Preparation of 2-Halogeno *S*-Phenyl Thioesters from 2-Phenylsulphonyl-2-phenylthiooxiranes. Crystal Structures of 2-Phenylsulphonyloxiranes

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1-Phenylsulphonyl-1-phenylthioalkenes **8** are prepared with high stereoselectivity as (*E*) isomers in a one-pot process by reaction of phenyl phenylthiomethyl sulphone **9** with aldehydes, followed by elimination. Nucleophilic epoxidation of these alkenes with lithium *tert*-butyl hydroperoxide yields 2-phenylsulphonyl-2-phenylthiooxiranes **4** as single diastereoisomers, without detectable oxidation of the phenylthio function. The oxiranes are also prepared by treatment of phenylsulphonyloxiranes **13** with butyllithium followed by diphenyl disulphide, which allows the preparation of 3,3-dialkyl-2-phenylsulphonyl-2-phenylthiooxiranes. The oxiranes **4** react with lithium or magnesium halides to give good yields of 2-halogeno *S*-phenyl thioesters **5**, **6** and **7**. 2-Iodo *S*-phenyl thioesters **7** are deiodinated by further treatment with magnesium iodide. In an analogous manner, 2-bromo *S*-methyl thioesters **15** and a 2-bromo *Se*-phenyl selenoester **17b** are also prepared from the corresponding oxiranes. X-Ray crystal structures of 2-phenylsulphonyloxiranes **4b**, **13e** and **14b**, reveal consistent lengthening of the C–O bond distant from the sulphonyl group, together with significant shortening of the C–O bond adjacent to the sulphonyl group.

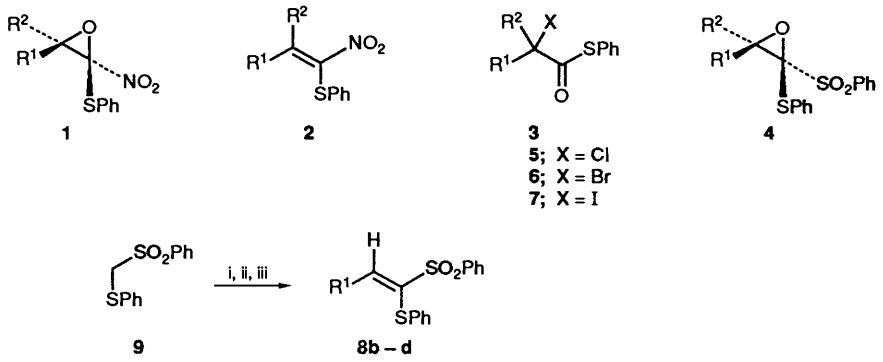
We have recently described synthetic applications of 2-nitro-2-phenylthiooxiranes **1**,[1] prepared by nucleophilic epoxidation of 1-nitro-1-phenylthioalkenes **2**. These oxiranes react efficiently with a variety of heteroatomic nucleophiles to give α-substituted *S*-phenylthioesters **3**,[2] which are themselves useful synthetic intermediates. Although the oxiranes **1** may be prepared efficiently, they are generally non-crystalline materials and we have therefore sought an alternative system in which the intermediates are stable and crystalline. We now report in full our investigations into the preparation of 2-phenylsulphonyl-2-phenylthiooxiranes **4**,[3] and their synthetic utility as precursors to 2-halogeno *S*-phenyl thioesters **5**, **6** and **7**,[4] which are inaccessible by direct halogenation of *S*-phenyl thioesters.[5]

Our first approach to the preparation of 2-phenylsulphonyl-2-phenylthiooxiranes involves epoxidation of 1-phenylsulphonyl-1-phenylthioalkenes **8** prepared by condensation of aldehydes with phenyl phenylthiomethyl sulphone **9**. Ogura has extensively investigated the synthetic utility of the closely related methylthiomethyl *p*-tolyl sulphone **10**,[6] developing methods for Knoevenagel condensation with aromatic aldehydes[7] and also a three step preparation of 2-alkyl-1-methylthio-1-(*p*-tolylsulphonyl)alkenes **11**, which proceeds with modest stereoselectivity.[8] Two direct methods for the condensation of **10** with unsaturated aldehydes have been reported.[9,10] Finally, contemporary with our own work, the direct condensation of **10** with α-oxygenated aldehydes using methanesulphonyl chloride–pyridine to dehydrate the initial adduct, was reported.[11]

Table 1 Preparation of alkenes **8** and **11**

Sulphone	Aldehyde	Product	R^1	Yield (%)
9	Pr^iCHO	**8b**	Pr^i	87
9	MeCHO	**8c**	Me	73
9	BuCHO	**8d**	Bu	83
10	Pr^iCHO	**11b**	Pr^i	70

Condensation of **9** with benzaldehyde was carried out using Ogura's general method to give the (*E*)-alkene **8a**.[7] We then investigated the direct condensation of phenyl phenylthiomethyl sulphone with simple aliphatic aldehydes. Treatment of **9** with butyllithium at −78 °C, followed by warming to 0 °C and re-cooling to −78 °C before addition of the aldehyde, gave the intermediate alkoxide adduct. The reaction could be quenched at this stage to give the β-hydroxy sulphone, or the mixture could be treated with acetic anhydride, triethylamine and a catalytic amount of 4-*N*,*N*-dimethylaminopyridine (DMAP) to give the (*E*)-alkenes **8b–d** in good yield, without detectable amounts of the (*Z*) isomers (Scheme 1, Table 1). The configurational assignment is based on the chemical shift of the vinyl proton in the ^1H NMR spectra. Analogous reaction of methylthiomethyl *p*-tolyl sulphone **10** with 2-methylpropanal



Scheme 1 *Reagents and conditions:* i, BuLi, THF, −78 to 0 °C; ii, RCHO, −78 °C; iii, Ac_2O, NEt_3, DMAP −78 to 0 °C

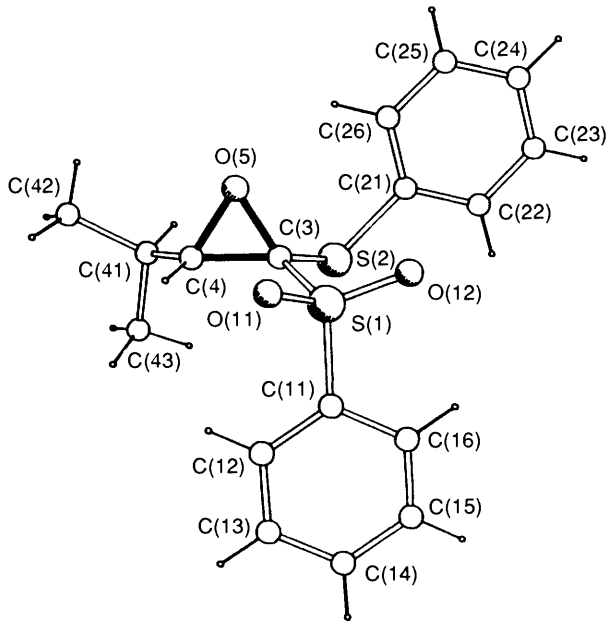
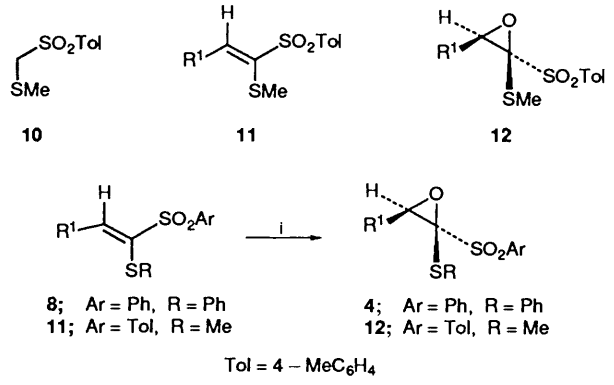


Fig. 1 The molecular structure of **4b**. Selected bond lengths (Å) and angles (°): C(3)–O(5) 1.425(4), C(4)–O(5) 1.450(3), C(3)–C(4) 1.481(3); C(3)–O(5)–C(4) 62.0(2), O(5)–C(3)–C(4) 59.8(2), O(5)–C(4)–C(3) 58.2(1)

to give the alkene **11b** was also efficient, although a trace of the (*Z*) isomer could be detected in this case.

Nucleophilic epoxidation of the alkenes **8a–d**, **11a** and **11b** was carried out using lithium *tert*-butyl hydroperoxide.[12] The reaction proceeded rapidly at temperatures between −78 and −18 °C to give the oxiranes **4a–d**, **12a** and **12b** in high yields as single stereoisomers (Scheme 2, Table 2). The structure of the



Scheme 2 *Reagents and conditions*: i, Bu^{t}O$_2$Li, THF, −78 to −18 °C.

Table 2 Preparation of oxiranes **4** and **12**

Alkene	Oxirane	R^1	Yield (%)
8a	**4a**	Ph	96
8b	**4b**	Pr^i	98
8c	**4c**	Me	99
8d	**4d**	Bu	92
11a	**12a**	Ph	99
11b	**12b**	Pr^i	92

oxirane **4b** was established by a single crystal X-ray structure determination (Fig. 1), and indicated that the epoxidation process had proceeded with retention of double bond configuration. Since previous epoxidations of unsaturated sulphones have also been shown to proceed with retention of

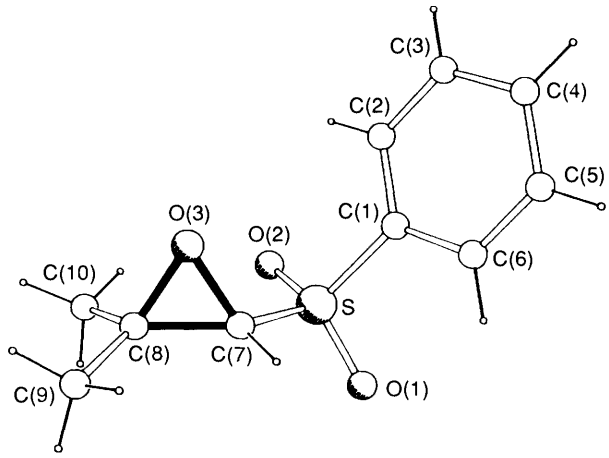
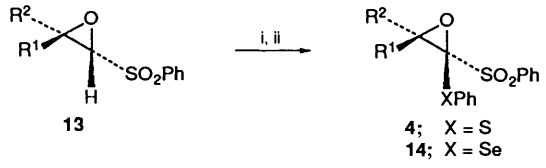


Fig. 2 The molecular structure of **13e**. Selected bond lengths (Å) and angles (°): C(7)–O(3) 1.410(3), C(8)–O(3) 1.457(5), C(7)–C(8) 1.476(4); C(7)–O(3)–C(8) 61.9(2), O(3)–C(7)–C(8) 60.6(2), O(3)–C(8)–C(7) 57.5(2)

configuration,[12,13] we feel confident of the stereochemical assignment of the remaining oxiranes.

