The generation and synthetic applications of episulfone α-anions

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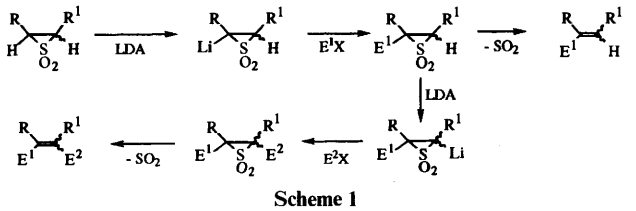
Treatment of the episulfone, 8,8-dimethyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S,S*-dioxide 1, with lithium diisopropylamide to generate the corresponding α-sulfonyl anion, and anion trapping with trimethylsilyl chloride or trimethylstannyl chloride *in situ*, produced the corresponding monosilyl, disilyl, monostannyl and distannyl episulfones as relatively stable, fully characterised crystalline solids. The structure of the disilylated episulfone 3a was also confirmed by X-ray crystallography: this is the first reported X-ray structure of a tetrasubstituted episulfone and the long carbon–carbon episulfone bond length (1.686 Å) is particularly noteworthy. With similar procedures the monotriethylsilyl, monotributylstannyl, and the triethyl, trimethyl disilyl adducts were prepared in reasonable to good yields. On treatment with potassium *tert*-butoxide or thermolysis the functionalized episulfones lost sulfur dioxide to produce the corresponding vinyl-silanes and -stannanes.

Attempts to use carbon electrophiles for α-sulfonyl anion trapping are also reported. The monobenzoylated adducts 9 and 10 were obtained by *in situ* trapping with benzoyl chloride. In addition, it was found that treatment of the disilylated episulfone 3a with caesium fluoride–benzaldehyde gave the monoalkylated adduct 11, albeit in low yield. Other reactions of the silylated/stannylated episulfones are also reported.

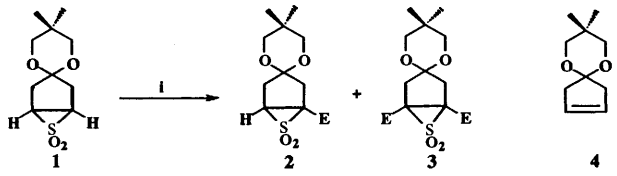
Since its discovery,[1] the Ramberg–Bäcklund reaction, the base-mediated conversion of α-halogeno sulfones into regio-defined alkenes, has attracted both mechanistic and synthetic interest.[2–4] The intermediacy of episulfones (thiirane 1,1-dioxides) in this reaction has long been established by indirect methods[2,3] but until recently these intermediates had not been isolated from α-halogeno sulfones under the conditions of the Ramberg–Bäcklund reaction. In 1989 we reported that the Ramberg–Bäcklund reaction could be carried out at low temperatures[4] and under these conditions a range of stable, functionalized episulfones were prepared from α-halogeno sulfones in high yields.[5,6]

Encouraged by earlier reports in which it was shown that it was possible to carry out base-catalysed deuterium exchange of episulfones,†[3] we initiated a study to investigate the generation and reactions of α-sulfonyl anions derived from episulfones obtained by the Ramberg–Bäcklund route.[7] Complementary research has recently been described by Simpkins *et al.*[8] using episulfones generated by other procedures.[9] We envisage that ultimately such methodology could provide a potentially useful new procedure for the stereocontrolled synthesis of alkenes with a range of substitution patterns as illustrated in Scheme 1 for the production of tri- and tetra-substituted alkenes.



Scheme 1

In order to establish the viability of this proposal we chose to study the deprotonation–trapping of the episulfone **1** (Scheme 2) due to its accessibility and stability,[5] and the fact that



Scheme 2 *Reagents and conditions:* i, 2.2 equiv. of LDA, THF, −78 °C, *n* equiv. E^+ (see Table 1)

stereoisomeric alkylated episulfones and alkenes are not possible, therefore simplifying product analysis. We had previously shown that episulfones of this type are rapidly converted into the corresponding alkenes under basic conditions,[6] and treatment of episulfones with organolithium reagents has been reported to give rapid decomposition.[10] We therefore envisaged that the generation of anions from episulfones would present a considerable challenge. Initial studies[7a] confirmed this view: using a range of bases and solvents at low temperature, followed by the addition of several reactive electrophiles, at best only trace amounts of adducts **2** were obtained, as the corresponding alkenes (the unsubstituted alkene **4** being the major reaction product). In view of these disappointing results, we turned our attention to an *in situ* trapping approach[11] in which the electrophilic trapping agent is pre-mixed with the substrate before the addition of the base. With this procedure we were extremely pleased to observe that it was indeed possible to generate and trap the α-sulfonyl anion using trimethylsilyl chloride as the electrophile and lithium diisopropylamide (LDA) as the base. The yields in this reaction were sometimes reasonable but were not reproducible. After considerable experimentation, it was eventually established that reproducible silylation yields could be obtained if a relatively dilute reaction mixture ($\leqslant 0.086$ mol dm^{-3} with respect to the episulfone) was employed, and the solution of LDA was added slowly over a period of 30 min using a syringe pump (Table 1, entries i and ii).[7b]

Under these conditions and with *ca.* 2 equiv. of trimethylsilyl

† For a recent study on the deprotonation of thiirane sulfoxides see M. D. Refvik, R. D. J. Froese, J. D. Goddard, H. H. Pham, M. F. Pippert and A. L. Schwan, *J. Am. Chem. Soc.*, 1995, **117**, 184.

Table 1 *In situ* silylation and stannylation of the episulfone **1**

	LDA (equiv.)	Electrophile (equiv.)	Yield product **2**	Yield product **3**
i	2.2	1.84 Me_3SiCl	**2a**, 54%	**3a**, < 6%
ii	2.2	4.7 Me_3SiCl	**2a**, trace	**3a**, 69%
iii	2.2	5 Me_3SiI [a]	**2a**, 0%	**3a**, 0%
iv	1.5	2 Et_3SiCl [b]	**2b**, 67%	**3b**, trace
v	2.2	5 Et_3SiCl	**2b**, 70%	**3b**, trace
vi	2.2	2 TBDMSTrif or TBDMSCl	0%	0%
vii	2.2	2 Me_3SnCl	**2c**, 35%	**3c**, 15%
viii	6.0	5 Me_3SnCl	**2c**, –	**3c**, 20%
ix	2.2	5.5 Bu_3SnCl	**2d**, 52%	**3d**, trace

[a] Me_3SiI appeared to catalyse the conversion of the episulfone **1** into the alkene **4**. [b] Use of Et_3SiOTf gave a lower yield (17%) of **2b**.

