A New Method for the Synthesis of α-Bromoacyl Silanes *via* Ring-opening of 2-Phenylsulphonyl-2-trimethylsilyloxiranes

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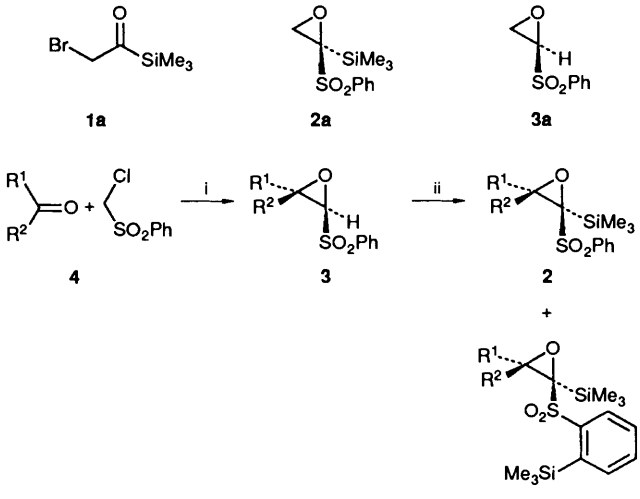
2-Phenylsulphonyl-2-trimethylsilyloxiranes **2** are efficiently prepared by treatment of 2-phenylsulphonyloxiranes **3** with butyllithium in the presence of chlorotrimethylsilane at low temperatures. Reaction of 3-alkyl-2-phenylsulphonyl-2-trimethylsilyloxiranes **2**, in which the alkyl group is primary, with magnesium bromide at room temperature gives 2-bromoacyl silanes **1** in good yield. Reaction at higher temperatures leads to competing formation of bromovinyl sulphones **7**. Reaction of 3,3-dialkyloxiranes with magnesium bromide occurs much more readily, leading to 2-bromoacyl silanes **1** in moderate yields. Other products derived from a common carbocationic intermediate are also isolated.

Acylsilanes are becoming increasingly important as synthetic intermediates.[1,2] While many effective methods are available for the synthesis of unfunctionalised acylsilanes,[1,2] methods for the preparation of functionalised derivatives are still being sought. In this context, direct access to α-halogeno acylsilanes **1** is a particularly attractive target, since these compounds can allow access to a wide variety of potentially useful intermediates.[3–7] The existing methods for the preparation of α-halogeno acylsilanes rely exclusively on the introduction of the halogen as an electrophilic reagent † (either as free halogen, or as *N*-halogenosuccinimide), either using an enol derivative of an acylsilane,[5,6,8–11] or directly from an acylsilane.[6,12] We had previously observed that treatment of 2-phenylsulphonyl-2-trimethylsilyloxirane **2a**, prepared by reaction of 2-phenylsulphonyloxirane **3a** with chlorotrimethylsilane and butyllithium in THF (tetrahydrofuran) at −102 °C, with magnesium bromide in diethyl ether gave 2-bromoacetyltrimethylsilane **1a** in good yield.[13] We now present a full account of our investigation into the scope and limitations of the reaction of 2-phenylsulphonyl-2-trimethylsilyloxiranes **2** with magnesium bromide as a method for the preparation of α-bromoacylsilanes.[14]

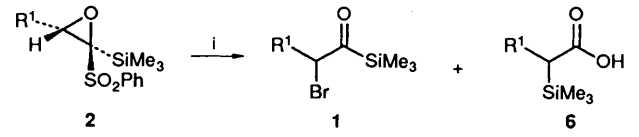


Scheme 1 *Reagents and conditions:* i, NaOH (50% aq.), $BnEt_3N^+Br^-$, CH_2Cl_2, 0 °C to room temp.; ii, Me_3SiCl, BuLi, THF, −100 °C

Results and Discussion

2-Phenylsulphonyloxiranes **3** were easily prepared by Darzens reaction of chloromethyl phenyl sulphone **4** with either aldehydes or ketones.[15,16] The reaction is generally efficient, unless the carbonyl compound is especially prone to enolate formation (*e.g.* 1-phenylbutan-2-one). *trans*-Oxiranes are obtained from aldehydes, and mixtures of stereoisomers are obtained from unsymmetrical ketones. Conversion of 2-phenylsulphonyloxiranes **3** into the corresponding 2-trimethylsilyl derivatives **2** was best achieved by treatment with butyllithium at −102 °C in the presence of chlorotrimethylsilane as an *in situ* trapping agent.‡ The reaction is extremely efficient for ketone derived phenylsulphonyloxiranes, and moderately efficient for aldehyde derived substrates (Scheme 1, Table 1). For the aldehyde derived substrates **3b–e**, by-products **5b–e** in which additional silylation at the *ortho* position of the phenylsulphonyl group had taken place were also isolated.[18] In one case **3f**, in which the alkyl substituent was Pr^i, it proved more effective to generate the lithiated oxirane and then add chlorotrimethylsilane subsequently. Use of the *in situ* method in this case led to significant amounts of starting material being recovered. It is likely that the relatively bulky *syn* substituent retards proton removal to such an extent that reaction of butyllithium with chlorotrimethylsilane becomes a competitive process.

Treatment of the 3-alkyl-2-phenylsulphonyl-2-trimethylsilyloxiranes **2b–e** with magnesium bromide in ether at room temperature led to slow but efficient formation of the α-bromoacylsilanes **1b–e** (Scheme 2, Table 2). In one case, a significant amount of the α-trimethylsilylcarboxylic acid **6** was also isolated, and these compounds are likely to represent the mass balance in the other reactions. Rearrangement of silyloxiranes to α-trimethylsilylcarbonyl compounds is well-documented,[19] and it is also well-established that acylsulphones are prone to



Scheme 2 *Reagents and conditions:* i, $MgBr_2{\cdot}Et_2O$, Et_2O, room temp.

† Conversion of an α-bromoacyl silane to an α-iodoacyl silane is described in ref. 7.

‡ *In situ* silylation of oxiranes has been extensively employed by Eisch,[17] although no examples of *in situ* silylation of phenylsulphonyl oxiranes had been described prior to our own observations.[13]

Table 1 Preparation of 2-phenylsulphonyl-2-trimethylsilyloxiranes **2**

R^1	R^2	Sulphonyl oxirane	Yield (%)	Silyl oxirane	Yield (%)	Disilyl derivative	Yield (%)
Me	H	**3b**	73	**2b**	86	**5b**	1
Et	H	**3c**	69	**2c**	72	**5c**	9
Pr	H	**3d**	93	**2d**	72	**5d**	13
Bu	H	**3e**	90	**2e**	80	**5e**	10
Pr^i	H	**3f**	99	**2f**	91		
Ph	H	**3g**	69	**2g**	73		
Me	Me	**3h**	96	**2h**	99		
Et/Me		**3i**	96[a]	**2i**	92[a]		
Et	Et	**3j**	84	**2j**	93		
$PhCH_2$/Et		**3k**	35[a]	**2k**	93[a]		
$(CH_2)_4$		**3l**	85	**2l**	91		
$(CH_2)_5$		**3m**	100	**2m**	91		

[a] Chromatographically inseparable mixtures of diastereoisomers.

Table 2 Reaction of 3-alkyl-2-phenylsulphonyl-2-trimethylsilyloxiranes with $MgBr_2$ in diethyl ether at room temp.

R^1	Silyl oxirane	α-Bromoacylsilane	Yield (%)
Me	**2b**	**1b**	79
Et	**2c**	**1c**	75
Pr	**2d**	**1d**	77[a]
Bu	**2e**	**1e**	80
Pr^i	**2f**	**1f**	8
Ph	**2g**	**1g**	0

[a] The α-trimethylsilyl carboxylic acid **6d** (17%) was also isolated.

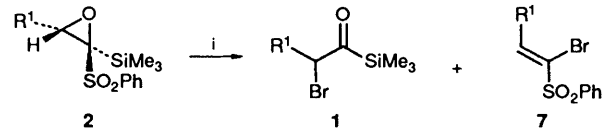
Table 3 Reaction of 3-alkyl-2-phenylsulphonyl-2-trimethylsilyloxiranes with $MgBr_2$ in THF at reflux

R^1	Silyl oxirane	α-Bromoacyl silane	Yield (%)	Vinyl sulphone	Yield (%)
Me	**2b**	**1b**	48	**7b**	30
Et	**2c**	**1c**	40	**7c**	40
Pr	**2d**	**1d**	27	**7d**	48
Bu[a]	**2e**	**1e**	41	**7e**	50
Pr^i	**2f**	**1f**	7	**7f**	64
Ph	**2g**	**1g**	0	**7g**	48

[a] No detectable reaction at room temp. in THF.

hydrolysis.[20] In the case of the more sterically hindered substrate **2f**, a mixture of products was formed with only a trace amount of the desired α-halogenoacylsilane **1f** under these conditions. Reactions of the 3-phenyl substrate **2g** under the same conditions gave no readily identifiable products. Interestingly, treatment of the oxirane **2e** with magnesium bromide in tetrahydrofuran (THF) had no effect even after an extended period. It is likely that THF competes more effectively than ether with the oxirane oxygen for the magnesium cation,[21] thus suppressing the ring-opening reaction.

However, when the substrates **2b–g** were treated with magnesium bromide in THF at reflux, the results were strikingly different. The straight-chain substrates **2b–e** gave mixtures of the previously isolated α-bromoacylsilanes **1b–e**, together with the bromovinyl sulphones **7b–e**, isolated as pure (*Z*)-isomers.[22] The other substrates, **2f** and **2g**, gave modest yields of the bromovinyl sulphones **7f** and **7g** (Scheme 3, Table 3). The

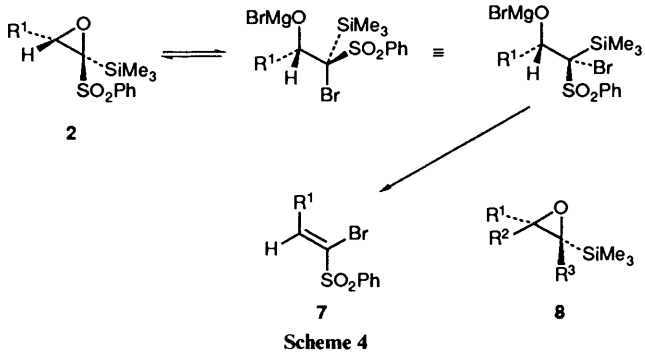


2 **1** **7**

Scheme 3 *Reagents and conditions*: i, $MgBr_2$·Et_2O, THF, reflux

bromovinyl sulphones **7** are most likely formed by nucleophilic attack of bromide at C-2, followed by *syn* elimination of trimethylsilanolate.[23] The (*Z*) stereochemistry of the bromovinyl sulphones, established by ^1H NMR spectroscopy, follows naturally from this mechanism (Scheme 4).