Unfortunately it was not possible to prepare 1-phenylsulphonyl-1-phenylthioalkenes from ketones using the method which had proved successful for aldehydes. This observation is consistent with the report that addition of the lithio anion of phenyl phenylthiomethyl sulphone **9** to cyclic ketones does not take place efficiently.[14] We therefore investigated an alternative route, using the introduction of a phenylthio group to an existing 2-phenylsulphonyloxirane. 2-Phenylsulphonyloxiranes **13** are easily prepared by Darzens reaction of chloromethyl phenyl sulphone with aldehydes and ketones under phase transfer conditions.[15,16] An X-ray crystal structure determination of the oxirane **13e**, derived from acetone, revealed that the C–O bond distant from the sulphonyl group is significantly longer than the C–O bond adjacent to the sulphonyl group (Fig. 2). Treatment of the oxirane **13b** with butyllithium at −102 °C, followed by reaction with diphenyl disulphide,[13] gave the oxirane **4b** (90%), identical with the compound prepared by nucleophilic epoxidation. When a similar reaction sequence was applied to the oxiranes **13e** and **13f** derived from acetone and cyclohexanone, respectively, more modest yields of the desired 2-phenylsulphonyl-2-phenylthiooxiranes were obtained (Scheme 3, Table 3). These reduced yields are most likely due to the greater instability of the fully substituted lithiated 2-phenylsulphonyloxiranes, rather than their lower reactivity. Analogous 2-nitro-2-phenylthiooxiranes are less



Scheme 3 *Reagents and conditions*: i, BuLi, THF, −100 °C; ii, PhSSPh or PhSeCl

Table 3 Preparation of oxiranes **4** and **14** from 2-phenylsulphonyloxiranes **13**

2-Phenylsulphonyloxirane	Product	R^1	R^2	Yield (%)
13b	**4b**	Pr^i	H	90
13e	**4e**	Me	Me	45
13f	**4f**	$(CH_2)_5$		50
13b	**14b**	Pr^i	H	92
13f	**14f**	$(CH_2)_5$		25

Table 4 Preparation of α-halogeno *S*-phenyl thioesters **5**, **6**, **7** and **15**

Oxirane	R^1	R^2	Reagent	Product	X	Yield (%)
4a	Ph	H	LiCl	**5a**	Cl	95
4b	Pr^i	H	LiCl	**5b**	Cl	79
4c	Me	H	LiCl	**5c**	Cl	99
4d	Bu	H	LiCl	**5d**	Cl	91
4a	Ph	H	$MgBr_2$	**6a**	Br	91
4b	Pr^i	H	$MgBr_2$	**6b**	Br	86
4c	Me	H	$MgBr_2$	**6c**	Br	73
4d	Bu	H	$MgBr_2$	**6d**	Br	82
4e	Me	Me	$MgBr_2$	**6e**	Br	92
4f	$(CH_2)_5$		$MgBr_2$	**6f**	Br	68[a]
12a	Ph	H	$MgBr_2$	**15a**	Br	74
12b	Pr^i	H	$MgBr_2$	**15b**	Br	62
4a	Ph	H	MgI_2	**7a**	I	80[b]
4b	Pr^i	H	LiI	**7b**	I	77
4c	Me	H	LiI	**7c**	I	69
4d	Bu	H	LiI	**7d**	I	72

[a] A small amount of the unsaturated thioester **16** was isolated. [b] This yield was determined from the ^1H NMR spectrum.

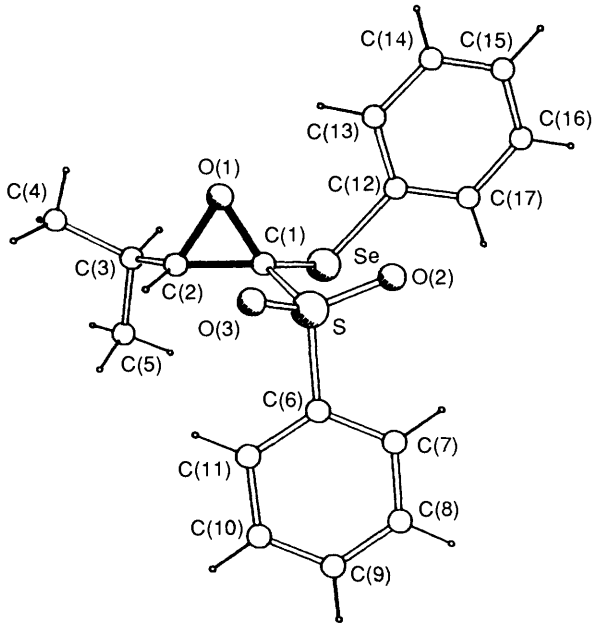


Fig. 3 The molecular structure of **14b**. Selected bond lengths (Å) and angles ( ): C(1)–O(1) 1.429(4), C(2)–O(1) 1.457(3), C(1)–C(2) 1.487(4); C(1)–O(1)–C(2) 62.0(2), O(1)–C(1)–C(2) 59.9(2), O(1)–C(2)–C(1) 58.1(2)

easily available, since, although (phenylthio)nitromethane does react with ketones to give the initial β-hydroxy nitro compounds,[17] dehydration of the adducts has not been reported. Direct Knoevenagel condensation of (phenylthio)nitromethane with ketones is possible, although the yields are rather poor.[1]

With the success of this alternative approach, we also briefly investigated the introduction of a phenylseleno substituent. Treatment of the lithio anion of **13b** with phenylselenenyl chloride gave the 2-phenylseleno-2-phenylsulphonyloxirane **14b**, with retention of stereochemistry, in excellent yield (92%). A much lower yield of the phenylselenooxirane **14f** (25%) was obtained using the fully substituted lithiated oxirane. A single crystal X-ray structure determination of **14b** (Fig. 3) confirmed the configurational assignment. It is noteworthy that the lengthening of the C–O bond distant from the sulphonyl group and the shortening of the C–O bond adjacent to the sulphonyl group observed in the 2-phenylsulphonyloxirane **13e**, is also observed in the crystal structures of both the 2-phenylsulphonyl-2-phenylthiooxirane **4b** and the 2-phenylseleno-2-phenylsulphonyloxirane **14b**. This difference presumably reinforces the normal tendency of a phenylsulphonyl group to suppress nucleophilic substitution at the α-position,[18] thus promoting nucleophilic attack at the β-position.

Reaction of the oxiranes **4a–d** with lithium chloride proceeded smoothly in acetone at reflux to give the 2-chloro *S*-phenyl thioesters **5a–d**. Treatment of the oxiranes **4a–f**, **12a** and **12b** with magnesium bromide at room temperature (or below) gave the 2-bromo *S*-phenyl thioesters **6a–d** and the 2-bromo *S*-methyl thioesters **15a** and **15b**, respectively. A small amount of the unsaturated thioester **16** was isolated from the reaction of **4f** with magnesium bromide. Analogous reaction of the phenylselenooxirane **14b** with magnesium bromide gave the 2-bromo *Se*-phenyl selenoester **17b** (69%), which suggests that the process may have significant scope. Finally, the oxiranes **4b–d** were converted in good yield into the 2-iodo *S*-phenyl thioesters **7b–d** using lithium iodide in acetone at reflux. 2-Iodo *S*-phenyl thioesters are unsurprisingly light-sensitive, particularly in solution, and it is advisable to handle them in the dark to avoid decomposition. The oxirane **4a** gave a complex mixture of unidentified products when treated with lithium iodide. Use of magnesium iodide at 0 °C allowed the isolation of the desired 2-iodo *S*-phenyl thioester **7a**, together with a small amount of the deiodinated *S*-phenyl thioester **18a** (Scheme 4, Table 4).

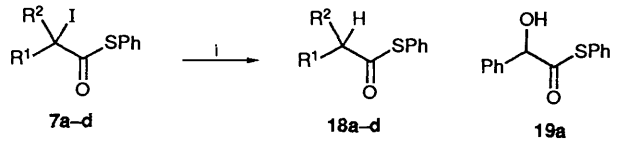
4; Ar = Ph, R = Ph
12; Ar = Tol, R = Me

5; X = Cl, R = Ph
6; X = Br, R = Ph
7; X = I, R = Ph
15; X = Br, R = Me

Scheme 4 *Reagents and conditions:* i, LiCl, $MgBr_2$, LiI or MgI_2

16 **17b**

Closer examination of the crude material from the preparation of the iodides **7b–d** also indicated the presence of trace amounts of the corresponding deiodinated compounds **18b–d**. We were therefore drawn to the conclusion that 2-iodo *S*-phenyl thioesters **7** can be converted into the corresponding deiodinated thioesters **18** by magnesium iodide. This hypothesis was confirmed by treatment of each of the 2-iodo *S*-phenyl thioesters **7a–d** with magnesium iodide in diethyl ether at room temperature in the dark, which led in good yield to the deiodinated compounds **18a–d**, respectively (Scheme 5, Table 5). While reductive dehalogenation of 2-halogeno ketones by iodide[19] and related reagents[20] is well-precedented, the analogous process with carboxylic acid derivatives appears to be restricted to 2-iodo lactones (prepared from the corresponding trifluoromethanesulphonates).[21]. Our observation of the



7a–d **18a–d** **19a**

Scheme 5 *Reagents and conditions:* i, MgI_2, Et_2O, room temp.

