Isolation of Episulfones from the Ramberg–Bäcklund Rearrangement. Part 2.† X-Ray Molecular Structure of 2,3-Epithio-8,8-dimethyl-6,10- dioxaspiro[4.5]-decane *S,S*-Dioxide and of *r*-6-Benzyl-*t*-7,*t*-8-epithio-1,4-dioxaspiro[4.4]nonane *S,S*-Dioxide

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For the first time, episulfones have been isolated by the treatment of α-halogeno sulfones with base under the conditions of the Ramberg–Bäcklund reaction. 3,3-Dialkoxy-6-thiabicyclo[3.1.0]hexane dioxides **3a–c** and **11a, b** have been fully characterised, X-ray crystal structures having been obtained for compounds **3c** and **11a**. Attempts to prepare episulfones with substituents at the bridgehead position were unsuccessful, however. The thermal stabilities of some of these episulfones have been studied, as have their reactions with base.

The Ramberg–Bäcklund rearrangement, the base-mediated conversion of an α-halogeno sulfone into a regio-defined alkene, has attracted considerable synthetic and mechanistic interest since its discovery in 1940.[1,2] Meyers' modification,[3] in which α-chlorination and *in situ* Ramberg–Bäcklund rearrangement are achieved by direct treatment of the sulfone with KOH–CCl_4–Bu^{t}OH, further extended the versatility of the process. Other recent innovations include the development of the Michael-induced Ramberg–Bäcklund rearrangement,[4] the use of sulfinyl leaving groups[5–7] and the introduction of α-trifluoromethylsulfonyl dimethyl sulfone[6] and α-halogenoalkanesulfonyl bromides[8] as novel Ramberg–Bäcklund precursors. The enduring utility of the Ramberg–Bäcklund rearrangement is demonstrated by recent applications to the synthesis of natural and novel cyclopentenes,[6,7,9,10] strained bicyclic alkenes,[5,11] enediynes related to esperamicin,[12] calicheamicin[12] and neocarzinostatin,[13] and (+)-eremantholide A.[14]

Detailed mechanistic studies have been carried out to establish the mechanism of the Ramberg–Bäcklund rearrangement as that shown in eqn. (1).[2,15,16] Although episulfones (thiirane 1,1-dioxides) have not previously been observed from this sequence, indirect support for their intermediacy has been obtained by taking authentic episulfones, prepared by other methods,[17] and showing that they give alkenes under the conditions normally employed for the Ramberg–Bäcklund reaction.[16] In addition, thiirene 1,1-dioxides have been obtained from α,α-dihalogeno sulfones by treatment with base.[18] We now report the first examples of episulfones obtained by the treatment of α-halogeno sulfones with base.[19] This discovery was made possible by the facile Ramberg–Bäcklund rearrangement of α-iodothiane dioxides we report recently.[10]

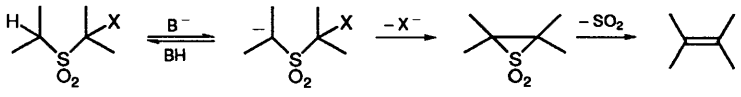
Scheme 1 illustrates studies carried out on unsubstituted thian-4-one ketals. Treatment of the readily available 2,3-dihydrothiin-4-one **1**[20] with trimethylsilyl iodide followed by *in situ* quenching[21] with ethylene glycol, butan-1-ol or 2,2-dimethylpropane-1,3-diol gave β-iodo acetals **2a–c** (X = I) in high yield. The bromo and chloro analogues of compound **2c** were also prepared, albeit in lower yield, by the use of trimethylsilyl bromide or chloride. The halogen atom adopts an equatorial position in all of the adducts **2** and so should be ideally positioned for 1,3-elimination.[2] This orientation was established by ^{1}H NMR spectroscopy in which the geminal methine protons exhibit clear axial–axial coupling (J 13.3–13.6 Hz for iodides, 12.8 Hz for the bromide and 12.3 Hz for the chloride), and so should be ideally positioned for 1,3-elimination.[2]

Table 1 Yields for the preparation of compounds **2–4** (%)

R,R	1 ⟶ 2	2 ⟶ 3	2 ⟶ 4	3 ⟶ 4
a CH_2CH_2	X = I, 88	87	*a*	*a*
b Bu	X = I, 84	82	93	91
c $CH_2C(Me)_2CH_2$	X = I, 85	85	91	93
	X = Br, 56	74		
	X = Cl, 14	85		

[a] Yield difficult to estimate due to volatility of product.

Attempts to study the Ramberg–Bäcklund rearrangement of iododioxolane **2a** were hampered by its poor solubility in tetrahydrofuran (THF) at low temperature. With an excess of potassium *tert*-butoxide in THF at −78 °C to room temperature the cyclopentene **4a**[22] was formed as expected. The yield of compound **4a** was difficult to estimate due to its volatility but it was readily identified by ^{1}H and ^{13}C NMR spectroscopy and by high-resolution mass spectroscopy. When a mixture of THF and dimethyl sulfoxide (DMSO) at 0 °C were used as solvent for this reaction, however, 7,8-epithio-1,4-dioxospiro[4.4]nonane *S,S*-dioxide **3a** was obtained in 87% yield as a cream-coloured solid, m.p. 148–150 °C (decomp.) which was fully characterised. Solubility problems and inadequate control over reaction temperature rendered this reaction somewhat capricious. Therefore ketals **2b, c** were investigated in an attempt to improve solubility in THF and thus make the transformation more reliable. This approach was successful as both compounds underwent smooth conversion into the corresponding episulfones **3b, c** in high, reproducible yield at −78 °C (Table 1). The dibutyl ketal **3b** is a viscous oil but the dioxane **3c** is a crystalline solid, with a sharp m.p. (94.0–



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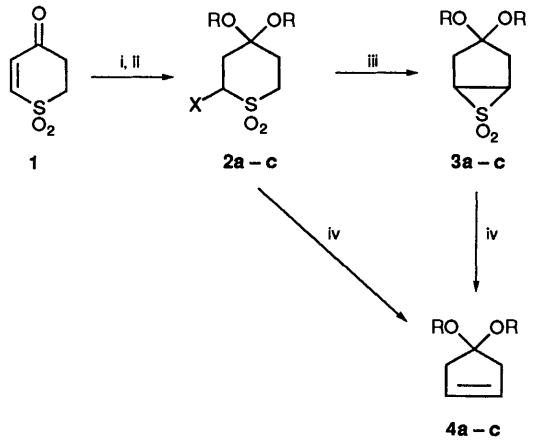


Scheme 1 *Reagents and conditions:* i, Me_3SiX, MeCN; ii, ROH; iii, $KOBu^t$, THF–DMSO, 0 °C *or* $KOBu^t$, THF, −78 °C; iv, $KOBu^t$

Table 2 Thermal decomposition of episulfones **3**[a]

Time (t/days)	3 Remaining (%)	
	3b	**3c**
0.7	87	95
1.7	78	90
2.8	70	85
3.75	63	81
6.7	46	71
9.7	*b*	64

[a] Determined by ^1H NMR spectroscopy in $CDCl_3$ at ~30 °C. [b] Not measured.

95.0 °C), and so was used for an X-ray crystal-structure determination (see later). It should be noted that this simple conversion of α-halogeno sulfone into episulfone is not dependent on the presence of an iodide leaving group: the α-bromo and α-chloro sulfones **2c** (X = Br, Cl) also gave compound **3c** in high yield on treatment with potassium *tert*-butoxide at low temperature. On treatment with base, episulfones **3b**, **c** underwent efficient conversion into the corresponding cyclopentenes **4b** and **4c**,[23] which were also prepared directly by conventional Ramberg–Bäcklund rearrangement of iodo sulfones **2b**, **c** using an excess of base.

All of the episulfones **3** could be kept at −20 °C for several months without the occurrence of significant decomposition. Even at room temperature, decomposition to cyclopentenes **4** was relatively slow, as can be seen from Table 2. The crystalline episulfone **3c** has a half-life of *ca.* 15 days in $CDCl_3$ solution at room temperature.

Alkyl-substituted thianes were also studied, as shown in Scheme 2. The requisite 2- and 3-substituted dihydrothiin-4-ones **8** and **14** were prepared by modifying methods previously developed in these laboratories.[10,24] Thus, conjugate reduction of the thiin-4-one **5**[10] to give allyl 3,4-dihydro-4-oxo-2*H*-thiine-3-carboxylate **6**, followed by alkylation and palladium-catalysed decarboxyallylation[24,25] of the adducts **7a**, **b** provided access to the 3-substituted sulfides **8a**, **b**. Conjugate addition to compound **6** readily afforded the β-keto esters **13a**, **b**,[10] which were decarboxyallylated to the sulfides **14a**, **b** using magnesium chloride in refluxing aq. dimethylformamide (DMF).[26] Tetrakis(triphenylphosphine)palladium(0) and morpholine can also be employed for the decarboxyallylation of compounds **13** but is less efficient (*e.g.*, **14a** was obtained in 91% using $MgCl_2$ and 58% using Pd^0).

Oxidation of sulfides **8** and **14** to the corresponding sulfones **9** and **15** was achieved in high yield with OXONE® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) in aq. methanol[27] and these compounds, in turn, were converted into β-iodo ketals **10** and **16** by the use of Me_3SiI–ethylene glycol, as before. The 3-substituted systems **10** were obtained as single diastereoisomers (>95%) which were assigned the *trans*-configuration by 400 MHz ^1H NMR spectroscopy. The 2-benzyl compound **16b** was predominantly the *cis*-isomer (*cis*:*trans* ~96:4) but, surprisingly, the 2-butyl sulfone **16a** was isolated as a 3:1 *cis*:*trans* diastereoisomeric mixture from which pure *cis*-isomer could be obtained by recrystallisation.* Analysis by 400 MHz ^1H NMR spectroscopy (*e.g.* Fig. 1 for **16a**) indicated that all of these iodo ketals appear to have iodine as the equatorial substituent. Given the reported[28] conformational free-energy differences of iodine (ΔG° ~0.4 kcal mol^{-1})† and ethyl (ΔG° ~1.8 kcal mol^{-1}) in cyclohexane derivatives, this observation indicates that there is an electronic/dipolar preference for equatorial halogen in these thiane dioxide systems which appears to override the usual equatorial preference of the alkyl substituents. It should be noted that the halogen substituents, when equatorial, are disposed within the internal bisector of the sulfonyl oxygen atoms. It is possible, however, that *trans*-**16a** exists in a twist-chair conformation; the consistent shielding of all ring carbon resonances in the ^{13}C NMR spectrum of *trans*-**16a** compared with the corresponding *cis*-isomer lends credence to this suggestion.[29]