Nucleophilic attack on 2-phenylsulphonyloxiranes **3** generally occurs at the 3-position.[13] By contrast, nucleophilic attack



2 **7** **8**

Scheme 4

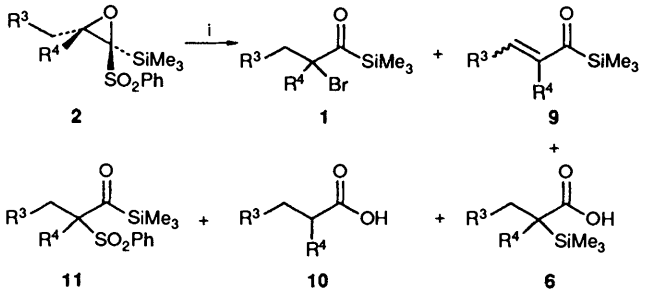
on 2-trimethylsilyloxiranes **8** occurs exclusively at the 2-position.[19,24] At room temperature we only observe products derived from attack at C-3, the normal process for nucleophilic attack on 2-phenylsulphonyloxiranes. In the case of the 2-phenylsulphonyl-2-trimethylsilyloxiranes, attack by bromide at C-2 results in an intermediate which can either re-close to the oxirane, or can undergo *syn*-elimination of trimethylsilanolate. It is unclear at present whether an increase in temperature promotes nucleophilic attack by bromide at C-2 rather than C-3, or increases the rate of trimethylsilanolate elimination, or both. Whatever the reason, the formation of products derived from attack at C-2 can compete at higher temperatures and, in cases where the substituent at C-3 is other than primary alkyl, become predominant.

In contrast to the slow reaction of 3-alkyl oxiranes, the reaction of 3,3-dialkyloxiranes **3h–m** with $MgBr_2$·Et_2O occurred much more rapidly at around 0 °C. The major product in all cases was the expected α-bromoacylsilane **1**, generally isolated in between 50 and 65% yield. However, variable amounts of α-trimethylsilyl carboxylic acids **6**, α,β-unsaturated acyl silanes **9** (isolated as pure (*Z*)-isomers as determined by ^1H NMR spectroscopy),[7] carboxylic acids **10** and traces of α-phenylsulphonyl acylsilanes **11** were also isolated (Scheme 5, Table 4). It is likely that the mechanism for attack on the 3,3-dialkylated oxiranes is closer to the S_N1 pathway than the S_N2 pathway, and it is possible to rationalise the formation of all the isolated products on the basis of an intermediate carbocation formed by magnesium ion induced cleavage of the C-3–oxygen

Table 4 Reaction of 3,3-dialkyl-2-phenylsulphonyl-2-trimethylsilyloxiranes with $MgBr_2$ in diethyl ether at 0 °C

Silyl-oxirane	R^3	R^4	2-Bromo-acylsilane	Yield (%)	Unsaturated acylsilane	Yield (%)	α-Trimethylsilyl carboxylic acid	Yield (%)	Carboxylic acid	Yield (%)
2h	H	Me	**1h**	57	**9h**	0	**6h**	24	**10h**	9
2i[a]	Me	Me	**1i**	65	**9i**	7	**6i**	5	**10i**	11[b]
2j	Me	Et	**1j**	57	**9j**	9	**6j**	0	**10j**	19[b]
2k[a]	Me	$PhCH_2$	**1k**	53	**9k**	11	**6k**	0	**10k**	22
2l	$(CH_2)_3$		**1l**	58	**9l**	3	**6l**	0	**10l**	0
2m	$(CH_2)_4$		**1m**	60	**9m**	6	**6m**	5	**10m**	11[b]

[a] These compounds are mixtures of diastereoisomers, of which only one is drawn. [b] Trace amounts of the α-phenylsulphonylacylsilanes **11** were also isolated.



Scheme 5 *Reagents and conditions:* i, $MgBr_2$·Et_2O, Et_2O, 0 °C

bond of the oxirane. In particular, the α-trimethylsilyl carboxylic acids **6** can be formed by trimethylsilyl migration, followed by hydrolysis of the acylsulphone function[20] as observed for one of the aldehyde derived oxiranes (*vide supra*). It is likely that the carboxylic acids **10** are derived from the α-trimethylsilyl carboxylic acids by desilylation.[26] The α-phenylsulphonyl acylsilanes **11** can be formed by phenylsulphonyl migration, which has good precedent.[27] Formation of the α,β-unsaturated acyl silanes **9** can be rationalised by proton loss from the intermediate carbocation; re-exposure of the α-bromoacyl silane **1m** to the reaction conditions did not lead to the formation of **9m**. Although the reaction of ketone derived oxiranes with $MgBr_2$ gives rise to the formation of several products, the isolation of the non-polar α-bromoacylsilanes in a high state of purity is easy.

In summary, we have described a simple, relatively efficient, method for the synthesis of a range of α-bromoacyl silanes in three steps from a carbonyl compound. The reactions are easy to carry out and use readily available starting materials. It is of particular note that the preparation of fully substituted α-bromoacyl silanes can be achieved by this method.

Experimental

General experimental procedures have been described.[16] *J* Values are given in Hz. Light petroleum refers to the fraction of b.p. 40–60 °C unless stated otherwise.

The oxiranes **3f**, **3h** and **3m** were prepared according to the general procedure already described.[15,16] The following new compounds were all prepared by the same method:

trans-3-*Methyl*-2-*phenylsulphonyloxirane* **3b**. The carbonyl compound was ethanal (3.7 cm^3, 65.6 mmol) which was added in eight equal portions over 4 h. Stirring was continued at 15 °C for 3.5 h. Flash chromatography using dichloromethane–light petroleum (3:1) as eluent yielded trans-3-*methyl*-2-*phenylsulphonyloxirane* **3b** (containing <2% of the *cis*-isomer by NMR spectroscopy) as a colourless oil which eventually solidified (0.949 g, 73%), m.p. 51–52 °C (from Et_2O) (Found: C, 54.5; H, 5.0. $C_9H_{10}O_3S$ requires C, 54.5; H, 5.1%); ν_{max}(film)/cm^{-1} 3067w, 3011w, 2975w, 1584w, 1375s, 1231m and 1154s; δ_H(300 MHz; standard $CHCl_3$) 1.44 (3 H, d, *J* 5.3), 3.71 (1 H, dq, *J* 1.6 and 5.3), 3.89 (1 H, d, *J* 1.6), 7.57–7.63 (2 H, m), 7.68–7.74 (1 H, m) and 7.91–7.95 (2 H, m); *m/z* (EI) 199 (MH^+, 38%), 141 (61), 125 (87), 94 (64) and 78 (87).

trans-3-*Ethyl*-2-*phenylsulphonyloxirane* **3c**. The carbonyl compound was propanal (0.77 cm^3, 10.7 mmol), which was added in five equal portions over 5 h. The mixture was then stirred at room temp for 25 h. Flash chromatography using light petroleum–ethyl acetate (15:1) as eluent yielded trans-3-*ethyl*-2-*phenylsulphonyloxirane* **3c** as a pale yellow oil (0.953 g, 69%) (Found: C, 56.8; H, 5.7. $C_{10}H_{12}O_3S$ requires C, 56.5; H, 5.7%); ν_{max}(film)/cm^{-1} 3096m, 3067m, 3007m, 2975m, 2940m, 2882m, 1586m, 1325s, 1244s and 1157s; δ_H(200 MHz; standard $CHCl_3$) 1.00 (3 H, t, *J* 7.5), 1.54–1.89 (2 H, m), 3.61–3.68 (1 H, m), 3.92 (1 H, d, *J* 1.7), 7.54–7.75 (3 H, m) and 7.90–7.96 (2 H, m); *m/z* (EI) 213 (MH^+, 2.4%), 195 (1.3), 183 (2.7), 157 (2.7), 142 (27), 125 (100), 94 (16) and 78 (93).

trans-2-*Phenylsulphonyl*-3-*propyloxirane* **3d**. The carbonyl compound was butanal (1.74 cm^3, 19.7 mmol) and the reaction mixture was stirred at 0 °C for 2 h before being warmed to room temperature and stirred for 24 h. Chromatography using light petroleum–ethyl acetate (15:1) as eluent yielded trans-2-*phenylsulphonyl*-3-*propyloxirane* **3d** as a pale yellow oil (1.376 g, 93%) (Found: C, 59.05; H, 6.4. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.2%); ν_{max}(film)/cm^{-1} 3058w, 2965m, 2935m, 2876m, 1580w, 1325s, 1217w and 1156s; δ_H(200 MHz; standard $CHCl_3$) 0.93–1.00 (3 H, m), 1.40–1.79 (4 H, m), 3.62–3.68 (1 H, m), 3.90 (1 H, d, *J* 1.7), 7.55–7.75 (3 H, m) and 7.90–7.96 (2 H, m); *m/z* (FAB) 227 (MH^+, 16%), 199 (13), 154 (8), 143 (48), 137 (35), 125 (88) and 85 (100).