Table 5 Reduction of 2-iodo *S*-phenyl thioesters **7** to thioesters **18** with MgI_2

Iodo thioester	Thioester	Yield (%)
7a	**18a**	55[a]
7b	**18b**	91
7c	**18c**	67
7d	**18d**	99

[a] In addition, the 2-hydroxy thioester **19a** was also isolated (33%).

great ease of reductive deiodination of 2-iodo *S*-phenyl thioesters is presumably a reflection of the enhanced acidity of the α-protons of thioesters compared with oxygen esters.[22]

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 and referenced to tetramethylsilane unless stated otherwise, *J* values are given in Hz. 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 either EI or FAB with MNBA as the matrix. Peaks due to ^{35}Cl, ^{79}Br and ^{80}Se 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 hypodermic 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 below −100 °C were prepared using liquid nitrogen and ethanol. All solvents were distilled: light petroleum refers to that fraction with boiling point between 40 and 60 °C, unless stated otherwise; dry tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl; dry diethyl ether was distilled from sodium benzophenone ketyl. 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 spectroscopy.[23] Butyllithium was obtained from Aldrich as nominal 2.5 mol dm^{-3} or 1.6 mol dm^{-3} solutions in hexanes, and the true concentration determined by titration using diphenylacetic acid as indicator.[24] Chloromethyl phenyl sulphone was obtained from Fluka, and used without further purification. Magnesium iodide in ether was prepared by reaction of an excess of magnesium turnings with iodine in dry diethyl ether under nitrogen, followed by filtration to give a concentration of MgI_2 of 0.17 mol dm^{-3}. *trans*-2-Methylthio-3-phenyl-2-*p*-tolylsulphonylethene **11a** was prepared by the literature procedure.[7] 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.

Phenyl Phenylthiomethyl Sulphone **9**.—A solution of bis(phenylthio)methane (20 g, 86.1 mmol) in acetic acid (64 cm^3) was cooled in an ice bath and hydrogen peroxide (14 cm^3, 123 mmol; 30% aqueous solution) was added with stirring. The flask was warmed to room temp. and stirring was continued for 80 min. Dichloromethane (500 cm^3) and water (100 cm^3) were added followed carefully by potassium carbonate (80 g, 0.58 mol). After effervescence had ceased, the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 50 cm^3). The organic extracts were combined, dried and the solvent removed under reduced pressure to yield phenyl phenylthiomethyl sulphoxide. This material was dissolved in acetone (400 cm^3) and water (14 cm^3) and cooled in an ice bath. Potassium permanganate (13.61 g, 86.1 mmol) was added to the stirred solution in several portions. The resulting mixture was warmed to room temp. and stirring was continued for 1 h. The insoluble matter was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in dichloromethane (200 cm^3), dried and the solvent was removed under reduced pressure. Crystallisation from diethyl ether–light petroleum yielded phenyl phenylthiomethyl sulphone [18.89 g, 83% overall from bis(phenylthio)methane], m.p. 62–64 °C (from Et_2O–light petroleum) (lit.,[18] 61–63 °C) (Found: C, 58.6; H, 4.4. Calc. for $C_{13}H_{12}O_2S_2$: C, 59.1; H, 4.6%); (Found: M^+, 264.026. Calc. for $C_{13}H_{12}O_2S_2$: M, 264.028); ν_{max}(KBr)/cm^{-1} 3058w, 3000w, 2944w, 1582w, 1306s and 1148s; δ_H(200 MHz) 4.35 (2 H, s), 7.16–7.28 (3 H, m), 7.30–7.41 (2 H, m), 7.46–7.55 (2 H, m), 7.59–7.67 (1 H, m) and 7.89–7.95 (2 H, m); *m/z* (EI) 264 (M^+, 32.5%), 186 (14) and 123 (100).

(E)-2-*Phenyl*-1-*phenylsulphonyl*-1-*phenylthioethene* **8a**.—Potassium carbonate (0.553 g, 4.0 mmol) and benzaldehyde (0.3 cm^3, 3.0 mmol) were added to a solution of phenyl phenylthiomethyl sulphone (0.529 g, 2.0 mmol) in isopropyl alcohol (5 cm^3) under nitrogen. The reaction mixture was refluxed for 3 h, water (10 cm^3) was added and the mixture was extracted with dichloromethane (3 × 15 cm^3). The extracts were dried and concentrated under reduced pressure. The resulting residue was chromatographed using light petroleum–ethyl acetate (10:1) to yield (E)-*phenyl*-1-*phenylsulphonyl*-1-*phenylthioethene* **8a** as white crystals (0.590 g, 84%), m.p. 112–113.5 °C (from ethyl acetate–light petroleum) (Found: C, 68.4; H, 4.4. $C_{20}H_{16}O_2S_2$ requires C, 68.15; H, 4.6%); ν_{max}(KBr)/cm^{-1} 3060w, 3018w, 1585m, 1565m, 1306s and 1149s; δ_H(300 MHz) 6.99–7.12 (5 H, m), 7.33–7.43 (5 H, m), 7.48–7.54 (1 H, m), 7.92–7.99 (4 H, m) and 8.58 (1 H, s); *m/z* (EI) 352 (M^+), 211 and 134.

General Procedure for Preparation of Alkenes **8b–d** *and* **11b**.—BuLi (1.1 cm^3, 1.95 mol dm^{-3} in hexanes; 2.15 mmol) was added to a solution of phenyl phenylthiomethyl sulphone (0.53 g, 2 mmol) in dry THF (5 cm^3) at −78 °C under nitrogen. The reaction mixture was warmed to 0 °C, stirred at that temp. for 30 min, cooled to −78 °C, and the aldehyde (2.2 mmol) was then added. Stirring was continued at −78 °C for 30 min, and then Ac_2O (0.23 cm^3, 2.4 mmol) was added. After a further 10 min, NEt_3 (0.67 cm^3, 4.8 mmol) and 4-dimethylaminopyridine (DMAP) (12 mg, 0.1 mmol) were added. The reaction mixture was then allowed to warm to 0 °C, and quenched with phosphate buffer (pH 7) (10 cm^3) when TLC analysis showed complete conversion into the desired alkene **8** or **11**. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (10 cm^3). The combined organic extracts were washed with saturated brine (10 cm^3) and dried. Solvent was removed, and the residue purified by flash chromatography.

(E)-3-*Methyl*-1-*phenylsulphonyl*-1-*phenylthiobut*-1-*ene* **8b**. 2-Methylpropanal was the aldehyde, and the reaction was carried out on a 20 mmol scale. Chromatography was carried out using light petroleum–ethyl acetate (20:1) as eluent to yield (E)-3-*methyl*-1-*phenylsulphonyl*-1-*phenylthiobut*-1-*ene* **8b** as a colourless oil which eventually solidified (5.550 g, 87%), m.p. 64–66 °C (from Et_2O–light petroleum) (Found: C, 64.3; H, 5.5. $C_{17}H_{18}O_2S_2$ requires C, 64.1; H, 5.7%); ν_{max}(film)/cm^{-1} 3062w, 2966m, 2930w, 2871w, 1582m, 1310s and 1144s; δ_H(300 MHz) 1.03 (6 H, d, *J* 6.7), 2.91–3.09 (1 H, m), 7.03–7.19 (5 H, m), 7.38–7.58 (3 H, m), 7.58 (1 H, d, *J* 10.2) and 7.86–7.92 (2 H, m); *m/z* (FAB) 637 (M_2H^+, 3%), 319 (MH^+, 14) and 177 (100).

(E)-1-*Phenylsulphonyl*-1-*phenylthioprop*-1-*ene* **8c**. Ethanal was the aldehyde. Chromatography was carried out using light petroleum–ethyl acetate (15:1) as eluent to yield (E)-1-*phenylsulphonyl*-1-*phenylthioprop*-1-*ene* **8c** as white crystals (0.425 g,

73%), m.p. 98.5–99 °C (from Et_2O) (Found: C, 62.2; H, 4.6. $C_{15}H_{14}O_2S_2$ requires C, 62.0; H, 4.85%); ν_{max}(KBr)/cm^{-1} 3030w, 2926w, 1596w, 1579w, 1304s and 1151; δ_H(300 MHz) 2.04 (3 H, d, *J* 6.9), 6.98–7.03 (2 H, m), 7.09–7.16 (3 H, m), 7.39–7.45 (2 H, m), 7.49–7.55 (1 H, m), 7.87 (1 H, q, *J* 6.9) and 7.89–7.92 (2 H, m); *m/z* (FAB) 290 (M^+, 26%) and 141 (100).

(E)-1-*Phenylsulphonyl*-1-*phenylthiohex*-1-*ene* **8d**. Pentanal was the aldehyde. Chromatography was carried out using light petroleum–ethyl acetate (15:1) as eluent to yield (E)-1-*phenylsulphonyl*-1-*phenylthiohex*-1-*ene* **8d** as a colourless oil which eventually became a white wax (550 mg, 83%) (Found: C, 65.1; H, 6.05. $C_{18}H_{20}O_2S_2$ requires C, 65.0; H, 6.1%); ν_{max}(film)/cm^{-1} 3062w, 3021w, 2958m, 2929m, 2869w, 1583w, 1308s and 1155s; δ_H(300 MHz) 0.86 (3 H, t, *J* 7.2), 1.24–1.36 (2 H, m), 1.39–1.48 (2 H, m), 2.42 (2 H, q, *J* 7.4), 7.00–7.03 (2 H, m), 7.07–7.16 (3 H, m), 7.40–7.45 (2 H, m), 7.50–7.55 (1 H, m), 7.77 (1 H, t, *J* 7.4) and 7.88–7.91 (2 H, m); *m/z* (EI) 332 (M^+) and 191.

(E)-3-*Methyl*-1-*methylthio*-1-p-*tolylsulphonylbut*-1-*ene* **11b**. Methylthiomethyl *p*-tolyl sulphone **10** was used in place of phenyl phenylthiomethyl sulphone **9**, and 2-methylpropanal was the aldehyde. Chromatography was carried out using light petroleum (b.p. 60–80 °C)–ethyl acetate (30:1) as eluent to yield (E)-3-*methyl*-1-*methylthio*-1-p-*tolylsulphonylbut*-1-*ene* **11b** as a colourless oil (0.380 g, 70%) (Found: M^+, 270.0768. $C_{13}H_{18}O_2S_2$ requires *M*, 270.0748); ν_{max}(film)/cm^{-1} 3024w, 2965m, 2928m, 2870w, 1598m, 1302s and 1142s; δ_H(200 MHz; standard $CHCl_3$) 1.09 (6 H, d, *J* 6.7), 2.26 (3 H, s), 2.43 (3 H, s), 2.99–3.17 (1 H, m), 7.32 (2 H, d, *J* 7.3), 7.34 (1 H, d, *J* 10.0) and 7.80 (2 H, d, *J* 8.3); *m/z* (EI) 270 (M^+, 17%), 115 (100), and 91 (25). NMR spectroscopy revealed the presence of a trace of what is suspected to be the (*Z*)-isomer with signals at δ 1.01 (6 H, d, *J* 6.6), 2.33 (3 H, s), 6.26 (1 H, d, *J* 10.8). The latter two signals are characteristic of the (*Z*)-isomer of this type of compound.[8]

General Procedure for the Preparation of Oxiranes **4a–d** *and* **12a, b**.—*tert*-Butyl hydroperoxide (2.7 cm^3; 3.6 mol dm^{-3} solution in toluene, 9.7 mmol) in dry THF (80 cm^3) under nitrogen was cooled to −78 °C and BuLi (3.9 cm^3, 1.85 mol dm^{-3} in hexanes; 7.2 mmol) was added. The alkene **4** or **12** (6.5 mmol) in dry THF (5 cm^3) was then added and the mixture either stirred at −78 °C or warmed to −18 °C. The mixture was stirred until TLC showed disappearance of alkene (30–120 min). Aqueous NH_4Cl (10%; 15 cm^3) was then added and, after separation of the organic layer, the aqueous phase was extracted with CH_2Cl_2 (3 × 30 cm^3). The organic extracts were washed with saturated brine (30 cm^3), dried, concentrated under reduced pressure and the residue purified by flash chromatography.

