dry THF (250 cm^3), and then treated with NaH (60% dispersion in mineral oil; 4.41 g). The mixture was refluxed for 30 min, and then cooled to room temp. Benzyl bromide (13.1 cm^3, 110 mmol) was added, and the mixture was stirred for 2 d. THF was removed under reduced pressure, and the residue partitioned between water (100 cm^3) and diethyl ether (100 cm^3). The ether layer was separated and the aqueous layer extracted with ether (100 cm^3). The combined organic extracts were dried and evaporated. The residue was dissolved in dichloromethane (250 cm^3) and the solution cooled to 0 °C. *m*-Chloroperbenzoic acid (24.7 g, 1.3 equiv.) was added as a solid over 1 h, and the mixture was then stirred at 0 °C for 1 h and warmed to room temp. Further *m*-CPBA (24.7 g, 1.3 equiv.) was added over an additional 1 h period. The reaction mixture was then washed with aqueous sodium sulphite (10%, 50 cm^3), aqueous sodium hydrogen carbonate (saturated, 50 cm^3), and then brine (50 cm^3). The organic extracts were dried and evaporated, and the residue purified by careful flash chromatography using 10:1 light petroleum–ethyl acetate as eluent to yield the *Z-vinyl sulphone* **12** (13.64 g, 43%) as a white crystalline solid, m.p. 50–51 °C (Found: C, 66.85; H, 5.55. $C_{16}H_{16}O_3S$ requires C, 66.65; H, 5.6%); ν_{max}(KBr)/cm^{-1} 3034, 2867, 1634, 1447, 1301, 1146, 1082 and 757; δ_H(300 MHz) 4.55 (2 H, s), 4.73 (2 H, dd, *J* 2.2 and 5.0), 6.26 (1 H, dt, *J* 11.5 and 2.2), 6.44 (1 H, dt, *J* 11.5 and 5.0), 7.28–7.38 (5 H, m), 7.51–7.56 (2 H, m), 7.61–7.67 (1 H, m) and 7.85–7.90 (2 H, m); *m/z* (EI) 288 (M^+), 232, 197 and 181; and the *E-vinyl sulphone* **13a** (12.67 g, 40%) as an oil; ν_{max}(film)/cm^{-1} 3063, 2861, 1632, 1447, 1312, 1147 and 753; δ_H(300 MHz) 4.22 (2

H, dd, *J* 2.1 and 3.2), 4.54 (2 H, s), 6.68 (1 H, dt, *J* 15.0 and 2.1), 7.01 (1 H, dt, *J* 15 and 3.4), 7.28–7.32 (5 H, m), 7.53–7.57 (2 H, m), 7.62–7.67 (1 H, m) and 7.86–7.89 (2 H, m); *m/z* (EI) 288 (M^+) and 257.

cis-3-*Benzyloxymethyl*-2-*phenylsulphonyloxirane* **9**.—Butyllithium (2.4 mol dm^{-3}; 3.28 cm^3, 7.89 mmol) was added dropwise to a solution of *tert*-butyl hydroperoxide (3.5 mol dm^3 in toluene; 3.07 cm^3, 10.77 mmol) in dry THF (35 cm^3) at −78 °C under nitrogen. A solution of *Z*-vinyl sulphone **12** (2.06 g, 7.17 mmol) in dry THF (10 cm^3) was then added, and the mixture warmed to −20 °C for 25 min. Aqueous NH_4Cl (15 cm^3) was added, and the mixture allowed to warm to room temp. The organic layer was separated and the aqueous layer extracted with ethyl acetate. The combined organic extracts were washed with aqueous sodium sulphite (10%, 20 cm^3) and then dried and evaporated. The residue was purified by flash chromatography using 5:1 light petroleum–ethyl acetate as eluent to give the cis-*oxirane* **9** as an oil (2.03 g, 93%) (Found: C, 63.7; H, 5.4. $C_{16}H_{16}O_4S$ requires C, 63.15; H, 5.3%); ν_{max}(film)/cm^{-1} 3065, 2862, 1585, 1449, 1328, 1158, 1085 and 731; δ_H(300 MHz) 3.54 (1 H, m), 4.01 (1 H, d, *J* 4.1), 4.17 (2 H, m), AB system (δ_A 4.55, δ_B 4.64, J_{AB} 11.7), 7.23–7.35 (5 H, m), 7.50–7.55 (2 H, m), 7.61–7.66 (1 H, m) and 7.89–7.92 (2 H, m); *m/z* (FAB) 305 (MH^+, 100%), 223 (24) and 197 (93).

trans-3-*Benzyloxymethyl*-2-*phenylsulphonyloxirane* **10a**.—Butyllithium (2.4 mmol dm^{-3}; 7.0 cm^3, 16.8 mmol) was added dropwise to a solution of *tert*-butylhydroperoxide (3.5 mol dm^{-3} in toluene; 6.5 cm^3, 22.75 mmol) in dry THF (80 cm^3) at −78 °C under nitrogen. A solution of *E*-vinyl sulphone **13a** (4.38 g, 15.2 mmol) in dry THF (20 cm^3) was then added, and the mixture warmed to −20 °C for 45 min. Aqueous NH_4Cl (30 cm^3) was added, and the mixture allowed to warm to room temp. The organic layer was separated and the aqueous layer extracted with ethyl acetate. The combined organic extracts were washed with aqueous sodium sulphite (10%; 40 cm^3) and then dried and evaporated. The residue was purified by flash chromatography using 10:1 light petroleum–ethyl acetate and then 5:1 light petroleum–ethyl acetate as eluent to give the trans-*oxirane* **10a** (4.08 g, 88%) as a white crystalline solid, m.p. 37–38 °C (Found: C, 63.25; H, 5.15. $C_{16}H_{16}O_4S$ requires C, 63.15; H, 5.3%); ν_{max}(film)/cm^{-1} 3064, 2864, 1585, 1449, 1326, 1155, 1088 and 750; δ_H(300 MHz) 3.63 (1 H, dd, *J* 4.2 and 12.6), 3.82–3.88 (2 H, m), 4.20 (1 H, d, *J* 1.5), 4.50 (2 H, s), 7.25–7.35 (5 H, m), 7.50–7.59 (2 H, m), 7.65–7.70 (1 H, m) and 7.86–7.93 (2 H, m); *m/z* (EI) 304 (M^+, 15%), 182 (24), 107 (84) and 91 (100).

