Applications of Methylsulfonylsulfene in Synthesis. Part 1. Conversion of 3,4-Dihydro-2*H*-pyran into *cis*-2-(*C*-Substituted)tetrahydropyran-3-sulfonates/sulfinates

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(1*R**,6*S**,8*R**)-8-Methylsulfonyl-2-oxa-7-thiabicyclo[4.2.0]octane 7,7-dioxide **10a**, available from the reaction of 3,4-dihydro-2*H*-pyran and methylsulfonylsulfene **1** (generated *in situ* from $MeSO_2Cl$ and Et_3N), underwent alkylation at position 8 in the presence of sodium hydride and alkyl halides. With methyl iodide and chloromethyl methyl ether, mixtures of the *endo*- and *exo*-methyl derivatives **10b** and **11b** (with **10b** in predominance) and the *endo*- and *exo*-methoxymethyl derivatives **10c** and **11c** (with **11c** in predominance) were produced. With benzyl chloride, *tert*-butyl bromoacetate and allyl bromide, only the *exo*-alkyl derivatives **11d–f** were isolated, the stereostructure of compound **11f** being established by X-ray crystallography.

In the presence of sodium thiophenoxide and thiophenol, compound **10a** underwent a reductive cleavage of its S(7)–C(8) bond to give, after acidification, the sulfinic acid **9a**; the sodium salt of the last-cited acid underwent methylation with methyl iodide to give (2*S**,3*S**)-3-methylsulfonyl-2-(methylsulfonylmethyl)tetrahydropyran **15d**. Under corresponding conditions (and also in the presence of a large excess of Na/Hg in MeOH), compound **11f** afforded the sulfinic acid **27c** which was transformed into (2*R**,3*S**)-3-methylsulfonyl-2-[(1'*R**)-1'-(methylsulfonyl)but-3'-enyl]-tetrahydropyran **21d**; the stereostructure of the last cited compound was determined by X-ray crystallography. The sulfinic acid **27c** also underwent reaction with diazomethane to give the methyl sulfinate **27b** as a ~1:1 mixture of diastereoisomers.

In the presence of Raney nickel, compound **10a** furnished (2*R**)-2-(methylsulfonylmethyl)-tetrahydrofuran **14** whereas compound **11f** underwent reduction of its olefinic linkage to give the propyl derivative **11h**.

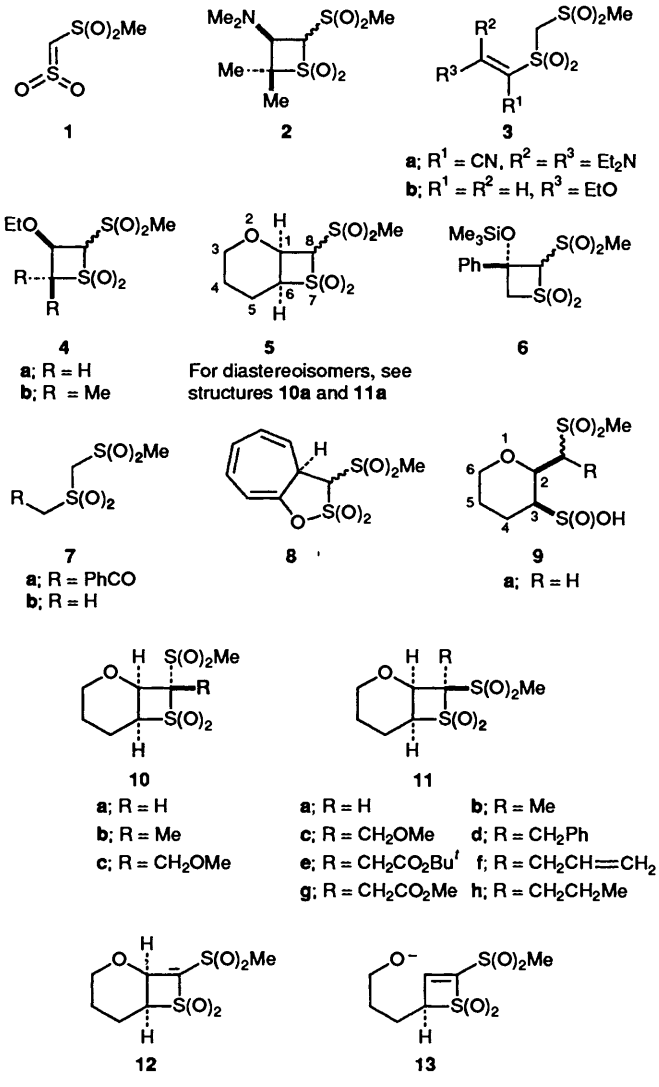
Sodium methoxide in methanol (and also Na/Hg in MeOH) induced an overall hydrolytic cleavage of the S(7)–C(8) bonds of compounds **10a** and **11f** to give, after acidification, the *cis*-sulfonic acids **15c** and **21b** (which were isolated as their methyl esters **15a** and **21a**). In the presence of sodium hydroxide, the *cis*-sulfonic acid **15c** underwent epimerisation at position 2 to give the *trans*-sulfonic acid **17c** (which was isolated as its methyl ester **17a**).

Opitz and his co-workers have postulated [1] that methylsulfonylsulfene **1** is generated in the reactions of triethylamine with methylsulfonylmethanesulfonyl chloride in tetrahydrofuran (THF) at −70 °C and with methanesulfonyl chloride in acetonitrile at −40 °C. The species undergoes addition reactions with amines,[2–5] *p*-nitrophenol,[2] trifluoroethanol [5] and water.[6] With enamines, it usually affords [2 + 2]-cycloadducts, *e.g.* **2** [2] [although 3,3-bis(diethylamino)propenenitrile furnishes compound **3a**].[7] The outcome of its reaction with enol ethers depends upon the structure of the enol ether: ethoxyethene affords a mixture of the vinyl sulfone **3b** and the thietane dioxide **4a**, 1-ethoxy-2-methylpropene gives the thietane dioxide **4b**, and 3,4-dihydro-2*H*-pyran yields the oxathiabicyclooctane dioxide **5**; compounds **4**–**5** are apparently isolated as single diastereoisomers although their geometries have not been assigned.[8] [2 + 2]-Cycloadducts are also usually formed in the reaction of the sulfene **1** with silyl enol ethers [although 1-phenyl-1-(trimethylsiloxy)ethene affords a mixture of compound **6** and the keto disulfone **7a** [9]] and thioenol ethers (vinyl sulfides).[10] Finally, compound **8** is produced in the reaction of the sulfene **1** with tropone.[11]