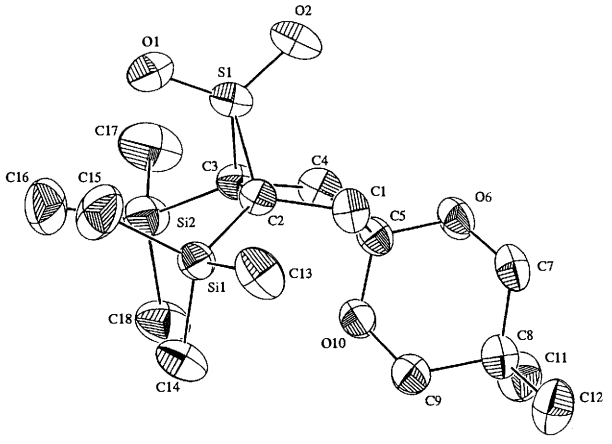


Fig. 1 ORTEP view of the silylated episulfone **3a** showing 50% thermal ellipsoids (with numbering scheme used in the tables of data)

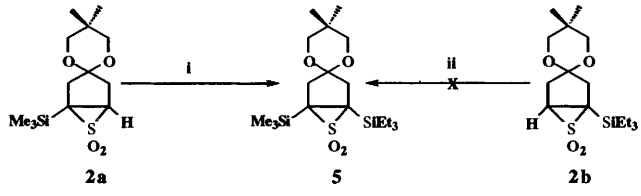
chloride and LDA the monosilylated episulfone **2a** was obtained in 54% yield with only trace amounts of the disilylated product **3a**. Even more remarkably, given the degree of steric compression involved, with a large excess of electrophile the 2,3-bis(trimethylsilyl)episulfone **3a** was formed in good yield (69%). The episulfones **2a** and **3a** were separated by column chromatography as crystalline, microanalytically pure compounds which could be stored at −20 °C for prolonged periods with only slight decomposition. The relative stability of these 2-silyl episulfones is surprising since the corresponding alkyl episulfones underwent rapid loss of SO_2 and could not be isolated.‡[5] The use of trimethylsilyl iodide as trapping agent was also investigated (entry iii) but silylated episulfones were not obtained from this reaction; the alkene **4** was the only product isolated.

The structure of compound **3a** has been confirmed by X-ray crystallographic analysis (Fig. 1 and Tables 2 and 3).§ Only three X-ray structures on episulfones have been reported before,[5,12] and this is the first on a tetrasubstituted compound. The earlier studies report[5,12] long carbon–carbon episulfone bond lengths (*e.g.* 1.65 Å[5]) but the value 1.686 Å for compound **3a** is particularly noteworthy. A slight staggering of the trimethylsilyl groups to avoid unfavourable eclipsing interactions is also noteworthy, resulting in significantly different Si–C–C episulfone bond angles (131.0° and 126.45°; Fig. 1 and Table 3).

Having established the optimum conditions for trimethylsilylation we were now interested in the scope and limitations of the trapping reaction (of course, the apparent need for *in situ* trapping greatly limits the range of suitable electrophiles). Other silyl halides were investigated first and the use of triethylsilyl chloride gave the mono-adduct **2b** as an oil in reasonable (67–70%) yield (Table 1, entries iv and v). Increasing the amount of silylating agent, however, did not produce the bis-silylated compound **3b** in significant quantities, although trace amounts were detected by mass spectrometry. This is presumably a steric effect, as the bis-trimethylsilyl derivative **3a** was obtained successfully. The steric congestion of these episulfone anions was further demonstrated when it was shown that *tert*-butyldimethylsilyl triflate failed to give even monosilylation (entry vi).

We next turned our attention to the use of tin electrophiles and a similar trend was observed. Thus, using trimethyltin chloride a mixture of the mono- and di-stannylated adducts **2c** and **3c** were observed, although it was not possible to obtain the distannylated adduct **3c** in yields > 20% (entries vii and viii). The use of the bulkier electrophile, tributyltin chloride, led only to the monostannylated adduct **2d** (with trace amounts of the distannylated adduct **3d** being identified by mass spectrometry), even when a large excess of tin halide was employed (entry ix). Both trimethylstannyl adducts were crystalline whereas the tributylstannyl compound was an oil: all were fully characterised by NMR spectroscopy and high resolution mass spectrometry.

The synthesis of unsymmetrical bis-silylated episulfones by the deprotonation–silylation of a mono-silylated episulfone was also investigated (Scheme 3). Initial studies utilized



Scheme 3 *Reagents and conditions:* i, 2 equiv. of LDA, THF, −78 °C, excess of Et_3SiCl (86%); ii, 2 equiv. of LDA, THF, −78 °C, excess of Me_3SiCl

2-triethylsilyl episulfone **2b** but all attempts to introduce a trimethylsilyl group proved unsuccessful and only starting material was recovered. Eventually, however, we found that it was possible to deprotonate trimethylsilyl episulfone **2a** and trap the anion using triethylsilyl chloride, to produce **5** as an oil in high yield. Attempts to produce mixed silyl/tin episulfones by this approach proved unsuccessful. These results indicate that the formation of tetrasubstituted episulfones by this deprotonation–trapping approach is extremely sensitive to steric effects: with electrophiles other than trimethylsilyl and trimethylstannyl chloride, the formation of the disubstituted adduct is not observed, even when an excess of base and trapping agent are employed.

With reasonable amounts of silyl and stannyl substituted episulfones in hand we were now interested in studying the chemistry of these compounds. As expected,[2,5] thermolysis of the episulfones, or treatment with potassium *tert*-butoxide in tetrahydrofuran (THF), led to the extrusion of sulfur dioxide to give the substituted alkenes (Scheme 4). The thermolysis was surprisingly slow, however (90 min in boiling THF were required for disilyl derivative **3a**), and the base-mediated method was normally preferred. In the case of the trimethylstannylated episulfone **2c** a substantial amount of decomposition was observed on treatment with potassium *tert*-butoxide and in this case the thermal extrusion method was preferred.