General Procedure for Reactions of cis-3-*Benzyloxymethyl*-2-*phenylsulphonyloxirane* **9**.—A solution of *cis*-3-benzyloxymethyl-2-phenylsulphonyloxirane **9** (1 mmol) in dry THF (7 cm^3) was cooled to −102 °C. Butyllithium (1.1 equiv.) was added slowly so that the temperature did not rise above −103 °C, and the electrophile in dry THF (0.5 cm^3) was then added immediately. After addition of the electrophile, aqueous NH_4Cl (10% solution; 5 cm^3) was added, and the reaction mixture was allowed to warm to room temp. The mixture was extracted with light petroleum (2 × 20 cm^3), and the combined organic extracts were dried and evaporated. The residue was then purified by flash column chromatography using 10:1 light petroleum–ethyl acetate to give the oxiranes **14**.

cis-3-*Benzyloxymethyl*-2-*deuterio*-2-*phenylsulphonyloxirane* **14a**. Dry pentane (4 cm^3) was used as co-solvent, and the electrophile was D_2O (22 equiv.). The *oxirane* **14a** (85%) was an oil; ν_{max}(film)/cm^{-1} 3064, 2926, 2861, 2260, 1449, 1327, 1166, 1084 and 734; δ_H(300 MHz) 3.59 (1 H, t, *J* 4.7), 4.21 (2 H, d, *J* 4.7), AB system (δ_A 4.60, δ_B 4.70, J_{AB} 1.7), 7.21–7.40 (5 H, m), 7.57–7.62 (2 H, m), 7.68–7.73 (1 H, m) and 7.92–7.98 (2 H, m); in addition, there were signals corresponding to the oxirane **15a**, including 4.52 (s), which allowed the proportion of **15a** to be determined; *m/z* (FAB) 328 (MNa^+, 7%), 306 (MH^+, 33), 198 (54), 125 (62) and 91 (100).

cis-3-*Benzyloxymethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **14b**. The electrophile was chlorotrimethylsilane (3 equiv.), which was added prior to addition of the butyllithium. The *oxirane* **14b** (63%) was an oil (Found: C, 60.8; H, 6.35. $C_{19}H_{24}O_4SSi$ requires C, 60.6; H, 6.4%); ν_{max}(film)/cm^{-1} 3065, 2958, 2903, 1448, 1308, 1253, 1156, 1084, 847 and 691; δ_H(300 MHz) 0.0 (9 H, s), ABX system (δ_A 4.12, δ_B 4.22, δ_X 3.37, J_{AX} 4.2, J_{BX} 2.2, J_{AB} 12.4), AB system (δ_A 4.56, δ_B 4.62, J_{AB} 11.7), 7.34–7.37 (5 H, m), 7.51–7.57 (2 H, m), 7.62–7.65 (1 H, m) and 7.88–7.91 (2 H, m); a signal at 0.22, due to the *trans* oxirane **15b**, indicated that the proportion of *trans* isomer was <5%; *m/z* (FAB) 377 (MH^+, 5%), 271 (4), 125 (20), 91 (59) and 73 (100).

cis-3-*Benzyloxymethyl*-2-*methyl*-2-*phenylsulphonyloxirane* **14c**. The electrophile was iodomethane (3 equiv.). The *oxirane* **14c** (71%) was an oil which solidified with time, m.p. 52–53 °C (Found: C, 64.1; H, 5.65. $C_{17}H_{18}O_4S$ requires C, 64.15; H, 5.7%); ν_{max}(film)/cm^{-1} 3064, 3032, 2927, 2856, 1448, 1324, 1144 and 1082; δ_H(300 MHz) 1.47 (3 H, s), 3.40 (1 H, t, *J* 4.4), 4.26 (2 H, d, *J* 4.4), AB system (δ_A 4.60, δ_B 4.69, J_{AB} 11.7), 7.28–7.38 (5 H, m), 7.56–7.61 (2 H, m), 7.67–7.72 (1 H, m) and 7.91–7.94 (2 H, m); a signal at 1.54, due to the *trans* isomer **15c**, indicated that the proportion of *trans* isomer was <5%; *m/z* (FAB) 319 (MH^+, 30%), 211 (42), 125 (86) and 91 (100).

cis-3-*Benzyloxymethyl*-2-(1′-*hydroxyethyl*)-2-*phenylsulphonyloxirane* **14d**. The electrophile was ethanal (4 equiv.). The *oxirane* **14d** (63%), a mixture of diastereoisomers, was an oil [Found: C, 61.85; H, 6.05. $C_{18}H_{20}O_5S$ requires C, 62.05; H, 5.8%); ν_{max}(film)/cm^{-1} 3055 br, 2925, 1449, 1323, 1168, 1080 and 737; δ_H(300 MHz) 0.94 (d, *J* 6.6) and 1.39† (d, *J* 6.3) (together 3 H), 2.15 (1 H, br s), 3.67 (1 H, t, *J* 4.2), 3.99† (q, *J* 6.3), 4.23† (d, *J* 4.1), 4.25 (d, *J* 4.3) and 4.26 (q, *J* 6.6) (together 3 H), two AB systems (δ_A 4.58, δ_B 4.67, J_{AB} 11.7) and (δ_A 4.59, δ_B 4.68, J_{AB} 11.7) (together 2 H), 7.30–7.38 (5 H, m), 7.54–7.60 (2 H, m), 7.66–7.72 (1 H, m) and 7.88–7.94 (2 H, m); additional signals at 1.21 (d) and 1.45 (d), due to the *trans* isomer **15d**, indicated that the proportion of *trans* isomer was <10%; *m/z* (FAB) 349 (MH^+, 16%), 241 (18), 125 (50) and 91 (100).

General Procedure for the Reactions of trans-3-*Benzyloxymethyl*-2-*phenylsulphonyloxirane* **10a**.—A solution of *trans*-3-benzyloxymethyl-2-phenylsulphonyloxirane **10a** (1 mmol) in dry THF (10 cm^3) was cooled to −102 °C. Butyllithium (1.2 equiv.) was added and the reaction mixture warmed to −95 °C and stirred at this temperature for 8 min. A solution of the electrophile in dry THF (0.5 cm^3) was then added. The reaction mixture was stirred for 5 min, aqueous NH_4Cl (10% solution; 5 cm^3) was added, and the reaction mixture was allowed to warm to room temp. The mixture was extracted with light petroleum (2 × 20 cm^3), and the combined organic extracts were dried and evaporated. The residue was then purified by flash chromatography using 3:1 light petroleum–ethyl acetate as eluent to give the oxiranes **15**.

trans-3-*Benzyloxymethyl*-2-*deuterio*-2-*phenylsulphonyloxirane* **15a**. The electrophile was D_2O (11.5 equiv.). The *oxirane* **15a** (80%) was an oil which solidified with time, m.p. 41 °C (Found: C, 63.35; H, 5.3. $C_{16}H_{15}DO_4S$ requires C, 63.35; H, 5.0%); ν_{max}(film)/cm^{-1} 3064, 2926, 2863, 2260, 1449, 1325, 1158 and 735; δ_H(300 MHz) 3.66 (1 H, dd, *J* 4.3 and 11.7), 3.84–3.90 (2 H, m), 4.52 (2 H, s), 7.26–7.37 (5 H, m), 7.52–7.62 (2 H, m), 7.67–7.73 (1 H, m) and 7.87–7.96 (2 H, m); *m/z* (FAB) 306 (MH^+, 2%), 304 (6), 155 (28), 127 (27) and 91 (100).

trans-3-*Benzyloxymethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **15b**. The electrophile was chlorotrimethylsilane (2.9 equiv.). The *oxirane* **15b** (80%) was an oil which crystallised with

time, m.p. 80–81 °C (Found: C, 60.8; H, 6.35. $C_{19}H_{24}O_4SSi$ requires C, 60.6; H, 6.4%); ν_{max}(film)/cm^{-1} 2956, 2931, 2858, 1471, 1447, 1308, 1225, 1148 and 842; δ_H(300 MHz) 0.22 (9 H, s), 3.35–3.44 (2 H, m), 3.77 (1 H, dd, *J* 1.8 and 10.1), AB system (δ_A 4.48, δ_B 4.55, J_{AB} 11.9), 7.28–7.68 (5 H, m), 7.51–7.53 (2 H, m), 7.55–7.68 (1 H, m) and 7.87–7.95 (2 H, m); *m/z* (FAB) 287 (MH^+ − Me_3SiOH, 19%), 215 (7), 199 (8), 125 (32), 89 (40) and 73 (100).