Very little has been published concerning the reactivity of the thietane dioxides **4**–**6** although, based upon the finding that compound **4a** is converted into the disulfone **7b** by aq. sodium hydroxide,[1] Opitz implies that they are unstable to alkali. Owing to their interesting array of reactive functionality which we considered could be exploited in synthesis, we have embarked on a study of the adducts of the sulfene **1** and enol ethers. In this paper, we describe some of our experiences with compound **5** which arose as a consequence of efforts to derive tetrahydropyrans of type **9** [the sulfinic acid oxidation level of the C(3) *S*-substituent was selected because of the extensive manipulative options which it offers[12]]. We hoped that compounds of type **9** (and, in due course, more complex representatives) would find application in the synthesis of *C*-glycopyranosides and tetrahydropyran-based spiroacetals—units which feature in a wide range of natural products with diverse biological properties.[13]

Discussion

Our plan for effecting transformations of the type **5** ⟶ **9** hinged upon achieving two key reactions. First, it would be necessary to install alkyl groups at position 8 of compound **5** to give products of types **10** and/or **11**. Although alkylations of thietane dioxides are uncommon,[14] examples involving 1,1-bis(sulfonyl)alkanes are well established.[15] Of course, in the case of compound **5** there is the possibility that the intermediate carbanion **12** might undergo β-elimination to the alkoxide **13**;



O-alkylations or other reactions of the last cited species would obviously foil our plan. Secondly, it would be necessary to cleave reductively the S(7)–C(8) bond of compounds of types **10** and/or **11**. Again, it is noteworthy that reductive ring openings of thietane dioxides are unknown although, seemingly, compounds of types **10** and/or **11** are well activated for such processes.

Full experimental details for the preparation of compound **5** have not been described in the literature. When methanesulfonyl chloride (0.45 mol) was added slowly to a solution of triethylamine (0.65 mol) in acetonitrile at −40 °C followed, after 1 h, by 3,4-dihydro-2*H*-pyran (0.23 mol), work-up, after 1.5 h at −40 °C, and recrystallisation gave compound **5** in 44% yield.

The ^{1}H NMR spectrum of compound **5** showed an interesting solvent dependence. In deuteriochloroform, a single species was present and, for example, the methylsulfonyl group appeared as a three-proton singlet at δ 3.22, the 1-hydrogen atom as a one-proton doublet (J 6 Hz) at δ 4.79 and the 8-hydrogen atom as a one-proton singlet at δ 5.07. In perdeuteriodimethyl sulfoxide, a 4:1 mixture of species was present; the 1-hydrogen atom resonated as a triplet (J 6 Hz) at δ 4.80 (0.2 H) and a double doublet (J 7 and 2 Hz) at δ 4.85 (0.8 H) and the 8-hydrogen atom as a doublet (J 2 Hz) at δ 6.14 (0.8 H) and a doublet (J 6 Hz) at δ 6.50 (0.2 H).

From the aforecited results, we infer that compound **5** exists as the diastereoisomer **10a** in deuteriochloroform and as a 4:1 mixture of the diastereoisomers **10a** and **11a** in perdeuteriodimethyl sulfoxide. Presumably, the diastereoisomer **10a** is favoured in the crystal state and this persists in the non-polar solvent. However, in the polar solvent, ionisation of the 8-hydrogen atom occurs and an equilibrium is established between the diastereoisomers **10a** and **11a**, in which the methylsulfonyl group favours the *exo*-position. In accord with the foregoing analysis, the addition of deuterium oxide caused no change to the ^{1}H NMR spectrum measured in deuteriochloroform. However, in that recorded in perdeuteriodimethyl sulfoxide, deuterium exchange of the 8-hydrogen atoms of the diastereoisomers **10a** and **11a** occurred rapidly.

When treated in *N*,*N*-dimethylformamide (DMF) at 0 °C with sodium hydride and methyl iodide, the bicycle **10a** was converted into a mixture of the *C*-methyl derivatives **10b** and **11b**, which was separated by chromatography. The more mobile component, identified as the *endo*-methyl derivative **10b**, was isolated in 38% yield after crystallisation; the less mobile component, assigned the *exo*-methyl stereostructure **11b**, was obtained in 12% yield after crystallisation. In the ^{1}H NMR spectrum of compound **10b** the 8-methyl group appeared as a singlet at δ 1.84, the methylsulfonyl group as a singlet at δ 3.17 and the 1-hydrogen atom as a doublet (J 6.5 Hz) at δ 4.65; in the case of compound **11b**, the corresponding protons appeared at δ 1.97, 3.46 and ~4.33. The stereochemical assignments rested upon nuclear Overhauser effect difference (NOED) spectroscopic studies. Irradiation of the 8-methyl group caused a 13% enhancement of the 1- and 6-hydrogen atoms (the signals of which overlapped) in compound **11b** but had no effect in compound **10b**.

The use of chloromethyl methyl ether in the alkylation reaction led, after chromatography and crystallisation, to the isolation of the *C*-methoxymethyl derivatives **10c** and **11c**. The more mobile compound, isolated in 16% yield, was assigned the *endo*-methoxymethyl stereostructure **10c**; the less mobile material, obtained in 59% yield, was identified as the *exo*-methoxymethyl derivative **11c**. The stereochemical assignment, which was tentative, was based upon the order of elution of the diastereoisomers and on the similarity in chemical shifts and coupling constants of the 1- and 6-hydrogen atoms of compounds **10b, c**.

A single product, isolated in 76% yield after crystallisation and formulated as the *exo*-benzyl derivative **11d**, was obtained when benzyl chloride was employed in the alkylation reaction. The stereostructure **11d** was inferred on the basis of ^{1}H NMR spectroscopic evidence, since the 6-hydrogen atom (δ 3.31) was substantially shielded compared with that of compounds **10a–c** and **11a–c** (δ 4.53 ± 0.2), implying that it resided in the shielding zone of the phenyl ring. Furthermore, in an NOED spectroscopic study, irradiation of the 1-hydrogen atom caused a 3.5% enhancement of a phenyl hydrogen atom.

The use of *tert*-butyl bromoacetate in the alkylation reaction led to the isolation of a single *tert*-butoxycarbonylmethyl derivative in 72% yield after crystallisation. Owing to an overlap of signals, the stereostructure of the last cited compound could not be unequivocally established by NOED spectroscopy. Tentatively, however, the *exo*-orientation of the *tert*-butoxycarbonylmethyl group was suggested by the 5.3% enhancement of one of its methylene hydrogen atoms when the 6-hydrogen atom was irradiated and by the 3.3% enhancement of its other methylene hydrogen atom when the 1-hydrogen atom was irradiated.