(E)-3-*Phenyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4a**. The alkene was **8a**, and the reaction was stirred at −78 °C for 80 min. Chromatography was carried out using light petroleum–ethyl acetate (10:1) as eluent to yield (E)-3-*phenyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4a** as a colourless oil which eventually solidified (2.31 g, 96%), m.p. 92.5–93.5 °C (Found: C, 65.65; H, 4.3. $C_{20}H_{16}O_3S_2$ requires C, 65.2; H, 4.4%); ν_{max}(film)/cm^{-1} 3062wbr, 3031wbr, 1583w, 1378w, 1325s and 1155s; δ_H(300 MHz) 5.08 (1 H, s), 7.01–7.07 (2 H, m), 7.10–7.19 (3 H, m), 7.32 (5 H, s), 7.43–7.49 (2 H, m), 7.58–7.64 (1 H, m) and 7.89–7.93 (2 H, m); *m/z* (EI) 368 (M^+), 258, 250, 226, 125 and 109.

(E)-3-*Isopropyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4b**. The alkene was **8b** (0.74 mmol scale), and the reaction mixture was stirred at −18 °C for 2 h. Chromatography was carried out using light petroleum–ethyl acetate (10:1) as eluent to yield (E)-3-*isopropyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4b** as a colourless oil which eventually solidified (0.242 g, 98%), m.p. 93–94.5 °C (from Et_2O–light petroleum) (Found: C, 61.1; H, 5.4. $C_{17}H_{18}O_3S_2$ requires C, 61.05; H, 5.4%); ν_{max}(film)/cm^{-1} 3063w, 2965m, 2932w, 2874w, 1579w, 1325s and 1157s; δ_H(200 MHz) 0.98 (3 H, d, *J* 6.8), 1.18 (3 H, d, *J* 6.7), 1.95–2.13 (1 H, m), 3.67 (1 H, d, *J* 9.2), 7.05–7.29 (5 H, m), 7.34–7.43 (2 H, m), 7.51–7.60 (1 H, m) and 7.77–7.82 (2 H, m); *m/z* (EI) 334 (M^+), 218 and 109.

(E)-3-*Methyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4c**. The alkene was **8c** (1 mmol scale), and the reaction was stirred at −78 °C for 30 min. Chromatography with light petroleum–ethyl acetate (10:1) as eluent gave (E)-3-*methyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4c** as white crystals (0.302 g, 99%), m.p. 87.5–90 °C (from Et_2O) (Found: C, 58.8; H, 4.5. $C_{15}H_{14}O_3S_2$ requires C, 58.8; H, 4.6%); ν_{max}(KBr)/cm^{-1} 3061w, 3002w, 1581m, 1393m, 1324s, 1259m and 1153s; δ_H(300 MHz) 1.58 (3 H, d, *J* 5.3), 4.08 (1 H, q, *J* 5.3), 7.10–7.23 (3 H, m), 7.25–7.29 (2 H, m), 7.40–7.45 (2 H, m), 7.55–7.61 (1 H, m) and 7.83 (2 H, m); *m/z* (EI) 306 (M^+), 197 and 165.

(E)-3-*Butyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4d**. The alkene was **8d** (0.5 mmol scale), and the reaction mixture was stirred at −78 °C for 10 min before being warmed to −18 °C and stirred for 55 min. Chromatography with light petroleum–ethyl acetate (10:1) as eluent yielded (E)-3-*butyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4d** as a colourless oil which eventually solidified (0.160 g, 92%), m.p. 45–47 °C [from Et_2O–light petroleum (b.p. 60–80 °C)] (Found: C, 61.6; H, 5.9. $C_{18}H_{20}O_3S_2$ requires C, 62.0; H, 5.8%); ν_{max}(film)/cm^{-1} 3063w, 2959m, 2930m, 2872m, 1584w, 1325s and 1157s; δ_H(200 MHz) 0.86–1.03 (3 H, m), 1.25–1.57 (4 H, m), 1.82–2.17 (2 H, m), 3.96 (1 H, t, *J* 6.1), 7.07–7.29 (5 H, m), 7.36–7.44 (2 H, m), 7.52–7.61 (1 H, m) and 7.79–7.85 (2 H, m); *m/z* (EI) 348 (M^+, 0.4%), 332 (0.9), 207 (56), 137 (60) and 109 (100).

(E)-2-*Methylthio*-3-*phenyl*-2-p-*tolylsulphonyloxirane* **12a**. The alkene was **11a** (1.78 mmol scale), and the reaction mixture was stirred at −78 °C for 10 min before being warmed to −18 °C and stirred for 80 min. Chromatography with light petroleum–ethyl acetate (10:1) as eluent yielded (E)-2-*methylthio*-3-*phenyl*-2-p-*tolylsulphonyloxirane* **12a** as a colourless oil (0.565 g, 99%) (Found: M^+, 320.0567. $C_{16}H_{16}O_3S_2$ requires *M*, 320.0541); ν_{max}(film)/cm^{-1} 3065w, 3030w, 2930w, 1596w, 1326m, 1216w and 1154s; δ_H(200 MHz) 1.96 (3 H, s), 2.49 (3 H, s), 4.98 (1 H, s), 7.37 (5 H, s), 7.41 (2 H, d, *J* 7.9) and 7.94 (2 H, d, *J* 7.9); *m/z* (EI) 320 (M^+), 304, 165 and 155.

(E)-3-*Isopropyl*-2-*methylthio*-2-p-*tolylsulphonyloxirane* **12b**. The alkene was **11b** (1.4 mmol scale) and the reaction mixture was warmed to −18 °C and stirred for 70 min. Chromatography with light petroleum–ethyl acetate (20:1) as eluent yielded (E)-3-*isopropyl*-2-*methylthio*-2-p-*tolylsulphonyloxirane* **12b** as a colourless oil (0.370 g, 92%) (Found: M^+, 286.0696. $C_{13}H_{18}O_3S_2$ requires *M*, 286.0697); ν_{max}(film)/cm^{-1} 3023m, 2967m, 2931w, 2874w, 1597w, 1326m, 1216s and 1154s; δ_H(300 MHz) 0.96 (3 H, d, *J* 6.8), 1.13 (3 H, d, *J* 6.7), 1.18–1.93 (1 H, m), 2.05 (3 H, s), 2.47 (3 H, s), 3.52 (1 H, d, *J* 9.2), 7.38 (2 H, d, *J* 7.9) and 7.83–7.89 (2 H, d, *J* 7.9); *m/z* (EI) 286 (M^+), 239, 170 and 155.

Preparation of 2-*Phenylsulphonyloxiranes* **13**.—The compounds were prepared by the following minor modification of the phase transfer Darzens condensation developed by Makosza,[15] and employed by Durst,[16] since consistently higher yields were obtained by the use of dichloromethane as solvent. Aqueous sodium hydroxide (15 cm^3; 50%) and tetrabutylammonium bromide (0.419 g, 1.30 mmol) were added to a solution of chloromethyl phenyl sulphone (1.250 g, 6.56 mmol) in dichloromethane (15 cm^3) and cooled to 0 °C. The carbonyl compound (7.2 mmol) was added and the reaction mixture was stirred at this temp. for 2 h before being warmed to room temp. and stirred for 24 h. Water (15 cm^3) was added and the mixture was extracted with dichloromethane (3 × 15 cm^3). The organic

extracts were combined and washed with hydrochloric acid (15 cm^3; 1 mol dm^{-3}), sodium hydrogen carbonate (15 cm^3; 1 mol dm^{-3}) and saturated brine (15 cm^3). They were then dried, filtered and concentrated under reduced pressure. Flash chromatography using light petroleum–ethyl acetate as eluent yielded the oxiranes **13**.

(E)-3-*Isopropyl*-2-*phenylsulphonyloxirane* **13b**. The carbonyl compound was 2-methylpropanal (0.66 cm^3, 7.2 mmol). Chromatography using light petroleum–ethyl acetate (10:1) gave (E)-3-*isopropyl*-2-*phenylsulphonyloxirane* **13b** as a white solid (1.470 g, 99%), m.p. 53.5–54.5 °C (from Et_2O–light petroleum) (Found: C, 58.3; H, 6.0. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.2%); ν_{max}(KBr)/cm^{-1} 3096w, 3076w, 3020w, 2972m, 2909w, 2871w, 1584w, 1313s, 1232m and 1147s; δ_H(200 MHz) 1.01 (3 H, d, *J* 6.8), 1.03 (3 H, d, *J* 6.8), 1.67–1.84 (1 H, m), 3.52 (1 H, dd, *J* 1.7 and 6.4), 3.94 (1 H, d, *J* 1.7), 7.56–7.76 (3 H, m) and 7.91–7.97 (2 H, m); *m/z* (FAB) 453 (M_2H^+, 3.2%), 227 (MH^+, 24), 143 (82) and 125 (100).

3,3-*Dimethyl*-2-*phenylsulphonyloxirane* **13e**. The carbonyl compound was propanone (0.53 cm^3, 7.2 mmol). Chromatography using light petroleum–ethyl acetate (15:1) as eluent yielded 3,3-dimethyl-2-phenylsulphonyloxirane **13e** as white crystals (96%), m.p. 76–76.5 °C (from Et_2O–light petroleum) (lit.,[16] 72–74 °C) (Found: C, 57.1; H, 5.8. Calc. for $C_{10}H_{12}O_3S$: C, 56.6; H, 5.7%); ν_{max}(KBr)/cm^{-1} 3076w, 3026w, 2982m, 2882w, 1583w, 1323s, 1239m and 1155s; δ_H(200 MHz) 1.42 (3 H, s), 1.83 (3 H, s), 3.81 (1 H, s), 7.56–7.75 (3 H, m) and 7.94–8.00 (2 H, m); *m/z* (EI) 212 (M^+, 14%), 184 (23), 169 (17), 142 (25) and 125 (64).