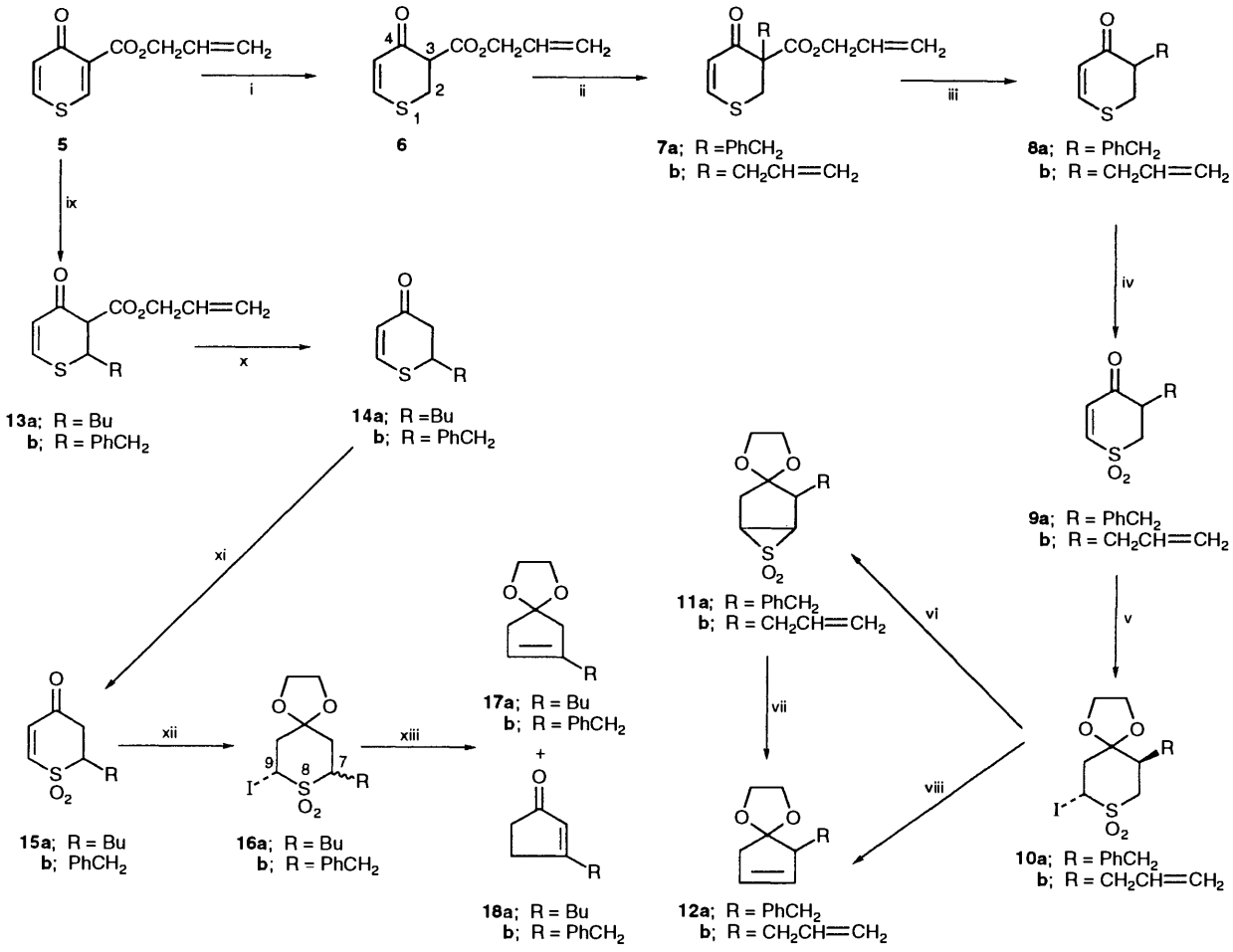
Treatment of compounds **10a**, **b** with potassium *tert*-butoxide in THF at −78 °C efficiently produced the corresponding episulfones **11a**, **b**, indicating that alkyl substitution β to the sulfonyl group does not preclude episulfone formation. In the case of compound **10b**, the reaction mixture was allowed to warm to room temperature and the episulfone **11b** was isolated in 65% yield together with the corresponding cyclopentene **12b**.[7] A similar result (**11a**, 69% + **12a**,[7] 28%) was observed when the reaction of sulfone **10a** was allowed to warm to room temperature,[19] but when the reaction was quenched at −78 °C the episulfone **11a** was produced almost exclusively (90%). *In order to optimise episulfone formation, quenching the reaction at −78 °C is obviously important.* Again, the use of higher reaction temperatures gave efficient Ramberg–Bäcklund rearrangement of iodo sulfones **10a**, **b** directly into the expected cycloalkenes **12a**, **b**. In addition, episulfone **11a** was efficiently converted into the cyclopentene **12a** on heating to its m.p. or by treatment with base. Episulfone **11a** can be stored as a solid at −18 °C without noticeable decomposition (<5%) over a 2 month period, whereas storage in solution at room temperature leads to significant decomposition to the cyclopentene **12a** (~66% conversion after 28 days according to ^1H NMR spectroscopy).

By contrast with the β-substituted substrates, the α-substituted compounds **16a**, **b** did not produce episulfones although their Ramberg–Bäcklund rearrangements to cyclopentenes occurred efficiently. The resulting cyclopentene ketals **17a**, **b** proved to be surprisingly labile on silica gel chromatography. In the rearrangement of the α-butyl compound **16a** the only product isolated after chromatography was the known[30] 3-butylcyclopent-2-enone **18a** (86%).* In the case of the α-benzyl analogue **16b**, the expected cyclopentene ketal **17b** (62%) was accompanied by 3-benzylcyclopent-2-enone **18b**[31] as a minor (29%) by-product.

Failure to isolate episulfones from the α-iodo sulfones **16a**, **b** (and from closely related α,β-disubstituted thiane dioxides)[10]

* The use of Me_3SiBr in this reaction also produced a diastereoisomeric mixture (*cis*:*trans* 6:5) of adducts **16a** (I = Br) with bromine equatorial according to ^1H NMR spectroscopy. This mixture underwent smooth Ramberg–Bäcklund rearrangement-hydrolysis to give compound **18a** in quantitative yield.

† 1 cal = 4.184 J.



Scheme 2 *Reagents and conditions:* i, $NaBH_4$, THF (67%); ii, RBr, K_2CO_3, acetone (**7a**, 92%; **7b**, 85%); iii, $Pd(PPh_3)_4$–morpholine, THF (**8a**, 83%; **8b**, 74%); iv, OXONE, aq. MeOH (**9a**, 94%; **9b**, 50%); v, Me_3SiI, MeCN; then $HOCH_2CH_2OH$ (**10a**, 93%; **10b**, 96%); vi, $KOBu^t$, THF, −78 °C (**11a**, 90%; **11b**, 65% + **12b**, 20%); vii, $KOBu^t$, THF, room temp. (**12a**, 85%; **12b**, 87%); viii, On **11a** only: $KOBu^t$, THF, room temp. (93%) or 110 °C, 20 min (88%); ix, RMgBr + catalytic CuBr·SMe_2; x, $MgCl_2·6H_2O$, aq. DMF, reflux (**14a**, 75% from **5**; **14b**, 43% from **5**); xi, as iv (**15a**, 91%; **15b**, 87%); xii, as v [**16a**, 90% (*cis*:*trans* 3:1); **16b**, 84% (*cis*)]; xiii, $KOBu^t$, THF, −78 °C; then SiO_2 chromatography (**16a** ⟶ **18a**, 86%; **16b** ⟶ **17b**, 62% + **18b**, 29%)

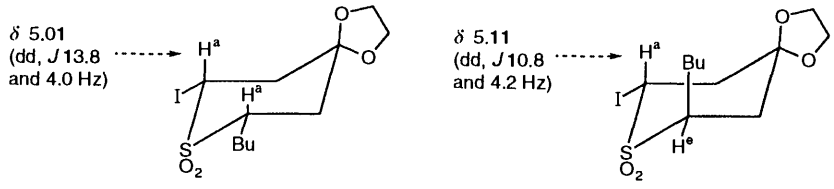


Fig. 1

suggests that the rate of loss of sulfur dioxide (either thermally or in a base-promoted process) from trisubstituted episulfones is fast compared with the disubstituted examples **3a–c** and **11a**, **b**, allowing isolation of the latter compounds from the basic reaction media.

It should be noted that α-iodo sulfone **16a**, as a 3:1 *cis*:*trans* mixture (see Fig. 1), afforded the expected Ramberg–Bäcklund reaction product in 86% yield, indicating that the disposition of the alkyl substituent has little bearing on the outcome of the reaction. However, the use of half a mole equivalent of base in this reaction led to isolation of compound **18a** (42%) together with the *cis*-disubstituted starting material **16a** (46%). This result indicates that *trans*-**16a**, which possesses the favoured W-plan arrangement,[2] reacts at a faster rate than the *cis*-diastereoisomer, which presumably undergoes equilibration prior to formation of episulfone.

*Structural Studies.**—The structures of compounds **3c** and **11a** have been confirmed by X-ray crystallographic analysis (see Fig. 2 and Tables 3 and 4).* Table 4 lists selected bond lengths. The X-ray crystal structures of compounds **3c** and **11a** were solved by Direct Methods using SHELXTL PLUS. Neutral-atom scattering factors (including anomalous scattering) were used.[32] All non-H atoms were refined with anisotropic thermal parameters. The hydrogen atoms were readily located from ΔF maps and their positions refined in successive cycles of least squares using fixed isotropic thermal parameters. Crystals of

* Full details of structures **3c** and **11a** have been deposited at the Cambridge Crystallographic Data Centre. See 'Instructions for Authors,' in the January issue.

Table 3 Crystallographic data

Compound	**3c**	**11a**
Formula	$C_{10}H_{16}O_4S$	$C_{14}H_{16}O_4S$
Formula wt.	232.3	280.3
Temp. (T/K)	293	293
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	5.635(6)	6.061(3)
b (Å)	5.913(6)	14.718(5)
c (Å)	18.180(15)	15.363(4)
α (deg)	89.48(7)	90
β (deg)	88.59(8)	95.32(3)
γ (deg)	68.22(8)	90
Z	2	4
$F(000)$	248	592
D_{calc} (g cm^{-3})	1.37	1.36
Crystal dimensions (mm)	0.18 × 0.20 × 0.30	0.20 × 0.22 × 0.24
Radiation	Mo-Kα (λ 0.7107 Å)	Mo-Kα
Monochromator	graphite	graphite
μ (mm^{-1})	0.267	0.233
Scan type	ω	ω
2θ range (deg)	2–47	2–50
Indices collected	$+h, \pm k, \pm l$	$+h, +k, \pm l$
Reflections collected	1685	2695
Independent	1487	2334
Observed	956 [$F > 6\sigma(F)$]	1729 [$F > 4\sigma(F)$]
Scan speed (deg min^{-1})	2–15.63	1.5–14.65
No. of L.S. parameters	131	220
Data/param.	7.3	7.86
R^a	14.05	9.66
$R_w{}^a$	12.45	8.74
g^a	0.004	0.0001
Min./max. e density (e Å^{-3})	−0.98/1.63	−0.63/0.56

^{a} $R = [\Sigma|(F_o - F_c)|]/\Sigma F_o$; $R_w = \{\Sigma[|(R_o - F_c)|]w^{\frac{1}{2}}\}/\Sigma F_o w^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F) + gF^2$.

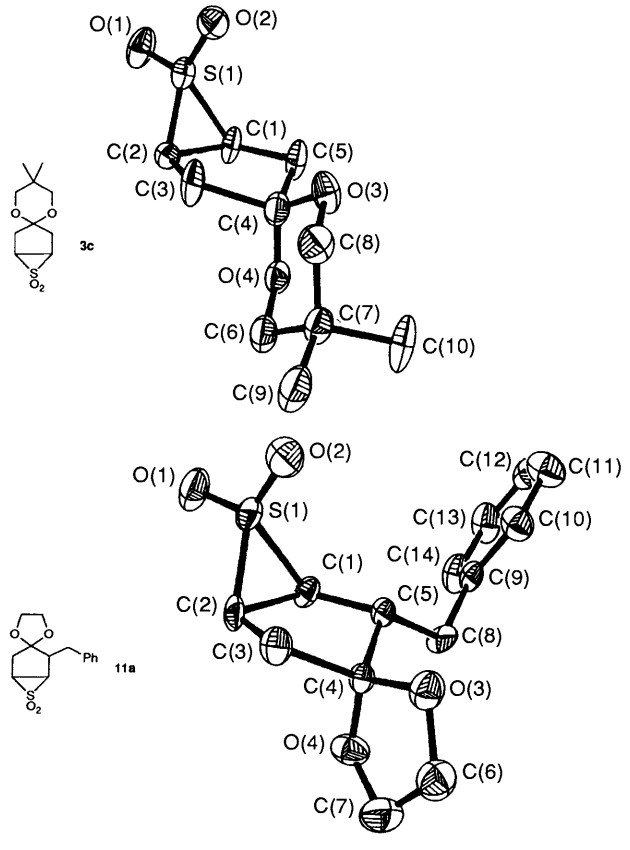


Fig. 2 ORTEP view of episulfones **3c** and **11a** with numbering system used in the tables of data

compound **3c** were particularly unstable to X-ray bombardment at ambient temperature and decomposed by ~15% over the period of data collection. The high R-values obtained for both compounds are further evidence of their instability.

The crystal structure of (*Z*)-2-but-2-ene episulfone has been reported[33] as has the microwave spectrum of ethylene episulfone.[34] These studies draw particular attention to the unusually long carbon–carbon bond length of episulfones at ~1.6 Å. Similar C–C bond lengths are observed for episulfones **3c** and **11a** [**3c**: 1.546(16) Å; **11a**: 1.655(10) Å] although, even allowing for the low accuracy of the structure determinations, the significantly shorter C–C bond length in compound **3c**, compared with the benzylated analogue **11a**, is noteworthy.

Concluding Remarks.—Episulfones have been isolated by the treatment of α-halogeno sulfones with base under the conditions of the Ramberg–Bäcklund reaction. Episulfones **3a–c** and **11a, b** have been fully characterised, X-ray crystal structures having been obtained for compounds **3c** and **11a**. Further work, including modification of ring size, ketal moiety, and substituent pattern, is in progress to evaluate the reasons for the stability of these novel episulfones and to obtain information concerning the mechanism of episulfone decomposition. The high stability and synthetic accessibility of the episulfones indicates that they might have synthetic potential in their own right. This area is also under current investigation.

Experimental

^{1}H NMR spectra (δ_H) were recorded using JEOL PMX 60, JEOL EX 90 and JEOL GSX 400 spectrometers and were assigned by use of either homonuclear decoupling or COSY-45 experiments at 400 MHz. ^{13}C NMR spectra (δ_C) were recorded using JEOL EX 90 and JEOL GSX 400 spectrometers (22.5 and 100 MHz respectively) and were assigned by use of either DEPT or heteronuclear correlation experiments at 100 MHz. Samples were prepared as solutions in $CDCl_3$ containing tetramethylsilane as internal standard. *J*-Values are given in Hz.