trans-3-*Benzyloxymethyl*-2-*methyl*-2-*phenylsulphonyloxirane* **15c**. The electrophile was iodomethane (3 equiv.). The *oxirane* **15c** (87%) was an oil which solidified with time, m.p. 80–81 °C (Found: C, 64.25; H, 5.6. $C_{17}H_{18}O_4S$ requires C, 64.15; H, 5.7%); ν_{max}(film)/cm^{-1} 2926, 1448, 1324, 1151 and 753; δ_H(300 MHz) 1.54 (3 H, s), 3.54 (1 H, dd, *J* 6.1 and 11.7), 3.78 (1 H, dd, *J* 3.9 and 11.7), 3.96 (1 H, dd, *J* 3.9 and 6.1), AB system (δ_A 4.53, δ_B 4.62, J_{AB} 11.9), 7.28–7.38 (5 H, m), 7.56–7.61 (2 H, m), 7.67–7.73 (1 H, m) and 7.90–7.95 (2 H, m); *m/z* (FAB) 241 (MH^+ − C_6H_6, 9%), 155 (50), 125 (47), 91 (100) and 73 (80).

trans-3-*Benzyloxymethyl*-2-(1′-*hydroxyethyl*)-2-*phenylsulphonyloxirane* **15d**. The electrophile was ethanal (4 equiv.). The *oxirane* **15d** (87%), a mixture of diastereoisomers, was an oil which eventually solidified, m.p. 94–96 °C (Found: C, 61.8; H, 5.7. $C_{18}H_{20}O_5S$ requires C, 62.05; H, 5.8%); ν_{max}(film)/cm^{-1} 3504(br), 2937, 1448, 1311, 1152, 1088 and 7.21; δ_H(300 MHz) 1.21 (d, *J* 6.8) and 1.45† (d, *J* 6.5) (together 3 H), 2.5† (d, *J* 4.9) and 2.76 (d, *J* 5.0) (together 1 H), 3.68 (dd, *J* 6.3) and 3.79–4.00 (m) (together 3 H), 4.19† (dq, *J* 4.9 and 6.5) and 4.40 (dq, *J* 5.0 and 6.8) (together 1 H), AB system (δ_A 4.53, δ_B 4.60, J_{AB} 11.7), 7.28–7.37 (5 H, m), 7.53–7.59 (2 H, m), 7.65–7.72 (1 H, m) and 7.89–7.94 (2 H, m); *m/z* (FAB) 349 (MH^+, 15%), 155 (81), 137 (58), 107 (34) and 91 (100).

(E)-3-*Hydroxyprop*-1-*enyl Phenyl Sulphone*.—Sodium benzenesulphinate (8.18 g, 50 mmol) and 1-chloro-2,3-epoxypropane (7.82 cm^3, 100 mmol) were dissolved in a mixture of DMF (dimethylformamide) (5 cm^3) and water (100 cm^3). The mixture was heated to reflux, and reflux was continued for 6 h. The mixture was then cooled to room temp., and set aside for 16 h. The white solid was filtered off using a sinter, washed with water, and dried (50 °C, 0.8 mmHg) to yield the vinyl sulphone (9.093 g, 92%) as a white solid, m.p. 140–141 °C (lit.,[28] 139–141 °C); δ_H(300 MHz) 1.80 (1 H, br s), 4.41 (1 H, t, *J* 3.0), 6.67 (1 H, dt, *J* 15.0 and 3.0), 7.07 (1 H, dt, *J* 15.0 and 3.0) and 7.88–7.91 (5 H, m); *m/z* (EI) 198 (M^+, 10%), 169 (70), 125 (50), 91 (50) and 78 (100).

(E)-3-(tert-*Butyldimethylsilyl*)*oxyprop*-1-*enyl Phenyl Sulphone* **13b**.—(*E*)-3-Hydroxyprop-1-enyl phenyl sulphone (8.13 g, 41.1 mmol), *tert*-butyldimethylsilyl chloride (6.81 g, 45.2 mmol), imidazole (3.075 g, 45.2 mmol) and dry DMF (100 cm^3) were stirred under nitrogen for 40 h. The reaction mixture was diluted with light petroleum (200 cm^3), and washed with saturated aqueous sodium hydrogen carbonate (50 cm^3) and saturated brine (50 cm^3). The light petroleum extract was dried and evaporated to yield the *vinyl sulphone* **13b** (11.31 g, 88%); ν_{max}(KBr)/cm^{-1} 3055, 1630, 1451, 1282, 1143, 1086 and 842; δ_H(300 MHz) 0.0 (6 H, s), 0.83 (9 H, s), 4.34 (2 H, t, *J* 2.6), 6.56 (1 H, dt, *J* 14.7 and 2.3), 7.00 (1 H, dt, *J* 14.7 and 2.9), 7.47–7.57 (3 H, m) and 7.83–7.87 (2 H, m); *m/z* (FAB) 313 (MH^+, 24%), 312 (M^+, 23), 171 (19), 125 (27) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*phenylsulphonyloxirane* **10b**.—Butyllithium (14.4 cm^3, 1.9 mol dm^{-3}, 27.4 mmol) was added dropwise to a solution of *tert*-butyl hydroperoxide (10.4 cm^3, 3.6 mol dm^{-3} in toluene, 37.4 mmol) in dry THF (130 cm^3) at −78 °C under nitrogen. A solution of *E*-vinyl sulphone **13b** (7.78 g, 24.9 mmol) in dry THF (20 cm^3) was then added, and the mixture warmed to −20 °C for 2 h. Aqueous NH_4Cl (30 cm^3) was added, and the mixture allowed to warm to room temp. The organic layer was separated and the aqueous layer extracted with light petroleum (2 × 100 cm^3). The combined organic extracts were washed with aqueous sodium sulphite (10%; 40 cm^3) and then dried and evaporated. The residue was purified by flash chromatography using 10:1 light petroleum–ethyl acetate as eluent to give the trans-*oxirane* **10b** (6.51 g, 80%) as a white crystalline solid, m.p. 53–54 °C (Found: C, 54.7; H, 7.65. $C_{15}H_{24}O_4SSi$ requires C, 54.85; H, 7.35%); ν_{max}(film)/cm^{-1} 2928, 2858, 1583, 1470, 1447, 1327, 1152 and 841; δ_H(300 MHz) 0.02 (3 H, s), 0.04 (3 H, s), 0.85 (9 H, s), 3.75–3.77 (1 H, m), 3.85 (1 H, dd, *J* 3.1 and 12.8), 4.01 (1 H, dd, *J* 1.7 and 12.8), 4.16 (1 H, d, *J* 1.5), 7.57–7.62 (2 H, m), 7.68–7.71 (1 H, m) and 7.92–7.96 (2 H, m); *m/z* (FAB) 329 (MH^+, 7%), 313 (15), 271 (68), 257 (27), 199 (43), 187 (85), 125 (100) and 73 (100).

General Procedure for the Reactions of trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*phenylsulphonyloxirane* **10b**.—A solution of *trans*-3-*tert*-butyldimethylsilyloxymethyl-2-phenylsulphonyloxirane **10b** (1 mmol) in dry THF (10 cm^3) was cooled to −102 °C. Butyllithium (1.1 equiv.) was added and the reaction mixture warmed to −95 °C and stirred at this temperature for 8 min. A solution of the electrophile in dry THF (0.5 cm^3) was then added. The reaction mixture was allowed to warm to the temperature indicated, aqueous NH_4Cl (10% solution; 5 cm^3) was added, and the reaction mixture was allowed to warm to room temp. The mixture was extracted with light petroleum (2 × 20 cm^3), and the combined organic extracts were dried and evaporated. The residue was then purified by flash chromatography using 10:1 light petroleum–ethyl acetate as eluent, unless stated otherwise.