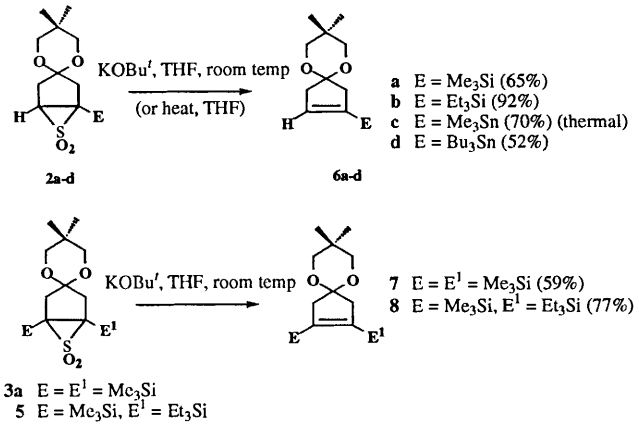
We next studied the desilylation of the silylated episulfones (Scheme 5) and discovered that the bistrimethylsilyl episulfone **3a** underwent smooth desilylation on treatment with tetrabutylammonium fluoride (TBAF) hydrate, to regenerate the

‡ It should be pointed out that under similar conditions, Simpkins *et al.*[8] prepared several silylated episulfones, including some that were tetrasubstituted.

§ Full details of structure **3a** have been deposited at the Cambridge Crystallographic Data Centre. See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1.

episulfone **1** in almost quantitative yield. This observation further demonstrates the robustness of these compounds. With CsF,[13] desilylation was more controlled and some of the monosilylated compound **2a** could be isolated along with the episulfone **1** (Scheme 5). Furthermore, the application of these conditions to the mixed disilyl episulfone **5** led to the selective removal of the trimethylsilyl group producing **2b** in 52% yield.

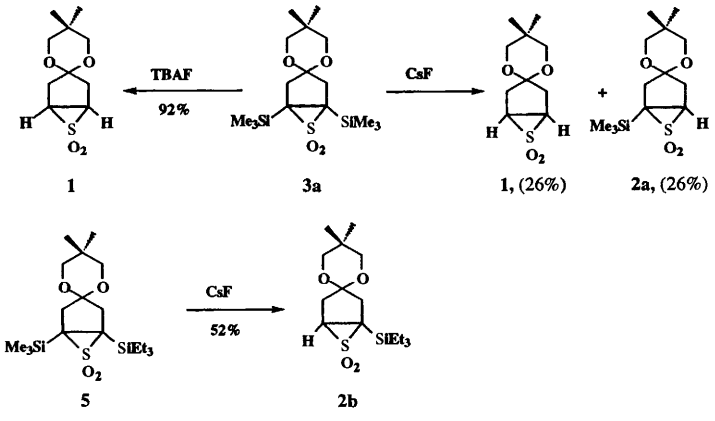
In the final phase of this investigation we studied procedures for the preparation of α-alkylated episulfones (Scheme 6). The use of carbon electrophiles in the episulfone trapping reaction was investigated first. Unsurprisingly, in view of the results of the silylation study, when alkyl halides, epoxides or aldehydes were employed in a sequential anion generation–trapping procedure the main product was the alkene **4** with recovered



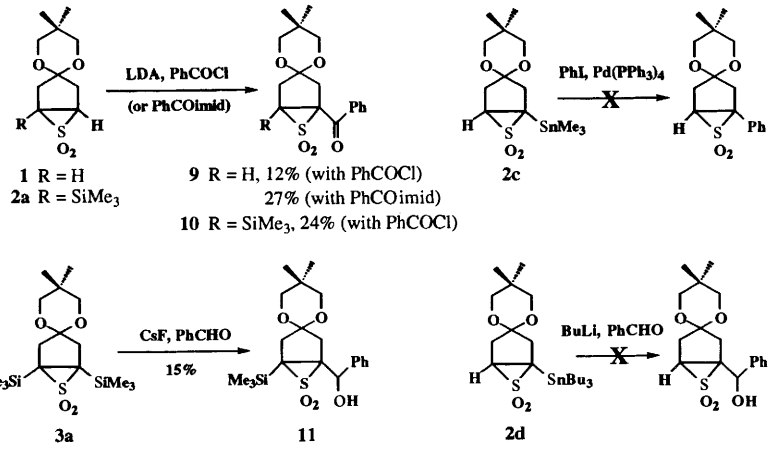
Scheme 4

starting material and only trace amounts of possible alkylated products.[7a] We were able, however, to trap the α-sulfonyl anions derived from **1** and **2a** with benzoyl chloride or benzoyl imidazole[14] using the *in situ* method to give the acylated adducts **9** and **10** in low yields. We also investigated the use of the stannylated episulfones **2c** and **2d** in carbon–carbon bond-forming processes (Scheme 6). Treatment of the trimethyltin episulfone **4c** with tetrakis(triphenylphosphine)palladium and iodobenzene[15] led to no observable product formation. Similarly, treatment of the tributyltin episulfone **4d** with butyllithium and benzaldehyde either sequentially or in an *in situ* fashion at low temperatures led to decomposition of the starting material. Treatment of bis-silyl episulfone **3a** with benzaldehyde and caesium fluoride[13] did produce the adduct **11**, albeit in low yield. Similar desilylation–aldehyde trapping reactions were reported by Simpkins *et al.*[8] but this group also made the exciting discovery that episulfones could be directly alkylated or hydroxyalkylated by treatment with benzyl bromide or benzaldehyde in the presence of an excess of Bu^t-P4-phosphazene base.[14]

In summary, we have shown that it is possible to generate α-sulfonyl anions from episulfones and to quench these anions efficiently with trialkylsilyl and trialkylstannyl chlorides using an *in situ* trapping procedure. This procedure can be used to produce tri- and tetra-subtituted episulfones and, by loss of sulfur dioxide, the corresponding vinylsilanes and vinylstannanes. Episulfone anion trapping was also achieved using selected carbon electrophiles although the yields were disappointing. These results indicate that the episulfone-based alkene synthesis outlined in Scheme 1 is viable. To realise the full potential of this methodology, however, improved methods of anion generation-trapping are required in order to extend the range of compatible electrophiles, preferably by removing the



Scheme 5



Scheme 6

requirement for *in situ* trapping. Research directed towards this end is in progress.