In a final example, allyl bromide was employed as the alkylating agent. The reaction gave rise to a single allyl derivative, formulated as the *exo*-allyl derivative **11f**, in 92% yield after crystallisation. The stereostructure **11f** was inferred from NOED spectroscopic studies. In particular, irradiation of the 6-hydrogen atom resulted in a 2.8% enhancement of one of the hydrogen atoms of the allylic methylene group and a 4.7%

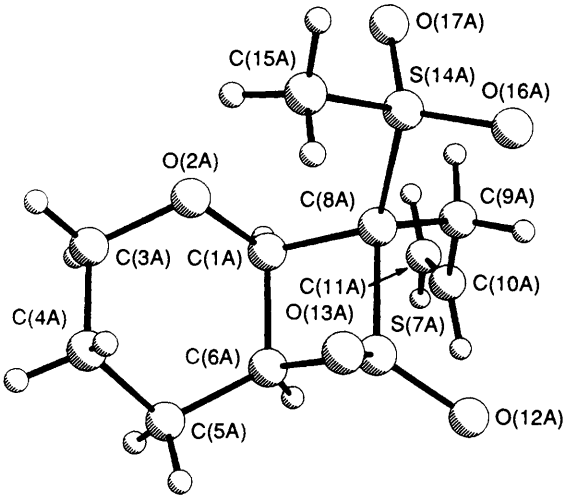


Fig. 1 Molecular structure of compound **11f**

Table 1 Fractional atomic co-ordinates for compound **11f** with estimated standard deviations (esds) in parentheses

Atom	*x*	*y*	*z*
S(7A)	0.964 9(1)	0.925 1(2)	0.694 52(6)
S(14A)	0.799 3(1)	1.179 0(2)	0.686 60(7)
O(2A)	0.746 7(3)	0.925 5(4)	0.600 2(2)
O(12A)	1.075 9(3)	0.957 5(5)	0.717 5(2)
O(13A)	0.906 3(3)	0.859 0(5)	0.734 2(2)
O(16A)	0.865 1(4)	1.234 2(5)	0.741 1(2)
O(17A)	0.745 4(4)	1.283 4(5)	0.642 4(2)
C(1A)	0.852 1(4)	0.966 0(6)	0.599 3(2)
C(3A)	0.717 3(5)	0.781 7(7)	0.574 7(3)
C(4A)	0.779 2(6)	0.662 9(7)	0.611 8(3)
C(5A)	0.896 8(5)	0.679 6(7)	0.613 8(3)
C(6A)	0.934 6(4)	0.841 3(6)	0.621 3(2)
C(8A)	0.893 2(4)	1.079 4(6)	0.651 0(2)
C(9A)	0.967 2(6)	1.202 8(8)	0.635 1(3)
C(10A)	1.041 6(6)	1.167(1)	0.596 7(4)
C(11A)	1.035 1(7)	1.214(4)	0.542 0(4)
C(11AB)	0.960(3)	1.258(4)	0.580(1)
C(15A)	0.703 4(5)	1.060 1(7)	0.705 1(3)
S(7B)	0.233 6(1)	0.610 9(2)	0.587 04(7)
S(14B)	0.360 2(1)	0.900 2(2)	0.566 58(7)
O(2B)	0.477 9(3)	0.611 2(4)	0.596 0(2)
O(12B)	0.134 2(3)	0.629 5(6)	0.604 5(2)
O(13B)	0.230 3(3)	0.575 6(5)	0.525 4(2)
O(16B)	0.266 3(4)	0.991 5(5)	0.554 3(2)
O(17B)	0.460 3(4)	0.966 8(5)	0.594 8(2)
C(1B)	0.414 8(4)	0.632 3(6)	0.638 2(3)
C(3B)	0.526 3(5)	0.465 8(7)	0.601 1(3)
C(4B)	0.441 5(6)	0.349 6(7)	0.582 6(3)
C(5B)	0.363 3(6)	0.348 8(7)	0.622 0(3)
C(6B)	0.333 0(5)	0.504 3(7)	0.637 8(2)
C(8B)	0.331 9(4)	0.756 8(6)	0.616 9(2)
C(9B)	0.295 0(5)	0.834 5(7)	0.669 8(3)
C(10B)	0.376 5(6)	0.932 2(8)	0.708 2(3)
C(11B)	0.357 0(8)	1.052(1)	0.732 6(5)
C(11BB)	0.365(4)	0.934(6)	0.759(2)
C(15B)	0.375 2(6)	0.819 9(7)	0.499 4(3)

Table 2 Bond lengths for compound **11f** with esds in parentheses

S(7A)–O(12A)	1.433(4)	S(7B)–O(12B)	1.425(4)
S(7A)–O(13A)	1.426(4)	S(7B)–O(13B)	1.435(4)
S(7A)–C(6A)	1.796(6)	S(7B)–C(6B)	1.799(6)
S(7A)–C(8A)	1.830(5)	S(7B)–C(8B)	1.841(6)
S(14A)–O(16A)	1.430(4)	S(14B)–O(16B)	1.431(4)
S(14A)–O(17A)	1.439(4)	S(14B)–O(17B)	1.433(5)
S(14A)–C(8A)	1.825(5)	S(14B)–C(8B)	1.814(6)
S(14A)–C(15A)	1.747(6)	S(14B)–C(15B)	1.743(6)
O(2A)–C(1A)	1.401(6)	O(2B)–C(1B)	1.397(7)
O(2A)–C(3A)	1.432(7)	O(2B)–C(3B)	1.439(7)
C(1A)–C(6A)	1.546(7)	C(1B)–C(6B)	1.554(8)
C(1A)–C(8A)	1.560(7)	C(1B)–C(8B)	1.544(7)
C(3A)–C(4A)	1.480(8)	C(3B)–C(4B)	1.499(9)
C(4A)–C(5A)	1.504(9)	C(4B)–C(5B)	1.485(9)
C(5A)–C(6A)	1.527(8)	C(5B)–C(6B)	1.513(8)
C(8A)–C(9A)	1.551(8)	C(8B)–C(9B)	1.555(7)
C(9A)–C(10A)	1.47(1)	C(9B)–C(10B)	1.493(9)
C(9A)–C(11AB)	1.34(3)	C(10B)–C(11B)	1.26(1)
C(10A)–C(11A)	1.30(1)	C(10B)–C(11BB)	1.21(5)
C(10A)–C(11AB)	1.31(3)	C(11B)–C(11BB)	1.22(5)
C(11A)–C(11AB)	1.48(3)		

enhancement of the allyl methine hydrogen atom; when the 1-hydrogen atom was irradiated, the olefinic hydrogen atoms of the allyl group were enhanced (CH:CH_2 by 1.8% and CH:CH_2 by 3.8%).