Table 4 Selected bond lengths (Å)

(*a*) Compound **3c**			
S(1)–O(1)	1.464(9)	S(1)–O(2)	1.436(13)
S(1)–C(1)	1.713(15)	S(1)–C(2)	1.705(15)
O(3)–C(4)	1.444(18)	O(3)–C(8)	1.439(16)
O(4)–C(4)	1.386(20)	O(4)–C(6)	1.430(14)
C(1)–C(2)	1.546(16)	C(1)–C(5)	1.541(16)
C(2)–C(3)	1.551(18)	C(3)–C(4)	1.570(18)
C(4)–C(5)	1.520(16)	C(6)–C(7)	1.541(22)
C(7)–C(8)	1.481(25)	C(7)–C(9)	1.516(18)
C(7)–C(10)	1.559(19)		
(*b*) Compound **11a**			
S(1)–O(1)	1.437(7)	S(1)–O(2)	1.414(7)
S(1)–C(1)	1.747(7)	S(1)–C(2)	1.741(9)
O(3)–C(4)	1.402(9)	O(3)–C(6)	1.417(13)
O(4)–C(4)	1.394(10)	O(4)–C(7)	1.418(13)
C(1)–C(2)	1.655(10)	C(1)–C(5)	1.504(9)
C(2)–C(3)	1.475(12)	C(3)–C(4)	1.576(9)
C(4)–C(5)	1.544(11)	C(5)–C(8)	1.559(9)
C(6)–C(7)	1.405(16)	C(8)–C(9)	1.500(11)
C(9)–C(10)	1.357(12)	C(9)–C(14)	1.359(12)
C(10)–C(11)	1.400(14)	C(11)–C(12)	1.349(16)
C(12)–C(13)	1.350(16)	C(13)–C(14)	1.422(15)

IR spectra (ν_{max}) were recorded on a Perkin-Elmer FT IR 1720X spectrophotometer as $CHCl_3$ solutions or mulls (Nujol) for solid samples and as thin films for liquid samples. Mass spectra were recorded on Kratos MS 25 (low resolution) or Kratos VG Zab-E (high resolution) instruments. Light petroleum refers to the fraction of boiling range 40–60 °C, which was redistilled before use. DMSO was stored over 4 Å sieves, THF was dried over sodium/benzophenone ketyl and distilled immediately before use, acetonitrile was distilled from calcium hydride, and morpholine from sodium before use. 2,3-Dihydrothiin-4-one 1,1-dioxide **1**,[20] allyl 4-oxo-4*H*-thiine-3-carboxylate **5**,[10] and tetrakis(triphenylphosphine)palladium[35] were prepared using literature procedures; other starting materials were used as received. Analytical TLC was performed on Merck 5554 aluminium-backed silica gel plates. A standard work-up refers to 2/3 extractions with the specified solvent, washing of the combined extracts with water, drying ($MgSO_4$) and removal of the solvent on a rotary evaporator. Column chromatography was carried out under gravity, using silica gel (Sorbsil C 60-H). Preparative centrifugal chromatography was carried out on a Chromatotron Model 7924T using silica gel plates (Merck 7749). M.p.s were recorded on a Kofler hot-stage m.p. apparatus and are uncorrected. Temperatures given for Kugelrohr distillations refer to the oven temperatures.

(a) *Preparation of Novel Sulfides.—Allyl* 3,4-*dihydro*-4-*oxo*-2H-*thiine*-3-*carboxylate* **6**. A solution of sodium borohydride (0.226 g, 5.97 mmol) in dry THF (450 cm^3) was added dropwise over a period of 2 h to a solution of allyl 4-oxo-4*H*-thiine-3-carboxylate **5** (1.17 g, 5.96 mmol) in dry THF (25 cm^3) at 0 °C. When the addition was complete the solution was stirred for a further 15 min prior to quenching with aq. ammonium chloride (50 cm^3). The two-phase mixture was stirred for 30 min and then was diluted with diethyl ether (400 cm^3) and water (100 cm^3). A standard ethereal work-up, followed by preparative centrifugal chromatography [CH_2Cl_2–ethyl acetate (9:1)] gave the *title compound* **6** (0.79 g, 67%) as a bright yellow oily mixture of keto and enol tautomers (85:15) (Found: C, 54.7; H, 5.3. $C_9H_{10}O_3S$ requires C, 54.53; H, 5.08%); R_f 0.31 [CH_2Cl_2–ethyl acetate (9:1)]; ν_{max}(film)/cm^{-1} 3454 (OH, enol), 1743 (C=O, ester) and 1630 (C=O, keto); δ_H(400 MHz) keto form: 3.34 (1 H, ddd, $J_{2ax,2eq}$ −13.2, $J_{2eq,3ax}$ 3.7, $J_{2eq,6eq}$ 1.1, 2-H_{eq}), 3.61 (1 H, dd, $J_{2ax,2eq}$ −13.2, $J_{2ax,3ax}$ 10.6, 2-H_{ax}), 3.69 (1 H, dd, $J_{2ax,3ax}$ 10.6, $J_{2eq,3ax}$ 3.7, 3-H_{ax}), 4.65–4.74 (2 H, m, OCH_2), 5.25 (1 H, ddt, J_{cis} 10.3, J_{gem} 1.5, $^4J_{allylic}$ 1.5, CH=C*H*H), 5.35 (1 H, ddt, J_{trans} 17.2, J_{gem} 1.5, $^4J_{allylic}$ 1.5, CH=CH*H*), 5.92 (1 H, ddt, J_{cis} 10.3, J_{trans} 17.2, J_{vic} 5.9, C*H*=CH_2), 6.23 (1 H, d, $J_{5,6}$ 10.3, 5-H) and 7.48 (1 H, dd, $J_{2eq,6}$ 1.1, $J_{5,6}$ 10.3, 6-H); enol form: 3.71 (2 H, m, 2-H_2), 4.65–4.74 (2 H, m, OCH_2), 5.27 (1 H, ddt, J_{cis} 10.3, J_{gem} 1.5, $^4J_{allylic}$ 1.5, CH=C*H*H), 5.35 (1 H, ddt, J_{trans} 17.2, J_{gem} 1.5, $^4J_{allylic}$ 1.5, CH=CH*H*), 5.92 (1 H, ddt, J_{cis} 10,3 J_{trans} 17.2, J_{vic} 5.9, C*H*=CH_2), 5.97 (1 H, d, $J_{5,6}$ 10.3, 5-H), 6.92 (1 H, br d, $J_{5,6}$ 10.3, 6-H) and 12.13 (1 H, s, OH); δ_C(100 MHz) keto form: 29.04 (C-2), 51.83 (C-3), 65.87 (OCH_2), 118.43 (CH=CH_2), 123.08 (C-5), 131.31 (*C*H=CH_2), 146.10 (C-6), 167.82 (C=O, ester) and 188.36 (C-4); enol form: 23.48 (C-2), 65.00 (OCH_2), 85.86 (C-3), 118.17 (CH=CH_2), 119.44 (C-5), 131.79 (*C*H=CH_2), 137.72 (C-6), 166.41 (C=O, ester) and 171.44 (C-4); *m/z* 198 (21%, M^+), 157 (22, M − CH_2CH=CH_2), 113 (100, 157 − CO_2).

3-*Benzyl*-2,3-*dihydro*-4H-*thiin*-4-*one* **8a**. (i) A solution of the dihydrothiinone **6** (0.53 g, 2.61 mmol) in dry acetone (15 cm^3) was treated with benzyl bromide (0.38 cm^3, 0.55 g, 3.22 mmol), then anhydrous potassium carbonate (1.11 g, 8.03 mmol) was added under nitrogen to the stirred mixture. The mixture was stirred for 24 h at room temp., then was concentrated at reduced pressure. The residue was taken up in water (30 cm^3) and CH_2Cl_2 (30 cm^3) and subjected to a standard CH_2Cl_2 work-up incorporating a brine wash. The crude material was purified by preparative centrifugal chromatography with CH_2Cl_2 as eluent to give allyl 3-benzyl-3,4-dihydro-4-oxo-2*H*-thiine-3-carboxylate **7a** (0.71 g, 92%) as a yellow oil which was fully characterised.

(ii) A solution of ester **7a** (1.83 g, 6.35 mmol) in dry THF (60 cm^3) under nitrogen was treated with morpholine (5.53 g, 60.35 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.37 g, 0.32 mmol). The mixture was stirred at room temp. for 3 h, then at 40 °C for 30 min. After cooling, the reaction mixture was filtered through Celite, then the solvent was removed. The crude material was purified by preparative centrifugal chromatography [diethyl ether–light petroleum (2:3)] to give the *title compound* **8a** (1.08 g, 83%) as a pale yellow oil (Found: C, 70.5; H, 5.9. $C_{12}H_{12}OS$ requires C, 70.55; H, 5.92%); R_f 0.46 [diethyl ether–light petroleum (2:3)]; ν_{max}($CHCl_3$)/cm^{-1} 1665 (C=O); δ_H(400 MHz) 2.69–2.87 (3 H, m, 2-H_{ax}, 3-H_{ax} and C*H*HPh), 3.12 (1 H, ddd, $J_{2ax,2eq}$ −13.3, $J_{2eq,3eq}$ 2.8, $J_{2eq,6}$ 0.9, 2-H_{eq}), 3.22 (1 H, dd, J_{gem} −12.3, J_{vic} 2.5, CH*H*Ph), 6.16 (1 H, d, $J_{5,6}$ 10.1, 5-H), 7.20–7.25 (3 H, m, 2′-, 4′-, 6′-H), 7.28–7.32 (2 H, m, 3′-, 5′-H) and 7.39 (1 H, dt, $J_{2,6}$ 0.9, $J_{5,6}$ 10.1, 3-H); δ_C(100 MHz) 30.26 (C-2), 33.82 (*C*H_2Ph), 46.73 (C-3), 122.83 (C-5), 126.36 (C-4′), 128.39 (C-3′, -5′), 128.88 (C-2′, -6′), 138.15 (C-1′), 145.38 (C-6) and 194.96 (C-4); *m/z* 204 (91%, M^+).

3-*Allyl*-2,3-*dihydro*-4H-*thiin*-4-*one* **8b**. The procedure (i) above was carried out using potassium carbonate (3.317 g, 24.0 mmol), compound **6** (1.586 g, 8.0 mmol), allyl bromide (1.161 g, 9.6 mmol) and dry acetone (32 cm^3) at room temp. for 20 h. Work-up as before, followed by column chromatography [ethyl acetate–light petroleum (1:4)], gave allyl 3-allyl-3,4-dihydro-4-oxo-2*H*-thiine-3-carboxylate **7b** (1.624 g, 85%) as a yellow oil which was fully characterised.

The procedure (ii) above was followed using morpholine (0.653 g, 7.50 mmol), tetrakis(triphenylphosphine)palladium(0) (0.043 g, 0.75 mmol), ester **7b** (0.179 g, 0.75 mmol) and dry THF (7.5 cm^3) at room temp. for 40 h. The reaction mixture was then filtered through a short column [diethyl ether–light petroleum (2:3)], then was further purified by column chromatography [diethyl ether–light petroleum (2:3)] to give the *title compound* **8b** (0.086 g, 74%) as a yellow oil (Found: C, 62.7; H, 6.7. $C_8H_{10}OS$ requires C, 62.30; H, 6.54%); R_f 0.62 [ethyl acetate–toluene (3:17)]; ν_{max}($CDCl_3$)/cm^{-1} 1660 (C=O) and 1550 (C=C); δ_H(60 MHz) 2.08–3.50 (5 H, m, 1′- and 2-H_2 and 3-H), 4.90–5.32 (2 H, m, 3′-H_2), 5.46–5.95 (1 H, m, 2′-H), 6.12 (1 H, d, $J_{5,6}$ 10.8, 5-H) and 7.38 (1 H, d, $J_{5,6}$ 10.8, 6-H); δ_C(22.5 MHz)

31.0 and 32.6 (C-1′ and -2), 44.8 (C-3), 118.0 (C-3′), 123.3 (C-5), 135.0 (C-2′), 145.5 (C-6) and 195.3 (C-4); *m/z* 154 (8%, M^+).

2-*Butyl*-2,3-*dihydro*-4H-*thiin*-4-*one* **14a**. (i) A solution of copper(I) bromide–dimethyl sulfide complex (0.21 g, 1.02 mmol) in dry dimethyl sulfide (5 cm^3) was added dropwise to a stirred solution of butylmagnesium bromide [prepared from butyl bromide (4.90 cm^3, 6.25 g, 45.63 mmol) and magnesium turnings (1.14 g, 46.89 mmol)] in dry THF (100 cm^3) at −78 °C under nitrogen. The mixture was stirred for 2 h, then a solution of allyl 4-oxo-4*H*-thiine-3-carboxylate (5.44 g, 27.72 mmol) in dry THF (85 cm^3) was added dropwise over a period of 30 min. The mixture was stirred for 1.5 h, then saturated aq. ammonium chloride (150 cm^3) was added. The mixture was warmed to room temp., then was diluted with water (50 cm^3) and subjected to a standard ethereal work-up incorporating a brine wash. Column chromatography [light petroleum–diethyl ether (9:1)] gave allyl 2-butyl-3,4-dihydro-4-oxo-2*H*-thiine-3-carboxylate **13a** (5.82 g, 82%) as a yellow oily mixture of keto and enol tautomers (1:2), R_f 0.80 [CH_2Cl_2–ethyl acetate (4:1)], which gave consistent IR, ^1H NMR and MS data.