Experimental

^{1}H NMR (δ_H) and ^{13}C NMR (δ_C) spectra were recorded on a Jeol EX 270 spectrometer; the carbon spectra were recorded at 67.5 MHz and were assigned using DEPT experiments. Samples were prepared as solutions in $CDCl_3$ containing tetramethylsilane as internal standard or were referenced to an internal chloroform standard. *J* Values are given in Hz. IR spectra (ν_{max}) were recorded on an ATI Mattson Genesis Series FT IR spectrometer as solutions ($CHCl_3$ or $CDCl_3$). Mass spectra were recorded on a Fisons Instruments VG Analytical Autospec Spectrometer system. Commercially available reagents were used as supplied unless otherwise stated. Commercial solutions of butyllithium were stored at 0 °C; the reagent was dispensed by syringe under nitrogen and standardized by titration with diphenylacetic acid.[17] Reactions requiring rigorously anhydrous conditions were carried out in glassware which had been dried for several hours at 150–200 °C. Reactions were carried out under an atmosphere of nitrogen and reagents and solvent were introduced by syringe or using cannula techniques, through a septum cap. Light petroleum refers to the fraction of boiling range 40–60 °C, which was redistilled before use. THF was dried over sodium benzophenone ketyl and distilled before use. Potassium *tert*-butoxide was recrystallized from dry THF before use.[18] A standard work-up refers to 2/3 extractions with the specified solvent, washing of the combined extracts with brine, drying ($MgSO_4$) and removal of the solvent on a rotary evaporator. Analytical TLC was performed on Merck 5554 aluminium-backed silica-gel plates. Compounds were visualized by spraying with ethanolic vanillin solution followed by charring where appropriate. Column chromatography was carried out under gravity, using silica gel (ICN Biomedicals GmbH silica 32–63, 60A). Melting points were recorded on an Electrothermal IA9100 digital melting-point apparatus and are uncorrected. Microanalyses were performed at The University of East Anglia.

Structural studies

The structure of **3a** was confirmed by X-ray crystallographic analysis. Experimental and refinement details are given in Table 2. A colourless rod-shaped crystal *ca.* 0.50 × 0.40 × 0.30 mm^3 which had been grown at −20 °C was mounted on a glass fibre and used for crystallographic measurements. To prevent crystal decomposition intensity data were collected at −50 °C. A Rigaku AFC6S four-circle diffractometer with graphite-monochromated Mo-Kα X-radiation, λ = 0.7107 Å, was used. Accurate unit cell dimensions were obtained by a least-squares refinement of the values of 25 centred reflections in the range 25° < 2θ < 30°. Intensities of 4081 reflections were measured in the range 5° < 2θ < 50° in a ω-2θ scan mode; of these reflections 3694 were unique (R_{int} = 0.023). No corrections for decay or absorption were applied since the measurement of three standard reflections every 150 reflections showed no sign of decay, and azimuthal scans of several reflections indicated no need for absorption corrections.

The structure was solved by direct methods using SHELXS-86.[19] Refinement was carried out using intensities, F^2, in SHELXL93.[20] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a rigid model [C(sp^2)–H = 0.93 Å, C(sp^3)–H = 0.96 Å] with U_{iso} {H[C-(sp^2)–H]} = 1.2U_{eq}[C(sp^2)] and U_{iso} {[C(sp^3)–H]} = 1.5 U_{eq}[C(sp^3)]. Full-matrix least squares refinement of 217 parameters for 3694 independent reflections [$I \geqslant \sigma(I)$] gave R_F = 0.0560 and wR_I = 0.1123 (R_F = 0.0388 and wR_I = 0.1012 on $I \geqslant 2\sigma(I)$ data). Selected bond lengths are given in Table 3 and an ORTEP diagram in Fig. 1.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.¶

Table 2 Crystallographic data

Compound	**3a**
Formula	$C_{16}H_{30}O_4SSi_2$
Formula wt.	374.64
Temperature	223 K
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	7.886(2)
b/Å	27.000(8)
c/Å	9.9996(12)
α/°	90
β/°	90.82(2)
γ/°	90
Z	4
F(000)	808
Density (calculated)	1.183 g cm^{-3}
Crystal dimensions (mm)	0.50 × 0.40 × 0.30
Radiation	Mo-Kα (0.7107 Å)
μ/mm^{-1}	0.282
Scan type	$\omega/2\theta$
Scan speed (deg min^{-1})	0.66 to 2.00
2θ Range (°)	5.10 to 50.00
Indices collected	$+h$, $+k$, $\pm l$
Reflections collected	4081
Independent reflections	3694 [R_{int} = 0.023]
Refinement method	Full-matrix least-squares on F^2
Number of parameters	217
Goodness-of-fit on F^2	1.050
Final R factors [$I > 2\sigma I$]	R_F = 0.0388, wR_{F^2} = 0.1012
R Factors (all data)	R_F = 0.0560, wR_{F^2} = 0.1123
Min./max. residual electron density (e Å^{-3})	0.280 and −0.210

$R_F = \Sigma||F_o| - |F_c||/\sigma|F_o|$; $wR_{F^2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$; Goodness of fit, $s = \{[\Sigma[w(F_o^2 - F_c^2)^2]/(\text{number of data} - \text{number of parameters})]\}^{\frac{1}{2}}$; weight, $w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.82P]$; where $P = [\text{Maximum}(F_o^2, 0) + 2F_c^2]/3$.

Table 3 Bond lengths (Å) and two selected angles (°) for **3a**

S(1)–O(1)	1.441(2)
S(1)–O(2)	1.446(2)
S(1)–C(3)	1.738(2)
S(1)–C(2)	1.741(2)
Si(1)–C(15)	1.845(3)
Si(1)–C(14)	1.850(3)
Si(1)–C(13)	1.868(3)
Si(1)–C(2)	1.910(2)
Si(2)–C(16)	1.860(3)
Si(2)–C(18)	1.864(3)
Si(2)–C(17)	1.866(3)
Si(2)–C(3)	1.902(2)
O(10)–C(5)	1.423(3)
O(10)–C(9)	1.436(3)
O(6)–C(5)	1.408(3)
O(6)–C(7)	1.433(3)
C(8)–C(7)	1.514(3)
C(8)–C(9)	1.526(3)
C(8)–C(11)	1.527(3)
C(8)–C(12)	1.527(4)
C(5)–C(4)	1.518(3)
C(5)–C(1)	1.540(3)
C(4)–C(3)	1.538(3)
C(1)–C(2)	1.538(3)
C(3)–C(2)	1.686(3)
C(2)–C(3)–Si(2)	131.0(2)
C(3)–C(2)–Si(1)	126.45(14)

Representative trapping procedure

8,8-Dimethyl-2-trimethylsilyl-2,3-epithio-6,10-dioxaspiro-[4.5]decane *S*,*S*-dioxide 2a. The episulfone **1**[5] (200 mg, 0.86

¶ For details see Instructions for Authors (1996), *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1.