2-*Phenylsulphonyl*-1-*oxaspiro*[2.5]*octane* **13f**. The carbonyl compound was cyclohexanone (0.68 cm^3, 6.56 mmol). Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded 2-phenylsulphonyl-1-oxaspiro[2.5]octane **13f** as a colourless oil which eventually solidified (1.660 g, 100%), m.p. 57–59 °C (from Et_2O–light petroleum) (lit.,[16] 56 °C) (Found: C, 62.1; H, 6.4. Calc. for $C_{13}H_{16}O_3S$: C, 61.9; H, 6.4%); ν_{max}(film)/cm^{-1} 3035w, 2938s, 2861m, 1586w, 1323s, 1269w and 1156s; δ_H(200 MHz) 1.42–1.87 (8 H, m), 2.05–2.33 (2 H, m), 3.77 (1 H, s), 7.55–7.74 (3 H, m) and 7.94–8.00 (2 H, m); *m/z* (FAB) 253 (MH^+, 40%), 235 (13), 143 (66), 125 (97) and 111 (100).

General Procedure for Work-up Used in the Preparation of Oxiranes **4b**, **4e**, **4f**, **14b** *and* **14f** *by Anion Formation*.—Aqueous ammonium chloride (5 cm^3; 10%) was added and the mixture was warmed to room temp. The organic layer was separated and the aqueous layer was washed with dichloromethane (3 × 15 cm^3). The extracts were dried, concentrated under reduced pressure and the resulting residue was purified by flash chromatography.

(E)-3-*Isopropyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4b**. *Anion quenching method*. A solution of the oxirane **13b** (0.113 g, 0.5 mmol) in dry THF (9 cm^3) was cooled to an internal temp. of −102 °C. Butyllithium (0.28 cm^3, 0.53 mmol; 1.9 mol dm^{-3}) was added dropwise keeping the internal temp. below −101 °C and the reaction mixture was stirred for 9 min at this temp. A solution of diphenyl disulphide (0.120 g, 0.55 mmol) in dry THF (1 cm^3) was added and the reaction mixture was stirred for a further 5 min, followed by usual work-up. Chromatography using light petroleum–ethyl acetate (10:1) as eluent gave (E)-3-*isopropyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4b** (0.150 g, 90%), identical with material prepared previously.

3,3-*Dimethyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4e**. A solution of 3,3-dimethyl-2-phenylsulphonyloxirane **13e** (0.106 g, 0.5 mmol) in dry THF (4 cm^3) and pentane (5 cm^3) was cooled to an internal temp. of −109 °C. Butyllithium (0.69 cm^3, 1.1 mmol; 1.6 mol dm^{-3}) was added dropwise keeping the internal temp. below −105 °C, followed immediately by the addition of a solution of diphenyl disulphide (0.218 g, 1.0 mmol) in dry THF (1 cm^3). The reaction mixture was stirred for a further 5 min during which time the temp. was not allowed to rise above −102 °C, and then worked-up as usual. Chromatography using light petroleum–ethyl acetate (10:1) as eluent gave 3,3-*dimethyl*-2-*phenylsulphonyl*-2-*phenylthiooxirane* **4e** as white crystals (0.072 g, 45%), m.p. 99–101 °C (from Et_2O) (Found: C, 59.7; H, 5.0. $C_{16}H_{16}O_3S_2$ requires C, 60.0; H, 5.0%); ν_{max}(KBr)/cm^{-1} 3062w, 3011w, 2967w, 2927w, 1582w, 1307sbr and 1148s; δ_H(200 MHz) 1.66 (3 H, s), 2.01 (3 H, s), 7.06–7.20 (5 H, m), 7.35–7.44 (2 H, m), 7.51–7.60 (1 H, m) and 7.82–7.88 (2 H, m); *m/z* (FAB) 321 (MH^+, 4.5%), 303 (1), 251 (10), 235 (4), 179 (27), 151 (100), 125 (18) and 109 (5).

2-*Phenylsulphonyl*-2-*phenylthio*-1-*oxaspiro*[2.5]*octane* **4f**. A solution of 2-phenylsulphonyl-1-oxaspiro[2.5]octane **13f** (0.126 g, 0.5 mmol) in dry THF (4 cm^3) and pentane (5 cm^3) was cooled to an internal temp. of −109 °C. Butyllithium (0.69 cm^3, 1.1 mmol; 1.6 mol dm^{-3}) was added dropwise keeping the internal temp. below −104 °C, followed immediately by the addition of a solution of diphenyl disulphide (0.218 g, 1.0 mmol) in dry THF (1 cm^3). The reaction mixture was stirred for a further 5 min during which time the temp. was not allowed to rise above −99 °C and then worked-up as usual. Chromatography using light petroleum–ethyl acetate (10:1) as eluent gave 2-*phenylsulphonyl*-2-*phenylthio*-1-*oxaspiro*[2.5]*octane* **4f** as white crystals (0.090 g, 50%), m.p. 125–127 °C (from Et_2O–light petroleum) (Found: C, 63.3; H, 5.5. $C_{19}H_{20}O_3S_2$ requires C, 63.3; H, 5.6%); ν_{max}(KBr)/cm^{-1} 3058w, 2944m, 2861m, 1584w, 1306s and 1150s; δ_H(200 MHz) 1.49–1.92 (6 H, m), 1.96–2.01 (2 H, m), 2.32–2.52 (2 H, m), 7.03–7.19 (5 H, m), 7.31–7.40 (2 H, m), 7.48–7.56 (1 H, m) and 7.79–7.85 (2 H, m); *m/z* (EI) 360 (M^+, 3%), 251 (7), 219 (94), 192 (97), 121 (49), 110 (83) and 109 (100).

(Z)-3-*Isopropyl*-2-*phenylseleno*-2-*phenylsulphonyloxirane* **14b**. A solution of 3-isopropyl-2-phenylsulphonyloxirane **13b** (0.113 g, 0.5 mmol) in dry THF (6 cm^3) and pentane (3 cm^3) was cooled to an internal temp. of −103 °C. Butyllithium (0.57 cm^3, 0.9 mmol; 1.58 mol dm^{-3}) was added dropwise whilst keeping the internal temp. below −100 °C. The reaction mixture was then stirred for 2 min at this temp. Benzeneselenenyl chloride (0.192 g, 1.0 mmol) in dry THF (0.5 cm^3) and pentane (0.5 cm^3) was then added over 5 min keeping the temp. below −100 °C. Stirring was continued for 1 min, and the reaction worked-up as usual. Chromatography using light petroleum–ethyl acetate (15:1) gave (Z)-3-*isopropyl*-2-*phenylseleno*-2-*phenylsulphonyloxirane* **14b** as a colourless oil which eventually solidified (0.175 g, 92%), m.p. 85.5–87.5 °C (from Et_2O–light petroleum) (Found: C, 53.6; H, 4.6. $C_{17}H_{18}O_3SSe$ requires C, 53.5; H, 4.8%); ν_{max}(film)/cm^{-1} 3062w, 3023w, 2966m, 2932w, 2875w, 1577w, 1324s, 1253w and 1154s; δ_H(300 MHz; standard CH_2Cl_2) 0.98 (3 H, d, *J* 6.8), 1.14 (3 H, d, *J* 6.7), 1.97–2.05 (1 H, m), 3.58 (1 H, d, *J* 9.3), 7.07–7.11 (2 H, m), 7.16–7.19 (3 H, m), 7.43–7.48 (2 H, m), 7.58–7.62 (1 H, m) and 7.86–7.90 (2 H, m); *m/z* (EI) 382 (M^+, 11%), 298 (9), 213 (25), 157 (100), 125 (41) and 77 (72).

2-*Phenylseleno*-2-*phenylsulphonyl*-1-*oxaspiro*[2.5]*octane* **14f**. A solution of 2-phenylsulphonyl-1-oxaspiro[2.5]octane **13f** (0.126 g, 0.5 mmol) in dry THF (6 cm^3) and pentane (3 cm^3) was cooled to an internal temp. of −104 °C. Butyllithium (1.1 cm^3, 1.3 mmol; 1.2 mol dm^{-3}) was added dropwise whilst keeping the internal temp. below −100 °C. The reaction mixture was then stirred for 5 min at this temp. A solution of benzeneselenenyl chloride (0.192 g, 1.0 mmol) in dry THF (0.5 cm^3) and pentane (0.5 cm^3) was then added over 3 min keeping the temp. below −100 °C. Stirring was continued at this temp. for a further 3 min, and then the reaction was worked-up as usual. Chromatography using light petroleum–ethyl acetate (20:1) gave 2-*phenylseleno*-2-*phenylsulphonyl*-1-*oxaspiro*[2.5]-

octane **14f** as a colourless oil which eventually solidified (0.050 g, 25%), m.p. 114.5–116.5 °C (from Et_2O) (Found: C, 55.9; H, 4.85. $C_{19}H_{20}O_3SSe$ requires C, 56.0; H, 4.95%); ν_{max}(film)/cm^{-1} 3057w, 2940m, 2860m, 1579w, 1316s and 1150s; δ_H(300 MHz; standard $CHCl_3$) 1.53–1.84 (6 H, m), 1.98–2.02 (2 H, m), 2.44–2.48 (2 H, m), 7.00–7.10 (4 H, m), 7.16–7.22 (1 H, m), 7.38–7.44 (2 H, m), 7.53–7.58 (1 H, m) and 7.85–7.88 (2 H, m); *m/z* (FAB) 409 (MH^+, 6%), 391 (3), 267 (13), 239 (85), 125 (67) and 109 (43).

General Procedure for Preparation of the 2-*Chloro* S-*Phenyl Thioesters* **5**.—The oxirane **4** (1 mmol) in dry acetone (2 cm^3) was added to a solution of lithium chloride (0.047 g, 1.10 mmol) in dry acetone (5 cm^3) at room temp. under nitrogen. The reaction mixture was then either stirred at room temp. or refluxed for the time indicated, and then quenched with water (3 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The organic extracts were combined, dried and concentrated under reduced pressure, and the residue then purified by flash chromatography using light petroleum–ethyl acetate (10:1) as eluent.