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*deuterio*-2-*phenylsulphonyloxirane* **16a**. The electrophile was D_2O (20 equiv.), and the reaction was quenched immediately. The *oxirane* **16a** (85%), was a white solid, m.p. 55–56 °C (Found: C, 54.85; H, 7.4. $C_{15}H_{23}DO_4SiS$ requires C, 54.7; H, 7.4%); ν_{max}(KBr)/cm^{-1} 2928, 2858, 1583, 1470, 1466, 1327, 1157 and 735; δ_H(300 MHz) 0.02 (3 H, s), 0.04 (3 H, s), 0.85 (9 H, s), 3.76 (1 H, dd, *J* 1.9 and 3.0), 3.84 (1 H, dd, *J* 3.0 and 12.7), 4.00 (1 H, dd, *J* 1.9 and 12.7), 7.57–7.63 (2 H, m), 7.68–7.74 (1 H, m) and 7.93–7.97 (2 H, m); *m/z* (FAB) 330 (MH^+, 3%), 314 (4), 300 (4), 272 (19), 257 (10), 188 (43), 125 (92) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **16b**. The electrophile was chlorotrimethylsilane (2 equiv.), and the reaction was quenched immediately. The *oxirane* **16b** (84%) was an oil (Found: C, 54.55; H, 8.15. $C_{18}H_{32}O_4Si_2S$ requires C, 53.95; H, 8.05%); ν_{max}(film)/cm^{-1} 2956, 2931, 2858, 1471, 1447, 1309, 1255, 1149 and 842; δ_H(300 MHz) 0.02 (3 H, s), 0.03 (3 H, s), 0.23 (9 H, s), 0.85 (9 H, s), 3.21 (1 H, dd, *J* 3.9 and 6.6), 3.58 (1 H, dd, *J* 6.6 and 12.0), 3.82 (1 H, dd, *J* 3.9 and 12.0), 7.48–7.50 (2 H, m), 7.52–7.61 (1 H, m) and 7.84–7.87 (2 H, m); *m/z* (FAB) 401 (MH^+, 1%), 385 (3), 343 (4), 287 (10), 147 (18), 135 (23), 89 (37) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*methyl*-2-*phenylsulphonyloxirane* **16c**. The electrophile was iodomethane (3.9 equiv.). The reaction mixture was warmed to −70 °C over 10 min. The *oxirane* **16c** (79%) was an oil (Found: C, 56.95; H, 7.65. $C_{16}H_{26}O_4SiS$ requires C, 56.1; H, 7.65%); ν_{max}(film)/cm^{-1} 2955, 2931, 2858, 1585, 1471, 1448, 1326, 1152 and 839; δ_H(300 MHz) 0.07 (3 H, s), 0.08 (3 H, s), 0.89 (9 H, s), 1.56 (3 H, s), 3.75 (1 H, dd, *J* 6.6 and 12.9), 3.83–3.90 (2 H, m), 7.56–7.62 (2 H, m), 7.67–7.73 (1 H, m) and 7.91–7.94 (2 H, m); *m/z* (FAB) 343 (MH^+, 6%), 327 (3), 313 (7), 201 (100), 159 (43) and 143 (69).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(1′-*hydroxyethyl*)-2-*phenylsulphonyloxirane* **16d**. The electrophile was ethanal (4 equiv.). The reaction mixture was warmed to −88 °C over 3 min. The residue was purified by flash chromatography using 3:1 ethyl acetate as eluent to yield the *oxirane* **16d** (85%), a

mixture of diastereoisomers, as an oil; ν_{max}(film)/cm^{-1} 3502, 2955, 2932, 2858, 1448, 1332, 1152 and 839; δ_H(200 MHz) 0.06 (6 H, s), 0.86 (9 H, s), 1.21 (d, *J* 6.9) and 1.45† (d, *J* 6.9) (together 3 H), 2.75 (1 H,br s), 3.85–4.10 (3 H, m), 4.19† (q, *J* 6.6) and 4.42 (q, *J* 6.9) (together 1 H), 7.51–7.59 (2 H, m), 7.62–7.68 (1 H, m) and 7.88–7.94 (2 H, m); *m/z* (FAB) 373 (MH^+, 9%), 355 (22), 215 (36), 159 (28), 125 (61) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **16e**. The electrophile was diphenyl disulphide (1.5 equiv.), and the reaction mixture was warmed to −75 °C over 5 min. The *oxirane* **16e** (76%) was an oil; ν_{max}(film)/cm^{-1} 3064, 2954, 2930, 2857, 1583, 1327, 1156 and 837; δ_H(300 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.89 (9 H, s), ABC system (δ_A 3.91, δ_B 3.95, δ_C 4.09, J_{AB} 12.0, J_{AC} 5.6, J_{BC} 4.3), 7.13–7.26 (3 H, m), 7.30–7.33 (2 H, m), 7.39–7.44 (2 H, m), 7.55–7.60 (1 H, m) and 7.80–7.83 (2 H, m); *m/z* (FAB) 421 ($MH^+ - CH_4$, 1%), 407 (11), 379 (4), 295 (18), 253 (35), 185 (33), 135 (66), 115 (88) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*ethyl*-2-*phenylsulphonyloxirane* **16f**. The electrophile, iodoethane (2 equiv.), was added as a solution in dry HMPA (0.6 cm^3), and the reaction mixture was warmed to −80 °C over 10 min. The *oxirane* **16f** (68%) was an oil which eventually solidified, m.p. 38–39 °C (Found: C, 56.9; H, 7.8. $C_{17}H_{28}O_4SiS$ requires C, 57.25; H, 7.9%); ν_{max}(film)/cm^{-1} 2954, 2932, 2858, 1469, 1447, 1324, 1151 and 839; δ_H(300 MHz) 0.07 (3 H, s), 0.08 (3 H, s), 0.89 (9 H, s), 1.02 (3 H, t, *J* 7.6), 1.81–1.98 (2 H, m), 3.74 (1 H, dd, *J* 4.1 and 10.0), 3.81–3.89 (2 H, m), 7.55–7.60 (2 H, m), 7.66–7.69 (1 H, m) and 7.92–7.95 (2 H, m); *m/z* (FAB) 357 (MH^+, 3%), 215 (89), 199 (32), 157 (58), 125 (86) and 73 (100).

trans-2-*Butyl*-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulphonyloxirane* **16g**. The electrophile was 1-iodobutane (2 equiv.), which was added as a solution in dry HMPA (0.6 cm^3), and the reaction mixture was warmed to −80 °C over 10 min. The *oxirane* **16g** (75%) was an oil (Found: C, 59.15; H, 8.4. $C_{19}H_{32}O_4SiS$ requires C, 59.35; H, 8.4%); ν_{max}(film)/cm^{-1} 2958, 2932, 2859, 1468, 1447, 1325, 1151, 1086 and 839; δ_H(300 MHz) 0.07 (3 H, s), 0.08 (3 H, s), 0.83 (3 H, t, *J* 7.3), 0.89 (9 H, s), 1.20–1.26 (3 H, m), 1.65–1.70 (1 H, m), 1.75–1.95 (2 H, m), 3.69–3.87 (3 H, m), 7.55–7.60 (2 H, m), 7.66–7.70 (1 H, m) and 7.91–7.95 (2 H, m); *m/z* (FAB) 385 (MH^+, 4%), 355 (7), 297 (4), 243 (64), 185 (46), 125 (78), 85 (100) and 73 (90).