(ii) Allyl 2-butyl-3,4-dihydro-4-oxo-2*H*-thiine-3-carboxylate **13a** (2.46 g, 9.67 mmol) and magnesium chloride hexahydrate (3.67 g, 18.06 mmol) in DMF (100 cm^3)–water (10 cm^3) were heated at reflux for 20 h. The reaction mixture was diluted with water (250 cm^3) and subjected to a standard ethereal work-up incorporating a brine wash. Column chromatography [light petroleum–diethyl ether (2:1)] gave the *title compound* **14a** (1.51 g, 91%) as a yellow oil (Found: C, 63.8; H, 8.5; S, 18.5. $C_9H_{14}OS$ requires C, 63.49; H, 8.29; S, 18.83%); R_f 0.22 [light petroleum–ethyl acetate (19:1)]; ν_{max}(film)/cm^{-1} 1663 (C=O); δ_H(400 MHz) 0.86 (3 H, t, $J_{3',4'}$ 7.3, 4′-H_3), 1.24–1.40 (4 H, m, 2′-, 3′-H_2), 1.59–1.71 (2 H, m, 1′-H_2), 2.53 (1 H, dd, $J_{2ax,3ax}$ 11.9, $J_{3ax,3eq}$ −16.3, 3-H_{ax}), 2.72 (1 H, dd, $J_{2ax,3eq}$ 3.3, $J_{3ax,3eq}$ −16.3, 3-H_{eq}), 3.41–3.48 (1 H, m, 2-H), 6.10 (1 H, d, $J_{5,6}$ 10.1, 5-H) and 7.39 (1 H, d, $J_{5,6}$ 10.1 6-H); δ_C(100 MHz) 13.83 (C-4′), 22.29 (C-3′), 28.67 (C-2′), 33.64 (C-1′), 43.05 (C-2), 44.84 (C-3), 123.29 (C-5), 145.80 (C-6) and 194.61 (C-4); *m/z* 170 (30%, M^+) and 113 (19, $M^+ - C_4H_9$).

2-*Benzyl*-2,3-*dihydro*-4H-*thiin*-4-*one* **14b**. (i) The procedure above was followed using copper(I) bromide–dimethyl sulfide complex (0.12 g, 0.58 mmol), dry dimethyl sulfide (3 cm^3) and benzylmagnesium chloride (12 cm^3 of a 2.0 mol dm^{-3} solution in THF, 24.00 mmol) in dry THF (60 cm^3), a solution of the ester **5** (4.05 g, 20.64 mmol) in dry THF (70 cm^3) being added dropwise during 60 min. The mixture was stirred for 25 min, saturated aq. ammonium chloride (90 cm^3) was added, and the reaction mixture was processed as above. The crude material was partially purified by column chromatography with CH_2Cl_2 as eluent to give allyl 2-benzyl-3,4-dihydro-4-oxo-2*H*-thiine-3-carboxylate **13b** (2.58 g) as an orange oily mixture of keto and enol tautomers (1:1), R_f 0.56 [light petroleum–ethyl acetate (3:2)], which gave consistent IR, ^1H NMR and MS data.

(ii) Conjugate adduct **13b** (1.60 g), magnesium chloride (1.35 g, 14.18 mmol) and pH 7.2 aq. phosphate buffer (ex-Aldrich; 5 cm^3) in DMF (60 cm^3) were heated at reflux for 16 h under nitrogen. The reaction mixture was diluted with water (150 cm^3) and subjected to a standard ethereal work-up incorporating a brine wash. Preparative centrifugal chromatography [light petroleum–ethyl acetate (3:2)] gave the *title compound* **14b** (0.89 g, 43% over two steps from **5**) as a yellow oil (Found: C, 70.4; H, 5.8. $C_{12}H_{12}OS$ requires C, 70.55; H, 5.92%); R_f 0.47 [light petroleum–ethyl acetate (3:2)]; ν_{max}(film)/cm^{-1} 1658 (C=O) and 1546; δ_H(400 MHz) 2.60 (1 H, dd, $J_{3ax,3eq}$ −16.2, $J_{2ax,3ax}$ 11.3, 3-H_{ax}), 2.78 (1 H, dd, $J_{3ax,3eq}$ −16.2, $J_{2ax,3eq}$ 3.4, 3-H_{eq}), 2.99 (2 H, d, J_{vic} 7.6, CH_2Ph), 3.65–3.75 (1 H, ddt, $J_{2ax,3ax}$ 11.3, $J_{2ax,3eq}$ 3.4, J_{vic} 7.6, 2-H), 6.18 (1 H, d, $J_{5,6}$ 10.1, 5-H) and 7.16–7.41 (6 H, m, 6-H + Ph); δ_C(100 MHz) 39.95 (*C*H_2Ph), 43.53 (C-3), 44.04 (C-2), 123.44 (C-5), 127.06 (C-4′), 128.59 (C-3′, -5′), 129.13 (C-2′, -6′), 136.73 (C-1′), 145.46 (C-6) and 194.12 (C-4); *m/z* 204 (48%, M^+).

(b) *General Procedure for Preparation of Sulfones from Sulfides*.—A solution of OXONE® in water was added to a stirred solution of the sulfide in methanol at 0 °C. The mixture was stirred for 6 h–2 days at room temp., and the reaction mixture was diluted with water and was then subjected to a standard CH_2Cl_2 work-up.

3-*Benzyl*-2,3-*dihydro*-4H-*thiin*-4-*one* 1,1-*dioxide* **9a**. A solution of the sulfide **8a** (1.08 g, 5.29 mmol) was treated with methanol (30 cm^3), OXONE® (3.28 g, 5.34 mmol) and water (30 cm^3) for 6 h as described above to give the *title compound* **9a** (1.18 g, 94%) as a solid, m.p. 142–144 °C (Found: C, 60.8; H, 5.1. $C_{12}H_{12}O_3S$ requires C, 61.00; H, 5.12%); R_f 0.25 (CH_2Cl_2); ν_{max}($CHCl_3$)/cm^{-1} 1700 (C=O), 1334 (SO_2, asym) and 1136 (SO_2, sym); δ_H(400 MHz) 2.79 (1 H, dd, J_{gem} −14.3, J_{vic} 9.2, C*H*HPh), 3.31 (1 H, dd, $J_{2ax,2eq}$ −14.0, $J_{2ax,3ax}$ 11.6, 2-H_{ax}), 3.36 (1 H, ddd, $J_{2ax,2ax}$ −14.0, $J_{2eq,3ax}$ 4.6, $J_{2eq,6}$ 3.1, 2-H_{eq}), 3.38 (1 H, dd, J_{gem} −14.3, J_{vic} 4.3, CH*H*Ph), 3.50 (1 H, dddd, $J_{2ax,3ax}$ 11.6, $J_{2eq,3ax}$ 4.6, J_{vic} 9.2, J_{vic} 4.3, 3-H_{ax}), 6.40 (1 H, d, $J_{5,6}$ 11.3, 5-H), 7.12 (1 H, dd, $J_{2eq,6}$ 3.1, $J_{5,6}$ 11.3, 6-H) and 7.15–7.35 (5 H, m, Ph); δ_C(100 MHz) 34.24 (*C*H_2Ph), 46.53 (C-3), 53.03 (C-2), 127.23 (C-4′), 128.96 (C-3′, -5′), 129.16 (C-2′, -6′), 132.44 (C-5), 136.19 (C-1′), 142.17 (C-6) and 193.17 (C-4); *m/z* 236 (8%, M^+).

3-*Allyl*-2,3-*dihydro*-4H-*thiin*-4-*one* 1,1-*dioxide* **9b**. 3-Allyl-2,3-dihydro-4*H*-thiin-4-one **8b** (0.580 g, 3.76 mmol) was treated with methanol (15 cm^3), OXONE® (3.467, g, 5.64 mmol) and water (15 cm^3) for 21 h as described above. Column chromatography with CH_2Cl_2 as eluent gave the *title compound* **9b** (0.353 g, 50%) as a solid, m.p. 53.0–55.5 °C (Found: C, 51.8; H, 5.5. $C_8H_{10}O_3S$ requires C, 51.60; H, 5.41%); R_f 0.43 (CH_2Cl_2); ν_{max}($CDCl_3$)/cm^{-1} 1695 (C=O), 1330 (SO_2, asymmetric) and 1135 (SO_2, symmetric); δ_H(60 MHz) 2.31–2.99 (2 H, m, 1′-H), 3.24–3.69 (3 H, m, 2-H_2 and 3-H), 4.95–6.13 (3 H, m, 2′-H and 3′-H_2), 6.38 (1 H, d, $J_{5,6}$ 11.4, 5-H) and 7.16 (1 H, dd, $J_{2eq,6}$ 2.4, $J_{5,6}$ 11.4 6-H); δ_C(22.5 MHz) 32.8 (C-1′), 44.5 (C-3), 53.6 (C-2), 119.9 (C-3′), 132.5 and 132.8 (C-2′ and -5), 142.3 (C-6) and 193.1 (C-4); *m/z* 186 (4%, M^+).

2-*Butyl*-2,3-*dihydro*-4H-*thiin*-4-*one* 1,1-*dioxide* **15a**. 2-Butyl-2,3-dihydro-4*H*-thiin-4-one **14a** (0.60 g, 3.52 mmol) was treated with methanol (30 cm^3), OXONE® (3.25 g, 5.29 mmol) and water (30 cm^3) for 2 days as described above. Preparative centrifugal chromatography [light petroleum–ethyl acetate (13:7)] gave the *title compound* **15a** (0.65 g, 91%) as a crystalline solid, m.p. 44–46 °C (Found: C, 53.6; H, 7.1; S, 15.6. $C_9H_{14}O_3S$ requires C, 53.44; H, 6.98; S, 15.85%); R_f 0.40 [light petroleum–ethyl acetate (7:3)]; ν_{max}(Nujol)/cm^{-1} 1685 (C=O), 1308 (SO_2, asym) and 1142 (SO_2, sym); δ_H(400 MHz) 0.99 (3 H, t, $J_{3',4'}$ 7.1, 4′-H_3), 1.36–1.71 (5 H, m, 1′-H, 2′- and 3′-H_2), 2.18–2.26 (1 H, m, 1′-H), 3.06 (1 H, dd, $J_{2ax,3ax}$ 10.7, $J_{3ax,3eq}$ −17.1 3-H_{ax}), 3.14 (1 H, ddd, $J_{2ax,3eq}$ 4.0, $J_{3ax,3eq}$ −17.1, $J_{3eq,5}$ 1.2, 3-H_{eq}), 3.60–3.53 (1 H, m, 2-H), 6.43 (1 H, dd, $J_{3eq,5}$ 1.2, $J_{5,6}$ 11.0, 5-H) and 7.25 (1 H, d, $J_{5,6}$ 11.0, 6-H); δ_C(100 MHz) 13.66 (C-4′), 22.30 (C-3′), 26.12 (C-2′), 28.04 (C-1′), 41.11 (C-3), 59.51 (C-2), 132.78 (C-5), 142.89 (C-6) and 192.00 (C-4); *m/z* 203 (1%, $M^+ + 1$).

2-*Benzyl*-2,3-*dihydro*-4*H*-*thiin*-4-*one* 1,1-*dioxide* **15b**. 2-Benzyl-2,3-dihydro-4*H*-thiin-4-one **14b** (0.91 g, 3.75 mmol) was treated with methanol (25 cm^3), OXONE® (3.51 g, 3.69 mmol) and water (25 cm^3) for 30 h as described above. Centrifugal chromatography [light petroleum–ethyl acetate (4:1 to 3:2)] followed by recrystallisation from CH_2Cl_2–light petroleum gave the *title compound* **15b** (0.91 g, 87%) as a solid, m.p. 108–109.5 °C (Found: C, 60.7; H, 5.1; S, 13.7. $C_{12}H_{12}O_3S$ requires C, 60.99; H, 5.12; S, 13.59%); ν_{max}(Nujol)/cm^{-1} 1693 (C=O), 1336 (SO_2, asym) and 1140 (SO_2, sym); δ_H(400 MHz) 2.79 (1 H, dd, J_{gem} −13.6, J_{vic} 11.3, C*H*HPh), 2.91 (1 H, ddd,

$J_{3ax,3eq}$ −17.4, $J_{2ax,3eq}$ 4.3, $J_{3eq,5}$ 1.2, 3-H_{eq}), 2.97 (1 H, dd, $J_{2ax,3ax}$ 10.2, $J_{3ax,3eq}$ −17.4, 3-H_{ax}), 3.59 (1 H, dd, J_{gem} −13.6, J_{vic} 3.7, CH*H*Ph), 3.70 (1 H, dddd, $J_{2ax,3ax}$ 10.2, $J_{2ax,3eq}$ 4.3, J_{vic} 11.3, J_{vic} 3.7, 2-H), 6.39 (1 H, dd, $J_{5,6}$ 11.0, $J_{3eq,5}$ 1.2, 5-H) and 7.18–7.37 (6 H, m, 6-H + Ph); δ_C(100 MHz) 31.83 (*C*H_2Ph), 39.92 (C-3), 60.73 (C-2), 127.72 (C-4'), 129.18 (C-3', -5'), 129.32 (C-2', -6'), 133.17 (C-5), 134.32 (C-1'), 142.48 (C-6) and 191.58 (C-4); *m*/*z* 236 (2%, M^+).