mmol) was dissolved in THF (10 cm^3) and trimethylsilyl chloride (0.2 cm^3, 1.58 mmol) was added to the solution; the mixture was then cooled to −78 °C. To this mixture was then added LDA (2.2 equiv.) in THF (10 cm^3) dropwise over a period of 30 min *via* a motor-driven syringe pump. Once addition was complete, the reaction was quenched at −78 °C by the addition of 10% aqueous NH_4OH–NH_4Cl to the mixture which was then allowed to warm to room temperature. A standard work-up procedure (CH_2Cl_2) gave the crude product as a yellow oil. Column chromatography (2→5% ethyl acetate–light petroleum) gave the *title compound* **2a** (141 mg, 54%) as a white solid, mp 60–66 °C (Found: C, 51.0; H, 8.1. $C_{13}H_{24}O_4SSi$ requires C, 51.3; H, 7.95%); R_F 0.11 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1366, 1325, 1150 and 1116; δ_H 0.20 (9 H, s, $SiMe_3$), 0.90 (3 H, s, 8-Me) and 0.95 (3 H, s, 8-Me), 2.30 (1 H, dd, *J* 14, 5, 4-CH), 2.35–2.45 (1 H, m, 1-CH), 2.57–2.70 (2 H, m, 1-CH and 4-CH), 3.32 (1 H, dd, *J* 8, 5, 3-CH), 3.39 (2 H, s, 7-CH_2) and 3.45 (2 H, s, 9-CH_2); δ_C −1.96, 22.23, 29.94, 34.04, 35.51, 47.84, 49.45, 71.45, 73.57 and 114.59; *m/z* (EI) 240 [100%, $(M - SO_2)^+$]. A small amount of the disilylated analogue **3a** (*ca.* 6%, slightly impure) was also obtained from the column.

8,8-Dimethyl-2,3-bis(trimethylsilyl)-2,3-epithio-6,10-dioxaspiro[4.5]decane *S*,*S*-dioxide 3a. A mixture of the episulfone **1** (200 mg, 0.86 mmol) and trimethylsilyl chloride (0.5 cm^3, 4.05 mmol) in THF (10 cm^3) was treated with LDA (2.2 equiv.) in THF (10 cm^3) at −78 °C and then worked-up and purified as described in the representative trapping procedure to give the *title compound* **3a** (223 mg, 69%) as a white solid, mp 75–76 °C (Found: C, 51.2; H, 8.4; S, 8.7%. $C_{16}H_{32}O_4SSi_2$ requires C, 51.02; H, 8.56; S, 8.51%); R_F 0.35 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1364, 1327, 1153 and 1116; δ_H 0.27 (18 H, s, 2 × $SiMe_3$), 0.93 (6 H, s, 8-Me_2) 2.45–2.65 (4 H, m, 1-CH_2 and 4-CH_2), 3.88 (2 H, s, 7-CH_2) and 3.91 (2 H, s, 9-CH_2); δ_C 0.28, 22.30, 29.94, 38.44, 52.98, 71.23, 73.55 and 113.37; *m/z* (CI) 313 [100%, $(M - SO_2 + H)^+$]. A small amount of the monosilylated analogue **2a** was observed by TLC analysis of the reaction mixture.

8,8-Dimethyl-2-triethylsilyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S*,*S*-dioxide 2b. A mixture of the episulfone **1** (200 mg, 0.86 mmol) and triethylsilyl chloride (0.72 cm^3, 4.3 mmol) in THF (10 cm^3) was treated with LDA (2.2 equiv.) in THF (10 cm^3) at −78 °C and then worked-up and purified as described in the representative trapping procedure to give the *title compound* **2b** (208 mg, 70%) as a clear oil {Found (CI): $[M - SO_2]^+$, 282.2024. $C_{16}H_{30}O_2Si$ requires 282.2015 (3.4 ppm error)}; R_F 0.21 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1363, 1322, 1158 and 1115; δ_H 0.60–0.97 (6 H, m, Si–CH_2), 1.0–1.09 (15 H, m, 5 × CH_3), 2.43–2.50 (1 H, m, 1-CH and 1 H, dd, *J* 13.5, 5, 4-CH), 2.69–2.79 (2 H, m, 1-CH and 4-CH), 3.47 (1 H, dd, *J* 8.25, 5, 3-CH) and 3.45–3.58 (4 H, m, 7-CH_2 and 9-CH_2); δ_C 2.50, 7.04, 22.12, 22.23, 29.84, 33.42, 36.83, 47.94, 48.07, 71.26, 73.47 and 114.53; *m/z* (CI) 283 [100%, $(M - SO_2 + H)^+$]. A trace amount of the disilylated analogue **3b** was detected in the mass spectrum of the reaction product.

8,8-Dimethyl-2-trimethylstannyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S*,*S*-dioxide 2c. A mixture of the episulfone **1** (400 mg, 1.72 mmol) and trimethyltin chloride (1 mol dm^{-3} in THF; 3.4 cm^3, 3.4 mmol) in THF (20 cm^3) was treated with LDA (2.2 equiv.) in THF (20 cm^3) at −78 °C as described in the representative trapping procedure. Once addition was complete, the reaction was quenched at −78 °C by addition of 10% aqueous NaF (20 cm^3) to the mixture which was then allowed to warm to room temperature. A standard work-up procedure (CH_2Cl_2) followed by successive washes with aqueous NaF and brine, and filtration through a short plug of Celite gave the crude product as a clear oil. Column chromatography (2→5% ethyl acetate–light petroleum) gave the *title compound* **2c** (233 mg, 35%) as a white solid, mp 87–90 °C {Found (CI): $[M - SO_2 + H]^+$, 333.0881. $C_{13}H_{25}O_2Sn$ requires 333.0876 (1.4 ppm error)}; R_F 0.12 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1364, 1322, 1158 and 1112; δ_H 0.97 (9 H, s, Sn–Me_3), 1.03 (6 H, s, 2 × CH_3), 2.28 (1 H, dd, *J* 14, 5.5, 4-CH), 2.30–2.50 (1 H, m, 1-CH), 2.63–2.76 (2 H, m, 1-CH and 4-CH), 3.23 (1 H, dd, *J* 7.5, 5.5, 3-CH), 3.44 (2 H, s, 7-CH_2) and 3.46 (2 H, s, 9-CH_2); δ_C −8.60, 22.14, 22.21, 29.92, 33.01, 36.83, 46.48, 49.25, 71.30, 73.55 and 114.35; *m/z* (CI) 333 [100%, $(M - SO_2 + H)^+$], as well as a smaller amount of the distannylated compound **3c** (145 mg, 15%) consistent with the data given below.