trans-3-*Butyl*-2-*phenylsulphonyloxirane* **3e**. The carbonyl compound was pentanal (0.73 cm^3, 6.9 mmol). The reaction mixture was stirred for 3.5 h at room temp. Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded trans-3-*butyl*-2-*phenylsulphonyloxirane* **3e** as an oil (1.415 g, 90%) (Found: C, 60.0; H, 6.7. $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7%); ν_{max}(film)/cm^{-1} 3067w, 3024w, 2959m, 2933m, 2870m, 1585w, 1326s, 1220m and 1156s; δ_H(200 MHz) 0.83–0.99 (3 H, m), 1.25–1.79 (6 H, m), 3.62–3.69 (1 H, m), 3.90 (1 H, d, *J* 1.7), 7.55–7.75 (3 H, m) and 7.91–7.97 (2 H, m); *m/z* (FAB) 481 (M_2H^+, 6%), 339 (M_2H^+ – $PhSO_2H$, 3), 241 (MH^+, 37), 225 (7), 143 (92) and 125 (100).

trans-3-*Phenyl*-2-*phenylsulphonyloxirane* **3g**.[15b] The carbonyl compound was benzaldehyde (0.67 cm^3, 6.56 mmol), which was added at 0 °C and the reaction mixture was stirred at this temperature for 80 min. Chromatography using dichloromethane–light petroleum (1:3) as eluent yielded *trans*-3-phenyl-2-phenylsulphonyloxirane **3g** as a white solid (1.014 g, 59%), m.p. 100–102 °C (from Et_2O) (lit.,[15b] 102–104 °C) (Found: C, 64.2; H, 4.5. Calc. for $C_{14}H_{12}O_3S$: C, 64.6; H, 4.6%); ν_{max}(KBr)/cm^{-1} 3068w, 3034w, 2993w, 1582w, 1322s, 1231w and 1151s; δ_H(200 MHz) 4.19 (1 H, d, *J* 1.6), 4.60 (1 H, d, *J* 1.6), 7.23–7.30 (2 H, m), 7.35–7.41 (3 H, m), 7.59–7.79 (3 H, m) and 7.97–8.03 (2 H, m); *m/z* (EI) 260 (M^+, 16%), 247 (12), 231 (16), 125 (71), 119 (67), 105 (88), 91 (91) and 77 (100).

trans- *and* cis-3-*Ethyl*-3-*methyl*-2-*phenylsulphonyloxirane* **3i**. The carbonyl compound was butan-2-one (1.8 cm^3, 19.7 mmol) which was added at room temp. and the mixture was stirred for 48 h. Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded 3-*ethyl*-3-*methyl*-2-*phenylsulphonyloxirane* **3i** as a colourless oil (1.430 g, 96%) (chromatographically inseparable mixture of the *trans* and *cis*-diastereoisomers in a 3:1 *trans*:*cis* ratio by NMR spectroscopy) (Found: C, 58.3; H, 6.2. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.2%); ν_{max}(film)/cm^{-1} 3075w, 2980m, 2945w, 2890w, 1590w, 1330s and 1160s; δ_H-(300 MHz) *trans*-Diastereoisomer: 0.95 (3 H, t, *J* 7.5), 1.54–1.71 (2 H, m), 1.80 (3 H, s), 3.80 (1 H, s), 7.58–7.63 (2 H, m), 7.67–7.73 (1 H, m) and 7.95–7.98 (2 H, m). *cis*-Diastereoisomer: 1.17 (3 H, t, *J* 7.6), 1.39 (3 H, s), 2.12–2.22 (2 H, m), 3.80 (1 H, s), 7.58–7.63 (2 H, m), 7.67–7.73 (1 H, m) and 7.95–7.98 (2 H, m). Assignments of the signals for the *trans*- and *cis*-diastereoisomers are tentative; *m*/*z* (EI) 227 (MH^+, 4%), 226 (M^+, 2), 198 (33), 183 (26), 142 (51), 125 (96), 85 (90) and 78 (100).

3,3-*Diethyl*-2-*phenylsulphonyloxirane* **3i**. The carbonyl compound was pentan-3-one (3.04 cm^3, 28.9 mmol) which was added at room temp. and the mixture was stirred for 6 d. Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded 3,3-*diethyl*-2-*phenylsulphonyloxirane* **3i** as a white solid (2.650 g, 84%), m.p. 70–71 °C (from Et_2O–light petroleum) (Found: C, 60.2; H, 6.6. $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7%); ν_{max}(KBr)/cm^{-1} 3092w, 3067w, 2978m, 2938m, 2882m, 1585w, 1310s and 1157s; δ_H(300 MHz) 0.91 (3 H, t, *J* 7.5), 1.16 (3 H, t, *J* 7.5), 1.68 (2 H, q, *J* 7.5), 2.20 (2 H, q, *J* 7.5), 3.80 (1 H, s), 7.57–7.63 (2 H, m), 7.67–7.73 (1 H, m) and 7.95–7.99 (2 H, m); *m*/*z* (EI) 240 (M^+), 212, 193, 143, 141, 125 and 98.

trans- *and* cis-3-*Benzyl*-3-*ethyl*-2-*phenylsulphonyloxirane* **3k**. The carbonyl compound was 1-phenylbutan-2-one (0.98 cm^3, 6.56 mmol) which was added at 0 °C and the reaction mixture was stirred for 1.5 h before being warmed to room temperature and stirred for 20 h. Chromatography using light petroleum–ethyl acetate (20:1) as eluent yielded 3-*benzyl*-3-*ethyl*-2-*phenylsulphonyloxirane* **3k** as a yellow oil (0.655 g, 33%) (chromatographically inseparable mixture of the *trans*- and *cis*-diastereoisomers in a 1:1 *trans*:*cis* ratio by NMR spectroscopy) (Found: C, 67.7; H, 5.75. $C_{17}H_{18}O_3S$ requires C, 67.5; H, 6.0%); ν_{max}(film)/cm^{-1} 3065w, 3030w, 2974w, 2940w, 2883w, 1604w, 1584w, 1497w, 1327, 1284w and 1155s; δ_H(200 MHz; standard CH_2Cl_2) *trans*-diastereoisomer: 1.20 (3 H, t, *J* 7.5), 2.00–2.28 (2 H, m), AB system (δ_A 2.89, δ_B 3.03, J_{AB} 14.8), 3.87 (1 H, s), 7.14–7.44 (5 H, m), 7.53–7.77 (3 H, m) and 7.90–8.06 (2 H, m); *cis*-diastereoisomer: 0.86 (3 H, t, *J* 7.5), 1.26–1.50 (1 H, m), 1.55–1.74 (1 H, m), AB system (δ_A 3.47, δ_B 3.75, J_{AB} 14.8), 3.74 (1 H, s), 7.14–7.44 (5 H, m), 7.53–7.77 (3 H, m) and 7.90–8.06 (2 H, m). Assignments for the *trans*- and *cis*-diastereoisomers are tentative; *m*/*z* (EI) 161 (M^+ – $PhSO_2$, 43%), 143 (11), 133 (10), 125 (7) and 91 (100).

2-*Phenylsulphonyl*-1-*oxaspiro*[2.4]*heptane* **31**. The carbonyl compound was cyclopentanone (0.64 cm^3, 7.2 mmol) which was added at room temp. and the mixture was stirred for 23 h. Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded 2-*phenylsulphonyl*-1-*oxaspiro*[2.4]*heptane* **31** as a colourless oil which eventually solidified (1.325 g, 85%), m.p. 60–61 °C (from Et_2O–light petroleum) (Found: C, 60.6; H, 5.8. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9%); ν_{max}(film)/cm^{-1} 3065w, 2964m, 2873w, 1331s, 1256w and 1154s; δ_H(200 MHz; standard $CHCl_3$) 1.21–1.97 (5 H, m), 2.01–2.26 (2 H, m), 2.35–2.73 (1 H, m), 4.07 (1 H, s), 7.52–7.74 (3 H, m) and 7.93–7.99 (2 H, m); *m*/*z* (FAB) 239 (MH^+, 17%), 221 (5), 143 (58), 125 (100) and 97 (68).

Silylation of 2-Phenylsulphonyloxiranes **3**.—*General procedure*. Chlorotrimethylsilane (2.5 equiv.) was added to a solution of the 2-phenylsulphonyloxirane **3** (1 equiv.) in dry THF (10 cm^3 $mmol^{-1}$) under nitrogen and the mixture was cooled to an internal temperature of −102 °C. Butyllithium (1.8 equiv. in hexane) was added dropwise over 10 min keeping the internal temperature below −100 °C. When the addition was complete aqueous ammonium chloride (10 cm^3; 10%) was added immediately and the reaction mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure and the resulting residue was chromatographed using light petroleum–ethyl acetate as eluent.

trans-3-*Methyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2b**. The oxirane was *trans*-3-methyl-2-phenylsulphonyl oxirane **3b** (0.612 g, 3.1 mmol). Chromatography was carried out using light petroleum–ethyl acetate (15:1) as eluent. trans-3-*Methyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2b** was obtained as a colourless oil which eventually solidified (0.720 g, 86%), m.p. 63–86 °C (from Et_2O) (Found: C, 53.4; H, 6.6. $C_{12}H_{18}O_3SSi$ requires C, 53.3; H, 6.7%); ν_{max}(film)/cm^{-1} 3067w, 2965w, 2903w, 1583w, 1306s, 1254s and 1148s; δ_H(200 MHz; standard $CHCl_3$) 0.28 (9 H, s), 1.39 (3 H, d, *J* 5.6), 3.23 (1 H, q, *J* 5.6), 7.48–7.71 (3 H, m) and 7.86–7.95 (2 H, m); *m*/*z* (FAB) 287 [$PhSO_2(Me_2Si)_2$, 1.2%], 271 (MH^+, 0.4), 255 (1.2), 198 (2), 109 (22) and 73 (100). trans-3-*Methyl*-2-*trimethylsilyl*-2-o-*trimethylsilylphenylsulphonyloxirane* **5b** (0.006 g, 1%) was also isolated as a colourless oil (Found: $M^+ - CH_3$, 327.0883. $C_{14}H_{23}O_3SSi_2$ requires $M - CH_3$, 327.0906); ν_{max}(film)/cm^{-1} 3058w, 2961m, 2901m, 1559w, 1310s, 1252s and 1150s; δ_H(200 MHz; standard $CHCl_3$) 0.37 (9 H, s), 0.41 (9 H, s), 1.31 (3 H, d, *J* 5.6), 2.66 (1 H, q, *J* 5.6), 7.46–7.62 (2 H, m), 7.76–7.80 (1 H, m) and 7.91–7.96 (1 H, m); *m*/*z* (FAB) 415 (M^+ + Me_3Si, 1%), 327 ($M^+ - CH_3$, 7), 271 (21), 241 (7), 129 (15) and 73 (100).