(c) *General Procedure for the Preparation of* β-*Halogeno Ketals.*—A solution of an unsaturated sulfone in acetonitrile at room temp. under nitrogen was treated with the appropriate trimethylsilyl halide. The resulting mixture was stirred for 1–24 h prior to the addition of the appropriate alcohol (or diol). After being stirred for a further 1–28 h, the reaction mixture was diluted with CH_2Cl_2, washed successively with water, aq. sodium hydrogen carbonate solution, and brine, and dried ($MgSO_4$), and then the solvent was removed. Where trimethylsilyl iodide was used, an additional wash with aq. sodium thiosulfate (10%) was incorporated after the initial water wash.

7-*Iodo*-1,4-*dioxa*-8-*thiaspiro*[4.5]*decane* 8.8-*dioxide* **2a** (X = I). A solution of 2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **1**[20] (3.84 g, 26.3 mmol) in acetonitrile (105 cm^3) was treated with trimethylsilyl iodide (10.51 g, 52.5 mmol) for 2 h and ethane-1,2-diol (8.15 g, 131.0 mmol) for 4 h as described above. The title compound **2a** (X = I) (7.32 g, 88%) precipitated from the reaction mixture as an off-white, microcrystalline solid (pure by ^1H NMR spectroscopy). Recrystallisation of an analytical sample from CH_2Cl_2–hexane gave the *title compound* as fine, off-white needles, m.p. 191–192 °C (decomp.) (Found: C, 26.4; H, 3.6. $C_7H_{11}IO_4S$ requires C, 26.43; H, 3.49%); R_f 0.79 (CH_2Cl_2); ν_{max}(Nujol)/cm^{-1} 1327 (SO_2, asym) and 1130 (SO_2, sym); δ_H(400 MHz) 2.09 (1 H, dddd, $J_{6eq,10eq}$ 3.6, $J_{9ax,10eq}$ 3.6, $J_{9eq,10eq}$ 3.6, $J_{10ax,10eq}$ −13.8, 10-H_{eq}), 2.45 (1 H, ddd, $J_{9ax,10ax}$ 14.0, $J_{9eq,10ax}$ 3.6, $J_{10ax,10eq}$ −13.8, 10-H_{ax}), 2.53 (1 H, ddd, $J_{6ax,6eq}$ −13.6 $J_{6eq,7ax}$ 3.7, $J_{6eq,10eq}$ 3.6, 6-H_{eq}), 2.77 (1 H, dd, $J_{6ax,6eq}$ −13.6, $J_{6ax,7ax}$ 13.6, 6-H_{ax}), 3.38 (1 H, ddd, $J_{9eq,9ax}$ −14.2, $J_{9eq,10ax}$ 3.6, $J_{9eq,10eq}$ 3.6, 9-H_{eq}), 3.48 (1 H, ddd, $J_{9ax,9eq}$ −14.2, $J_{9ax,10ax}$ 14.0, $J_{9ax,10eq}$ 3.6, 9-H_{ax}), 3.96–4.07 (4 H, m, 2-, 3-H_2) and 5.13 (1 H, dd, $J_{6ax,7ax}$ 13.6, $J_{6eq,7ax}$ 3.7, 7-H_{ax}); δ_C(100 MHz) 32.30 (C-7), 33.10 (C-10), 45.83 (C-6), 46.01 (C-9), 64.90 and 65.27 (C-2, -3) and 105.87 (C-5); *m*/*z* 191 (18%, M^+ − I).

4,4-*Dibutoxy*-2-*iodothiane* 1,1-*dioxide* **2b** (X = I). A solution of 2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **1** (4.75 g, 32.5 mmol) in acetonitrile (150 cm^3) was treated with trimethylsilyl iodide (13.00 g, 65.0 mmol) for 2 h and butan-1-ol (24.1 g, 325 mmol) for 4 h as described above. Column chromatography of the crude product with CH_2Cl_2 as eluent gave, after recrystallisation from diethyl ether–pentane, the *title compound* **2b** (X = I) (11.01 g, 84%) as pale yellow needles, m.p. 39.5–41.0 °C (Found: C, 39.0; H, 6.4; S, 7.7. $C_{13}H_{25}IO_4S$ requires C, 38.6; H, 6.2; S, 7.9%); R_f 0.56 (CH_2Cl_2); ν_{max}($CHCl_3$)/cm^{-1} 1334 (SO_2, asymm), 1133 (SO_2, sym) and 1104 (ketal); δ_H(400 MHz) 0.92 and 0.95 (2 × 3 H, 2 × t, *J* 6.9 and 6.9, 4'-H_3), 1.31–1.45 (4 H, m, 3'-H_2), 1.47–1.61 (4 H, m, 2'-H_2), 2.22 (1 H, ddd, $J_{5ax,5eq}$ −14.3, $J_{5ax,6ax}$ 13.5, $J_{5ax,6eq}$ 4.0, 5-H_{ax}), 2.42 (1 H, dddd, $J_{3eq,5eq}$ 3.4, J_{5ax5eq} −14.3, $J_{5eq,6ax}$ 3.7, $J_{5eq,6eq}$ 3.7, 5-H_{eq}), 2.54 (1 H, dd, $J_{2ax,3ax}$ 13.3, $J_{3ax,3eq}$ −13.8, 3-H_{ax}), 2.84 (1 H, ddd, $J_{2ax,3eq}$ 3.7, $J_{3ax,3eq}$ −13.8, $J_{3eq,5eq}$ 3.4, 3-H_{eq}), 3.26–3.31 (2 H, m, 6-H_{ax} and 6-H_{eq}), 3.38 and 3.40 (2 × 2 H, 2 × t, *J* 6.9 and 6.9, 1'-H_2) and 5.01 (1 H, dd, $J_{2ax,3ax}$ 13.3, $J_{2ax,3eq}$ 3.7, 2-H_{ax}); δ_C(100 MHz) 13.79 and 13.86 (C-4'), 19.31 and 19.57 (C-3'), 30.88 (C-5), 31.75 and 31.80 (C-2'), 32.63 (C-2), 44.44 (C-3), 45.34 (C-6), 60.35 and 60.97 (C-1') and 97.74 (C-4); *m*/*z* 277 (3%, M^+ − I).

8-*Iodo*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5.]*undecane* 9,9-*dioxide* **2c** (X = I). A solution of 2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **1** (0.50 g, 3.42 mmol) in acetonitrile (15 cm^3) was treated with trimethylsilyl iodide (1.37 g, 6.85 mmol) for 2 h and 2,2-dimethylpropane-1,3-diol (1.78 g, 17.1 mmol) for 4 h as described above. Preparative centrifugal chromatography of the crude product with CH_2Cl_2 as eluent gave, after recrystallisation from ethanol, the *title compound* **2c** (X = I) (1.04 g, 85%) as off-white needles, m.p. 152.5–153.5 °C (Found: C, 33.3; H, 4.8; S, 8.9. $C_{10}H_{17}IO_4S$ requires C, 33.5; H, 4.8; S, 8.8%); R_f 0.55 (CH_2Cl_2); ν_{max}($CHCl_3$)/cm^{-1} 1397, 1367 (*gem*-dimethyl), 1334 (SO_2, asym), 1135 (SO_2, sym), 1115 and 1103 (ketal); δ_H(400 MHz) 0.98 and 0.99 (2 × 3 H, 2 × s, 3-Me), 2.19 (1 H, ddd, $J_{10ax,11ax}$ 13.6, $J_{10eq,11ax}$ 4.3, $J_{11ax,11eq}$ −14.6, 11-H_{ax}), 2.52 (1 H, dd, $J_{7ax,7eq}$ −14.0, $J_{7ax,8ax}$ 13.4, 7-H_{ax}), 2.63 (1 H, dddd, $J_{7eq,11eq}$ 3.7, $J_{10eq,11eq}$ 3.7, $J_{10ax,11eq}$ 3.7, $J_{11ax,11eq}$ −14.6, 11-H_{eq}), 3.05 (1 H, ddd, $J_{7eq,7ax}$ −14.0, $J_{7eq,8ax}$ 3.7, $J_{7eq,11eq}$ 3.7, 7-H_{eq}), 3.30 (1 H, ddd, $J_{10ax,10eq}$ −14.0, $J_{10eq,11ax}$ 4.3, $J_{10eq,11eq}$ 3.7, 10-H_{eq}), 3.37 (1 H, ddd, $J_{10ax,10eq}$ −14.0, $J_{10ax,11ax}$ 13.6, $J_{10ax,11eq}$ 3.7, 10-H_{ax}), 3.50 and 3.51 (2 × 2 H, 2 × s, 2- and 4-H_2) and 5.04 (1 H, dd, $J_{7ax,8ax}$ 13.4, $J_{7eq,8ax}$ 3.7, 8-H_{ax}); δ_C(22.4 MHz) 22.43 (C-*Me*$_2$), 30.22 (C-3), 30.38 (C-11), 31.99 (C-8), 42.98 (C-7), 45.09 (C-10), 70.38 and 70.75 (C-2 and -4) and 95.35 (C-6); *m*/*z* 233 (26%, M^+ − I).

8-*Bromo*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]*undecane* 9,9-*dioxide* **2c** (X = Br). A solution of 2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **1** (1.00 g, 6.84 mmol) in acetonitrile (25 cm^3) was treated with trimethylsilyl bromide (2.09 g, 13.7 mmol) for 2 h and 2,2-dimethylpropane-1,3-diol (3.56 g, 34.2 mmol) for 4 h as described above. Preparative centrifugal chromatography of the crude product with CH_2Cl_2 as eluent gave, after recrystallisation from ethanol, the *title compound* **2c** (X = Br) (1.20 g, 56%) as fine needles, m.p. 162–163 °C (Found: C, 38.6; H, 5.2; S, 10.25. $C_{10}H_{17}BrO_4S$ requires C, 38.35; H, 5.47; S, 10.24%); R_f 0.68 (CH_2Cl_2); ν_{max}($CHCl_3$)/cm^{-1} 1398 and 1368 (*gem*-dimethyl), 1337 (SO_2, asym), 1118 (SO_2, sym) and 1103 (ketal); δ_H(400 MHz) 0.99 (6 H, s, 3-Me_2), 2.20 (1 H, ddd, $J_{10ax,11ax}$ 12.2, $J_{10eq,11ax}$ 5.2, $J_{11ax,11eq}$ −14.7, 11-H_{ax}), 2.43 (1 H, dd, $J_{7ax,7eq}$ −14.0, $J_{7ax,8ax}$ 12.8, 7-H_{ax}), 2.60 (1 H, dddd, $J_{7eq,11eq}$ 3.7, $J_{10ax,11eq}$ 3.7, $J_{10eq,11eq}$ 4.0, $J_{11ax,11eq}$ −14.7, 11-H_{eq}), 3.01 (1 H, ddd, $J_{7ax,7eq}$ −14.2, $J_{7eq,8ax}$ 4.0, $J_{7eq,11eq}$ 3.7, 7-H_{eq}), 3.24 (1 H, ddd, $J_{10ax,10eq}$ −14.5, $J_{10eq,11ax}$ 5.2, $J_{10eq,11eq}$ 4.0, 10-H_{eq}), 3.29 (1 H, ddd, $J_{10ax,10eq}$ −14.5, $J_{10ax,11ax}$ 12.2, $J_{10ax,11eq}$ 3.7, 10-H_{ax}), 3.48–3.55 (4 H, m, 2-, 4-H_2) and 4.84 (1 H, dd, $J_{7ax,8ax}$ 12.8, $J_{7eq,8ax}$ 4.0, 8-H_{ax}); δ_C(100 MHz) 22.39 and 22.45 (3-*Me*), 30.20 (C-3), 30.46 (C-11), 40.92 (C-7), 46.31 (C-10), 55.60 (C-8), 70.33 and 70.71 (C-2 and -4) and 95.29 (C-6); *m*/*z* 233 (75%, M^+ − Br).

8-*Chloro*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]*undecane* 9,9-*dioxide* **2c** (X = Cl). A solution of 2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **1** (1.00 g, 6.84 mmol) in acetonitrile (25 cm^3) was treated with trimethylsilyl chloride (1.49 g, 13.7 mmol) for 2 h and 2,2-dimethylpropane-1,3-diol (3.56 g, 34.2 mmol) for 4 h as described above. Preparative centrifugal chromatography of the crude product with CH_2Cl_2 as eluent gave two compounds.