S-*Phenyl* 2-*chloro*-2-*phenyl*(*thioethanoate*) **5a**. The oxirane was **4a**, and the reaction mixture was refluxed for 30 min. S-*Phenyl* 2-*chloro*-2-*phenyl*(*thioethanoate*) **5a** was obtained as a yellow solid (0.250 g, 95%), m.p. 29.5–30.5 °C (from Et_2O–light petroleum) (Found: C, 63.6; H, 4.1. $C_{14}H_{11}ClOS$ requires C, 64.0; H, 4.2%); ν_{max}(film)/cm^{-1} 3063w, 3032w, 2953w, 1694s, 1583w and 1494w; δ_H(300 MHz) 5.52 (1 H, s), 7.35–7.44 (8 H, m) and 7.50–7.55 (2 H, m); *m/z* (EI) 262 (M^+), 234, 199, 137, 125 and 109.

S-*Phenyl* 2-*chloro*-3-*methyl*(*thiobutanoate*) **5b**. The oxirane was **4b**, and the reaction mixture was refluxed for 22 h. *S*-Phenyl 2-chloro-3-methyl(thiobutanoate) **5b** was obtained as a yellow oil (0.180 g, 79%), identical with the material prepared from the 2-nitro-2-phenylthiooxirane.[1]

S-*Phenyl* 2-*chloro*(*thiopropanoate*) **5c**. The oxirane was **4c**, and the reaction was stirred at room temp. for 5 h. The product, S-*phenyl* 2-*chloro*(*thiopropanoate*) **5c**, was obtained pure without chromatography as a pale yellow oil (0.199 g, 99%) (Found: M^+, 200.0095. C_9H_9ClOS requires *M*, 200.0063); ν_{max}(film)/cm^{-1} 3061w, 2986w, 2934w, 1698s and 1582w; δ_H(300 MHz) 1.77 (3 H, d, *J* 6.9), 4.59 (1 H, q, *J* 6.9) and 7.43 (5 H, s); *m/z* (EI) 200 (M^+), 144, 137, 110, 109 and 63.

S-*Phenyl* 2-*chloro*(*thiohexanoate*) **5d**. The oxirane was **4d**, and the reaction mixture was refluxed for 50 min. S-*Phenyl* 2-*chloro*(*thiohexanoate*) **5d** was obtained as a pale yellow oil (0.220 g, 91%) (Found: M^+, 242.0517. $C_{12}H_{15}ClOS$ requires *M*, 242.0532); ν_{max}(film)/cm^{-1} 3062w, 2959m, 2931m, 2868m, 1693s and 1583w; δ_H(300 MHz) 0.93 (3 H, t, *J* 7.2), 1.31–1.59 (4 H, m), 1.93–2.17 (2 H, m), 4.47 (1 H, dd, *J* 8.2, *J* 5.3) and 7.43 (5 H, s); *m/z* (EI) 242 (M^+), 144, 137, 109 and 105.

S-*Phenyl* 2-*Bromo*-2-*phenyl*(*thioethanoate*) **6a**.—Magnesium bromide–diethyl ether (0.123 g, 0.48 mmol) was added to a solution of the oxirane **4a** (0.160 g, 0.43 mmol) in dry diethyl ether (5 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 2 h, poured into light petroleum (15 cm^3), filtered and concentrated under reduced pressure to yield pure S-*phenyl* 2-*bromo*-2-*phenyl*(*thioethanoate*) **6a** as white crystals (0.120 g, 91%), m.p. 68.5–69.5 °C [from Et_2O–light petroleum (60–80 °C)] (Found: C, 54.9; H, 3.4. $C_{14}H_{11}BrOS$ requires C, 54.7; H, 3.6%); ν_{max}(KBr)/cm^{-1} 3056w, 3024w, 2985w, 1691s and 1492w; δ_H(300 MHz) 5.58 (1 H, s), 7.36–7.44 (8 H, m), 7.53–7.57 (2 H, m); *m/z* (EI) 306 (M^+), 277, 199, 196, 169, 137, 118 and 109.

S-*Phenyl* 2-*Bromo*-3-*methyl*(*thiobutanoate*) **6b**.—Magnesium bromide–diethyl ether (0.301 g, 1.17 mmol) was added to a solution of the oxirane **4b** (0.234 g, 0.70 mmol) in dry diethyl ether (10 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 22 h, poured into light petroleum (25 cm^3), filtered and concentrated under reduced pressure to yield pure *S*-phenyl 2-bromo-3-methyl(thiobutanoate) **6b** as a yellow oil (0.165 g, 86%) identical with the material prepared from the 2-nitro-2-phenylthiooxirane.[1]

S-*Phenyl* 2-*Bromo*(*thiopropanoate*) **6c**.—Magnesium bromide–diethyl ether (0.284 g, 1.10 mmol) was added to a solution of the oxirane **4c** (0.306 g, 1.00 mmol) in dry diethyl ether (12 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 6 h, poured into light petroleum (25 cm^3), filtered and concentrated under reduced pressure. Chromatography with light petroleum–ethyl acetate (10:1) as eluent yielded S-*phenyl* 2-*bromo*(*thiopropanoate*) **6c** as a pale yellow oil (0.180 g, 73%) (Found: M^+, 243.9568. C_9H_9BrOS requires *M*, 243.9557); ν_{max}(film)/cm^{-1} 3061w, 2978w, 2926w, 1705s and 1577w; δ_H(300 MHz) 1.90 (3 H, d, *J* 6.9), 4.62 (1 H, q, *J* 6.9) and 7.44 (5 H, s); *m/z* (EI) 244 (M^+), 188, 135 and 109.

S-*Phenyl* 2-*Bromo*(*thiohexanoate*) **6d**.—Magnesium bromide–diethyl ether (0.284 g, 1.10 mmol) was added to a solution of the oxirane **4d** (0.348 g, 1.00 mmol) in dry diethyl ether (12 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 4.5 h, poured into light petroleum (20 cm^3), filtered and concentrated under reduced pressure. Chromatography with light petroleum–ethyl acetate (10:1) as eluent yielded S-*phenyl* 2-*bromo*(*thiohexanoate*) **6d** as a dark yellow oil (0.235 g, 82%) (Found: M^+, 286.0055. $C_{12}H_{15}BrOS$ requires *M*, 286.0027); ν_{max}(film)/cm^{-1} 3061w, 2958s, 2930s, 2868m, 1705s and 1576w; δ_H(300 MHz) 0.93 (3 H, t, *J* 7.3 and 7.0), 1.33–1.58 (4 H, m), 2.03–2.18 (2 H, m), 4.46 (1 H, dd, *J* 6.4, *J* 7.9) and 7.44 (5 H, s); *m/z* (EI) 286 (M^+), 218, 188, 177, 149 and 109.

S-*Phenyl* 2-*Bromo*-2-*methyl*(*thiopropanoate*) **6e**.—Magnesium bromide–diethyl ether (0.062 g, 0.24 mmol) was added to a solution of the oxirane **4e** (0.052 g, 0.16 mmol) in dry diethyl ether (5 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 24 h, poured into light petroleum (15 cm^3), filtered and concentrated under reduced pressure. Chromatography using light petroleum–ethyl acetate (15:1) as eluent yielded S-*phenyl* 2-*bromo*-2-*methyl*(*thiopropanoate*) **6e** as a yellow oil (0.038 g, 92%) (Found: M^+, 257.9679. $C_{10}H_{11}BrOS$ requires *M*, 257.9715); ν_{max}(film)/cm^{-1} 3061w, 2978w, 2928w, 1696s and 1584m; δ_H(200 MHz) 2.02 (6 H, s) and 7.43 (5 H, s); *m/z* (EI) 258 (M^+, 10%), 188 (14), 151 (50), 121 (50) and 109 (100).

1-*Bromo*-1-*phenylthiocarbonylcyclohexane* **6f**.—Magnesium bromide–diethyl ether (0.051 g, 0.20 mmol) was added to a solution of the oxirane **4f** (0.047 g, 0.13 mmol) in dry diethyl ether (5 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 21 h, water (3 cm^3) was added and extracted with dichloromethane (3 × 10 cm^3). The extracts were combined, dried and concentrated under reduced pressure. Chromatography using light petroleum (b.p. 60–80 °C)–ethyl acetate (30:1) as eluent yielded 1-*bromo*-1-*phenylthiocarbonylcyclohexane* **6f** as a colourless oil which solidified after being stored at −20 °C (0.027 g, 68%) (Found: M^+, 298.0014. $C_{13}H_{15}BrOS$ requires *M*, 298.0028); ν_{max}(film)/cm^{-1} 3058w, 2938s, 2861m and 1694s; δ_H(200 MHz) 1.25–2.02 (6 H, m), 2.08–2.33 (4 H, m) and 7.43 (5 H, s); *m/z* (EI) 298 (M^+, 18%), 218 (48), 191 (56), 163 (74), 110 (91), 109 (75) and 81 (100); and 1-*phenylthiocarbonylcyclohex*-1-*ene* **16** as a colourless oil (0.008 g), contaminated with 1-bromo-1-phenylthiocarbonylcyclohexane **6f** as the minor component in approx. a 2:1 ratio by NMR spectroscopy (Found: M^+, 218.0725. $C_{13}H_{14}OS$ requires *M*, 218.0765); ν_{max}(film)/cm^{-1} 3061w, 2936s, 2861m, 1670s and

1584w; δ_H(200 MHz) 1.66–1.78 (4 H, m), 2.18–2.33 (4 H, m), 7.11–7.15 (1 H, m) and 7.42 (5 H, s); *m/z* (EI) 218 (M^+, 2%), 137 (4), 109 (100) and 81 (63).

S-*Methyl* 2-*Bromo*-2-*phenyl*(*thioethanoate*) **15a**.—Magnesium bromide–diethyl ether (0.480 g, 1.86 mmol) was added to a solution of the oxirane **12a** (0.540 g, 1.7 mmol) in dry diethyl ether (20 cm^3) under nitrogen. The reaction mixture was stirred at room temp. for 100 min, poured into light petroleum (35 cm^3), filtered and concentrated under reduced pressure. Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded S-*methyl* 2-*bromo*-2-*phenyl*(*thioethanoate*) **15a** as a yellow oil which solidified on freezing (0.308 g, 74%) (Found: M^+, 243.9564. C_9H_9BrOS requires *M*, 243.9557); ν_{max}(film)/cm^{-1} 3062w, 3030w, 2965w, 2929w, 1695s and 1493m; δ_H(300 MHz) 2.35 (3 H, s), 5.49 (1 H, s), 7.34–7.41 (3 H, m) and 7.49–7.54 (2 H, m); *m/z* (EI) 244 (M^+), 169, 165, 118, 90 and 75.