trans-3-*Ethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2c** The oxirane was *trans*-3-ethyl-2-phenylsulphonyloxirane **3c** (0.962 g, 4.5 mmol). Chromatography was carried out using light petroleum–ethyl acetate (20:1) as eluent. trans-3-*Ethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2c** was obtained as a colourless oil which eventually solidified (0.925 g, 72%), m.p. 48–50 °C (from Et_2O–light petroleum) (Found: C, 55.3; H, 7.1. $C_{13}H_{20}O_3SSi$ requires C, 54.9; H, 7.1%); ν_{max}(film)/cm^{-1} 3069w, 2975m, 2940w, 2903w, 2882w, 1584w, 1306s, 1254s and 1148s; δ_H(200 MHz; standard $CHCl_3$) 0.23 (9 H, s), 1.03 (3 H, t, *J* 7.5), 1.41–1.83 (2 H, m), 3.15 (1 H, dd, *J* 5.0 and 7.6), 7.48–7.68 (3 H, m) and 7.86–7.94 (2 H, m); *m*/*z* (FAB) 357 (M^+ + Me_3Si, 2%), 287 [$PhSO_2(Me_3Si)_2$, 3], 285 (MH^+, 1), 269 (2), 215 (5), 143 (13), 125 (9), 109 (1) and 73 (100). trans-3-*Ethyl*-2-*trimethylsilyl*-2-o-*trimethylsilylphenylsulphonyloxirane* **5c** was also isolated as a colourless oil (0.152 g, 9%); δ_H(60 MHz; solvent CCl_4; standard external Me_4Si) 0.43 (9 H, s), 0.54 (9 H, s), 0.90–1.25 (3 H, m), 1.30–1.94 (2 H, m), 2.49 (1 H, dd, *J* 4.6 and 6.8) and 7.23–7.88 (4 H, m).

trans-2-*Phenylsulphonyl*-3-*propyl*-2-*trimethylsilyloxirane* **2d**. The oxirane was *trans*-2-phenylsulphonyl-3-propyloxirane **3d** (1.092 g, 4.8 mmol). Chromatography using light petroleum–ethyl acetate (30:1) as eluent gave trans-2-*phenylsulphonyl*-3-*propyl*-2-*trimethylsilyloxirane* **2d** as a pale yellow oil (1.041 g, 72%) (Found: M^+, 298.1068. $C_{14}H_{22}O_3SSi$ requires *M*, 298.1059); ν_{max}(film)/cm^{-1} 3066w, 2963m, 2876w, 1559w, 1306s, 1254m and 1148s; δ_H(200 MHz; standard $CHCl_3$) 0.22 (9 H, s), 0.92 (3 H, m), 1.37–1.52 (3 H, m), 1.64–1.75 (1 H, m), 3.16–3.21 (1 H, m), 7.46–7.66 (3 H, m) and 7.85–7.90 (2 H, m); *m*/*z* (FAB) 371 (M^+ + Me_3Si, 2%), 299 (MH^+, 1), 298 (M^+, 0.5), 287 (5), 226 (1), 215 (6), 157 (14), 125 (8), 83 (6) and 73 (100). trans-3-*Propyl*-2-*trimethylsilyl*-2-o-*trimethylsilylphenylsulphonyloxirane* **5d** was also isolated as a colourless oil (0.228 g, 13%); ν_{max}(film)/cm^{-1} 3058w, 2963m, 2903m, 2876m, 1559w, 1310s, 1252s and 1152s; δ_H(200 MHz; standard $CHCl_3$) 0.30 (9 H, s), 0.40 (9 H, s), 0.82–0.89 (3 H, m), 1.24–1.44 (3 H, m),

1.58–1.73 (1 H, m), 2.65 (1 H, m), 7.45–7.60 (2 H, m), 7.74–7.78 (1 H, m) and 7.90–7.95 (1 H, m); *m/z* (FAB) 443 (M^+ + Me_3Si, 1%), 371 (MH^+, 0.6), 355 (5), 287 (3), 157 (28) and 73 (100).

trans-3-*Butyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2e**. The oxirane was *trans*-3-butyl-2-phenylsulphonyloxirane **3e** (0.349 g, 1.46 mmol). Chromatography using light petroleum–ethyl acetate (15:1) as eluent gave trans-3-*butyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2e** as a colourless oil which solidified on freezing (0.363 g, 80%) (Found: C, 57.8; H, 7.9. $C_{15}H_{24}O_3SSi$ requires C, 57.65; H, 7.7%); ν_{max}(film)/cm^{-1} 3069w, 2961m, 2932m, 2874m, 1586w, 1306s, 1254s and 1148s; δ_H(200 MHz; standard $CHCl_3$) 0.22 (9 H, s), 0.84–0.91 (3 H, m), 1.22–1.55 (5 H, m), 1.57–1.80 (1 H, m), 3.18 (1 H, dd, *J* 4.4 and 7.45), 7.47–7.69 (3 H, m) and 7.85–7.94 (2 H, m); *m/z* (FAB) 385 (M^+ + Me_3Si, 7%), 341 (2), 313 (MH^+, 4), 287 (50), 215 (44), 171 (100), 125 (38) and 73 (45). trans-3-*Butyl*-2-*trimethylsilyl*-2-o-*trimethylsilylphenylsulphonyloxirane* **5e** was also isolated as a colourless oil (0.055 g, 10%); δ_H(60 MHz; solvent CCl_4; standard external Me_4Si) 0.32 (9 H, s), 0.42 (9 H, s), 0.55–1.06 (3 H, m), 1.06–1.85 (6 H, m), 2.30–2.60 (1 H, m) and 7.00–7.75 (4 H, m).

trans-3-(1-*Methylethyl*)-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2f**. *External Quench Method.*—A solution of *trans*-3-(1-methylethyl)-2-phenylsulphonyloxirane **3f** (0.226 g, 1.0 mmol) in dry THF (20 cm^3) under nitrogen was cooled to an internal temperature of −102 °C. Butyllithium (0.56 cm^3, 1.06 mmol; 1.9 mol dm^{-3}) was added dropwise keeping the internal temperature below −100 °C, and the mixture was then stirred for 8 min before the addition of chlorotrimethylsilane (0.14 cm^3, 1.1 mmol). Stirring was then continued for a further 2 min, aqueous ammonium chloride (7 cm^3; 10%) was added and the reaction mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 12 cm^3). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure and the resulting residue was chromatographed using light petroleum–ethyl acetate (15:1) as eluent. *trans*-3-(1-*Methylethyl*)-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2f** (0.272 g, 91%) was obtained as a colourless oil (Found: C, 56.9; H, 7.4. $C_{14}H_{22}O_3SSi$ requires C, 56.3; H, 7.4%) (Found: $M^+ - CH_3$, 283.0866. $C_{13}H_{19}O_3SSi$ requires $M - CH_3$, 283.0824); ν_{max}(film)/cm^{-1} 3067w, 2970m, 2904w, 2875w, 1585w, 1307s, 1254s and 1154s; δ_H(200 MHz; standard $CHCl_3$) 0.22 (9 H, s), 1.00 (3 H, d, *J* 6.5), 1.02 (3 H, d, *J* 6.6), 1.50–1.68 (1 H, m), 2.94 (1 H, d, *J* 9.8), 7.49–7.69 (3 H, m) and 7.87–7.93 (2 H, m); *m/z* (FAB) 371 (M^+ + Me_3Si, 1%), 299 (MH^+, 0.9), 287 (6), 283 (0.5), 226 (2), 215 (5), 157 (9), 125 (9) and 73 (100).

trans-3-*Phenyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2g**. The oxirane was *trans*-3-phenyl-2-phenylsulphonyloxirane **3g** (0.950 g, 3.65 mmol). Chromatography using light petroleum–ethyl acetate (15:1) as eluent gave trans-3-*phenyl*-2-*phenylsulphonyl*-2-*trimethylsiloxirane* **2g** as a colourless oil which eventually solidified (0.882 g, 73%), m.p. 95–96 °C (MeOH) (lit.,* 95–97 °C from methanol) (Found: C, 61.2; H, 5.9. $C_{17}H_{20}O_3SSi$ requires C, 61.4; H, 6.1%); ν_{max}(film)/cm^{-1} 3065m, 3032w, 2959m, 2901m, 1586m, 1497m, 1306s, 1252s and 1146s; δ_H(200 MHz; standard $CHCl_3$) −0.08 (9 H, s), 4.40 (1 H, s), 7.33 (5 H, s), 7.54–7.72 (3 H, m) and 7.99–8.03 (2 H, m); *m/z* (FAB) 391 (3%), 333 (MH^+, 0.7), 317 (0.5), 287 (5), 226 (4), 215 (10), 191 (10), 163 (30), 125 (13) and 73 (100).

3,3-*Dimethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2h**. The oxirane was 3,3-dimethyl-2-phenylsulphonyloxirane **3h** (3.900 g, 18.4 mmol). Chromatography using light petroleum–ethyl acetate (10:1) as eluent gave 3,3-*dimethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2h** as a white solid (5.220 g, 100%), m.p. 74–76 °C (Found: C, 55.0; H, 7.0. $C_{13}H_{20}O_3SSi$ requires C, 54.9; H, 7.1%); ν_{max}(KBr)/cm^{-1} 3094w, 3059w, 3017w, 2972w, 2938w, 2902w, 1301s, 1254m and 1142s; δ_H(200 MHz; standard $CHCl_3$) 0.22 (9 H, s), 1.46 (3 H, s), 1.63 (3 H, s), 7.47–7.65 (3 H, m) and 7.86–7.92 (2 H, m); *m/z* (FAB) 357 (M^+ + Me_3Si, 0.3%), 342 (M^+ + Me_2Si, 0.3), 287 (5), 269 (0.5), 169 (11), 143 (15), 125 (6), 115 (4) and 73 (Me_2Si, 100).