That the allyl derivative possessed the stereostructure **11f** was unequivocably established by an X-ray crystallographic analysis. The molecular structure (see Experimental section for crystal data and other information), together with its crystallographic labelling, is shown in Fig. 1. Refined atomic co-ordinates are included in Table 1, bond lengths in Table 2 and bond angles in Table 3.

To consolidate the stereochemistries of compounds **11d** and **11e**, it was decided to correlate them chemically with the allyl derivative **11f**. Hence, when subjected sequentially to the action of ozone, hydrogen peroxide and diazomethane, the benzyl derivative **11d** and the allyl derivative **11f** were transformed into the methoxycarbonylmethyl derivative **11g** (isolated, after chromatography, in 23% overall yield from the former sequence and in 56% overall yield from the latter sequence). Compound **11g** was also obtained (81% yield after chromatography) by subjection of the *tert*-butyl ester **11e** to the action of trifluoroacetic acid (TFA) and treatment of the product with diazomethane.

From the foregoing results, it is clear that the thietane dioxide **10a** readily undergoes alkylation reactions at position 8 by way of the anion **12**. The stereochemical outcome appears to depend on the 'size' of the alkylating agent. With methyl iodide and chloromethyl methyl ether, both *endo*- and *exo*-alkylated products are observed (with a preference for *endo*-methylation and *exo*-methoxymethylation). With benzyl chloride, *tert*-butyl bromoacetate and allyl bromide, only *exo*-alkylated products are obtained.

The next objective was to devise conditions which would effect the conversion of compounds of types **10** and **11** into products of type **9**. It was decided to explore this avenue using the parent bicycle **10a** and the allyl derivative **11f**.

The use of hydride reducing agents proved unproductive and led either to complex mixtures {$(Me_2CHCH_2)_2AlH$, CH_2Cl_2; $LiAlH_4$, THF; $NaBH_4$, THF; $LiBH[CH(Me)Et]_3$, THF} or no reaction [$LiAlH(OBu^t)_3$, THF].

Raney nickel is known to cleave reductively the C–S bond of activated sulfones.[16] However, when the thietane dioxide **10a** was heated with the reagent in boiling ethanol, only a poor recovery of material resulted. Following chromatographic fractionation, compound **14** was isolated in 21% yield (14% of the starting material was also recovered). The structure of compound **14** rested upon its elemental composition and its ^1H NMR spectroscopic properties.

When the allyl derivative **11f** was subjected to the action of Raney nickel under similar conditions, only reduction of the olefinic bond was observed, to give the propyl derivative **11h** in 81% yield after crystallisation.

It is known that aluminium amalgam reduces the C–S bond of β-keto sulfones.[17] However, the thietane dioxides **10a** and **11f** were unaffected by the reagent in aq. THF.

Table 3 Bond angles (°) for compound **11f** with esds in parentheses

O(12A)–S(7A)–O(13A)	117.9(3)	S(14A)–C(8A)–C(9A)	104.5(4)
O(12A)–S(7A)–C(6A)	114.9(3)	C(1A)–C(8A)–C(9A)	114.3(5)
O(12A)–S(7A)–C(8A)	112.7(3)	C(8A)–C(9A)–C(10A)	119.5(6)
O(13A)–S(7A)–C(6A)	112.4(3)	C(8A)–C(9A)–C(11AB)	124(1)
O(13A)–S(7A)–C(8A)	112.9(2)	C(10A)–C(9A)–C(11AB)	56(1)
C(6A)–S(7A)–C(8A)	80.2(3)	C(9A)–C(10A)–C(11A)	126.1(8)
O(16A)–S(14A)–O(17A)	119.0(3)	C(9A)–C(10A)–C(11AB)	57(1)
O(16A)–S(14A)–C(8A)	103.8(3)	C(11A)–C(10A)–C(11AB)	69(2)
O(16A)–S(14A)–C(15A)	108.2(3)	C(10A)–C(11A)–C(11AB)	56(1)
O(17A)–S(14A)–C(8A)	105.5(3)	C(9A)–C(11AB)–C(10A)	67(2)
O(17A)–S(14A)–C(15A)	108.2(3)	C(9A)–C(11AB)–C(11A)	122(2)
C(8A)–S(14A)–C(15A)	112.0(3)	C(10A)–C(11AB)–C(11A)	55(1)
C(1A)–O(2A)–C(3A)	113.4(4)	O(12B)–S(7B)–O(13B)	117.7(3)
O(2A)–C(1A)–C(6A)	113.5(4)	O(12B)–S(7B)–C(6B)	115.6(3)
O(2A)–C(1A)–C(8A)	109.0(4)	O(12B)–S(7B)–C(8B)	113.2(3)
C(6A)–C(1A)–C(8A)	97.6(4)	O(13B)–S(7B)–C(6B)	112.3(3)
O(2A)–C(3A)–C(4A)	110.8(5)	O(13B)–S(7B)–C(8B)	113.1(3)
C(3A)–C(4A)–C(5A)	110.7(5)	C(6B)–S(7B)–C(8B)	79.0(3)
C(4A)–C(5A)–C(6A)	112.8(5)	O(16B)–S(14B)–O(17B)	118.7(3)
S(7A)–C(6A)–C(1A)	89.6(3)	O(16B)–S(14B)–C(8B)	104.8(3)
S(7A)–C(6A)–C(5A)	120.1(4)	O(16B)–S(14B)–C(15B)	108.2(3)
C(1A)–C(6A)–C(5A)	118.3(5)	O(17B)–S(14B)–C(8B)	107.0(3)
S(7A)–C(8A)–S(14A)	115.4(3)	O(17B)–S(14B)–C(15B)	108.0(3)
S(7A)–C(8A)–C(1A)	87.9(3)	C(8B)–S(14B)–C(15B)	109.9(3)
S(7A)–C(8A)–C(9A)	114.0(4)	C(1B)–O(2B)–C(3B)	111.8(4)
S(14A)–C(8A)–C(1A)	120.7(4)	O(2B)–C(1B)–C(6B)	112.7(4)
O(2B)–C(1B)–C(8B)	110.0(4)	S(7B)–C(8B)–C(9B)	107.9(4)
C(6B)–C(1B)–C(8B)	96.7(4)	S(14B)–C(8B)–C(1B)	119.6(4)
O(2B)–C(3B)–C(4B)	109.6(5)	S(14B)–C(8B)–C(9B)	108.1(4)
C(3B)–C(4B)–C(5B)	112.1(6)	C(1B)–C(8B)–C(9B)	112.6(5)
C(4B)–C(5B)–C(6B)	112.5(5)	C(8B)–C(9B)–C(10B)	115.3(5)
S(7B)–C(6B)–C(1B)	89.5(3)	C(9B)–C(10B)–C(11B)	125.5(8)
S(7B)–C(6B)–C(5B)	121.3(4)	C(9B)–C(10B)–C(11BB)	111(2)
C(1B)–C(6B)–C(5B)	118.4(5)	C(11B)–C(10B)–C(11BB)	59(2)
S(7B)–C(8B)–S(14B)	119.0(3)	C(10B)–C(11B)–C(11BB)	58(2)
S(7B)–C(8B)–C(1B)	88.3(3)	C(10B)–C(11BB)–C(11B)	63(3)