trans-2-*Benzyl*-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulphonyloxirane* **16h**. The electrophile, benzyl bromide (2 equiv.), was added as a solution in dry HMPA (0.6 cm^3), and the reaction mixture was warmed to −82 °C over 5 min. The *oxirane* **16h** (61%) was an oil (Found: C, 63.3; H, 7.35. $C_{22}H_{30}O_4SiS$ requires C, 63.1; H, 7.2%); δ_H(300 MHz) 0.01 (3 H, s), 0.02 (3 H, s), 0.85 (9 H, s), AB system (δ_A 3.30, δ_B 3.40, J_{AB} 16.0), 3.58 (1 H, dd, *J* 5.7 and 12.2), 3.77 (1 H, dd, *J* 4.3 and 12.2), 3.96 (1 H, dd, *J* 4.3 and 5.7), 7.06–7.12 (5 H, m), 7.33–7.39 (2 H, m), 7.49–7.55 (1 H, m) and 7.63–7.67 (2 H, m); *m/z* (FAB) 419 (MH^+, 3%), 371 (4), 361 (48), 331 (51), 277 (55), 219 (50), 115 (78) and 91 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(1′-*hydroxy*-2′-*methylpropyl*)-2-*phenylsulphonyloxirane* **16i**. The electrophile was 2-methylpropanal (2 equiv.), and the mixture was stirred at −90 °C before quenching. The residue was purified by flash chromatography using 20:1 light petroleum–ethyl acetate as eluent to yield the two diastereoisomeric *oxiranes* **16i**. The oxirane with higher R_F (52%) was an oil; ν_{max}(film)/cm^{-1} 3519, 2928, 2931, 2858, 1471, 1447, 1308, 1151 and 837; δ_H(300 MHz) 0.07 (6 H, s), 0.60 (3 H, d, *J* 6.6), 0.88 (9 H, s), 0.96 (3 H, d, *J* 6.6), 1.92–1.98 (1 H, m), 2.1–2.4 (1 H, br s), 3.77–3.85 (3 H, m), 4.01–4.07 (1 H, m), 7.54–7.60 (2 H, m), 7.66–7.69 (1 H, m) and 7.91–7.95 (2 H, m); *m/z* (FAB) 401 (MH^+, 23%), 259 (18), 159 (87), 125 (62) and 73 (100). The oxirane with lower R_f (29%) eventually solidified, m.p. 30–34 °C (Found: C, 56.45; H, 7.95. $C_{19}H_{32}O_5SiS$ requires C, 56.8; H, 8.3%); ν_{max}(film)/cm^{-1} 3527, 2958, 2932, 2859, 1586, 1470, 1309, 1149 and 838; δ_H(300 MHz) 0.06 (3, H, s), 0.07 (3 H, s), 0.70 (3 H, d, *J* 6.7), 0.87 (9 H, s), 0.99 (3 H, d, *J* 6.6), 2.2–2.3 (1 H, m), 2.35 (1 H, br s), 3.33 (1 H, d, *J* 8.9), 3.70 (1 H, dd, *J* 3.5 and 5.9), 3.84 (1 H, dd, *J* 5.9 and 12.4), 4.07 (1 H, dd, *J* 3.5 and 12.4), 7.54–7.60 (2 H, m), 7.66–7.72 (1 H, m) and 7.93–7.96 (2 H, m); *m/z* (FAB) 401 (MH^+, 4%), 159 (21) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(1′-*hydroxycyclohex*-2′-*enyl*)-2-*phenylsulphonyloxirane* **16j**. The electrophile was cyclohex-2-enone (1.1 equiv.), and the reaction mixture was stirred at −98 °C for 10 min. The residue was purified by flash chromatography using 10:1 light petroleum–ethyl acetate as eluent to yield the two diastereoisomeric *oxiranes* **16j**. The oxirane with higher R_F (43%) was an oil; ν_{max}(film)/cm^{-1} 3495, 2953, 2932, 2858, 1470, 1447, 1308, 1150 and 837; δ_H(300 MHz) 0.08 (6 H, s), 0.90 (9 H, s), 1.66–1.73 (4 H, m), 2.05 (1 H, br s), 2.27–2.35 (2 H, m), 3.94 (1 H, dd, *J* 3.1 and 5.4), 4.05–4.14 (2 H, m), 5.36 (1 H, br d, *J* 10), 5.86 (1 H, dt, *J* 10.0 and 4.0), 7.49–7.56 (2 H, m), 7.62–7.68 (1 H, m) and 7.88–7.93 (2 H, m); *m/z* (FAB) 407 ($MH^+ - H_2O$, 1%), 125 (17), 97 (33) and 73 (100). The oxirane with lower R_F (30%) was an oil; ν_{max}(film)/cm^{-1} 3495, 2954, 2857, 1470, 1447, 1308, 1150, 1091 and 838; δ_H(300 MHz) 0.05 (3 H, s), 0.06 (3 H, s), 0.88 (9 H, s), 1.67–1.90 (4 H, m), 2.05–2.13 (1 H, m), 2.20 (1 H, br s), 2.58–2.63 (1 H, m), 3.84–3.94 (3 H, m), 5.61 (dt, *J* 10.1 and 1.3), 5.91 (1 H, ddd, *J* 2.2, 5.5 and 10.1), 7.48–7.55 (2 H, m), 7.60–7.66 (1 H, m) and 7.92–7.97 (2 H, m); *m/z* (FAB) 407 ($MH^+ - H_2O$, 1%), 125 (27), 97 (62) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(*methoxycarbonyl*)-2-*phenylsulphonyloxirane* **16k**. The electrophile was methyl chloroformate (1.3 equiv.), and the reaction mixture was warmed to −80 °C over 5 min. The residue was purified by flash chromatography using 5:1 light petroleum–ethyl acetate as eluent to yield the *oxirane* **16k** (77%), as an oil; ν_{max}(film)/cm^{-1} 2956, 2931, 2858, 1753, 1449, 1329, 1159 and 839; δ_H(300 MHz) 0.01 (3 H, s), 0.03 (3 H, s), 0.84 (9 H, s), 3.74 (3 H, s), 3.78–4.03 (3 H, m), 7.53–7.62 (2 H, m), 7.67–7.75 (1 H, m) and 7.87–7.93 (2 H, m); *m/z* (FAB) 387 (MH^+, 3%), 371 (3), 355 (4), 329 (38), 245 (40), 125 (70) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(*ethoxalyl*)-2-*phenylsulphonyloxirane* **16l**. The electrophile was ethyl oxalyl chloride (1.7 equiv.), and the reaction mixture was warmed to −80 °C over 2 min. Addition of 10:1 light petroleum–ethyl acetate (2 cm^3) to the crude product caused the *oxirane* **16l** (50%) to crystallise out, m.p. 117–118 °C (Found: C, 52.55; H, 6.3. $C_{19}H_{28}O_7SiS$ requires C, 53.25; H, 6.6%); ν_{max}(KBr)/cm^{-1} 2931, 2858, 1750, 1471, 1448, 1333, 1297, 1257, 1154, 836 and 783; δ_H(300 MHz) −0.08 (3 H, s), −0.05 (3 H, s), 0.77 (9 H, s), 1.42 (3 H, t, *J* 7.1), 4.14–4.16 (2 H, m), 4.22 (1 H, t, *J* 1.0), AB part of ABX_3 system (δ_A 4.39, δ_B 4.41, J_{AB} 14.4, J_{AX}, J_{BX} 7.1) 7.54–7.60 (2 H, m), 7.69–7.75 (1 H, m) and 7.77–7.80 (2 H, m); *m/z* (FAB) 371 ($MH^+ - C_4H_{10}$, 5%), 355 (2), 297 (5), 287 (8), 269 (3), 185 (11), 125 (32) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(4′-*hydroxybutanoyl*)-2-*phenylsulphonyloxirane* **16m**. The electrophile was γ-butyrolactone (1.5 equiv.), and the reaction mixture was warmed to −68 °C over 4 min. The residue was purified using 3:1 light petroleum–ethyl acetate as eluent to yield the *oxirane* **16m** (76%), as an oil which eventually solidified, m.p. 87–88 °C; ν_{max}(film)/cm^{-1} 3498, 2956, 2931, 2858, 1723, 1329, 1157, 838 and 757; δ_H(300 MHz) 0.00(s), 0.03(s), 0.09(s) and 0.10(s) (together 6 H), 0.84(s) and 0.92(s) (together 9 H), 1.74–1.81(m), 1.94–2.13(m), 2.49–2.61(m) and 2.95–3.06(m) (together 5 H), 3.56 (dt, *J* 0.9 and 6.2), 3.81–4.01(m), 4.17 (dd, *J* 4.0 and 5.8) (together 5 H), 7.49–7.65 (2 H, m), 7.69–7.75 (1 H, m) and 7.85–7.95 (2 H, m); *m/z* (FAB) 437 (MNa^+, 1%), 397 ($MH^+ - H_2O$, 39), 255 (53), 125 (88) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(5′-*hydroxypentanoyl*)-2-*phenylsulphonyloxirane* **16n**. The electrophile was δ-valerolactone (1.5 equiv.), and the reaction mixture was warmed to −70 °C over 5 min. The residue was purified by flash chromatography using 50:1 dichloromethane–ethanol as eluent to yield the *oxirane* **16n** (87%), as an oil; ν_{max}(film)/cm^{-1} 3407br, 2955, 2933, 2884, 2859, 1723, 1448, 1328, 1158 and 730; δ_H(300 MHz) 0.00(s), 0.02(s), 0.09(s) and 0.10(s) (together 6 H), 0.84(s) and 0.92(s) (together 9 H), 1.44–1.60(m), 1.72–1.78(m), 2.38–2.47(m) and 2.83–2.92(m) (together 7 H), 3.58 (t, *J* 6.2), 3.81 (dd, *J* 2.6 and 11.8), 3.85–3.95(m), 4.01–4.04(m) and 4.20 (dd, *J* 4.3 and 5.6) (together 5 H), 7.46–7.51(m), 7.56–7.61(m), 7.69–7.75(m) (together 3 H) and 7.84–7.89 (2 H, m); *m/z* (FAB) 451 (MNa^+, 4%), 429 (MH^+, 2), 411 (16), 381 (7), 297 (9), 273 (15), 154 (77), 136 (90) and 73 (100).