8,8-Dimethyl-2,3-bis(trimethylstannyl)-2,3-epithio-6,10-dioxaspiro[4.5]decane *S*,*S*-dioxide 3c. A mixture of the episulfone **1** (200 mg, 0.86 mmol) and trimethyltin chloride (1 mol dm^{-3} in THF; 4.3 cm^3, 4.3 mmol) in THF (10 cm^3) was treated with LDA (2.2 equiv.) in THF (10 cm^3) at −78 °C as described in the representative trapping procedure. TLC analysis at this time showed substantial amounts of starting material and mono-stannylated compound to be present. Thus, further equivalents of LDA (*ca.* 6 equiv. in total) were added until no starting material or mono-stannylated compound were present. The reaction was quenched and worked-up as described for the mono-stannylated case above to give the *title compound* **3c** (97 mg, 20%) as a white solid, mp 98–104 °C {Found (CI): $[M - SO_2 + H]^+$, 489.0523. $C_{16}H_{33}O_2Sn_2$ requires 489.0524 (1.6 ppm error)}; R_F 0.26 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1395, 1364, 1321, 1167 and 1112; δ_H 0.34 (18 H, s, $SnMe_3$), 0.95 (6 H, s, 2 × CH_3), 2.41–2.66 (4 H, m, 1-CH_2 and 4-CH_2), 3.41 (2 H, s, 7-CH_2) and 3.43 (2 H, s, 9-CH_2); δ_C −6.90, 22.30, 29.95, 38.24, 51.87, 71.16, 73.58 and 114.25; *m/z* (CI) 559 [65%, $(M + H)^+$].

8,8-Dimethyl-2-tributylstannyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S*,*S*-dioxide 2d. A mixture of the episulfone **1** (200 mg, 0.86 mmol) and tributyltin chloride (1.2 cm^3, 4.7 mmol) in THF (10 cm^3) was treated with LDA (2.2 equiv.) in THF (10 cm^3) at −95 °C as described in the representative trapping procedure. Once addition was complete, the reaction was quenched and worked-up as described for the mono-stannylated case **2c** to give the *title compound* **2d** (230 mg, 52%) as a clear oil {Found (CI): $[M - SO_2 + H]^+$, 459.2287. $C_{22}H_{43}O_2Sn$ requires 459.2285 (0.6 ppm error)}; R_F 0.14 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1395, 1376, 1321, 1157 and 1112; δ_H 0.78–1.60 (33 H, m, $SnBu_3$ and 2 × CH_3), 2.17 (1 H, dd, *J* 14, 5, 4-CH), 2.25–2.45 (1 H, m, 1-CH), 2.48–2.68 (2 H, m, 1-CH and 4-CH), 3.25 (1 H, dd, *J* 8, 5, 3-CH), 3.35 (2 H, s, 7-CH_2) and 3.44 (2 H, s, 9-CH_2); δ_C 10.51, 13.49, 13.53, 17.43, 22.06, 22.24, 29.90, 32.09, 38.22, 46.47, 49.57, 71.21, 73.51 and 114.44; *m/z* (CI) 459 [100%, $(M - SO_2 + H)^+$]. A trace amount of the distannylated analogue **3d** was detected in the mass spectrum of the reaction product.

8,8-Dimethyl-3-triethylsilyl-2-trimethylsilyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S*,*S*-dioxide 5. A mixture of trimethylsilyl episulfone **2a** (100 mg, 0.33 mmol) and triethylsilyl chloride (0.2 cm^3, 1.2 mmol) in THF (10 cm^3) was treated with LDA (2.0 equiv.) in THF (10 cm^3) at −78 °C and then worked-up and purified as described in the representative trapping procedure to give the *title compound* **5** (115 mg, 86%) as a clear oil {Found (CI): $[M + H]^+$, 419.2105. $C_{19}H_{39}O_4SSi_2$ requires 419.2107 (0.4 ppm error)}; R_F 0.41 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1365, 1315, 1150 and 1121; δ_H 0.28 (9 H, s, $SiMe_3$), 0.88–1.04 (21 H, m, 3 × Si–CH_2CH_3 and 2 × CH_3), 2.53–2.59 (4 H, m, 1-CH_2 and 4-CH_2), 3.41 and 3.43 (2 × 2 H, 2 × s, 7-CH_2 and 9-CH_2); δ_C 3.28, 6.12, 6.50, 22.26, 29.86, 37.98, 39.10, 50.85, 51.08, 71.12, 73.42 and 113.44; *m/z* (CI) 419 [10%, $(M + H)^+$].

Representative desulfonylation procedure

8,8-Dimethyl-2-trimethylsilyl-6,10-dioxa[4.5]dec-2-ene 6a. The episulfone **2a** (100 mg, 0.33 mmol) was dissolved in THF (10 cm^3) and potassium *tert*-butoxide (315 mg, 2.81 mmol) and the reaction mixture stirred at room temperature for 5 min after

which time TLC analysis showed that all of the starting material had been consumed. The reaction was quenched by addition of saturated aqueous ammonium chloride to the mixture which was then subjected to a standard work-up procedure (CH_2Cl_2) to give the product as a yellow oil. Column chromatography of this (light petroleum→2% ethyl acetate–light petroleum) gave the *title compound* **6a** (50 mg, 65%) as a clear oil {Found (CI): $[M + H]^+$, 241.1622. $C_{13}H_{25}O_2Si$ requires 241.1624 (0.6 ppm error)}; R_F 0.75 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1363 and 1113; δ_H 0.07 (9 H, s, $SiMe_3$), 0.95 and 1.03 (6 H, s, 2 × CH_3), 2.70–2.74 (4 H, m, 1-CH_2 and 4-CH_2), 3.52 (4 H, s, 7-CH_2 and 9-CH_2) and 5.87–5.89 (1 H, m, 3-CH); δ_C −2.01, 22.36, 22.41, 30.01, 43.88, 45.82, 72.06, 110.42, 136.48 and 142.28; *m/z* (CI) 241 [100%, $(M + H)^+$].

8,8-Dimethyl-2-triethylsilyl-6,10-dioxa[4.5]dec-2-ene 6b. The episulfone **2b** (200 mg, 0.58 mmol) in THF (10 cm^3) was treated with potassium *tert*-butoxide (150 mg, 1.34 mmol) at room temperature as described in the representative desulfonylation procedure (5 min) to give the *title compound* **6b** (150 mg, 92%) as a clear oil {Found (CI): $[M + H]^+$, 283.2096. $C_{16}H_{31}O_2Si$ requires 283.2093 (1.0 ppm error)}; R_F 0.78 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1363 and 1113; δ_H 0.49–0.64 (6 H, m, 3 × Si–CH_2), 0.91 (3 H, s, Me), 0.94 (3 H, s, Me), 0.96 (3 H, s, Me), 0.97 (3 H, s, Me), 1.03 (3 H, s, Me), 2.64–2.68 (4 H, m, 1-CH_2 and 4-CH_2), 3.46 (4 H, s, 7-CH_2 and 9-CH_2) and 5.84–5.86 (1 H, m, 3-CH); δ_C 3.36, 7.87, 22.82, 22.87, 30.46, 44.17, 47.11, 72.50, 110.76, 138.27 and 139.85; *m/z* (CI) 283 [100%, $(M + H)^+$].