3-*Ethyl*-3-*methyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2i**. The oxirane was 3-ethyl-3-methyl-2-phenylsulphonyloxirane **3i** (*trans*:*cis*, 3:1) (1.339 g, 5.9 mmol). Chromatography using light petroleum–ethyl acetate (15:1) as eluent gave 3-*ethyl*-3-*methyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2i** as a colourless oil which solidified on freezing (1.639 g, 93%) (chromatographically inseparable mixture of the *trans*- and *cis*-diastereoisomers in a 2.8:1 *trans*:*cis* ratio by NMR spectroscopy) (Found: C, 56.55; H, 7.4. $C_{14}H_{22}O_3SSi$ requires C, 56.3; H, 7.4%); ν_{max}(film)/cm^{-1} 3067w, 2971m, 2902w, 2883w, 1304s, 1253m and 1145s; δ_H(300 MHz; standard $CHCl_3$) shows *trans*- and *cis*-diastereoisomers in a 2.8:1 *trans*:*cis* ratio. *trans*-Diastereoisomer: 0.28 (9 H, s), 1.03 (3 H, t, *J* 7.4), 1.52 (3 H, s), 1.58–1.67 (2 H, m), 7.50–7.60 (3 H, m) and 7.85–7.93 (2 H, m); *cis*-diastereoisomer: 0.20 (9 H, s), 1.04 (3 H, t, *J* 7.5), 1.46 (3 H, s), 1.87–1.95 (1 H, m), 3.08–3.18 (1 H, m), 7.50–7.60 (3 H, m) and 7.85–7.93 (2 H, m). Assignments of the signals for the *trans*- and *cis*-diastereoisomers are tentative; *m/z* (FAB) 299 (MH^+, 7%), 287 (88), 226 (9), 215 (74), 199 (36), 157 (100) and 73 (45).

3,3-*Diethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2j**. The oxirane was 3,3-diethyl-2-phenylsulphonyloxirane **3j** (1.270 g, 5.3 mmol). Chromatography using light petroleum–ethyl acetate (15:1) as eluent gave 3,3-*diethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2j** as a colourless oil which eventually solidified (1.573 g, 95%), m.p. 41–42 °C [from Et_2O–light petroleum (b.p. 60–80 °C)] (Found: C, 58.1; H, 7.7. $C_{15}H_{24}O_3SSi$ requires C, 57.65; H, 7.7%); ν_{max}(film)/cm^{-1} 3066w, 2971m, 2942w, 2901w, 2883w, 1305s, 1253m and 1145s; δ_H(300 MHz; standard $CHCl_3$) 0.22 (9 H, s), 0.98 (3 H, t, *J* 7.5), 1.03 (3 H, t, *J* 7.4), 1.52–1.63 (1 H, m), 1.70–1.83 (1 H, m), 1.91–2.00 (2 H, m), 7.49–7.59 (3 H, m) and 7.89–7.92 (2 H, m); *m/z* (FAB) 385 (M^+ + Me_2Si, 0.2%), 313 (MH^+, 0.4), 287 (5), 215 (5), 171 (27), 125 (5) and 73 (100).

3-*Benzyl*-3-*ethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2k**. The oxirane was 3-benzyl-3-ethyl-2-phenylsulphonyloxirane **3k** (*trans*:*cis*, 1:1) (0.600 g, 2.0 mmol). Chromatography using light petroleum–ethyl acetate (13:1) as eluent gave 3-*benzyl*-3-*ethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2k** as a colourless oil (0.692 g, 93%) (chromatographically inseparable mixture of the *trans*- and *cis*-diastereoisomers in a 1:1 *trans*:*cis* ratio by NMR spectroscopy) (Found: C, 63.9; H, 7.1. $C_{20}H_{26}O_3SSi$ requires C, 64.1; H, 7.0%); ν_{max}(film)/cm^{-1} 3064w, 3028w, 2968m, 2900w, 1603w, 1584w, 1497m, 1305s, 1253m and 1143s; δ_H(200 MHz) *trans*-Diastereoisomer: 0.32 (9 H, s), 1.00 (3 H, t, *J* 7.3), 0.76–2.00 (2 H, m), AB system (δ_A 2.88, δ_B 3.08, J_{AB} 14.7), 7.10–7.34 (5 H, m), 7.48–7.61 (3 H, m) and 7.89–7.96 (2 H, m); *cis*-diastereoisomer: 0.28 (9 H, s), 0.97 (3 H, t, *J* 7.5), 1.38–1.58 (2 H, m), 3.21 (2 H, s), 7.10–7.34 (5 H, m), 7.48–7.61 (3 H, m) and 7.89–7.96 (2 H, m); *m/z* (FAB) 375 (MH^+, 1%), 287 (16), 233 (71), 159 (12), 125 (28), 91 (55) and 73 (100).

2-*Phenylsulphonyl*-2-*trimethylsilyl*-1-*oxaspiro*[2.4]*heptane* **21**. The oxirane was 2-phenylsulphonyl-1-oxaspiro[2.4]heptane **31** (1.305 g, 5.5 mmol). Chromatography using light petroleum–ethyl acetate (13:1) as eluent gave 2-*phenylsulphonyl*-2-*tri*-

* There is some ambiguity as to the structure of the compound with this melting point prepared by Eisch and Galle.[17b] Our results on the subsequent reactions of this compound suggest that silylation had occurred α- to the phenylsulphonyl group, rather than α- to the phenyl group, which supports the structure implied in the discussion section of Eisch and Galle's paper, rather than that explicitly stated in the experimental section of their paper.

methylsilyl-1-oxaspiro[2.4]*heptane* **21** as a pale yellow oil (1.550 g, 91%) (Found: C, 58.1; H, 7.0. $C_{15}H_{22}O_3SSi$ requires C, 58.0; H, 7.1%); ν_{max}(film)/cm^{-1} 3066w, 2960m, 2900w, 2872w, 1306s, 1252m and 1141s; δ_H(200 MHz; standard $CHCl_3$) 0.20 (9 H, s), 1.50–1.96 (6 H, m), 1.99–2.10 (1 H, m), 2.15–2.35 (1 H, m), 7.47–7.69 (3 H, m) and 7.87–8.00 (2 H, m); *m/z* (FAB) 383 ($M^+ + Me_3Si$, 5%), 311 (MH^+, 6), 287 (33) and 169 (100).

2-*Phenylsulphonyl-2-trimethylsilyl-1-oxaspiro*[2.5]*octane* **2m**. The oxirane was 2-phenylsulphonyl-1-oxaspiro[2.5]octane **3m** (1.114 g, 4.4 mmol). Chromatography using light petroleum–ethyl acetate (10:1) as eluent gave 2-*phenylsulphonyl-2-trimethylsilyl-1-oxaspiro*[2.5]*octane* **2m** as a colourless oil which eventually solidified (1.300 g, 91%), m.p. 45–48 °C (from Et_2O–light petroleum) (Found: C, 59.3; H, 7.4. $C_{16}H_{24}O_3SSi$ requires C, 59.2; H, 7.45%); ν_{max}(film)/cm^{-1} 2934s, 2859m, 1559w, 1306s, 1252m and 1146s; δ_H(200 MHz; standard $CHCl_3$) 0.22 (9 H, s), 1.16–1.93 (9 H, m), 2.09–2.18 (1 H, m), 7.46–7.63 (3 H, m) and 7.80–7.90 (2 H, m); *m/z* (FAB) 325 (MH^+, 3.5%), 287 (7), 251 (5) and 183 (100).

Magnesium Bromide–Diethyl Ether Ring Opening of Aldehyde Derived 2-Phenylsulphonyl-2-trimethylsilyloxiranes.—General procedure. Magnesium bromide–diethyl ether (1.9 equiv.) was added to a solution of the oxirane **2** (1 equiv.) in dry diethyl ether (12 cm^3 mmol^{-1}) or dry THF (12 cm^3 mmol^{-1}) under nitrogen. The reaction mixture was stirred at room temperature or heated at reflux for the time indicated, phosphate buffer (10 cm^3; pH 7) was added and the organic phase was separated. The aqueous layer was washed with diethyl ether (3 × 20 cm^3), the organic phases were then combined and dried ($MgSO_4$). Removal of the solvent on the rotary evaporator gave the crude product.

Reactions in Ether at Room Temp.—Ring opening of trans-3-*methyl-2-phenylsulphonyl-2-trimethylsiloxirane* **2b**. The oxirane was *trans*-3-methyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2b** (0.540 g, 2.0 mmol) and the mixture was stirred at room temp. in ether for 44 h. The crude product, 2-*bromopropanoyltrimethylsilane* **1b**, was obtained as an unstable yellow oil without chromatography (0.332 g, 79%) (Found: C, 33.9; H, 5.4. $C_6H_{13}BrOSi$ requires C, 34.45; H, 6.3%) (Found: M^+ – CO, 179.9965. $C_5H_{13}BrSi$ requires *M* – CO, 179.9971); ν_{max}(film)/cm^{-1} 2963m, 2928w, 2903w and 1647s; δ_H(200 MHz; standard $CHCl_3$) 0.30 (9 H, s), 1.66 (3 H, d, *J* 6.8) and 4.61 (1 H, q, *J* 6.8); *m/z* (EI) 180 (M^+ – CO, 17%), 137 (64), 101 (40), 73 (100) and 56 (49).