Bromoacetyltrimethylsilane **17d**.—A solution of magnesium bromide in diethyl ether–toluene[42] (1 mol dm^{-3}; 1.38 cm^3) was added to a solution of the silyloxirane **6d** (0.352 g, 1.38 mmol) in dry diethyl ether (30 cm^3), and the mixture was stirred at room temp. for 2 h. The reaction mixture was then poured into water (20 cm^3), the organic layer separated and the aqueous layer extracted with light petroleum (2 × 10 cm^3). The combined organic layers were dried and concentrated, and the residue purified by Kugelrohr distillation (oven temp. 100 °C, 15 mmHg) to give the *acylsilane* **17d** (0.176 g, 66%) as an oil; ν_{max}/cm^{-1} 2958, 2930, 1644 and 1251; δ_H(300 MHz) 0.24 (9 H, s) and 4.08 (2 H, s).

1-*Bromobutane*-2,3-*dione* **17f**.—A solution of magnesium bromide in diethyl ether–toluene[42] (1 mol dm^{-3}; 1.46 cm^3) was added to a solution of the oxirane **6f** (0.300 g, 1.33 mmol) in dry diethyl ether (10 cm^3). The mixture was stirred for 2 h at room temp., then diluted with light petroleum (20 cm^3) and filtered through Celite. The Celite was washed with a further portion of light petroleum (20 cm^3), and the combined filtrates were concentrated to yield the bromo dione **17f** as an oil (Found: MH^+, 164.9615. $C_4H_6BrO_2$ requires *M*H 164.9552); ν_{max}(film)/cm^{-1} 3483, 2987, 1719, 1358 and 1038; δ_H(300 MHz) 2.44 (3 H, s) and 4.32 (2 H, s); *m/z* (EI) 165 (MH^+, 1%) and 83 (100).

1-*Bromo*-3-*hydroxybutanone* **17a**.—A solution of magnesium bromide in diethyl ether–toluene (1 mol dm^{-3}; 0.93 cm^3) was added to a solution of the oxirane **8a** (0.193 g, 0.85 mmol) in dry diethyl ether (10 cm^3). The mixture was stirred for 2 h at room temp. and pH 7 phosphate buffer (5 cm^3) was then added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 cm^3). The combined organic extracts were dried and concentrated to yield the *bromo ketone* **17a** (0.097 g, 68%) as an oil; ν_{max}(film)/cm^{-1} 3427, 2983, 1730, 1450, 1386, 1127 and 1046; δ_H(300 MHz) 1.40 (3 H, d, *J* 7.0), 2.98 (1 H, br s), AB system (δ_A 4.06, δ_B 4.12, J_{AB} 13.3), and 4.60 (1 H, q, *J* 7.0).

1-(*Bromoacetyl*)*cyclopentanol* **17e**.—A solution of magnesium bromide (1 mol dm^{-3}; 0.92 cm^3) was added to a solution of the oxirane **8e** (0.234 g, 0.88 mmol) in dry diethyl ether (10 cm^3), and the mixture was stirred at room temp. for 2 h. The reaction mixture was diluted with more ether (10 cm^3) and then filtered through Celite. The Celite was washed with ether (10 cm^3), and the combined filtrates were concentrated to give the *bromo ketone* **17e** (0.145 g, 80%) as an oil (Found: MH^+, 206.9992. $C_7H_{12}BrO_2$ requires 207.0021); ν_{max}/cm^{-1} 3490, 2958, 1720, 1386, 1035, 1017 and 638; δ_H(300 MHz) 1.76–1.98 (6 H, m), 2.10–2.13 (2 H, m), 2.8 (1 H, br s) and 4.23 (2 H, s); *m/z* (EI) 207 (MH^+, 14%), 189 (33) and 83 (100).