Sodium amalgam has been reported to be an effective reagent for the reductive removal of arylsulfonyl groups.[18] When the thietane dioxide **10a** was treated with the reagent in methanol at 0 °C and the product was then deionised [Amberlite IR-120(H^+)], an acidic material was obtained which reacted with diazomethane to give, after chromatography and crystallisation, the *cis*-sulfonate **15a** in 70% yield. The structure of compound **15a** was deduced by elemental analysis and ^{1}H NMR spectroscopy (involving extensive decoupling experiments). On the basis of the coupling constant of 2 Hz between the 2- and 3-hydrogen atoms and the width at half-height[19] ($w_{\frac{1}{2}}$ 7 Hz) of the signal for the 3-hydrogen atom, the material is considered to adopt the conformation **16a** in deuteriochloroform solution.

Clearly, an overall hydrolysis rather than a reduction had occurred in the reaction involving sodium amalgam and methanol. Presumably, methanolysis leads initially to the methyl sulfonate **15a**, which reacts with sodium methoxide to give the sodium sulfonate **15b** (and MeOMe). Deionisation then affords the sulfonic acid **15c**, which reacts with diazomethane to give the product **15a**.

In accord with the aforementioned proposal, the bicycle **10a** underwent reaction with methanolic methoxide to give, after acidification and esterification, the methyl sulfonate **15a** in 81% yield (after chromatography and crystallisation).

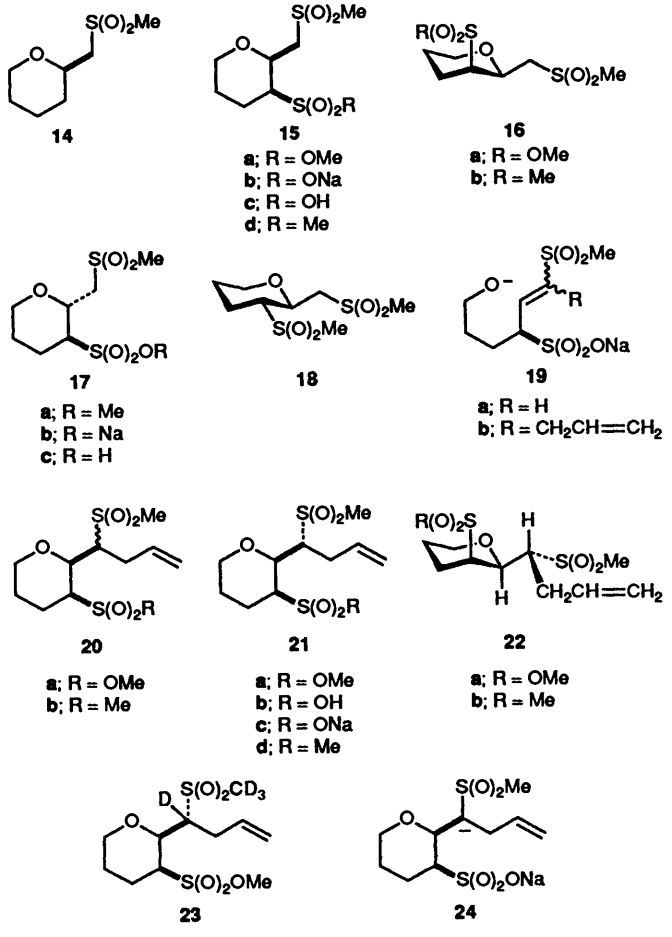
Interestingly, when the bicycle **10a** was heated with sodium hydroxide in aq. THF and the product was then treated with Amberlite IR-120(H^+), an acidic material was isolated; it reacted with diazomethane to give, after chromatography and crystallisation, the *trans*-sulfonate **17a** in 63% yield. The structure of compound **17a** was assigned on the basis of elemental analysis and ^{1}H NMR spectroscopy (involving extensive decoupling experiments). From the coupling constant of 8 Hz between the 2- and 3-hydrogen atoms, the material is considered to adopt the conformation **18** in deuteriochloroform solution.

Presumably, the bicycle **10a** reacts with sodium hydroxide to form the *cis*-sulfonate **15b** which then epimerises to the thermodynamically more stable *trans*-sulfonate **17b** by an elimination–addition pathway involving the species **19a**.

To test this notion, the *cis*-sulfonate **15a** was heated with sodium hydroxide in aq. THF; acidification and esterification led, after chromatography and crystallisation, to the isolation of the *trans*-sulfonate **17b** in 83% yield.

Subjection of the allyl derivative **11f** to the action of sodium amalgam in methanol at 0 °C led, after acidification and esterification with diazomethane, to the formation of a syrupy product in 75% yield (after chromatography). ^{1}H NMR spectroscopic considerations left little doubt that the material possessed the structure **20a** and that it was present as a single diastereoisomer. On the basis of subsequent evidence (to be discussed later), the stereostructure **21a** is assigned to the material. The coupling constants of 2 Hz between the 2- and 3-hydrogen atoms and 11 Hz between the 2- and 1′-hydrogen atoms together with the $w_{\frac{1}{2}}$-value of 8 Hz for the signal of the 3-hydrogen atom indicate that compound **21a** adopts the geometry **22a** in deuteriochloroform solution.