S-*Methyl* 2-*Bromo*-3-*methyl*(*thiobutanoate*) **15b**.—Magnesium bromide–diethyl ether (0.396 g, 1.5 mmol) was added to a solution of the oxirane **12b** (0.365 g, 1.3 mmol) in dry diethyl ether (15 cm^3) at 0 °C and was stirred at this temp. under nitrogen for 27 h. The reaction mixture was then poured into light petroleum (b.p. 30–40 °C) (30 cm^3), filtered and concentrated on the rotary evaporator with care since the product is volatile. Chromatography using light petroleum (b.p. 30–40 °C)–diethyl ether (30:1) as eluent yielded S-*methyl* 2-*bromo*-3-*methyl*(*thiobutanoate*) **15b** as a volatile colourless oil (0.166 g, 62%) (Found: M^+, 209.9691. $C_6H_{11}BrOS$ requires *M*, 209.9715); ν_{max}(film)/cm^{-1} 2967s, 2930s, 2874m, 1692s and 1669s; δ_H(200 MHz; standard $CHCl_3$) 1.03 (6 H, t, *J* 6.5), 2.21–2.41 (1 H, m), 2.33 (3 H, s) and 4.24 (1 H, d, *J* 6.8); *m/z* (EI) 210 (M^+, 4%), 163 (30), 135 (40), 83 (44) and 55 (100). Unchanged starting material was also recovered (0.056 g, 15%).

Se-*Phenyl* 2-*Bromo*-3-*methyl*(*selenobutanoate*) **17b**.—Magnesium bromide–diethyl ether (0.177 g, 0.68 mmol) was added to a solution of the oxirane **14b** (0.137 g, 0.36 mmol) in dry diethyl ether (6 cm^3) and stirred under nitrogen at room temp. for 24 h. Phosphate buffer (4 cm^3; pH 7) was added, and the mixture was extracted with diethyl ether (3 × 10 cm^3). The combined extracts were dried and concentrated. Chromatography using light petroleum–diethyl ether (80:1) as eluent yielded Se-*phenyl* 2-*bromo*-3-*methyl*(*selenobutanoate*) **17b** as a pale brown oil (0.080 g, 69%) (Found: M^+, 319.9453. $C_{11}H_{13}BrOSe$ requires *M*, 319.9316); ν_{max}(film)/cm^{-1} 3055w, 2967s, 2932m, 2872m and 1711s; δ_H(300 MHz; standard $CHCl_3$) 1.09 (3 H, d, *J* 6.7), 1.10 (3 H, d, *J* 6.6), 2.31–2.42 (1 H, m), 4.43 (1 H, d, *J* 5.9), 7.36–7.45 (3 H, m) and 7.48–7.53 (2 H, m); *m/z* (EI) 320 (M^+, 16%), 236 (76), 157 (72), 135 (44), 77 (38) and 55 (100).

S-*Phenyl* 2-*Iodo*-2-*phenyl*(*thioethanoate*) **7a**.—Freshly prepared magnesium iodide (0.54 mmol) in dry diethyl ether (4 cm^3) was added to a solution of (*E*)-3-phenyl-2-phenylsulphonyl-2-phenylthiooxirane **4a** (0.182 g, 0.49 mmol) in dry diethyl ether (5 cm^3) at 0 °C under nitrogen and in the absence of light. The reaction mixture was stirred at this temp. for 1 h, saturated aqueous sodium thiosulphate (3 cm^3) was added and the organic layer was separated by pipette. The aqueous layer was extracted with diethyl ether (3 × 6 cm^3) and the extracts were combined and dried. The solvent was removed under reduced pressure to give a mixture of S-*phenyl* 2-*iodo*-2-*phenyl*(*thioethanoate*) **7a** (80% yield by NMR spectroscopy) and S-*phenyl* 2-*phenyl*(*thioethanoate*) **18a** (15% yield by NMR spectroscopy). Due to the susceptibility of the iodide to deiodinate, a separate sample was purified for characterisation. Chromatography using light petroleum (b.p. 60–80 °C)–ethyl acetate (30:1) as eluent yielded: S-*phenyl* 2-*iodo*-2-*phenyl*(*thioethanoate*) **7a** as a pale yellow solid, m.p. 90–91 °C (from Et_2O) (Found: C, 47.75; H, 2.9. $C_{14}H_{11}IOS$ requires C, 47.5; H, 3.1%); ν_{max}(KBr)/cm^{-1} 3056w, 3031w, 2980w, 1686s and 1489w; δ_H(200 MHz) 5.83 (1 H, s), 7.29–7.37 (3 H, m), 7.40 (5 H, s) and 7.54–7.61 (2 H, m); *m/z* (EI) 354 (M^+, 0.6%), 236 (13), 217 (61), 199 (100) and 118 (97); and S-*phenyl* 2-*phenyl*(*thioethanoate*) **18a** as a colourless oil (Found: M^+, 228.0593. $C_{14}H_{12}OS$ requires *M*, 228.0609); ν_{max}(film)/cm^{-1} 3063m, 3031w, 2926m, 1705s, 1584w and 1495m; δ_H(200 MHz) 3.92 (2 H, s), 7.34 (5 H, s) and 7.38 (5 H, s); *m/z* (EI) 228 (M^+, 18%), 199 (6), 118 (83), 109 (33) and 91 (100).

General Procedure for Preparation of 2-*Iodo* S-*Phenyl Thioesters* **7**.—Lithium iodide (0.201 g, 1.5 mmol) was added to a solution of the 2-phenylsulphonyl-2-phenylthiooxirane **4b–d** (1.0 mmol) in dry acetone (10 cm^3) under nitrogen and the mixture was then refluxed for the time indicated in the absence of light. Saturated aqueous sodium thiosulphate (5 cm^3) was added and the mixture was extracted with light petroleum (3 × 15 cm^3). The organic extracts were combined, dried and the solvent removed under reduced pressure in the absence of light.

S-*Phenyl* 2-*iodo*-3-*methyl*(*thiobutanoate*) **7b**. The oxirane was **4b**, and the mixture was refluxed for 42 h. Chromatography with light petroleum as eluent yielded *S*-phenyl 2-iodo-3-methyl(thiobutanoate) **7b** as a yellow oil (0.245 g, 77%) identical with material prepared from the 2-nitro-2-phenylthiooxirane.[1]

S-*Phenyl* 2-*iodo*(*thiopropanoate*) **7c**. The oxirane was **4c**, and the mixture was refluxed for 1 h. Chromatography with light petroleum–ethyl acetate (30:1) as eluent yielded S-*phenyl* 2-*iodo*(*thiopropanoate*) **7c** as a yellow oil (0.202 g, 69%) (Found: M^+, 291.9436. C_9H_9IOS requires *M*, 291.9419); ν_{max}(film)/cm^{-1} 3061w, 2975w, 2921w and 1701s; δ_H(200 MHz) 2.02 (3 H, d, *J* 7.0), 4.79 (1 H, q, *J* 7.0) and 7.44 (5 H, s); *m/z* (EI) 292 (M^+, 82%), 236 (100), 183 (67), 155 (67), 137 (32) and 109.

S-*Phenyl* 2-*Iodo*(*thiohexanoate*) **7d**. The oxirane was **4d**, and the mixture was refluxed for 6 h. Chromatography with light petroleum–ethyl acetate (30:1) as eluent yielded S-*phenyl* 2-*iodo*(*thiohexanoate*) **7d** as a yellow oil (0.242 g, 72%) (Found: M^+, 333.9917. $C_{12}H_{15}IOS$ requires *M*, 333.9888); ν_{max}(film)/cm^{-1} 3060w, 2957m, 2928m, 2866m, 1699s and 1581w; δ_H(200 MHz) 0.89–0.96 (3 H, m), 1.26–1.52 (4 H, m), 1.98–2.10 (2 H, m), 4.60 (1 H, t, *J* 7.45) and 7.44 (5 H, s); minor contamination (3%) by S-phenyl thiohexanoate **18d** was evident; *m/z* (EI) 334 (M^+), 236, 225, 218, 197, 137, 128, 127, 123 and 109.

General Work-up Procedure for Reduction of 2-*Iodo* S-*Phenyl Thioesters* **7**.—Saturated aqueous sodium thiosulphate (3 cm^3) was added to the reaction mixture, which was then extracted with diethyl ether (3 × 10 cm^3). The diethyl ether extracts were combined, dried and concentrated under reduced pressure.

Reduction of S-*Phenyl* 2-*Iodo*-2-*phenyl*(*thioethanoate*) **7a**.—Freshly prepared magnesium iodide (0.68 mmol) in diethyl ether (4 cm^3) was added to a solution of *S*-phenyl 2-iodo-2-phenyl(thioethanoate) **7a** [containing *S*-phenyl 2-phenyl(thioethanoate)] **18a** as the minor contaminant in a 5.3:1 ratio by NMR spectroscopy) (0.120 g, 0.34 mmol) in dry diethyl ether (3 cm^3). The reaction mixture was then stirred at room temp. under nitrogen and in the absence of light for 4 d, before the usual work-up. Chromatography using light petroleum (b.p. 60–80 °C)–ethyl acetate (30:1) gave *S*-phenyl 2-phenyl(thioethanoate) **18a** (0.042 g, 55%) and S-*phenyl* 2-*hydroxy*-2-*phenyl*(*thioethanoate*) **19a** as an orange oil (0.027 g, 33%)