1-*Bromo*-3-*hydroxy*-3-*methylpentane*-2-*one* **17g**.—A solution of magnesium bromide in diethyl ether–toluene (1 mol dm^{-3}; 0.69 cm^3) was added to a solution of the oxirane **8g** (0.161 g, 0.63 mmol) in dry ether (5 cm^3), and the mixture was stirred at room temp. for 2 h. The reaction mixture was diluted with ether (5 cm^3) and then filtered through Celite. The Celite was washed with ether (5 cm^3), and the combined filtrates were concentrated to give the *bromo ketone* **17g** (0.076 g, 62%) as an oil (Found: $MH^+ - H_2O$, 179.9634. $C_5H_6BrO_2$ requires 176.9552); ν_{max}/cm^{-1} 3485, 2930, 1730 and 1150; δ_H(300 MHz) 0.88 (3 H, t, *J* 7.4), 1.43 (3 H, s), 1.69–1.86 (2 H, m), 3.10 (1 H, br s) and 4.25 (2 H, s); *m/z* (EI) 195 (MH^+, 15%), 177 (33), 135 (32), 121 (48) and 83 (100).

trans-2-*Butyl*-3-*hydroxymethyl*-2-*phenylsulphonyloxirane* **19g**.—The oxirane **16g** (0.31 g, 0.81 mmol) was dissolved in toluene (2 cm^3) and boron trifluoride–diethyl ether (0.10 cm^3, 0.81 mmol) was added. The reaction mixture was stirred for 16 h at room temp., diluted with ether (10 cm^3) and then aqueous sodium hydrogen carbonate (5 cm^3) was added. The organic layer was separated, dried, and concentrated to give the *oxirane* **19g** (0.163 g, 75%), as an oil; ν_{max}/cm^{-1} 3517, 2961, 1447, 1308, 1148 and 727; δ_H(200 MHz) 0.82 (3 H, t, *J* 7.0), 1.11–1.28 (3 H, m), 1.49–1.64 (1 H, m), 1.74–2.02 (2 H, m), 2.45 (1 H, br s), 3.69 (1 H, dd, *J* 5.3 and 11.6), 3.84 (1 H, dd, *J* 3.7 and 5.3), 3.93 (1 H, dd, *J* 3.7 and 11.6), 7.54–7.75 (3 H, m) and 7.90–7.96 (2 H, m); *m/z* (FAB) 271 (MH^+, 8%), 125 (100) and 85 (55).

2-*Bromo*-1-(tert-*butyldimethylsilyloxy*)-4-*phenylbutan*-3-*one* **20**.—Solid magnesium bromide–diethyl ether (0.232 g, 0.90 mmol) was added to a solution of the oxirane **16h** (0.289 g, 0.69 mmol) in dry diethyl ether (5 cm^3). The mixture was stirred at room temp. for 4.5 h, diluted with light petroleum (20 cm^3) and filtered through Celite. The Celite was washed with light petroleum (20 cm^3) and the combined filtrates were concentrated to yield the *bromo ketone* **20** (0.211 g, 85%) as an oil (Found: $MH^+ - C_4H_9$, 299.0110. $C_{12}H_{16}BrO_2Si$ requires 299.0103); ν_{max}(film)/cm^{-1} 2955, 2930, 2857, 1725, 1256, 1100 and 837; δ_H(300 MHz) 0.05 (3 H, s), 0.06 (3 H, s), 0.85 (9 H, s), 3.89 (1 H, dd, *J* 5.5 and 10.5), AB system (δ_A 3.90, δ_B 4.04, J_{AB} 16.1), 40.9 (1 H, dd, *J* 8.2 and 10.5), 4.35 (1 H, dd, *J* 5.5 and 8.2) and 7.19–7.34 (5 H, m); *m/z* (EI) 299 ($MH^+ - C_4H_9$, 100%), 271 (40), 219 (42), 189 (38), 129 (36) and 91 (62).

2-*Bromo*-1-*hydroxy*-4-*phenylbutan*-3-*one* **21**.—The silyl ether **20** 0.211 g, 0.59 mmol) was dissolved in dichloromethane (3 cm^3), and boron trifluoride–diethyl ether (0.11 cm^3, 0.89 mmol) was added. The mixture was stirred at room temp. for 2.5 h, diluted with dichloromethane (10 cm^3), and washed with saturated aqueous sodium hydrogen carbonate (5 cm^3). The organic layer was separated, the aqueous layer extracted with dichloromethane (10 cm^3), and the combined organic extracts were dried and concentrated to give the *bromo alcohol* **21** (0.100 g, 70%) as an oil (Found: M^+, 241.9903. $C_{10}H_{11}BrO_2$ requires *M*, 241.9943); ν_{max}/cm^{-1} 3416, 1719, 1497, 1454, 1075, 1049, 1032, 739 and 698; δ_H(300 MHz) 2.40 (1 H, br s), 3.89 (1 H, dd, *J* 5.0 and 12.2), 4.03 (1 H, dd, *J* 7.4 and 12.2), 4.03 (2 H, s), 4.45 (1 H, dd, *J* 5.0 and 7.4) and 7.14–7.42 (5 H, m); *m/z* (EI) 242 (M^+, 4%), 163 (24), 136 (58) and 91 (100).

1-*Phenylsulphonyl*-3,6-*dioxabicyclo*[3.1.0]*hexan*-2-*one* **22**.—The oxirane **16k** (0.340 g, 0.881 mmol) was dissolved in dichloromethane (7 cm^3), and trifluoromethanesulphonic acid (0.156 cm^3, 1.76 mmol) was added. The mixture was stirred at room temp. until TLC (3:1 light petroleum–ethyl acetate) indicated consumption of **16k**. Aqueous sodium hydrogen carbonate (5 cm^3) was added and, after separation of the organic layer, the aqueous layer was extracted with

Table 5 Atomic coordinates (× 10^4) for **24a**

	x	*y*	*z*
C(1)	−1 886(3)	7 108(3)	8 653(2)
O(2)	−2 496(2)	7 594(2)	7 795(1)
C(3)	−3 767(4)	6 764(4)	7 374(2)
C(4)	−4 078(4)	5 846(5)	8 078(3)
C(5)	−2 533(4)	5 688(3)	8 702(2)
O(6)	−2 301(2)	8 039(2)	9 260(1)
C(7)	−1 127(4)	8 132(3)	10 058(2)
C(8)	287(4)	7 883(3)	9 769(2)
O(9)	322(3)	8 634(2)	8 985(1)
C(10)	−171(3)	7 245(3)	8 902(2)
S(11)	1 095(1)	6 124(1)	8 528(1)
O(12)	2 575(3)	6 581(4)	8 944(2)
O(13)	665(3)	4 723(2)	8 675(2)
C(14)	718(3)	6 447(3)	7 383(2)
C(15)	1 379(4)	7 567(4)	7 087(3)
C(16)	1 014(5)	7 838(4)	6 192(3)
C(17)	48(4)	6 990(4)	5 612(2)
C(18)	−579(4)	5 879(4)	5 912(2)
C(19)	−258(3)	5 595(3)	6 801(2)

dichloromethane (10 cm^3). The combined organic layers were dried and concentrated to give the *lactone* **22** (0.190 g, 90%) as a white solid, m.p. 153–154 °C (Found: C, 50.0; H, 3.3. $C_{10}H_8O_5S$ requires C, 50.0; H, 3.35%); ν_{max}(KBr)/cm^{-1} 1794, 1450, 1328, 1164, 1062 and 594; δ_H(300 MHz) 4.45 (2 H, s), 4.89 (1 H, s), 7.62–7.68 (2 H, m), 7.75–7.81 (1 H, m) and 8.11–8.15 (2 H, m); *m/z* (EI) 240 (M^+), 141, 135 and 78.