When the allyl derivative **11f** was heated with sodium hydroxide in aq. THF and the product was then acidified and esterified with diazomethane, compound **21a** was isolated in 43% yield (after chromatography). Interestingly, when the sulfonic acid **21b** was subjected to the action of sodium deuteroxide in deuterium oxide–THF and the product was then treated with Amberlite IR-120(H^+) and diazomethane, the tetradeuteriated material **23** was obtained. Evidently, the allyl group does not impede the reversible generation of the



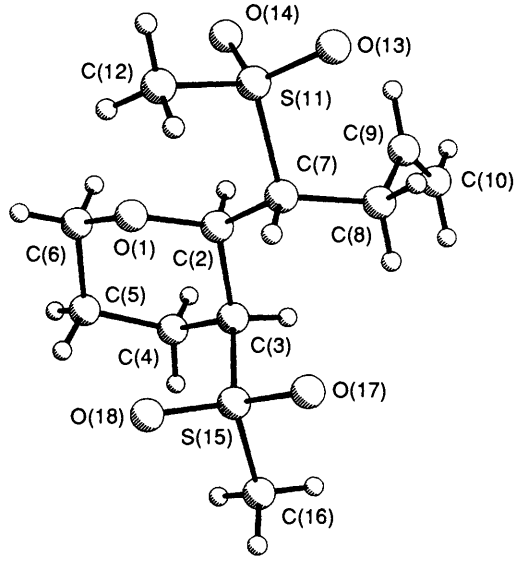
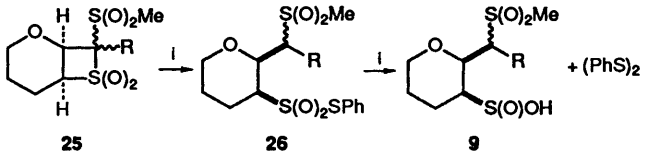


Fig. 2 Molecular structure of compound **21d**

carbanionic intermediate **24** from the the sulfonate salt **21c** but blocks its β-elimination to the species **19b** (assuming that diastereoisomers of **21c** with a *trans*-arrangement of the 2- and 3-substituent are thermodynamically more stable than is *cis*-isomer **21c**). The formation of compound **21c** as a single diastereoisomer is of note, implying that the 1′-epimer is thermodynamically unfavoured. However, since there is evidence that α-sulfonyl carbanions can exhibit configurational stability,[20] the possibility that the **11f** → **21c** transformation (which proceeds with retention of configuration at the carbon centre) is under kinetic control cannot be excluded.

The speculation depicted in Scheme 1 prompted us to examine the behaviour of the bicycles **10a** and **11f** towards thiophenol under basic conditions. If initial attack by the nucleophile were to occur at S(8) of a precursor of type **25** (*cf.* **10**, **11**), a thiosulfonate of type **26** would be expected to arise. However, thiosulfonates are known to react with thiols to give sulfinic acids and disulfides.[21] Accordingly, it was hoped that a thiosulfonate of type **26** would be further transformed into a sulfinic acid of type **9** and diphenyl disulfide.



Scheme 1 *Reagent:* i, PhSH

When the bicycle **10a** was heated with sodium thiophenoxide and thiophenol in THF and the product was then treated sequentially with Amberlite IR-120(H^+), sodium hydrogen carbonate in aq. methanol, and methyl iodide in DMF, two fractions were isolated after chromatography. The first fraction (6% yield) was diphenyl disulfide [when the ion-exchange resin was stirred with $CHCl_3$ and the filtrate was evaporated, a further quantity (65% yield) of PhSSPh was isolated]. The second fraction, obtained in 38% yield, was the disulfone **15d**. On the basis of the coupling constant of 2 (or 3) Hz between the 2- and 3-hydrogen atoms and the $w_{\frac{1}{2}}$-value of 7 Hz for the signal of the 3-hydrogen atom, the disulfone **15d** is considered to adopt the conformation **16b** in deuteriochloroform. Clearly, the conformational bias of compounds **15a** and **15d** is very similar.

Evidently, sodium thiophenoxide/thiophenol had effected the desired reductive ring opening of the bicycle **10a** to give, after acidic work-up, the sulfinic acid **9a**. *S*-Alkylation of the sodium salt of the last cited species by methyl iodide had afforded the sulfone **15d**.

When subjected to corresponding conditions, the allyl derivative **11f** gave, after chromatography, diphenyl disulfide in 7% yield [when the ion-exchange resin was processed as before, a further quantity (67% yield) of PhSSPh was isolated] and a second product in 66% yield. ^1H NMR spectroscopic considerations left little doubt that the material possessed the structure **20b** and that it was present as a single diastereoisomer. An X-ray crystallographic examination established that the material possessed the stereostructure **21d**. The molecular structure (see Experimental section for crystal data and other information), together with its crystallographic labelling, is shown in Fig. 2. Refined atomic co-ordinates are included in Table 4, bond lengths in Table 5 and bond angles in Table 6.

Obviously, the sulfinate salt **27a** was the primary product of the reaction of the bicycle **11f** with sodium thiophenoxide/thiophenol and it had served as the precursor of compound **21d**. On the basis of the coupling constants of 2 Hz between the 2- and 3-hydrogen atoms and 11 Hz between the 2- and 1′-hydrogen atoms, together with the $w_{\frac{1}{2}}$-value of 9 Hz for the signal of the 3-hydrogen atom, it is clear that compound **21d** adopts the geometry **22b** in deuteriochloroform solution. From Fig. 2, it is evident that this geometry is also present in the crystalline state.

The establishment that compound **20b** possessed the stereostructure **21d** strongly suggested that compound **20a** had the stereostructure **21a** alluded to earlier. Therefore, both compounds were formed as single diastereoisomers in related ring-opening reactions of the same precursor and both compounds

Table 4 Fractional atomic co-ordinates for compound **21d** with esds in parentheses

Atom	*x*	*y*	*z*
S(11)	0.380 9(3)	0.380 3(3)	0.533 7(1)
S(15)	0.562 3(4)	0.470 3(3)	0.265 3(2)
O(1)	0.250 8(8)	0.375 8(7)	0.372 2(3)
O(13)	0.500 8(8)	0.389 2(7)	0.594 3(3)
O(14)	0.222 9(8)	0.432 5(7)	0.550 2(4)
O(17)	0.703(1)	0.465(1)	0.316 3(4)
O(18)	0.503(1)	0.352 9(8)	0.234 8(5)
C(2)	0.335(1)	0.490(1)	0.388 5(5)
C(3)	0.339(1)	0.555(1)	0.311 8(6)
C(4)	0.254(1)	0.579(1)	0.261 3(6)
C(5)	0.148(1)	0.462(1)	0.250 8(6)
C(6)	0.105(1)	0.402(1)	0.329 8(6)
C(7)	0.470(1)	0.459(1)	0.450 5(5)
C(8)	0.571(1)	0.576(1)	0.475 9(6)
C(9)	0.475(2)	0.688(1)	0.514 2(9)
C(10)	0.482(2)	0.798(2)	0.491(1)
C(12)	0.361(1)	0.214(1)	0.511 0(6)
C(16)	0.616(1)	0.569(1)	0.185 7(5)