The less polar fraction, after recrystallisation from ethanol, gave the *title compound* **2c** (X = Cl) (0.261 g, 14%) as fine off-white needles, m.p. 160.5–162 °C (Found: C, 44.8; H, 6.5; S, 12.05. $C_{10}H_{17}ClO_4S$ requires C, 44.69; H, 6.38; S, 11.93%); R_f 0.72 (CH_2Cl_2); ν_{max}($CHCl_3$)/cm^{-1} 1398 and 1365 (*gem*-dimethyl), 1337 (SO_2, asym), 1116 (SO_2, sym) and 1103 (ketal); δ_H(400 MHz) 0.99 and 1.00 (2 × 3 H, 2 × s, 3-Me_2), 2.20 (1 H, ddd, $J_{10ax,11ax}$ 11.9, $J_{10eq,11ax}$ 5.2, $J_{11ax,11eq}$ −14.7, 11-H_{ax}), 2.35 (1 H, dd, $J_{7ax,7eq}$ −14.0, $J_{7ax,8ax}$ 12.5, 7-H_{ax}), 2.58 (1 H, dddd, $J_{7eq,11eq}$ 3.7, $J_{10ax,11eq}$ 3.7, $J_{10eq,11eq}$ 4.0, $J_{11ax,11eq}$ −14.7, 11-H_{eq}), 2.94 (1 H, ddd, $J_{7eq,7ax}$ −14.0, $J_{7eq,8ax}$ 4.0, $J_{7eq,11eq}$ 3.7, 7-H_{eq}), 3.18 (1 H, ddd, $J_{10ax,10eq}$ −14.3, $J_{10eq,11ax}$ 5.2, $J_{10eq,11eq}$ 4.0, 10-H_{eq}), 3.22 (1 H, ddd, $J_{10ax,10eq}$ −14.3, $J_{10ax,11ax}$ 11.9, $J_{10ax,11eq}$ 3.7, 10-H_{ax}), 3.45–3.56 (4 H, m, 2- and 4-H_2) and 4.79 (1 H, dd, $J_{7ax,8ax}$ 12.5, $J_{7eq,8ax}$ 4.0, 8-H_{ax}); δ_C(22.4 MHz) 22.43 (3-*Me*$_2$), 30.46 (C-3), 30.56 (C-11), 40.13 (C-7),

46.56 (C-10), 66.29 (C-8), 70.36 and 70.67 (C-2, -4) and 94.81 (C-6); *m/z* 269 (1%, $M^+ - 1$) and 233 (2, $M^+ - Cl$).

The more polar fraction, after recrystallisation from ethanol–light petroleum, gave 3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]-*undec*-7-*ene* (1.02 g, 64%) as off-white needles, m.p. 85–88 °C {Found: (CI) $[M + NH_4]^+$, 250.1113. $C_{10}H_{16}O_4S$ requires $[M - NH_4]$, 250.1113}, R_f 0.41 (CH_2Cl_2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1398 and 1367 (*gem*-dimethyl), 1308 (SO_2, asym), 1113 (SO_2, sym) and 1099 (ketal); δ_H(400 MHz) 0.91 and 1.07 (2 × 3 H, 2 × s, C-Me_2), 2.50–2.56 (2 H, m, 11-H_2), 3.33–3.53 (2 H, m, 10-H), 3.50 and 3.64 (4 H, ABq, J_{AB} 11.9, 2- and 4-H_2), 6.36 (1 H, dt, $J_{7,8}$ 11.4, $J_{7,11}$ 1.5, 7-H) and 6.79 (1 H, dt, $J_{7,8}$ 11.4, $J_{8,10}$ 1.2, 8-H); δ_C(22.5 MHz) 21.80 and 22.24 (3-Me_2), 29.70 (C-3), 30.83 (C-11), 47.46 (C-10), 70.39 (C-2, -4), 91.20 (C-6), 129.61 (C-7) and 132.95 (C-8); *m/z* 168 (9%, $M^+ - SO_2$).

trans-6-*Benzyl*-9-*iodo*-1,4-*dioxa*-8-*thiaspiro*[4.5]*decane* 8,8-*dioxide* **10a**. A solution of unsaturated sulfone **9a** (1.00 g, 4.23 mmol) in acetonitrile (100 cm^3) was treated with trimethylsilyl iodide (1.69 g, 8.45 mmol) for 1 h and ethylene glycol (1.31 g, 21.1 mmol) for 24 h as described above. The crude material was purified by preparative centrifugal chromatography with CH_2Cl_2 as eluent to give the *title compound* **10a** (1.61 g, 93%) as a solid, m.p. 195–199 °C (decomp.) (Found: C, 41.2; H, 4.1. $C_{14}H_{17}IO_4S$ requires C, 41.19; H, 4.20%); R_f 0.39 (CH_2Cl_2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1322 (SO_2, asym) and 1124 (SO_2, sym); δ_H(400 MHz) 2.27 (1 H, dd, J_{gem} −13.3, J_{vic} 11.5, C*H*HPh), 2.59 (1 H, dd, $J_{9ax,10eq}$ 4.4, $J_{10ax,10eq}$ −13.9, 10-H_{eq}), 2.66 (1 H, dd, $J_{9ax,10ax}$ 12.8. $J_{10ax,10eq}$ −13.9, 10-H_{ax}), 2.68–2.74 (1 H, m, 6-H_{ax}), 3.15 (1 H, dd, J_{gem} −13.3, J_{vic}[1c] 3.7, CH*H*Ph), 3.16–3.18 (2 H, m, 7-H_2), 4.09–4.15 (4 H, m, 2- and 3-H), 5.08 (1 H, dd, $J_{9ax,10ax}$ 12.8, $J_{9ax,10eq}$ 4.4 9-H_{ax}), 7.09–7.13 (2 H, m, 2′-, 6′-H) and 7.25–7.35 (3 H, m, 3′-, 4′-, 5′-H); δ_C(100 MHz) 32.40 (C-9, 33.20 (*C*H_2Ph), 45.20 (C-6), 45.34 (C-10), 49.70 (C-7), 65.72 and 65.86 (C-2, -3), 107.71 (C-5), 126.91 (C-4′), 128.90 (C-3′, -5′), 129.12 (C-2′, -6′) and 137.17 (C-1′); *m/z* 279 (25%).

trans-6-*Allyl*-9-*iodo*-1,4-*dioxa*-8-*thiaspiro*[4.5]*decane* 8,8-*dioxide* **10b**. A solution of 3-allyl-2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **9b** (0.084, g, 0.45 mmol) in acetonitrile (1.5 cm^3) was treated with trimethylsilyl iodide (0.198 g, 0.99 mmol) for 100 min and ethylene glycol (0.140 g, 2.25 mmol) for 28 h as described above. Column chromatography (CH_2Cl_2 as eluent) gave the *title compound* **10b** as a solid (0.154 g, 96%), m.p. 140.5–144 °C; R_f 0.54 (CH_2Cl_2) (Found: C, 33.9; H, 4.2. $C_{10}H_{15}IO_4S$ requires C, 33.53; H, 4.22%); {Found: (CI) $[M + NH_4]^+$, 376.0079. $C_{10}H_{15}IO_4S$ requires $[M + NH_4]$, 376.0080}; $\nu_{max}(CDCl_3)/cm^{-1}$ 1320 (SO_2, asym) and 1135 (SO_2, sym); δ_H(60 MHz) 1.52–3.68 (7 H, m, 1′-, 7- and 10-H_2 and 6-H), 4.07 (4 H, br s, 2- and 3-H_2), 4.80–5.31 (3 H, m, 9-H and 3′-H_2) and 5.35–6.08 (1 H, m, 2′-H); δ_C(22.5 MHz) 31.7 (C-1′), 32.5 (C-9), 42.8 (C-6), 45.5 (C-10), 50.0 (C-7), 65.8 and 65.6 (C-2, -3), 107.7 (C-5), 118.6 (C-3′) and 134.3 (C-2′); *m/z* 231 ($M^+ - I$, 22%).

7-*Butyl*-9-*iodo*-1,4-*dioxa*-8-*thiaspiro*[4.5]*decane* 8,8-*dioxide* **16a**. A solution of 2-butyl-2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **15a** (0.64 g, 3.16 mmol) in acetonitrile (12 cm^3) was treated with trimethylsilyl iodide (1.46 g, 7.31 mmol) for 1 h and ethane-1,3-diol (1.17 g, 18.83 mmol) for 18 h as described above. Preparative centrifugal chromatography [light petroleum–ethyl acetate (7:3)] gave the *title compound* **16a** (1.07 g, 90%) as a solid, chromatographically identical mixture of diastereoisomers (3:1), m.p. 81–83 °C (Found: C, 35.55; H, 5.1; S, 8.5. $C_{11}H_{19}IO_4S$ requires C, 35.30; H, 5.12; S, 8.57%); R_f 0.27 [light petroleum–ethyl acetate (7:3)]; ν_{max}(Nujol)/cm^{-1} 1309 (SO_2, asym) and 1115 (SO_2, sym); *m/z* 247 ($M^+ - I$, 15%). Successive recrystallisation of the mixture of isomers from ethyl acetate–light petroleum afforded a sample of the major *cis*-isomer (> 99:1, *cis*:*trans*).

cis-Isomer: δ_H(400 MHz) 0.92 (3 H, t, $J_{3',4'}$ 7.2, 4′-H_3), 1.21–1.44 (4 H, m, 2′- and 3′-H_2), 1.44–1.55 (2 H, m, 1′-H), 2.07 (1 H, ddd, $J_{10eq,6eq}$ 4.0, $J_{7ax,6eq}$ 4.0, $J_{6ax,6eq}$ −14.0, 6-H_{eq}), 2.15 (1 H, dd, $J_{7ax,6ax}$ 14.0, $J_{6ax,6eq}$ −14.0, 6-H_{ax}), 2.51 (1 H, ddd, $J_{10ax,10eq}$ −13.8, $J_{10eq,9ax}$ 3.7, $J_{10eq,6eq}$ 4.0, 10-H_{eq}), 2.73 (1 H, dd, $J_{10ax,10eq}$ −13.8, $J_{10ax,9ax}$ 13.8, 10-H_{ax}), 3.23–3.33 (1 H, m, 7-H_{ax}), 3.99–4.02 (4 H, m, 2- and 3-H_2) and 5.01 (1 H, dd, $J_{10ax,9ax}$ 13.8, $J_{10eq,9ax}$ 4.0, 9-H_{ax}); δ_C(100 MHz) 13.90 (C-4′), 22.02 (C-3′), 26.08 (C-2′), 28.05 (C-1′), 32.42 (C-9), 38.57 (C-6), 45.63 (C-10), 56.25 (C-7), 64.90 and 64.67 (C-2 and -3) and 105.96 (C-5).

trans-Isomer: δ_H(400 MHz) 0.94 (3 H, t, $J_{3',4'}$ 7.2, 4′-H_3), 1.21–1.44 (4 H, m, 2′- and 3′-H_2), 1.82–1.94 (2 H, m, 1′-H_2), 2.09–2.16 (1 H, m, 6-H_{eq}), 2.36 (1 H, dd, $J_{7eq,6ax}$ 4.7, $J_{6ax,6eq}$ −14.7, 10-H_{ax}), 2.54 (1 H, ddd, $J_{10ax,10eq}$ −10.8, $J_{10eq,9ax}$ 4.2, $J_{10eq,6eq}$ 2.4, 10-H_{eq}), 2.62 (1 H, dd, $J_{10ax,10eq}$ −10.8, $J_{10ax,9ax}$ 10.8, 10-H_{ax}), 3.32–3.39 (1 H, m, 7-H_{eq}), 3.99–4.02 (4 H, m, 2- and 3-H_2) and 5.11 (1 H, dd, $J_{10ax,9ax}$ 4.2, 9-H_{ax}); δ_C(100 MHz) 13.90 (C-4′), 21.91 (C-3′), 26.97 (C-2′), 28.75 (C-1′), 29.47 (C-9), 35.33 (C-6), 44.61 (C-10), 55.82 (C-7), 64.20 and 64.84 (C-2, -3) and 105.68 (C-5).