Ring opening of trans-3-*ethyl-2-phenylsulphonyl-2-trimethylsilyloxirane* **2c**. The oxirane was *trans*-3-ethyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2c** (0.658 g, 2.3 mmol) and the mixture was stirred at room temp. in ether for 49 h. Chromatography of the resulting residue using light petroleum (b.p. 30–40 °C)–diethyl ether (20:1) as eluent yielded 2-*bromobutanoyltrimethylsilane* **1c** as a volatile, unstable yellow oil (0.388 g, 75%) (Found: M^+ – CO, 194.0091. $C_6H_{15}BrSi$ requires *M* – CO, 194.0127); ν_{max}(film)/cm^{-1} 2971s and 1647s; δ_H(200 MHz; standard $CDCl_3$) 0.30 (9 H, s), 1.01 (3 H, t, *J* 7.3), 1.83–1.93 (1 H, m), 1.98–2.07 (1 H, m) and 4.41 (1 H, dd, *J* 5.9 and 8.2); *m/z* (EI) 194 (M^+ – CO, 12%), 137 (55), 101 (32) and 73 (100).

Ring opening of trans-2-*phenylsulphonyl-3-propyl-2-trimethylsilyloxirane* **2d**. The oxirane was *trans*-2-phenylsulphonyl-3-propyl-2-trimethylsilyloxirane **2d** (0.596 g, 2.0 mmol) and the mixture was stirred at room temp. in ether for 48 h. Chromatography using light petroleum (b.p. 30–40 °C)–diethyl ether (15:1) as eluent gave 2-bromopentanoyltrimethylsilane[8] **1d** as a yellow oil (0.365 g, 77%) (Found: M^+ – CO, 208.0244. Calc. for $C_7H_{17}BrSi$: *M* – CO, 208.0283); ν_{max}(film)/cm^{-1} 2963s, 2876m and 1645s; δ_H(200 MHz; standard $CHCl_3$) 0.29 (9 H, s), 0.93 (3 H, t, *J* 7.4), 1.33–1.39 (1 H, m), 1.47–1.52 (1 H, m), 1.82–1.98 (2 H, m) and 4.47 (1 H, dd, *J* 6.0 and 8.4); *m/z* (EI) 208 (M^+ – CO, 9%), 137 (47), 129 (26), 101 (40) and 73 (100). Further elution with ethyl acetate gave 2-trimethylsilylpentanoic acid[28] **6d** as a yellow oil (0.059 g, 17%) (Found: $M^+ - CH_3$, 159.0831. Calc. for $C_7H_{15}O_2Si$: *M* – CH_3, 159.0841); ν_{max}(film)/cm^{-1} 3650–2350brm, 2961s, 2936s, 2874m and 1686s; δ_H(200 MHz; standard $CHCl_3$) 0.10 (9 H, s), 0.86–0.93 (3 H, m), 1.25–1.57 (3 H, m), 1.68–1.88 (1 H, m), 2.01 (1 H, dd, *J* 2.3 and 11.6). The carboxylic acid singlet is too broad to be observed; *m/z* (EI) 159 (M^+ – CH_3, 28%), 145 (83), 129 (90), 73 (97) and 55 (98).

Ring opening of trans-3-*butyl-2-phenylsulphonyl-2-trimethylsilyloxirane* **2e**. The oxirane was *trans*-3-butyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2e** (0.156 g, 0.5 mmol) and the mixture was stirred at room temp. in ether for 5 d. Chromatography using light petroleum (b.p. 30–40 °C)–diethyl ether (20:1) as eluent gave 2-bromohexanoyltrimethylsilane **1e**[5,9] as a pale yellow oil (0.100 g, 80%) (Found: MH^+, 251.0428. Calc. for $C_9H_{20}BrOSi$: *M*H, 251.0468); ν_{max}(film)/cm^{-1} 2959m, 2874w and 1645m; δ_H(300 MHz; standard $CHCl_3$) 0.30 (9 H, s), 0.89–0.95 (3 H, m), 1.25–1.50 (4 H, m), 1.79–1.92 (1 H, m), 1.94–2.06 (1 H, m) and 4.46 (1 H, dd, *J* 6.1 and 8.3); *m/z* (EI) 251 (MH^+, 0.6%), 222 (4.5), 207 (1), 171 (14), 137 (23), 101 (25) and 73 (100).

Ring opening of trans-3-(1-*methylethyl*)-2-*phenylsulphonyl-2-trimethylsilyloxirane* **2f**. Magnesium bromide–diethyl ether (0.491 g, 1.9 mmol) was added to a solution of *trans*-3-(1-methylethyl)-2-phenylsulphonyl-2-trimethylsilyloxirane **2f** (0.298 g, 1.0 mmol) in dry diethyl ether (10 cm^3) under nitrogen and stirred at room temperature for 20 d. The reaction mixture was then poured into light petroleum (b.p. 30–40 °C) (50 cm^3). The resulting suspension was decanted from the sticky residue formed and the solvent was removed on the rotary evaporator with care since the product from this reaction is volatile. Chromatography using light petroleum (b.p. 30–40 °C)–diethyl ether (80:1) as eluent gave 2-bromo-3-methylbutanoyltrimethylsilane **1f** as a yellow oil (0.019 g, 8%) (Found: M^+, 236.0162. $C_8H_{17}BrOSi$ requires *M*, 236.0233); ν_{max}(film)/cm^{-1} 2957s, 2924s, 2872m, 2855m and 1647w; δ_H(300 MHz; standard $CHCl_3$) 0.30 (9 H, s), 0.97 (3 H, d, *J* 6.7), 1.06 (3 H, d, *J* 6.6), 2.27–2.34 (1 H, m) and 4.26 (1 H, d, *J* 8.0); *m/z* (EI) 237 (MH^+, 3%), 236 (M^+, 0.5), 208 (28), 193 (7), 137 (65), 101 (65) and 73 (100). Further elution using light petroleum (b.p. 30–40 °C)–diethyl ether (15:1) gave unchanged 3-(1-methylethyl)-2-phenylsulphonyl-2-trimethylsilyloxirane **2f** (0.066 g, 22%) and 3-(1-methylethyl)-2-phenylsulphonyloxirane **3f** (0.060 g, 26%) resulting from desilylation of the starting material.

Reactions in THF at Reflux.—Ring opening of trans-3-*methyl-2-phenylsulphonyl-2-trimethylsilyloxirane* **2b**. Magnesium bromide–diethyl ether (0.611 g, 2.4 mmol), *trans*-3-methyl-2-phenylsulphonyl-2-trimethylsiloxirane **2b** (0.336 g, 1.25 mmol) and dry THF 15 cm^3) were heated at reflux under nitrogen for 47 h. The reaction mixture was poured into light petroleum (b.p. 30–40 °C) (40 cm^3) and the solvent was removed under reduced pressure at 40 °C. The resulting residue was immediately applied to a column in a little dichloromethane and chromatographed using light petroleum (b.p. 30–40 °C)–diethyl ether (30:1) as eluent, yielding 2-bromopropanoyltrimethylsilane **1b** (0.125 g, 48%). Further elution with light petroleum (b.p. 30–40 °C)–diethyl ether (20:1) gave (*Z*)-1-bromo-1-phenylsulphonylprop-1-ene **7b** as a white solid (0.098 g, 30%), m.p. 117.5–120 °C (lit.,[22b] 116–118 °C from ethanol) (Found: C, 42.0; H, 3.4. Calc. for $C_9H_9BrO_2S$: C, 41.4; H, 3.5%); ν_{max}(KBr)/cm^{-1} 3065w, 3023w, 1613w, 1318s and 1159s; δ_H(200 MHz) 1.96 (3 H, d, *J* 6.8), 7.53 (1 H, q, *J* 6.8), 7.51–7.71 (3 H, m) and 7.92–7.97 (2 H, m); *m/z* (EI) 260 (M^+, 57%), 181 (18), 141 (9), 125 (97), 77 (100) and 39 (77).

Ring opening of trans-3-*ethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2c**. The oxirane was *trans*-3-ethyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2c** (0.568 g, 2.0 mmol) and the mixture was heated at reflux in THF for 75 h. Chromatography of the resulting residue using light petroleum–ethyl acetate (20:1) as eluent gave 2-bromobutanoyltrimethylsilane **1c** (0.177 g, 40%) together with (Z)-1-*bromo*-1-*phenylsulphonylbut*-1-*ene* **7c** as a white solid containing *trans*-3-ethyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2c** as a minor contaminant in *ca.* 91:9 ratio by NMR spectroscopy (0.220 g, 40%), m.p. 73–75 C (from Et_2O) (Found: C, 44.2; H, 4.1. $C_{10}H_{11}BrO_2S$ requires C, 43.65; H, 4.0%) (Found: M^+, 273.9664. $C_{10}H_{11}BrO_2S$ requires *M*, 273.9664); ν_{max}(KBr)/cm^{-1} 3063w, 2982m, 2940w, 2876w, 1613m, 1584w, 1306s and 1161s; δ_H(200 MHz) 1.13 (3 H, t, *J* 7.6), 2.25–2.40 (2 H, m), 7.44 (1 H, t, *J* 7.1), 7.51–7.63 (2 H, m), 7.64–7.71 (1 H, m) and 7.92–7.97 (2 H, m); *m/z* (EI) 274 (M^+, 74%), 195 (16), 125 (73), 77 (89) and 53 (100).

Ring opening of trans-2-*phenylsulphonyl*-3-*propyl*-2-*trimethylsilyloxirane* **2d**. The oxirane was *trans*-2-phenylsulphonyl-3-propyl-2-trimethylsilyloxirane **2d** (0.596 g, 2.0 mmol) and the mixture was heated at reflux in THF for 72 h. Chromatography of the resulting residue using light petroleum–ethyl acetate (20:1) as eluent gave 2-bromopentanoyltrimethylsilane **1d** (0.129 g, 27%) together with (Z)-1-*bromo*-1-*phenylsulphonylpent*-1-*ene* **7d** as a yellow oil containing trans-2-*phenylsulphonyl*-3-*propyl*-2-*trimethylsilyloxirane* **2d** as a minor contaminant in *ca.* 84:16 ratio by NMR spectroscopy (0.277 g, 48%) (Found: M^+, 287.9811. $C_{11}H_{13}BrO_2S$ requires *M*, 287.9820); ν_{max}(film)/cm^{-1} 3067w, 2963m, 2934m, 2874w, 1611w, 1586w, 1327s and 1159s; δ_H(200 MHz; standard $CHCl_3$) 0.96 (3 H, t, *J* 7.4), 1.50–1.62 (2 H, m), 2.29 (2 H, q, *J* 7.2 and 14.6), 7.45 (1 H, t, *J* 7.2), 7.50–7.61 (2 H, m), 7.61–7.69 (1 H, m) and 7.92–7.96 (2 H, m); *m/z* (EI) 288 (M^+, 32%), 209 (12), 166 (8), 143 (46), 125 (58) and 77 (100).