Table 5 Bond lengths for compound **21d** with esds in parentheses

S(11)–O(13)	1.434(6)	O(1)–C(6)	1.42(1)
S(11)–O(14)	1.431(7)	C(2)–C(3)	1.57(1)
S(11)–C(7)	1.794(9)	C(2)–C(7)	1.57(1)
S(11)–C(12)	1.76(1)	C(3)–C(4)	1.49(1)
S(15)–O(17)	1.451(8)	C(4)–C(5)	1.49(1)
S(15)–O(18)	1.402(9)	C(5)–C(6)	1.53(1)
S(15)–C(3)	1.79(1)	C(7)–C(8)	1.53(1)
S(15)–C(16)	1.760(9)	C(8)–C(9)	1.54(2)
O(1)–C(2)	1.39(1)	C(9)–C(10)	1.20(2)

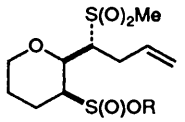
Table 6 Bond angles (°) for compound **21d** with esds in parentheses

O(13)–S(11)–O(14)	116.9(4)	O(1)–C(2)–C(7)	108.4(8)
O(13)–S(11)–C(7)	105.6(4)	C(3)–C(2)–C(7)	114.9(8)
O(13)–S(11)–C(12)	106.7(5)	S(15)–C(3)–C(2)	114.5(7)
O(14)–S(11)–C(7)	111.1(4)	S(15)–C(3)–C(4)	114.7(7)
O(14)–S(11)–C(12)	108.8(5)	C(2)–C(3)–C(4)	107.1(9)
C(7)–S(11)–C(12)	107.3(5)	C(3)–C(4)–C(5)	113.5(9)
O(17)–S(15)–O(18)	117.9(6)	C(4)–C(5)–C(6)	110.7(9)
O(17)–S(15)–C(3)	110.3(5)	O(1)–C(6)–C(5)	109.6(9)
O(17)–S(15)–C(16)	106.9(5)	S(11)–C(7)–C(2)	110.0(7)
O(18)–S(15)–C(3)	109.1(5)	S(11)–C(7)–C(8)	110.4(7)
O(18)–S(15)–C(16)	107.1(5)	C(2)–C(7)–C(8)	114.5(8)
C(3)–S(15)–C(16)	104.6(5)	C(7)–C(8)–C(9)	116(1)
C(2)–O(1)–C(6)	111.1(8)	C(8)–C(9)–C(10)	122(2)
O(1)–C(2)–C(3)	111.1(8)		

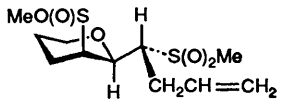
exhibited common conformational properties in deuteriochloroform solution.

To complete this phase of the work, it only remained to demonstrate that derivatives of compound **27a**, at the sulfinic acid oxidation level, could be isolated. When the allyl derivative **11f** was heated with sodium thiophenoxide and thiophenol in THF and the product was then treated sequentially with Amberlite IR-120(H^+) in aq. THF and diazomethane in diethyl ether, three fractions were obtained after chromatography. The first fraction (79% yield) was diphenyl sulfide. The second and third fractions, isolated in yields of 33 and 31%, were diastereoisomers (designated *A* and *B*) of the desired methyl sulfinate **27b**. From the coupling constants of 1.5 Hz between the 2- and 3-hydrogen atoms and 11 Hz between the 2- and 1′-hydrogen atoms (it was not possible to determine $w_{\frac{1}{2}}$-values[19] for the 3-hydrogen atoms because of signal overlap), we infer that both diastereoisomers of the sulfinate **27b** adopt the conformation **28** in deuteriochloroform solution.

As already mentioned, the allyl derivative **11f** was converted into the sulfonate salt **21c** when subjected to the action of



27
a; R = Na
b; R = Me
c; R = H



28

sodium amalgam (~4 mass equiv.) in ice-cold methanol. However, in a re-examination of the reaction, it was discovered that use of a large amount of the reducing agent (~36 mass equiv.) brought about the desired reaction to give the sulfinate salt **27a**. An acidic work-up and treatment of the product with diazomethane led, after chromatography, to the isolation of isomer *A* of the sulfinate **27b** in 31% yield and isomer *B* of the sulfinate **27b** in 30% yield.

The unlikely possibility that the sulfinate salt **27a** formed in the foregoing reaction arose by reduction of the sulfonate salt **21c** was excluded by subjecting the sulfonate **21c** to the modified conditions. Only the sulfonate **21a** was obtained following acidic work-up and treatment of the product with diazomethane. Clearly, in the presence of a large excess of sodium amalgam, the allyl derivative **11f** undergoes a reductive cleavage of its S(7)–C(8) bond to give the sulfinate salt **27a**.

In summary, methodology has been devised which permits the hydrolytic and reductive cleavage of the S(7)–C(8) bond of the thietane dioxide **10a** to give both the sulfonic acids **15c** and **17c** and the sulfinic acid **9a**. A range of alkyl groups can be introduced at C(8) of compound **10a** in a stereoselective manner. When applied to the allyl derivative **11f**, the ring-opening reactions lead to the formation of the sulfonic acid **21b** and the sulfinic acid **27c** as single diastereoisomers. Overall, therefore, it is possible to install functional *C*-appendages at position 6 and sulfonic/sulfinic acid groups at position 5 of 3,4-dihydro-2*H*-pyran in a *syn*-selective manner.

Experimental

Dry solvents/reagents, referred to in the ensuing experiments, were prepared in the following manner: acetonitrile and DMF were stored over 4 Å molecular sieves; THF was stored over calcium chloride and, immediately prior to use, was distilled from sodium–benzophenone; methanol was distilled from magnesium turnings and iodine; triethylamine was stored over sodium hydroxide pellets. Light petroleum refers to that fraction boiling in the range 40–60 °C. Sodium hydride (60% dispersion in mineral oil) was washed (× 3) with sodium-dried light petroleum and dried (*in vacuo*; $CaCl_2$) prior to use. Ozone was generated using a Wallace and Tieman ozonator. Diazomethane (in Et_2O) was prepared from Diazald and potassium hydroxide.[22]

TLC was performed on Schleicher and Schull plastic sheets coated with silica gel (F 1500 LS254); the plates were initially examined under UV light and spots were visualised with iodine vapour. Column chromatography was effected, under pressure, using Merck Kieselgel (Type 60H). Evaporations refer to the removal of solvents at ≤40 °C using a Buchi rotary evaporator. M.p.s were determined using a Kofler hot-stage apparatus. IR spectra were recorded using a Hilger and Watts Infrascan, a Perkin-Elmer Type 257, a Perkin-Elmer Type 783 or a Nicolet 20 SXB FT spectrometer. A Unicam SP 800 or a Perkin-Elmer Lambda 15 was employed to measure UV spectra; extinction coefficients (ε) are presented in cm^2 $mmol^{-1}$. ^1H NMR spectra were recorded at 300 MHz on either a Bruker WM 300-WB or a Bruker AC 300 spectrometer; coupling constants (*J*) and separations are given in Hz. EI mass spectra were

determined using an AEI MS9 spectrometer; FAB mass spectra were recorded with a Kratos MS45 instrument using *m*-nitrobenzyl alcohol as the sample matrix.