cis-7-*Benzyl*-9-*iodo*-1,4-*dioxa*-8-*thiaspiro*[4.5]*decane* 8,8-*dioxide* **16b**. A solution of 2-benzyl-2,3-dihydro-4*H*-thiin-4-one 1,1-dioxide **15b** (0.76 g, 3.2 mmol) in acetonitrile (20 cm^3) was treated with trimethylsilyl iodide (1.35 g, 6.76 mmol) for 1 h and ethane-1,2-diol (1.00 g, 16.14 mmol) for 24 h as described above. Preparative centrifugal chromatography [light petroleum–ethyl acetate (3:2)] gave the *title compound* **16b** (1.10 g, 84%) as a crystalline solid, m.p. 128–130 °C (Found: C, 41.4; H, 4.1; S, 7.95. $C_{14}H_{17}IO_4S$ requires C, 41.19; H, 4.19; S. 7.85%); R_f 0.76 [light petroleum–ethyl acetate (3:2)]; ν_{max}(Nujol)/cm^{-1} 1318 (SO_2, asym) and 1116 (SO_2, sym); δ_H(400 MHz) 1.83 (1 H, ddd, $J_{10eq,6eq}$ 3.7, $J_{7ax,6eq}$ 3.7, $J_{6ax,6eq}$ −14.0, 6-H_{eq}), 2.12 (1 H, dd, $J_{7ax,6ax}$ 13.7, J_{6ax6eq} −14.0 6-H_{ax}), 2.50 (1 H, ddd, $J_{10ax,10eq}$ −13.4, $J_{10eq,9ax}$ 3.7, $J_{10eq,6eq}$ 3.7 10-H_{eq}), 2.75 (1 H, dd, $J_{10ax,10eq}$ −13.4, $J_{10ax,9ax}$ 13.4, 10-H_{ax}), 2.77 (1 H, dd, J_{gem} −14.0, J_{vic} 12.0, C*H*HPh), 3.55–3.61 (2 H, m, 7-H and C*H*HPh), 3.76–3.95 (4 H, m, 2- and 3-H_2), 5.10 (1 H, dd, $J_{10ax,9ax}$ 13.4, $J_{10ax,9eq}$ 3.7, 9-H_{ax}) and 7.17–7.35 (5 H, m, Ph); δ_C(100 MHz) 32.16 (C-9), 32.31 (*C*H_2Ph), 37.92 (C-6), 46.00 (C-10), 57.39 (C-7), 64.76 and 65.04 (C-2, -3), 106.15 (C-5), 127.19 (C-4′), 128.90 (C-3′, -5′), 129.27 (C-2′, -6′) and 135.72 (C-1′); *m/z* 204 ($M^+ - I - Ph$, 100%). Careful analysis of the product by ^1H NMR spectroscopy indicated the presence of a small amount of the *trans*-isomer (*cis*:*trans* ~ 96:4).

(d) *General Procedure for Preparation of Episulfones.*—A solution of the β-halogeno ketal in dry THF at −78 °C under nitrogen was treated with a solution of freshly sublimed potassium *tert*-butoxide in dry THF. The solution was stirred, then quenched at −78 °C with saturated aq. ammonium chloride. The mixture was then diluted with water and subjected to a standard CH_2Cl_2 work-up.

7,8-*Epithio*-1,4-*dioxaspiro*[4.4]*nonane* S,S-*dioxide* **3a**. A solution of 7-iodo-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxide **2a** (0.50 g, 1.57 mmol) in a mixture of dry DMSO (20 cm^3) and dry THF (30 cm^3) at 0 °C under nitrogen was treated with a THF solution of freshly sublimed potassium *tert*-butoxide (1.0 mol dm^{-3}; 2.00 cm^3, 2.00 mmol). After being stirred for 3 h, the reaction mixture was worked up as described above to give, after preparative centrifugal chromatography [CH_2Cl_2–ethyl acetate (9:1)], the *title episulfone* **3a** (0.26 g, 87%) as a cream-coloured solid, m.p. 148–150 °C (decomp.) (Found: C, 43.9; H, 5.3. $C_7H_{10}O_4S$ requires C, 44.2; H, 5.3%); R_f 0.08 [CH_2Cl_2–ethyl acetate (9:1)]; ν_{max}(Nujol)/cm^{-1} 1311 (SO_2, asym) and 1105 (SO_2, sym); δ_H(400 MHz) 2.35–2.43 (2 H, m, 6- and 9-H_{ax}), 2.44–2.48 (2 H, m, 6- and 9-H_{eq}), 3.69–3.73 (2 H, m, 7- and 8-H) and 3.85–3.98 (4 H, s, 2- and 3-H_2); δ_C(100 MHz) 35.82, (C-6, -9), 46.27 (C-7, -8), 64.17 and 65.88 (C-2, -3) and 122.11 (C-5); *m/z* 191 (1%, $M^+ \pm 1$) and 126 (100, $M^+ - SO_2$).

3,3-*Dibutoxy*-6-*thiabicyclo*[3.1.0]*hexane* 6,6-*dioxide* **3b**. A

solution of 4,4-dibutoxy-2-iodothiane 1,1-dioxide **2b** (0.50 g, 1.23 mmol) in dry THF (25 cm^3) was treated with potassium *tert*-butoxide (0.30 g, 2.67 mmol) for 10 min as described above to give, after preparative centrifugal chromatography [CH_2Cl_2–light petroleum (1:1)], the *title episulfone* **3b** (0.28 g, 82%) as a pale yellow viscous oil {Found: (CI) $[M + 1]^+$, 277.1470. $C_{13}H_{24}O_4S$ requires [M + 1], 277.1474}; R_f 0.46 [CH_2Cl_2–light petroleum (1:1)]; $\nu_{max}(CHCl_3)/cm^{-1}$ 1323 (SO_2, asym), 1134 (SO_2, sym) and 1104 (ketal); δ_H(400 MHz) 0.92 and 0.93 (2 × 3 H, 2 × t, *J* 6.9 and 6.9, 4'-H_3), 1.31–1.42 (4 H, m, 3'-H_2), 1.48–1.57 (4 H, m, 2'-H_2), 2.18–2.27 (2 H, m, 2-, 4-H), 2.52–2.58 (2 H, m, 2-, 4-H), 3.36 (2 H, t, *J* 6.7, 1'-H_2), 3.44 (2 H, t, *J* 6.7, 1'-H_2) and 3.57–3.62 (2 H, m, 1-, 5-H); δ_C(100 MHz) 13.78 (C-4'), 19.30 and 19.41 (C-3'), 31.76 and 31.83 (C-2'), 33.07 (C-2, -4), 46.70 (C-1, -5), 60.87 and 63.93 (C-1') and 115.50 (C-3); *m/z* 275 (17%, $M^+ - 1$) and (3, $M^+ - SO_2$).

2,3-*Epithio*-8,8-*dimethyl*-6,10-*dioxaspiro*[4.5]*decane* S,S-*dioxide* **3c**. 1. *From* 8-*iodo*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]*undecane* 9,9-*dioxide* **2c** (X = I). A solution of 8-iodo-3,3-dimethyl-1,5-dioxa-9-thiaspiro[5.5]undecane 9,9-dioxide **2c** (X = I) (0.129 g, 0.47 mmol) in dry THF (10 cm^3) was treated with potassium *tert*-butoxide (0.079 g, 0.70 mmol) for 10 min as described above to give, after preparative centrifugal chromatography [CH_2Cl_2–light petroleum (4:1)], the *title episulfone* **3c** (0.092 g, 85%) as a solid, m.p. 94.0–95.0 °C (Found: C, 51.8; H, 6.95; S, 13.76. $C_{10}H_{16}O_4S$ requires C, 51.71; H, 6.94; S, 13.80%) {Found: (CI) $[M + NH_4]^+$, 250.1113. $C_{10}H_{16}O_4S$ requires [M + NH_4], 250.1113}; R_f 0.44 (CH_2Cl_2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1397 and 1365 (*gem*-dimethyl), 1325 (SO_2, asym), 1138 (SO_2, sym) and 1115 (ketal); δ_H(400 MHz) 0.98 (6 H, s, 8-Me_2), 2.26 (2 H, m, 1-, 4-H_{ax}), 2.76 (2 H, m, 1-, 4-H_{eq}), 3.45 (2 H, s, 7-H_2), 3.49 (2 H, s, 9-H_2) and 3.61 (2 H, m, 2-, 3-H); δ_C(100 MHz) 22.25 (8-*Me*$_2$), 29.95 (C-8), 32.95 (C-1, -4), 46.58 (C-2, -3), 71.38 and 73.61 (C-7, -9) and 113.56 (C-5); *m/z* 168 (50%, $M^+ - SO_2$).

2. *From* 8-*bromo*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]*undecane* 9,9-*dioxide* **2c** (X = Br). A solution of 8-bromo-3,3-dimethyl-1,5-dioxa-9-thiaspiro[5.5]undecane 9,9-dioxide **2c** (X = Br) (0.200 g, 0.64 mmol) in dry THF (15 cm^3) was treated with potassium *tert*-butoxide (0.110 g, 0.98 mmol) for 15 min as described above to give, after preparative centrifugal chromatography [CH_2Cl_2–light petroleum (4:1)], the title episulfone **3c** (0.110 g, 74%) as a solid, with data identical with those above.

3. *From* 8-*chloro*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]*undecane* 9,9-*dioxide* **2c** (X = Cl). A solution of 8-chloro-3,3-dimethyl-1,5-dioxa-9-thiaspiro[5.5]undecane 9,9-dioxide **2c** (X = Cl) (0.129 g, 0.47 mmol) in THF (10 cm^3) was treated with potassium *tert*-butoxide (0.079 g, 0.70 mmol) for 10 min as described above to give, after preparative centrifugal chromatography [CH_2Cl_2–light petroleum (4:1)], the title episulfone **3c** (0.092 g, 85%) as a solid, with data identical with those above.

r-6-*Benzyl*-t-7,t-8-*epithio*-1,4-*dioxaspiro*[4.4]*nonane* S,S-*dioxide* **11a**. A solution of iodo ketal **10a** (0.130 g, 0.32 mmol) in THF (20 cm^3) was treated with potassium *tert*-butoxide (0.080 g, 0.71 mmol) in THF (5 cm^3) for 3 min as described above. Preparative centrifugal chromatography with CH_2Cl_2 as eluent gave the *title compound* **11a** (0.076 g, 90%) as a solid, m.p. 106–108 °C (decomp.) (Found: C, 60.1; H, 5.7. $C_{14}H_{16}O_4S$ requires C, 59.98; H, 5.75%) {Found: (CI) $[M + NH_4]^+$, 298.1120. $C_{14}H_{16}O_4S$ requires [M + NH_4], 298.1113}; R_f 0.55 (CH_2Cl_2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1310 (SO_2, asym) and 1135 (SO_2, sym); δ_H(400 MHz) 2.30–2.40 (2 H, m, CH_2Ph), 2.74 (1 H, dd, $J_{9\alpha,9\beta}$ −14.3, $J_{8,9\alpha}$ 11.2, 9-H_α), 2.95 (1 H, dd, $J_{9\alpha,9\beta}$ 4.8, 9-H_β), 3.05 (1 H, ddd, $J_{7,8}$ 5.8, $J_{8,9\alpha}$ 11.2, $J_{8,9\beta}$ 4.8, 8-H), 3.36 (1 H, dd, $J_{6,7}$ 10.3, $J_{7,8}$ 5.8, 7-H), 3.56 (1 H, ddd, J_{vic} 6.6, J_{vic} 7.7, $J_{6,7}$ 10.3, 6-H), 3.84–4.08 (4 H, m, 2-, 3-H_2) and 7.18–7.33 (5 H, m, Ph); δ_C(100 MHz) 32.07 (C-9), 34.44 (*C*H_2Ph), 44.85 (C-6), 46.64 (C-8), 50.17 (C-7), 64.82 and 66.08 (C-2, -3), 121.33 (C-5), 126.62 (C-4'), 128.44 (C-2', -6'), 128.77 (C-3', -5') and 134.41 (C-1'); *m/z* 216 (27%, $M^+ - SO_2$).

r-6-*Allyl*-t-7,t-8-*epithio*-1,4-*dioxaspiro*[4.4]*nonane* S,S-*dioxide* **11b**. A solution of the iodo ketal **10b** (0.107 g, 0.30 mmol) in THF (5 cm^3) was treated with potassium *tert*-butoxide (0.040 g, 0.36 mmol) in THF (2 cm^3) for 2.5 h at −78 °C as described above and was then allowed to warm to room temp. over a period of 1.5 h. The reaction mixture was then quenched by the addition of water (5 cm^3) and worked up as described above. The residue was purified by column chromatography [diethyl ether–light petroleum (2:3)] to give 6-allyl-1,4-dioxaspiro-[4.4]non-7-ene **12b** (0.010 g, 20%) (see later) followed by the *title compound* **11b** (0.045 g, 65%) as a solid, m.p. 64–68 °C {Found: (CI) $[M + NH_4]^+$, 248.0962. $C_{10}H_{14}O_4S$ requires [M + NH_4], 248.0956}; R_f 0.48 [diethyl ether–light petroleum (7:3)] J; ν_{max}(Nujol)/cm^{-1} 1305 (SO_2, asym) and 1140 (SO_2, sym); δ_H(60 MHz) 2.04–2.84 (5 H, m, 1'- and 9-H_2, and 6-H), 3.14–3.80 (2 H, m, 7-, 8-H), 3.96 (4 H, br s, 2-, 3-H), 4.84–5.38 (2 H, m, 3'-H_2) and 5.46–6.16 (1 H, m, 2'-H); *m/z* (CI) 248 (12%, $M + NH_4]^+$ and 167 (100, $[M + 1 - SO_2]$)$^+$.