Ring opening of trans-3-*butyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2e**. The oxirane was *trans*-3-butyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2e** (0.470 g, 1.5 mmol) and the mixture was heated at reflux in THF for 69 h. Chromatography using light petroleum–ethyl acetate (10:1) as eluent gave 2-bromohexanoyltrimethylsilane **1e** (0.156 g, 41%) together with (Z)-1-*bromo*-1-*phenylsulphonylhex*-1-*ene* **7e** as a pale yellow oil which solidified on cooling (0.205 g, 50%) (Found: C, 48.0; H, 5.2. $C_{12}H_{15}BrO_2S$ requires C, 47.5; H, 5.0%); ν_{max}(film)/cm^{-1} 3062w, 2959m, 2932m, 2872m, 2863m, 1613m, 1327s and 1157s; δ_H(300 MHz; standard $CHCl_3$) 0.92 (3 H, t, *J* 7.2), 1.23–1.42 (2 H, m), 1.46–1.56 (2 H, m), 2.31 (2 H, dt, *J* 7.2 and 7.4), 7.45 (1 H, t, *J* 7.2), 7.53–7.58 (2 H, m), 7.63–7.69 (1 H, m) and 7.92–7.95 (2 H, m); *m/z* (EI) 302 (M^+, 13%), 223 (11), 125 (37), 81 (100) and 77 (78).

Ring opening of trans-3-(1-*methylethyl*)-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2f**. The oxirane was *trans*-3-(1-methylethyl)-2-phenylsulphonyl-2-trimethylsilyloxirane **2f** (0.596 g, 2.0 mmol) and the mixture was heated at reflux in THF for 22 d. Chromatography of the resulting residue using light petroleum–ethyl acetate (15:1) as eluent gave 2-bromo-3-methylbutanoyltrimethylsilane **1f** (0.035 g, 7%), together with (Z)-1-*bromo*-3-*methyl*-1-*phenylsulphonylbut*-1-*ene* **7f** as a colourless oil which eventually solidified (0.372 g, 64%), m.p. 74–75 °C (from Et_2O) (Found: C, 45.85; H, 4.5. $C_{11}H_{13}BrO_2S$ requires C, 45.7; H, 4.5%); ν_{max}(film)/cm^{-1} 3065m, 3007m, 2969s, 2909m, 2872s, 1586m, 1319s and 1159s; δ_H(300 MHz; standard $CHCl_3$) 1.11 (6 H, d, *J* 6.7), 2.66–2.78 (1 H, m), 7.27 (1 H, d, *J* 9.3), 7.54–7.59 (2 H, m), 7.64–7.69 (1 H, m) and 7.91–7.94 (2 H, m); *m/z* (EI) 288 (M^+, 42%), 166 (12) and 67 (100).

Ring opening of trans-3-*phenyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2g**. The oxirane was *trans*-3-phenyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2g** (0.332 g, 1.0 mmol) and the mixture was heated at reflux in THF for 46h. Chromatography using light petroleum–ethyl acetate (10:1) as eluent yielded (Z)-1-bromo-2-phenyl-1-phenylsulphonylethene **7g** as a pale yellow solid (0.156 g, 48%), m.p. 102–103 °C (from Et_2O) (lit.,[22b] 101–103 °C from ethanol) (Found: C, 52.0; H, 3.2. Calc. for $C_{14}H_{11}BrO_2S$: C, 52.0; H, 3.4%); ν_{max}(KBr)/cm^{-1} 3083vw, 3055vw, 3022vw, 2959m, 1595m, 1306s and 1150s; δ_H(300 MHz; standard $CHCl_3$) 7.32–7.49 (3 H, m), 7.54–7.60 (2 H, m), 7.62–7.71 (1 H, m), 7.79–7.84 (2 H, m), 7.98–8.03 (2 H, m) and 8.37 (1 H, s); *m/z* (EI) 322 (M^+, 28%), 243 (19), 180 (55), 125 (10), 102 (43) and 77 (27).

Magnesium Bromide–Diethyl Ether Ring Opening of Ketone Derived 2-*Phenylsulphonyl*-2-*trimethylsilyloxiranes in Diethyl Ether.—General procedure*. A solution of the oxirane **2** (1 equiv.) in dry diethyl ether (12 cm^3 mmol^{-1}) was cooled to 0 °C under nitrogen. Magnesium bromide–diethyl ether (1.9 equiv.) was added and the reaction mixture was stirred at this temperature for the time indicated. The mixture was then poured into light petroleum (b.p. 30–40 °C) (80 cm^3) and the remaining sticky residue was washed thoroughly with diethyl ether. The organic washings were combined and the solvent was removed with care under reduced pressure at 25 °C since the products of the reactions are volatile. The crude mixture of organic and inorganic products was washed thoroughly with a little light petroleum (b.p. 30–40 °C)–diethyl ether (80:1) and the washings were applied to a column. Chromatography using light petroleum (b.p. 30–40 °C)–diethyl ether (80:1) as eluent then gave the products.

Ring opening of 3,3-*dimethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2h**. The oxirane was 3,3-dimethyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2h** (1.134 g, 4.0 mmol) and the mixture was stirred for 140 min. Chromatography gave 2-bromo-2-methylpropanoyltrimethylsilane **1h** as a volatile orange liquid (0.508 g, 57%) (Found: C, 37.7; H, 6.8. $C_7H_{15}BrOSi$ requires C, 37.7; H, 6.8%); ν_{max}(film)/cm^{-1} 2973m, 2928m, 2901m and 1642s; δ_H(300 MHz; standard $CHCl_3$) 0.35 (9 H, s) and 1.78 (6 H, s); *m/z* (EI) 194 (10%), 137 (43), 101 (18), 73 (100) and 70 (23). Further elution with light petroleum–ethyl acetate (10:1) gave 2-methyl-2-trimethylsilylpropanoic acid **6h** as a white solid (0.153 g, 24%) which sublimed from 70 °C onwards (Found: C, 52.6; H, 10.2. $C_7H_{16}O_2Si$ requires C, 52.45; H, 10.1%); ν_{max}(KBr)/cm^{-1} 3650–2400mbr, 2961m, 2874m and 1674sbr; δ_H(200 MHz; standard $CHCl_3$) 0.08 (9 H, s) and 1.22 (6 H, s). The carboxylic acid singlet is too broad to be observed; *m/z* (EI) 160 (M^+, 37%), 143 (65), 129 (11), 115 (13), 87 (68), 85 (91), 83 (100) and 73 (77); and finally 2-methylpropanoic acid **10h** (0.032 g, 9%).

Ring opening of 3-*ethyl*-3-*methyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2i**. The oxirane was 3-ethyl-3-methyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2i** (2.8:1) *trans*:*cis* ratio) (1.034 g, 3.5 mmol) and the mixture was stirred for 4.5 h. Chromatography gave 2-bromo-2-methylbutanoyltrimethylsilane **1i** as a volatile yellow liquid (0.507 g, 65%) (Found: C, 41.0; H, 7.2. $C_8H_{17}BrOSi$ requires C, 40.5; H, 7.2%); (Found: M^+, 236.0231. $C_8H_{17}BrOSi$ requires *M*, 236.0232); ν_{max}(film)/cm^{-1} 2957s, 2926s, 2874m, 2857m and 1640s; δ_H(300 MHz; standard $CHCl_3$) 0.33 (9 H, s), 0.97 (3 H, t, *J* 7.4), 1.71 (3 H, s), 1.90–2.03 (1 H, m) and 2.09–2.22 (1 H, m); *m/z* (EI) 236 (M^+), 222, 208, 193, 137, 118, 101 and 73. (*E*)-2-Methylbut-2-enoyltrimethylsilane **9i** was also obtained as a volatile yellow oil (0.036 g, 7%) (Found: M^+, 156.0972. $C_8H_{16}OSi$ requires *M*, 156.0970); ν_{max}(film)/cm^{-1} 2959s, 2926s, 2872m, 2857m and 1591s; δ_H(300 MHz; standard $CHCl_3$) 0.25 (9 H, s), 1.66 (3 H, s), 1.93 (3 H, d, *J* 6.9) and 6.69 (1 H, brq); *m/z* (EI) 156 (M^+, 49%), 141 (71), 113 (18), 83 (13) and 73 (100). Further elution using light petroleum–diethyl ether (10:1) gave impure 2-*methyl*-2-*phenylsulphonylbutanoyltrimethylsilane* **11i** as an oil (0.051 g, 5%) (Found: $M^+ - CO$, 270.1118. $C_{13}H_{22}O_2SSi$

requires M − CO, 270.1109); ν_{max}(film)/cm^{-1} .3065w, 2965w, 1634m, 1584w, 1306s and 1146s; δ_H(200 MHz; standard $CHCl_3$) 0.36 (9 H, s), 0.78 (3 H, t, J 7.5), 1.42 (3 H, s), 1.70–1.84 (1 H, m), 2.46–2.57 (1 H, m) and 7.28–7.71 (5 H, m); m/z (EI) 270 (M^+ − CO, 5.8%), 255 (57), 125 (88), 109 (56), 77 (91) and 73 (100); and 2-methyl-2-trimethylsilylbutanoic acid **6i** as a colourless oil which eventually became a soft waxy solid (0.013 g, 2%) (Found: $M^+ - CH_3$, 159.0847. $C_7H_{15}O_2Si$ requires $M - CH_3$, 159.0841); ν_{max}(film)/cm^{-1} 3660–2200brs and 1673brs; δ_H(200 MHz; standard $CHCl_3$) 0.07 (9 H, s), 0.92 (3 H, t), 1.16 (3 H, s), 1.21–1.45 (1 H, m) and 1.94–2.17 (1 H, m). The carboxylic acid singlet is too broad to be observed; m/z (EI) 174 (M^+, 16%), 159 (56), 157 (85), 85 (86), 83 (93) and 73 (99). Further elution using diethyl ether gave a mixture of 2-methyl-2-trimethylsilylbutanoic acid **6i** and 2-methylbutanoic acid **10i** (0.073 g). The yields were calculated from the NMR spectrum to be 5% and 11% respectively.