8,8-Dimethyl-2-trimethylstannyl-6,10-dioxa[4.5]dec-2-ene 6c. The episulfone **2c** (90 mg, 0.23 mmol) in THF (10 cm^3) was refluxed for 1 h at which time TLC analysis showed that all of the starting material had been consumed. The solvent was removed to give the product as a yellow oil. Column chromatography of this (light petroleum→2% ethyl acetate–light petroleum) gave the *title compound* **6c** (51 mg, 70%) as a clear oil {Found (CI): $[M + H]^+$, 333.0880. $C_{13}H_{25}O_2Sn$ requires 333.087 65 (1.2 ppm error)}; R_F 0.79 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1395, 1364 and 1109; δ_H 0.14 (9 H, s, $SnMe_3$), 1.16 (3 H, s, CH_3), 1.22 (3 H, s, CH_3), 2.74–2.76 (4 H, m, 1-CH_2 and 4-CH_2), 3.53 (4 H, s, 7-CH_2 and 9-CH_2), 5.80–5.82 (1 H, m, 3-H); δ_C −10.01, 22.39, 29.66, 43.46, 48.51, 71.86, 110.3, 137.56 and 141.92; *m/z* (CI) 333 [100%, $(M + H)^+$].

8,8-Dimethyl-2-tributylstannyl-6,10-dioxa[4.5]dec-2-ene 6d. The episulfone **2d** (200 mg, 0.38 mmol) in THF (10 cm^3) was treated with potassium *tert*-butoxide (104 mg, 0.93 mmol) at room temperature as described in the representative desulfonylation procedure (30 min) to give the *title compound* **6d** (91 mg, 52%) as a clear oil {Found (CI): $[M + H]^+$, 459.2369. $C_{22}H_{43}O_2Sn$ requires 459.2374 (1.1 ppm error)}; R_F 0.78 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1395, 1364 and 1106; δ_H 0.92–1.77 (33 H, m, $SnBu_3$ and 2 × CH_3), 2.75–2.83 (4 H, m, 1-CH_2 and 4-CH_2), 3.61 (4 H, s, 7-CH_2 and 9-CH_2), 5.76–5.82 (1 H, m, 3-H); δ_C 9.13, 13.56, 13.65, 17.46, 22.35, 29.66, 43.55, 49.43, 71.84, 110.2, 127.67 and 137.48; *m/z* (CI) 459 [100%, $(M + H)^+$].

8,8-Dimethyl-2,3-bis(triethylsilyl)-6,10-dioxa[4.5]dec-2-ene 7. (a) The episulfone **3a** (100 mg, 0.265 mmol) in THF (10 cm^3) was treated with potassium *tert*-butoxide (315 mg, 2.81 mmol) at room temperature as described in the representative desulfonylation procedure (30 min) to give the *title compound* **7** (49 mg, 59%) as a clear oil {Found (EI): $[M]^+$, 312.1942. $C_{16}H_{32}O_2Si_2$ requires 312.1941 (0.4 ppm error)}; R_F 0.77 (ethyl acetate–light petroleum, 1:9); ν_{max} 1396, 1363 and 1113 cm^{-1}; δ_H 0.12 (18 H, s, 2 × $SiMe_3$), 0.96 (6 H, s, 2 × CH_3), 2.84 (4 H, s, 1-CH_2 and 4-CH_2), 3.48 (4 H, s, 7-CH_2 and 9-CH_2); δ_C 0.36, 22.37, 30.05, 51.02, 72.15, 119.20 and 151.00; *m/z* (CI) 313 [100%, $(M + H)^+$].

(b) The episulfone **3a** (41 mg, 0.11 mmol) in THF (10 cm^3) was boiled under reflux for 90 min. Removal of the solvent followed by column chromatography (light petroleum→2% ethyl acetate–light petroleum) gave the title compound **7** (15.4 mg, 45%) as a clear oil with properties as in (a).

8,8-Dimethyl-3-triethylsilyl-2-trimethylsilyl-6,10-dioxa[4.5]-dec-2-ene 8. The episulfone **5** (100 mg, 0.24 mmol) in THF (10 cm^3) was treated with potassium *tert*-butoxide (52 mg, 0.45 mmol) at room temperature as described in the representative desulfonylation procedure (10 min) to give the *title compound* **8** (65 mg, 77%) as a clear oil {Found (CI): $[M + H]^+$, 355.2491. $C_{19}H_{39}O_2Si_2$ requires 355.2489 (0.7 ppm error)}; R_F 0.81 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1396, 1363 and 1112; δ_H 0.16 (9 H, s, $SiMe_3$), 0.64–0.73 (6 H, m, 3 × $SiCH_2$), 0.86–0.99 (15 H, m, 5 × CH_3), 2.86 (4 H, s, 1-CH_2 and 4-CH_2), 3.50 (4 H, s, 7-CH_2 and 9-CH_2); δ_C 0.45, 4.17, 7.60, 22.37, 30.02, 50.88, 51.24, 72.12, 109.20, 148.94 and 151.76; *m/z* (CI) 355 [100%, $(M + H)^+$].

Treatment of 8,8-dimethyl-2,3-bis(trimethylsilyl)-2,3-epithio-6,10-dioxaspiro[4.5]decane *S,S*-dioxide 3a with TBAF. The disilyl episulfone **3a** (65 mg, 0.17 mmol) was dissolved in THF (3 cm^3) and TBAF hydrate (88 mg, 0.34 mmol) was added to the solution; the mixture was then stirred at room temperature under nitrogen. The appearance of the product was monitored by TLC and after 30 min the reaction mixture was diluted with water to quench the reaction and subjected to a standard work-up procedure (CH_2Cl_2) to give the product as a yellow oil. Column chromatography of this (2→5% ethyl acetate–light petroleum) gave 8,8-dimethyl-2,3-epithio-6,10-dioxaspiro-[4.5]decane *S,S*-dioxide **1** (36 mg, 92%) as a white solid the data for which were consistent with those of an authentic sample.[5]

Treatment of 8,8-dimethyl-2,3-bis(trimethylsilyl)-2,3-epithio-6,10-dioxaspiro[4.5]decane *S,S*-dioxide 3a with CsF

The disilyl episulfone **3a** (40 mg, 0.1 mmol) was added to flame-dried caesium fluoride (30 mg, 0.2 mmol) and dissolved in benzene (3 cm^3). To this solution was added a catalytic quantity of 18-crown-6 (5 mg, 0.019 mmol) and the reaction mixture was stirred under nitrogen. The appearance of the monosilyl compound **2a** was monitored by TLC and after 3 h the reaction was quenched by addition of water to the mixture which was then subjected to a standard work-up procedure (CH_2Cl_2) to give the product as a yellow oil. Column chromatography of this (2→5% ethyl acetate–light petroleum) gave the *S,S*-dioxide **2a** (8 mg, 26%) as a white solid the data for which were consistent with those given above. In addition, a small portion of the doubly desilylated compound **1** was also isolated (6 mg, 26%) the data for which were consistent with those given above.