(e) *Preparation of Cyclopentenes.*—1,4-*Dioxaspiro*[4.4]*non*-7-*ene* **4a**. A solution of potassium *tert*-butoxide in THF (1.0 mol dm^{-3}; 3.30 cm^3, 3.30 mmol) was added to a stirred suspension of 7-iodo-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxide **2a** (0.42 g, 1.32 mmol) in dry diethyl ether (50 cm^3) at −78 °C under nitrogen. The reaction mixture was allowed to warm to room temp. during 6 h. Saturated aq. ammonium chloride (60 cm^3) was added and a standard ethereal work-up was carried out. ^1H NMR spectroscopy of the resulting oil (0.134 g) indicated the presence of Bu^{t}OH and the highly volatile 1,4-dioxaspiro-[4.4]non-7-ene **4a** [22] (Found: $[M + H]^+$, 127.0759. Calc. for $C_7H_{10}O_2$: [M + H], 127.0759); R_f 0.30 (CH_2Cl_2); ν_{max}(film)/cm^{-1} 2884 (CH str), 1327 and 1019; δ_H(90 MHz) 2.65 (4 H, br s, 6-, 9-H_2), 3.91 (4 H, br s, 2-, 3-H_2) and 5.62 (2 H, br s, 7-, 8-H); δ_C(22.5 MHz) 43.14 (C-6, -9), 64.21 (C-2, -3), 117.45 (C-5) and 128.07 (C-7, -8).

4,4-*Dibutoxycyclopentene* **4b**. 1. *From* 4,4-*dibutoxy*-2-*iodothiane* 1,1-*dioxide* **2b**. A solution of 4,4-dibutoxy-2-iodothiane, 1,1-dioxide **2b** (0.80 g, 1.98 mmol) in dry THF (25 cm^3) at room temp. under nitrogen was treated with a solution of potassium *tert*-butoxide (0.67 g, 5.97 mmol) in dry THF (5 cm^3). After being stirred for 2 h at room temp., the reaction mixture was quenched with saturated aq. ammonium chloride (25 cm^3), then was subjected to a standard CH_2Cl_2 work-up. The crude product was purified by distillation (Kugelrohr) to give the *title alkene* **4b** (0.39 g, 93%) as a mobile liquid, b.p. 80 °C/0.5 mmHg (Found: C, 73.7; H, 11.7. $C_{13}H_{24}O_2$ requires C, 73.54; H, 11.39%); R_f 0.92 (CH_2Cl_2); ν_{max}(film)/cm^{-1} 1622 (C=C) and 1105 (ketal); δ_H(400 MHz) 0.92 (6 H, t, *J* 7.0, 4'-H_3), 1.24–1.58 (8 H, m, 2'-, 3'-H_2), 2.54 (4 H, br s, 3-, 5-H_2), 3.43 (4 H, t, *J* 6.7, 1'-H_2) and 5.65 (2 H, br s, 1-, 2-H); δ_C(100 MHz) 13.89 (C-4'), 19.50 (C-3'), 32.14 (C-2'), 41.92 (C-3, -5), 61.38 (C-1'), 111.16 (C-4) and 127.80 (C-1, -2); *m/z* 212 (10%, M^+).

2. *From* 3,3-*dibutoxy*-6-*thiabicyclo*[3.1.0]*hexane* 6,6-*dioxide* **3b**. A solution of 3,3-dibutoxy-6-thiabicyclo[3.1.0]hexane 6,6-dioxide **3b** (0.124 g, 0.45 mmol) in dry THF (10 cm^3) at room temp. under nitrogen was treated with a solution of potassium *tert*-butoxide (0.10 g, 0.91 mmol) in dry THF (5 cm^3) for 2 h. Work-up and purification as described above gave the title alkene **4b** (0.086 g, 91%) with data identical with those above.

8,8-*Dimethyl*-6,10-*dioxaspiro*[4.5]*dec*-2-*ene* **4c**. 1. *From* 8-*iodo*-3,3-*dimethyl*-1,5-*dioxa*-9-*thiaspiro*[5.5]*undecane* 9,9-*dioxide* **2c**. Freshly sublimed potassium *tert*-butoxide (0.62 g, 5.56 mmol) was added to a solution of 8-iodo-3,3-dimethyl-1,5-dioxa-9-thiaspiro[5.5]undecane 9,9-dioxide **2c** (1.00 g, 2.78 mmol) in dry THF (50 cm^3) under nitrogen at room temp. The solution was stirred for 1 h, then was quenched with saturated

aq. ammonium chloride (50 cm^3). A standard CH_2Cl_2 work-up, followed by Kugelrohr distillation of the crude material, gave the title alkene **4c**[23] (0.425 g, 91%) as a liquid, b.p. 35 °C/0.5 mmHg (Found: C, 71.2; H, 9.4. Calc. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%); R_f 0.90 (CH_2Cl_2); ν_{max}(film)/cm^{-1} 1622 (C=C), 1395, 1363 (*gem*-dimethyl), 1120 and 1106 (ketal); δ_H(400 MHz) 0.99 (6 H, s, 8-Me_2), 2.66 (4 H, s, 1-, 4-H_2), 3.52 (4 H, s, 7-, 9-H_2) and 5.67 (2 H, s, 2-, 3-H); δ_C(100 MHz) 22.37 (8-Me_2), 29.97 (C-8), 49.32 (C-1, -4), 71.85 (C-7, -9), 109.16 (C-5) and 127.69 (C-2, -3); *m/z* 168 (44%, M^+).

2. *From* 2,3-*epithio*-8,8-*dimethyl*-6,10-*dioxaspiro*[4.5]*decane* S,S-*dioxide* **3c**. A solution of 2,3-epithio-8,8-dimethyl-6,10-dioxaspiro[4.5]decane *S,S*-dioxide **3c** (0.232 g, 1.00 mmol) in dry THF (15 cm^3) under nitrogen at room temp. was treated with a solution of potassium *tert*-butoxide (0.224 g, 2.00 mmol) in dry THF (5 cm^3) for 1 h. Work-up and purification as described above gave the title alkene **4c** (0.156 g, 93%) with data identical with those above.

6-*Benzyl*-1,4-*dioxaspiro*[4.4]*non*-7-*ene* **12a**. 1. *From* trans-6-*benzyl*-9-*iodo*-1,4-*dioxa*-8-*thiaspiro*[4.5]*decane* 8.8-*dioxide* **10a**. A solution of potassium *tert*-butoxide (0.050 g, 0.45 mmol) in dry THF (5 cm^3) was added dropwise under nitrogen to a stirred solution of compound **10a** (0.122 g, 0.30 mmol) in dry THF (5 cm^3) in a solid CO_2–carbon tetrachloride-bath. The mixture was allowed to attain room temp. and was stirred for a further 20 h, when TLC (CH_2Cl_2) indicated the continued presence of episulfone **11a**. A further portion of potassium *tert*-butoxide (0.034 g, 0.30 mmol) was added and the mixture was stirred for a further 2.5 h, when brine (10 cm^3) was added. A standard CH_2Cl_2 work-up, followed by column chromatography (CH_2Cl_2), gave 6-benzyl-1,4-dioxaspiro[4.4]non-7-ene **12a**[7] (0.055 g, 85%) as an oil, R_f 0.72 (CH_2Cl_2); ν_{max}/cm^{-1} 1495 and 700; δ_H(400 MHz) 2.49–2.63 (3 H, m, 9-H_2 and CH*H*Ph), 2.89 (1 H, dd, J_{gem} −13.6, J_{vic} 5.9, C*H*HPh), 2.96–3.01 (1 H, m, 6-H), 3.77–3.96 (4 H, m, 2-, 3-H_2), 5.59–5.63 (1 H, m, 7-H), 5.70–5.74 (1 H, m, 8-H) and 7.15–7.29 (5 H, m, Ph); δ_C(100 MHz) 35.67 (*C*H_2Ph), 43.02 (C-9), 53.54 (C-6), 64.03 and 64.71 (C-2, -3), 117.53 (C-5), 125.68 (C-4), 127.44 (C-7), 128.13 (C-2′, -6′), 128.99 (C-3′, -5′), 132.91 (C-8) and 140.81 (C-1′); *m/z* 216 (29%, M^+).

2. *From* r-6-*benzyl*-t-7,t-8-*epithio*-1,4-*dioxaspiro*[4.4]*nonane* S,S-*dioxide* **11a** *and base*. A solution of episulfone **11a** (0.034 g, 0.12 mmol) in dry THF (2 cm^3), stirred under nitrogen in a solid CO_2–carbon tetrachloride-bath, was treated dropwise with a solution of potassium *tert*-butoxide (0.017 g, 0.15 mmol) in dry THF (1 cm^3). The mixture was stirred at the same temperature for 30 min, then at room temp. for 2 h, when a further portion of potassium *tert*-butoxide (0.017 g, 0.15 mmol) was added. The mixture was stirred for 30 min and then was quenched with brine (2 cm^3). Work-up and purification as described above gave the title alkene **12a** (0.156 g, 93%) with data identical with those above.

3. *By thermolysis of* r-6-*benzyl*-t-7,t-8-*epithio*-1,4-*dioxaspiro*-[4.4]*nonane* S,S-*dioxide* **11a**. Episulfone **11a** (0.065 g, 0.23 mmol) was heated, under nitrogen in a Kugelrohr oven, rapidly to 90 °C then to 110 °C during 20 min, when no solid material remained. The residue was subjected to column chromatography as described above to give the title alkene **12a** (0.044 g, 88%) with data identical with those above.

6-*Allyl*-1,4-*dioxaspiro*[4.4]*non*-7-*ene* **12b**. A solution of potassium *tert*-butoxide (0.140 g, 1.25 mmol) in dry THF (7 cm^3) was added dropwise under nitrogen to a solution of the iodo ketal **10b** (0.179 g, 0.50 mmol) in dry THF (7 cm^3) at −78 °C. The mixture was allowed to attain room temp. and was stirred for 16 h. A further portion of potassium *tert*-butoxide (0.056 g, 0.50 mmol) was added and the mixture was stirred at room temp. for a further 1 h. The reaction mixture was diluted with brine (5 cm^3) and water (5 cm^3), and a standard CH_2Cl_2 work-up followed by column chromatography (CH_2Cl_2) gave 6-allyl-1,4-dioxaspiro[4.5]non-7-ene **12b**[7] (0.072 g, 87%) as an oil, R_f 0.86 [diethyl ether–light petroleum (1:1)]; ν_{max}/cm^{-1} 2880, 1640 (C=C), 1140 and 1030; δ_H(60 MHz) 1.81–2.90 (5 H, m, 1′- and 9-H_2 and 6-H), 3.91 (4 H, s, C-2, 3-H), 4.77–5.21 (2 H, m, 3′-H_2) and 5.31–6.23 (3 H, m, 7-, 8- and 2′-H); δ_C(22.5 MHz) 33.9 (C-1′), 43.0 (C-9), 51.6 (C-6), 64.8 and 64.0 (C-2, -3), 115.5 (C-3′), 117.5 (C-5) and 127.3, 132.9 and 137.1 (C-7, -8 and -2′); *m/z* 166 (4%, M^+).

3-*Butylcyclopent*-2-*enone* **18a**. A solution of potassium *tert*-butoxide in THF (1.0 mol dm^{-3}; 2.05 cm^3, 2.05 mmol) was added to a stirred solution of 7-butyl-9-iodo-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxide **16a** (~3:1 mixture of diastereoisomers) (0.506 g, 1.35 mmol) in dry THF (20 cm^3) at −78 °C under nitrogen. The reaction mixture was allowed to warm to 0 °C, then saturated aq. ammonium chloride (10 cm^3) was added. The mixture was given a standard ethereal work-up followed by preparative centrifugal chromatography [hexane–ethyl acetate (7:3)] to produce 3-butylcyclopent-2-enone **18a** (0.16 g, 86%) as an oil with consistent spectral properties (which were also in accord with literature[28] data).

7-*Benzyl*-1,4-*dioxaspiro*[4.4]*non*-7-*ene* **17b**. A solution of potassium *tert*-butoxide in THF (1.0 mol dm^{-3}; 2.35 cm^3, 2.35 mmol) was added to a stirred solution of 7-benzyl-9-iodo-1,4-dioxa-8-thiaspiro[4.5]decane-8,8-dioxide **16b** (0.53 g, 1.29 mmol) in dry THF (35 cm^3) at −78 °C under nitrogen. The reaction mixture was allowed to warm to room temp., then saturated aq. ammonium chloride (10 cm^3) was added. A standard CH_2Cl_2 work-up, followed by preparative centrifugal chromatography [light petroleum to light petroleum–ethyl acetate (7:3)], gave 7-benzyl-1,4-dioxaspiro[4.4]non-7-ene **17b** (0.175 g, 62%) as an oil with consistent spectral properties (which were also in accord with literature[7] data).

The more polar fractions were found to contain 3-benzylcyclopent-2-enone **18b** (0.065 g, 29%) as a pale yellow oil with consistent spectral properties (which were also in accord with literature[30] data).

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