Table 6 Crystallographic data

Compound	**4b**	**13e**	**14b**
Formula	$C_{17}H_{18}O_3S_2$	$C_{10}H_{12}O_3S$	$C_{17}H_{18}O_3SSe$
M	334.5	212.3	381.4
Crystal system	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	*Pbca*	$P\bar{1}$
a/Å	9.152(2)	7.450(1)	9.203(4)
b/Å	10.156(3)	11.414(1)	10.344(4)
c/Å	10.345(3)	24.940(2)	10.344(4)
α/°	104.51(1)		104.34(2)
β/°	109.64(2)		109.71(2)
γ/°	98.21(1)		98.07(2)
U/Å^3	849.1	2120.8	856.3
Z	2	8	2
D_x/g cm^{-3}	1.308	1.329	1.479
Radiation, λ/Å	Cu-$K\alpha$, 1.541 84	Cu-$K\alpha$, 1.541 84	Mo-$K\alpha$, 0.710 73
μ/mm^{-1}	2.87	2.51	2.29
F(000)	352	896	388
Crystal size/mm	0.15 × 0.31 × 0.58	0.20 × 0.36 × 0.36	0.40 × 0.44 × 0.52
No. refns. for cell, 2θ range/°	32, 20–35	32, 35–40	32, 20–25
$2\theta_{max}$/°	130	130	50
Maximum indices khl	10, 11, 12	8, 13, 29	10, 12, 12
Transmission factors	0.44–0.60	0.26–0.41	0.43–0.58
Reflections measured	5548	3060	3745
Unique reflections	2729	1496	2996
Observed reflections	2572	1173	2515
R_{int}	0.069	0.015	0.030
Weighting parameters A_n	2, −5, 25, −4, 2, −17	−23, 107, 13, 70, −39, −375	−6, 85, 30, 11, −3, −109
Extinction parameter x	1.7(2) × 10^{-5}	5.4(1) × 10^{-5}	0
R	0.049	0.051	0.051
$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.032	0.037	0.055
Goodness of fit	1.10	1.67	1.25
No. of parameters	209	137	208
Mean, max. shift/esd	0.007, 0.066	0.001, 0.004	0.003, 0.026
Max., min. el. density/eÅ^{-3}	0.43, −0.47	0.21, −0.46	0.87, −0.94

(Found: M$^+$ − O, 228.0552. $C_{14}H_{12}OS$ requires M − O, 228.0609); ν_{max}(film)/cm^{-1} 3468mbr, 3063w, 3032w, 2924w, 1701s and 1495m; δ_H(200 MHz) 3.59 (1 H, d, J 4.5), 5.32 (1 H, d, J 4.2) and 7.28–7.52 (10 H, m); m/z (EI) 245 (MH$^+$, 70%), 228 (28), 227 (52), 119 (100) and 110 (97).

Reduction of S-*Phenyl* 2-*Iodo*-3-*methyl*(*thiobutanoate*) **7b**.—Freshly prepared magnesium iodide (0.5 mmol) in diethyl ether (3 cm^3) was added to a solution of *S*-phenyl 2-iodo-3-methyl-(thiobutanoate) **7b** (0.079 g, 0.25 mmol) in dry diethyl ether (3 cm^3) and the mixture was stirred at room temp. under nitrogen and in the absence of light for 11 d. Pure S-*phenyl* 3-*methyl*(*thiobutanoate*) **18b** was obtained using the usual work-up as a pale yellow oil (0.044 g, 91%) (Found: M$^+$, 194.0801. $C_{11}H_{14}OS$ requires M, 194.0765); ν_{max}(film)/cm^{-1} 3068w, 2961s, 2930m, 2872m and 1709s; δ_H(200 MHz) 1.00 (6 H, d, J 6.6), 2.11–2.31 (1 H, m), 2.53 (2 H, d, J 7.1) and 7.40 (5 H, s); m/z (EI) 194 (M$^+$, 24%), 137 (9), 109 (70), 85 (98) and 57 (100).

Reduction of S-*Phenyl* 2-*Iodo*(*thiopropanoate*) **7c**.—Freshly prepared magnesium iodide (0.86 mmol) in dry diethyl ether (5 cm^3) was added to a solution of *S*-phenyl 2-iodo(thiopropanoate) **7c** (0.126 g, 0.43 mmol) in dry diethyl ether (4 cm^3). The reaction mixture was then stirred at room temp. under nitrogen and in the absence of light for 5 d and then subjected to usual work-up. ^{1}H NMR spectroscopy indicated partial reaction, so the residue was dissolved in diethyl ether (3 cm^3) and additional freshly prepared magnesium iodide (0.9 mmol) in dry diethyl ether (3 cm^3) was added, and stirring was continued for a further 7 d. Usual work-up gave pure *S*-phenyl-thiopropanoate **18c** as a pale yellow oil (0.048 g, 67%) (Found: MH$^+$, 167.0524. $C_9H_{11}OS$ requires MH, 167.0530); ν_{max}-(film)/cm^{-1} 3066w, 2980w, 2938w, 1709s and 1584w; δ_H(200 MHz) 1.22 (3 H, t, J 7.5), 2.67 (2 H, q, J 7.5) and 7.40 (5 H, s); m/z (EI) 218 (35%), 167 (MH$^+$, 48), 166 (M$^+$, 56), 137 (18), 110 (67), 77 (28), 57 (100) and 29 (70).

Reduction of S-*Phenyl* 2-*Iodo*(*thiohexanoate*) **7d**.—Freshly prepared magnesium iodide (0.5 mmol) in dry diethyl ether (3 cm^3) was added to a solution of *S*-phenyl 2-iodo(thiohexanoate) **7d** (containing <3% *S*-phenyl thiohexanoate **18d** by NMR spectroscopy) (0.100 g, 0.3 mmol) in dry diethyl ether (3 cm^3). The reaction mixture was then stirred at room temp. under nitrogen and in the absence of light for 10 d. Usual work-up gave S-*phenyl thiohexanoate* **18d** as a pale yellow oil (0.062 g, 99%) (Found: M$^+$, 208.0915. $C_{12}H_{16}OS$ requires M, 208.0921); ν_{max}(KBr)/cm^{-1} 3061w, 2957s, 2930s, 2872m, 2861m and 1709s; δ_H(200 MHz) [shows the presence of <3% of *S*-phenyl 2-iodo(thiohexanoate) **7d**] 0.86–0.94 (3 H, m), 1.24–1.42 (4 H, m), 1.58–1.79 (2 H, m), 2.61–2.69 (2 H, m) and 7.40 (5 H, s); m/z (EI) 208 (M^+, 9%), 137 (15), 121 (9), 110 (30), 99 (55) and 69 (100).

X-Ray Crystallography.—Crystal data for **4b**, **13e** and **14b** are given in Table 6, together with information on data collection and structure determination procedures. Crystals were examined at room temperature on a Stoe–Siemens diffractometer with graphite-monochromated radiation. Unit cell parameters were refined from 2θ values of reflections measured at $\pm\omega$. Data collection employed ω/θ scans and on-line profile fitting.[25] In each case, semiempirical absorption corrections were applied, and no significant variation was observed in standard reflections monitored at regular intervals during data collection.

The structures were determined by direct methods and refined by blocked-cascade least-squares methods[26] on F, from

Table 7 Atomic coordinates (× 10^4) for **4b**

	x	y	z
S(1)	2630(1)	4237(1)	7297(1)
O(11)	2889(1)	4258(2)	8756(1)
O(12)	1045(1)	3640(2)	6207(2)
C(11)	3314(2)	5952(3)	7321(2)
C(12)	4697(2)	6841(3)	8410(2)
C(13)	5153(3)	8203(4)	8439(3)
C(14)	4209(3)	8681(4)	7397(3)
C(15)	2833(3)	7788(4)	6318(3)
C(16)	2369(2)	6433(3)	6251(2)
S(2)	3863(1)	3057(1)	4976(1)
C(21)	2065(2)	1694(3)	3912(2)
C(22)	984(4)	1875(5)	2724(4)
C(23)	−372(4)	773(6)	1838(4)
C(24)	−679(3)	−389(4)	2148(3)
C(25)	391(5)	−533(5)	3326(3)
C(26)	1759(5)	502(4)	4205(3)
C(3)	3970(2)	3278(3)	6760(2)
C(4)	5477(2)	3383(3)	7959(2)
C(41)	6992(2)	3167(4)	7768(3)
C(42)	7909(4)	2606(6)	8969(4)
C(43)	7954(3)	4543(5)	7835(4)
O(5)	4124(1)	2172(2)	7377(2)

Table 8 Atomic coordinates (× 10^4) for **13e**

	x	y	z
S	1893(1)	4466(1)	6290(1)
O(1)	330(2)	4040(3)	6568(1)
O(2)	2401(4)	5675(2)	6340(2)
O(3)	5335(2)	3710(2)	6236(1)
C(1)	1722(3)	4115(2)	5607(1)
C(2)	2526(3)	4837(3)	5235(2)
C(3)	2434(3)	4555(3)	4699(2)
C(4)	1530(3)	3543(3)	4535(2)
C(5)	726(3)	2836(3)	4918(2)
C(6)	820(3)	3115(2)	5453(2)
C(7)	3675(3)	3519(2)	6493(1)
C(8)	5261(3)	3835(3)	6817(1)
C(9)	6158(4)	2850(4)	7109(2)
C(10)	5654(5)	5025(4)	7022(3)

reflections with $F > 4\sigma_c(F)$; σ_c was obtained from counting statistics only. Hydrogen atoms were constrained to give C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring angle external bisectors, $U(H) = 1.2\ U_{eq}(C)$; anisotropic thermal parameters were refined for all other atoms. The weighting scheme[27] was $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$ ($G = F_0/F_{max}$, $H = sin\theta/\sin\theta_{max}$). Atomic scattering factors were taken from ref. 28. An isotropic extinction parameter x was refined whereby $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$.

Refined coordinates are given in Tables 7–9.

Other parameters, together with full lists of bond lengths and angles, are available as supplementary material from the CCDC.*

* For details of the crystallographic deposition scheme see Instructions for Authors (1991), *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.

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Table 9 Atomic coordinates (× 10^4) for **14b**

	x	y	z
Se	3916(1)	3095(1)	4847(1)
S	2648(1)	4243(1)	7292(1)
O(1)	4131(2)	2185(2)	7354(2)
O(2)	1075(2)	3642(2)	6185(2)
O(3)	2884(2)	4264(2)	8738(2)
C(1)	4011(3)	3320(3)	6772(3)
C(2)	5490(3)	3395(3)	7988(3)
C(3)	7008(4)	3164(3)	7819(4)
C(4)	7850(5)	2562(5)	8987(5)
C(5)	7994(4)	4538(4)	7915(5)
C(6)	3301(3)	5975(3)	7315(3)
C(7)	2332(4)	6466(3)	6296(4)
C(8)	2767(4)	7844(4)	6392(4)
C(9)	4130(5)	8701(4)	7449(5)
C(10)	5098(4)	8224(3)	8442(4)
C(11)	4697(3)	6838(3)	8421(3)
C(12)	1994(4)	1637(3)	3767(3)
C(13)	1726(6)	458(4)	4136(5)
C(14)	293(5)	−574(4)	3298(5)
C(15)	−735(4)	−505(4)	2099(4)
C(16)	−432(5)	613(4)	1693(5)
C(17)	919(5)	1719(4)	2552(5)

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