Treatment of the *S,S*-dioxide 5 with CsF

The disilyl episulfone **5** (40 mg, 0.096 mmol) was added to flame-dried caesium fluoride (45 mg, 0.3 mmol) and dissolved in benzene (3 cm^3). To this solution was added a catalytic quantity of 18-crown-6 (5 mg, 0.019 mmol) and the reaction mixture was stirred under nitrogen. The appearance of the monosilyl compound was monitored by TLC. After 90 min the reaction was quenched by the addition of water to the mixture which was then subjected to a standard work-up procedure (CH_2Cl_2) to give the product as a yellow oil. Column chromatography of this (2→5% ethyl acetate–light petroleum) gave the *S,S*-dioxide **2b** (17 mg, 52%) as a clear oil, the data for which were consistent with those given above.

2-Benzoyl-8,8-dimethyl-2,3-epithio-6,10-dioxaspiro[4.5]-decane *S,S*-dioxide 9

(a) A mixture of the episulfone **1** (200 mg, 0.86 mmol) and benzoyl chloride (0.5 cm^3, 4.3 mmol) in THF (10 cm^3) was treated with LDA (2.2 equiv.) in THF (10 cm^3) at −78 °C and then worked-up and purified as described in the representative trapping procedure to give the *title compound* **9** (35 mg, 12%) as a white solid, mp 88–94 °C {Found (CI): $[M - SO_2 + H]^+$, 273.1490. $C_{17}H_{21}O_3$ requires 273.1491 (1.2 ppm error)}; R_F 0.54 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1669, 1396,

1363, 1322, 1165 and 1113; δ_H 0.84 (3 H, s, CH_3), 1.03 (3 H, s, CH_3), 2.88–2.90 (2 H, m, 1-CH and 4-CH), 3.02–3.03 (2 H, m, 1-CH and 4-CH), 3.40–3.58 (4 H, m, 7-CH_2 and 9-CH_2), 6.39–6.41 (1 H, m, 3-CH), 7.32–7.46 and 7.61–7.66 (5 H, m, ArH); δ_C 22.19, 22.48, 29.97, 39.69, 45.89, 71.86, 107.67, 128.23, 128.84, 131.91, 138.16, 141.00, 142.51 and 193.38; *m/z* (CI) 273 [100%, $(M - SO_2 + H)^+$].

(b) The above procedure was repeated using benzoylimidazole (1.72 mmol, generated[15] from benzoyl chloride and imidazole) in place of benzoyl chloride. The title compound **9** (77 mg, 27%) was isolated as a white solid the data for which were identical with those described above.

3-Benzoyl-8,8-dimethyl-2-trimethylsilyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S,S*-dioxide 10

A mixture of the trimethylsilyl episulfone **2a** (77 mg, 0.25 mmol) and benzoyl chloride (0.1 cm^3, 0.86 mmol) in THF (10 cm^3) was treated with LDA (2.2 equiv.) in THF (10 cm^3) at −78 °C and then worked-up and purified as described in the representative trapping procedure to give the *title compound* **10** (23 mg, 24%) as a clear oil {Found (CI): $[M - SO_2 + H]^+$, 345.1885. $C_{20}H_{29}O_3Si$ requires 345.1885}; R_F 0.36 (ethyl acetate–light petroleum, 1:9); ν_{max}/cm^{-1} 1669, 1396, 1363, 1322, 1165 and 1113; δ_H 0.00 (9 H, s, $SiMe_3$), 0.88 (3 H, s, CH_3), 1.08 (3 H, s, CH_3), 2.95 (2 H, m, 1-CH and 4-CH), 3.06 (2 H, m, 1-CH and 4-CH), 3.51 (4 H, s, 7-CH_2 and 9-CH_2), 7.39–7.59 and 7.83–7.87 (5 H, m, ArH); δ_C −1.50, 22.03, 22.26, 29.83, 45.59, 48.85, 71.92, 108.61, 128.38, 129.10, 132.91, 137.13, 146.72, 147.05 and 197.10; *m/z* (CI) 345 [100%, $(M - SO_2 + H)^+$].

3-[Hydroxy(phenyl)methyl]-8,8-dimethyl-2-trimethylsilyl-2,3-epithio-6,10-dioxaspiro[4.5]decane *S,S*-dioxide 11

The disilyl episulfone **3a** (100 mg, 0.27 mmol) was added to flame-dried caesium fluoride (100 mg, 0.66 mmol) and molecular sieves (1 g) and dissolved in benzene (3 cm^3). To this solution was added benzaldehyde (0.5 cm^3, 4.9 mmol) and a catalytic quantity of 18-crown-6 (20 mg, 0.075 mmol). The reaction mixture was cooled to −78 °C and stirred under nitrogen. The appearance of the product was monitored by TLC and after 5 h at −78 °C the reaction mixture was warmed to room temperature, quenched with water and subjected to a standard work-up procedure (CH_2Cl_2) to give the product as a yellow oil. Column chromatography of this (2→5% ethyl acetate–light petroleum) gave the *title compound* **11** (17 mg, 15%) as a white solid {Found (CI): $[M - SO_2 + H]^+$, 347.2041. $C_{20}H_{31}O_3Si$ requires 347.2042 (0.3 ppm error)}, R_F 0.48 (ethyl acetate–light petroleum, 2:8); ν_{max}/cm^{-1} 3425, 1396, 1364, 1323, 1138 and 1113; δ_H 0.22 (9 H, $SiMe_3$), 0.83 (3 H, s, CH_3), 1.04 (3 H, s, CH_3), 2.34–2.41 (1 H, br s, OH), 2.89–2.72 (4 H, m, 1-CH_2 and 4-CH_2), 3.38–3.68 (4 H, m, 7-CH_2 and 9-CH_2), 5.62 (1 H, s, 3-CH) and 7.23–7.39 (5 H, m, Ph); δ_C −0.12, 22.17, 22.46, 29.97, 40.30, 48.98, 71.78, 72.04, 108.41, 125.64, 128.33, 127.15, 137.35, 141.50 and 150.67; *m/z* (CI) 347 [100%, $(M + H)^+$].

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