Ring opening of 3,3-*diethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2j**. The oxirane was 3,3-diethyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2j** (1.248 g, 4.0 mmol) and the mixture was stirred for 2 h. Chromatography gave 2-bromo-2-ethylbutanoyltrimethylsilane **1j** as a volatile yellow liquid (0.574 g, 57%) (Found: C, 43.6; H, 7.75. $C_9H_{19}BrOSi$ requires C, 43.0; H, 7.6%) (Found: M^+, 250.0362. $C_9H_{19}BrOSi$ requires M, 250.0389); ν_{max}(film)/cm^{-1} 2972m, 2883w, 2856w and 1637s; δ_H(200 MHz; standard $CHCl_3$) 0.32 (9 H, s), 0.90 (6 H, t, J 7.4), 2.04 (2 H, q, J 7.3) and 2.06 (2 H, q, J 7.5); m/z (EI) 250 (M^+), 235, 222, 171, 137, 101, 98 and 73; and (E)-2-*ethylbut*-2-*enoyltrimethylsilane* **9j** as an unstable volatile yellow liquid (0.059 g, 9%) (Found: M^+, 170.1131. $C_9H_{18}OSi$ requires M, 170.1127); ν_{max}(film)/cm^{-1} 2963s, 2930s, 2874m, 2857m, 1642w and 1591s; δ_H(300 MHz; standard $CHCl_3$) 0.25 (9 H, s), 0.88 (3 H, t, J 7.5), 1.94 (3 H, d, J 6.9), 2.21 (2 H, q, J 7.5) and 6.62 (1 H, q, J 7.0); m/z (EI) 170 (M^+), 155, 141, 101, 97 and 73 (Me_3Si). Further elution using light petroleum–diethyl ether (5:1) gave impure 2-*ethyl*-2-*phenylsulphonylbutanoyltrimethylsilane* **11j** as a colourless oil (0.006 g, 0.5%) ν_{max}(film)/cm^{-1} 3063w, 2975m, 1634m, 1304s and 1142s; δ_H(200 MHz; standard $CHCl_3$) 0.35 (9 H, s), 0.92 (6 H, t, J 7.5), 1.93–2.20 (4 H, m) and 7.32–7.68 (5 H, m); m/z (FAB) 385 (M^+ + Me_3Si, 12%), 313 (MH^+, 16), 297 (24), 284 (33), 171 (100), 141 (18), 125 (83) and 97 (55); and 2-ethylbutanoic acid **10j** (0.087 g, 19%).

Ring opening of 3-*benzyl*-3-*ethyl*-2-*phenylsulphonyl*-2-*trimethylsilyloxirane* **2k**. The oxirane was 3-benzyl-3-ethyl-2-phenylsulphonyl-2-trimethylsilyloxirane **2k** (*trans*:*cis* 1:1) (0.362 g, 0.97 mmol) and the mixture was stirred at 0 °C for 5.5 h followed by 9 °C for 16 h. Chromatography gave 2-*benzyl*-2-*bromobutanoyltrimethylsilane* **1k** as a yellow oil (0.160 g, 53%) (Found: M^+, 312.0504. $C_{14}H_{21}BrOSi$ requires M, 312.0545); ν_{max}(film)/cm^{-1} 3088w, 3065w, 3032w, 2971m and 1638s; δ_H(300 MHz; standard $CHCl_3$) 0.27 (9 H, s), 0.97 (3 H, t, J 7.3), 1.91–200 (1 H, m), 2.05–2.15 (1 H, m), AB system (δ_A 3.28, δ_B 3.34, J_{AB} 14.5), 7.17–7.20 (2 H, m) and 7.24–7.31 (3 H, m); m/z (EI) 312, 297, 284, 233, 217, 160, 101, 91 and 73; and (*E*)-2-benzylbut-2-enoyltrimethylsilane **9k**[25] as a yellow oil (0.024 g, 11%) (Found: MH^+, 231.1205. Calc. for $C_{14}H_{19}OSi$: MH, 231.1205); ν_{max}(film)/cm^{-1} 3087w, 3063w, 3029w, 2957s, 2926s, 2855m and 1593s; δ_H(200 MHz; standard $CHCl_3$) 0.27 (9 H, s), 1.99 (3 H, d, J 6.9), 3.60 (2 H, s), 6.85 (1 H, q, J 6.9) and 7.09–7.32 (5 H, m); m/z (EI) 231 (MH^+, 33%), 217 (46), 203 (10), 129 (9), 91 (24) and 73 (100). Further elution with light petroleum–diethyl ether (10:1) gave 2-benzylbutanoic acid **10k** (0.038 g, 22%).

Ring opening of 2-*phenylsulphonyl*-2-*trimethylsilyl*-1-*oxaspiro*[2.4]*heptane* **21**. The oxirane was 2-phenylsulphonyl-2-trimethylsilyl-1-oxaspiro[2.4]heptane **21** (0.696 g, 2.24 mmol) and the mixture was stirred for 3 h. Chromatography gave 1-*bromo*-1-*trimethylsilylcarbonylcyclopentane* **1l** as a pale yellow oil which rapidly decomposes at room temperature when concentrated (0.323 g, 58%) (Found: C, 43.9; H, 6.9. $C_9H_{17}BrOSi$ requires C, 43.4; H, 6.9%); ν_{max}(film)/cm^{-1} 2959s, 2874m and 1638s; δ_H(300 MHz; standard $CHCl_3$) 0.35 (9 H, s), 1.64–1.75 (2 H, m), 1.91–2.01 (2 H, m), 2.11–2.20 (2 H, m) and 2.23–2.34 (2 H, m); m/z (EI) 233 (M^+ − CH_3, 9%), 169 (81), 137 (42), 101 (47) and 73 (100); and trimethylsilylcarbonylcyclopent-1-ene **91** as a yellow oil (0.011 g, 3%) (Found: M^+, 168.0972. $C_9H_{16}OSi$ requires M, 168.0971); ν_{max}(film)/cm^{-1} 2955s, 2926s, 2855m and 1587w; δ_H(300 MHz; standard $CHCl_3$) 0.26 (9 H, s), 1.82–1.92 (2 H, m), 2.44–2.64 (4 H, m) and 6.79–6.82 (1 H, brs); m/z (EI) 168 (M^+, 20%), 153 (7), 140 (9), 95 (10), 73 (100) and 67 (15).

Ring opening of 2-*phenylsulphonyl*-2-*trimethylsilyl*-1-*oxaspiro*[2.5]*octane* **2m**. The oxirane was 2-phenylsulphonyl-2-trimethylsilyl-1-oxaspiro[2.5] octane **2m** (0.746 g, 2.3 mmol) and the mixture was stirred for 3.5 h. Chromatography gave 1-*bromo*-1-*trimethylsilylcarbonylcyclohexane* **1m** as a yellow oil which solidified on freezing (0.364 g, 60%) (Found: C, 45.6; H, 7.3. $C_{10}H_{19}BrOSi$ requires C, 45.6; H, 7.3%); ν_{max}(film)/cm^{-1} 2937s, 2860m and 1636s; δ_H(300 MHz; standard $CHCl_3$) 0.32 (9 H, s), 1.23–1.39 (1 H, m), 1.54–1.67 (3 H, m), 1.73–1.97 (4 H, m) and 2.07–2.17 (2 H, m); m/z (EI) 262 (M^+), 247, 234, 219, 183, 137, 110, 101, 82 and 73; and trimethylsilylcarbonylcyclohex-1-ene **9m** as a volatile yellow oil (0.026 g, 6%) (Found: M^+, 182.1164. Calc. for $C_{10}H_{18}OSi$: M, 182.1127); ν_{max}(film)/cm^{-1} 3040w, 2935s, 2860m and 1586s; δ_H(300 MHz; standard $CHCl_3$) 0.26 (9 H, s), 1.60–1.64 (4 H, m), 2.11–2.13 (2 H, m), 2.29–2.32 (2 H, m) and 6.86–6.89 (1 H, brs); m/z (EI) 182 (M^+, 18%), 167 (14), 154 (6), 109 (8), 73 (85) and 69 (100). Further elution using light petroleum–diethyl ether (20:1) gave 1-*phenylsulphonyl*-1-*trimethylsilylcarbonylcyclohexane* **11m** as a white wax (0.017 g, 2%), m.p. broad range around 70 °C (Found: M^+ − CHO, 295.1203. $C_{15}H_{23}O_2SSi$ requires M −CHO, 295.1188); ν_{max}(film)/cm^{-1} 2926m, 2855m, 1628m, 1586w, 1300m and 1140m; δ_H(200 MHz) 0.37 (9 H, s), 0.96–1.83 (8 H, m), 2.48–2.54 (2 H, m) and 7.47–7.68 (5 H, m); m/z (FAB) 398 (M^+ + Me_3Si, 18%), 326 (MH^+, 9), 310 (13), 297 (17), 183 (7), 77 (20) and 73 (100). Further elution with light petroleum–diethyl ether (10:1) gave 1-(trimethylsilyl)cyclohexanecarboxylic acid **6m** as white crystals (0.022 g, 5%) which sublime from 100 °C onwards (Found: M^+, 200.1243. $C_{10}H_{20}O_2Si$ requires M, 200.1232); ν_{max}(KBr)/cm^{-1} 3600–2400brm, 2928s, 2851m and 1674s; δ_H(200 MHz; standard $CHCl_3$) 0.05 (9 H, s), 1.09–1.73 (8 H, m) and 2.16–2.22 (2 H, m); m/z (EI) 200 (M^+, 1.6%), 183 (17), 110 (40), 83 (62) and 73 (93); and cyclohexanecarboxylic acid **10m** (0.031 g, 11%).

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