4-*Bromofuran*-2,3-*dione* **23**.—The oxirane **22** (0.109 g, 0.453 mmol) was dissolved in THF (6 cm^3) and solid magnesium bromide–diethyl etherate (0.117 g, 0.453 mmol) was added. The reaction mixture was stirred for 4 h at room temp., and then diluted with diethyl ether (10 cm^3) before being filtered through Celite. The Celite was washed with more diethyl ether (10 cm^3) and the combined filtrates were concentrated to give the *bromo dione* **23** (0.073 g, 90%) as a solid, m.p. 90–94 °C (Found: M^+, 177.9275. $C_4H_3BrO_3$ requires *M*, 177.9266); ν_{max}(KBr)/cm^{-1} 3328, 1762, 1700, 1345, 1168 and 1104; δ_H(300 MHz) 4.82 (2 H, s) and 7.11 (1 H, br s); *m/z* 178 (M^+, 30%), 133 (79), 77 (61) and 69 (100).

(1α,2α,5α)- *and* (1α,2β,5α)-*Dihydro*-1-(*phenylsulphonyl*)-*spiro*[3,6-*dioxabicyclo*[3.1.0]*hexane*-2,2′(3′,H)*furan*] **24a** *and* **24b**.—Crude oxirane **16m** prepared by the previously described procedure using oxirane **10b** (0.312 g, 0.95 mmol) was dissolved in acetone (5 cm^3) and treated with 2 drops of aqueous perchloric acid. The reaction mixture was stirred for 3 h at room temp. and then poured into water (0.5 cm^3) and extracted with light petroleum (30 cm^3). The light petroleum extracts were dried, concentrated and the residue purified by flash chromatography using 3:1 light petroleum–ethyl acetate as eluent to give the two diastereoisomeric *spiroacetals* **24a** and **24b**. The spiroacetal with higher R_F **24b** (0.015 g, 6%) was a solid, m.p. 109–112 °C; ν_{max}(KBr)/cm^{-1} 2873, 1448, 1324, 1155, 1040, 727 and 622; δ_H(300 MHz) 1.95–2.06 (3 H, m), 2.29–2.43 (1 H, m), AB system (δ_A 3.84, δ_B 3.90, J_{AB} 10.9), 3.93–4.03 (2 H, m), 4.05 (1 H, s), 7.56–7.62 (2 H, m), 7.68–7.74 (1 H, m) and 7.93 (2 H, m); *m/z* 283 (MH^+, 77%), 141 (51) and 125 (100). The spiroacetal with lower R_F was a solid, m.p. 85 °C (Found: C, 55.25; H, 4.9. $C_{13}H_{14}O_3S$ requires C, 55.3; H, 5.0%); ν_{max}(KBr)/cm^{-1} 2960, 2884, 1448, 1330, 1158, 1046, 724 and 689; δ_H(300 MHz) 1.97–2.12 (3 H, m), 2.78–2.91 (1 H, m), 3.43–3.52 (1 H, m), 3.74 (1 H, d, *J* 11.3), 3.89–3.96 (1 H, m), 4.08 (1 H, d, *J* 11.3), 4.31 (1 H, s), 7.55–7.61 (2 H, m), 7.67–7.73 (1 H, m) and 7.93–7.97 (2 H, m); *m/z* (FAB) 283 (MH^+, 29%), 215 (21), 125 (89) and 73 (100).

(1α,2α,5α)- *and* (1α,2β,5α)-*Tetrahydro*-1-(*phenylsulphonyl*)-*spiro*[3,6-*dioxabicyclo*-[3.1.10]-*hexane*-2,2′(2′H)*pyran*] **25a** *and* **25b**.—Crude oxirane **16n** prepared by the previously described procedure using oxirane **10b** (0.481 g, 1.46 mmol) was dissolved in acetone (5 cm^3) and treated with 2 drops of aqueous perchloric acid. The reaction mixture was stirred for 3 h at room temp. and then poured into water (0.5 cm^3) and extracted with light petroleum (30 cm^3). The light petroleum extracts were dried, concentrated and the residue purified by flash chromatography using 3:1 light petroleum–ethyl acetate as eluent to give the two diastereoisomeric *spiroacetals* **25a** and **25b** (0.250 g, 58%), an oil, as a 2:1 mixture. Recrystallisation from light petroleum–ethyl acetate allowed the isolation of a sample of **25a** containing < 15% of **25b**. This sample of **25a** had m.p. 156–157 °C (Found: C, 56.9; H, 5.35. $C_{14}H_{16}O_5S$ requires C, 56.75; H, 5.45%). The following data refer to the mixture of diastereoisomers; ν_{max}(film)/cm^{-1} 2948, 1448, 1329, 1159, 1074 and 726; δ_H(300 MHz) 1.44–1.82(m) and 2.17–2.47(m) (together 6 H), 3.53–3.60(m) and 3.68–3.73(m) (together 2 H), 3.78† (d, *J* 11.4), AB system (δ_A 3.86, δ_B 3.92, J_{AB} 11.0) and 4.10† (d, *J* 11.4) (together 2 H), 4.03(s) and 4.29†(s) (together 1 H), 7.54–7.60 (2 H, m), 7.65–7.72 (1 H, m) and 7.96–8.00 (2 H, m); *m/z* 297 (MH^+, 20%), 155 (33) and 125 (100).

Crystal Data for **24a**.—$C_{13}H_{14}O_5S$, M_r = 282.3, monoclinic, *a* = 9.170(3), *b* = 9.713(3), *c* = 15.569(4) Å, β = 104.58(3)°, *V* = 1342.3 $Å^3$ (from 2θ values of 32 reflections measured at ±ω, 20 < 2θ < 25°), *Z* = 4, D_c = 1.397 g cm^{-3}, *F*(000) = 592, μ(Mo-Kα) = 0.24 mm^{-1}, λ = 0.710 73 Å, space group $P2_1/n$, *T* = 22 °C.

Data Collection and Processing.—Stoe–Siemens diffractometer, crystal size 0.06 × 0.48 × 0.56 mm, ω/θ scan mode with on-line profile fitting,[43] $2\theta_{max}$ 50°, index ranges *h* −10 to 10, *k* 0 to 11, *l* 0 to 18, together with two symmetry equivalent sets and part of a fourth set, no variation observed for three standard reflections, no absorption correction; 7812 reflections measured, 2360 unique, 1650 with $F > 4\sigma_c(F)$ (σ_c from counting statistics only), R_{int} = 0.035.

Structure solution and refinement.[44] Direct methods, blocked-cascade refinement on *F*, weighting[45] $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 12G - 7G^2 + H^2 - 18GH$ ($G = F_0/F_{max}$, $H = \sin\theta/\sin\theta_{max}$), isotropic extinction parameter $x = 1.5(4) \times 10^{-6}$, such that $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$; anisotropic thermal parameters, scattering factors from reference 46, constrained H atoms [C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring angle external bisectors, $U(H) = 1.2U_{eq}(C)$], *R* = 0.052, *wR* = 0.046, *S* = 1.06 for 173 parameters, max. shift/e.s.d. 0.003, final difference electron density within ±0.31 e $Å^{-3}$.

Atomic coordinates are given in Table 5. Other parameters, together with full lists of bond lengths and angles, are available as supplementary material from the CCDC.*

Acknowledgements

We thank the SERC for postdoctoral support (M. A.) and for a research grant (W. C.), and the Nuffield Foundation for an equipment grant. We also thank Dr. M. N. S. Hill, Mr. I. McKeag, Mr. P. Kelly, Mr. S. Addison and Mr. D. Dunbar for obtaining spectroscopic and microanalytical data.

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Paper 0/04666C
Received 16*th October* 1990
Accepted 12*th December* 1990