Preparation of (1R*,6S*,8R*)-8-*Methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*Dioxide* **10a**.—Methanesulfonyl chloride (34 cm^3, 51.5 g, 0.45 mol) was added during 1 h to a vigorously stirred, cooled (solid CO_2–MeCN) solution of dry triethylamine (91 cm^3, 66.0 g, 0.65 mol) in dry acetonitrile (175 cm^3). After a further 1 h, 3,4-dihydro-2*H*-pyran (20.5 cm^3, 18.9 g, 0.23 mol) was added during 15 min and the mixture was stirred at ~ −40 °C for 1 h and then allowed to warm to room temperature. The insoluble material was filtered off and washed twice with hot ethyl acetate. Evaporation of the combined filtrate and washings left a dark-brown oil which crystallised. Recrystallisation of the material from ethyl acetate gave the title compound **10a** (24.0 g, 44%), m.p. 169–170 °C (lit.,[3] 166–167 °C); ν_{max}(KBr)/cm^{-1} 1335, 1305, 1170 and 1160 (SO_2); λ_{max}(EtOH)/nm no absorption; δ(300 MHz; $CDCl_3$) 1.51–1.62, 1.96–2.24 and 2.40–2.48 [1, 2 and 1 H, m, m and dm (separation 12), 4- and 5-H_2], 3.22 (3 H, s, $MeSO_2$), 3.45 and 3.99–4.06 [each 1 H, dt (*J* 11.5, 11.5 and 2.5) and dm (separation 11.5), 3-H_2], 4.70 (1 H, dt, *J* 6, 6 and 2, 6-H), 4.79 (1 H, d, *J* 6, 1-H) and 5.07 (1 H, s, 8-H) (addition of D_2O caused no change); δ(300 MHz; CD_3SOCD_3) 1.50–1.60, 1.85–2.00, 2.05–2.20 and 2.25–2.40 (each 1 H, m, 4- and 5-H_2), 3.34 (3 H, s, $MeSO_2$), 3.42–3.60 and 3.90–4.05 (each 1 H, m, 3-H_2), 4.58 and 4.73 [0.2 and 0.8 H, t (separation 6) and dt (*J* 7, 7 and 3), 6-H], 4.80 and 4.85 [0.2 and 0.8 H, t (*J* 6) and dd (*J* 7 and 2), 1-H], and 6.14 and 6.50 [0.8 and 0.2 H, d (*J* 2) and d (*J* 6), 8-H] [addition of D_2O caused the signals at δ 6.14 and 6.50 to disappear, the signal at δ 4.80 to appear as a doublet (*J* 6), and the signal at δ 4.85 to appear as a doublet (*J* 7)]; *m*/*z* (FAB) 394 (M + $C_7H_8NO_3^+$, 68%), 376 (M + $C_7H_6NO_2^+$, 50), 241 (MH^+, 100) and 97 (31) (Found: C, 35.2; H, 5.0; S, 27.1. Calc. for $C_7H_{12}O_5S_2$: C, 35.0; H, 5.05; S, 26.7%).

Reaction of the Bicycle **10a** *with Methyl Iodide*.—An ice-cooled mixture of the bicycle **10a** (0.550 g, 2.29 mmol) and sodium hydride (0.061 g, 2.5 mmol) in dry DMF (20 cm^3) was stirred for 0.5 h and then treated with methyl iodide (1.0 cm^3, 2.3 g, 16 mmol). The mixture was allowed to warm to room temperature and, after 2 h, it was diluted with diethyl ether (75 cm^3) and washed with brine (3 × 50 cm^3). Evaporation of the dried ($MgSO_4$) organic phase and subjection of the residue to silica gel column chromatography gave two fractions.

The first fraction, eluted with light petroleum–diethyl ether (2:1) and recrystallised from methylene dichloride–carbon tetrachloride, was (1R*,6S*,8R*)-8-*methyl*-8-*methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*dioxide* **10b** (0.221 g, 38%), m.p. 135–137 °C; ν_{max}(KBr)/cm^{-1} 1330, 1325, 1305, 1285 and 1150 (SO_2); λ_{max}(EtOH)/nm no absorption; δ(300 MHz; $CDCl_3$) 1.47–1.57, 1.92–2.17 and 2.38–2.48 [1, 2 and 1 H, m, m and dm (separation 13), 4- and 5-H_2], 1.84 (3 H, s, 8-Me), 3.17 (3 H, s, $MeSO_2$), 3.44 and 4.01–4.07 [each 1 H, dt (*J* 11.5, 11.5 and 2.5) and dm (separation 11.5), 3-H_2], 4.65 (1 H, d, *J* 6.5, 1-H) and 4.82 (1 H, dt, *J* 6.5, 6.5 and 2, 6-H) [irradiation at δ 3.44 caused the signal at δ 4.03 to appear as a multiplet; irradiation at δ 4.03 caused the signal at δ 1.92–2.17 to simplify and that at δ 3.44 to appear as a double doublet (*J* 11.5 and 2); irradiation at δ 4.65 resulted in the collapse of the signal at δ 4.82 to a broad doublet (*J* 6.5); irradiation at δ 4.82 caused the signal at δ 1.92–2.17 to simplify and that at δ 4.65 to collapse to a singlet] (in an NOED spectroscopic experiment, the signals at δ 1.84 and 3.17 were irradiated; no enhancements were observed); *m*/*z* (EI) 254 (M^+), 175, 110 and 84 (base peak) (Found: C, 38.1; H, 5.5; M^+, 254.0271. $C_8H_{14}O_5S_2$ requires C, 37.8; H, 5.55%; *M*, 254.0283).

The second fraction, eluted with light petroleum–diethyl ether (1:1) and recrystallised from methylene dichloride–carbon tetrachloride, was (1R*,6S*,8S*)-8-*methyl*-8-*methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*dioxide* **11b** (0.070 g, 12%), m.p. 144–145 °C; ν_{max}(KBr)/cm^{-1} 1315, 1300, 1150 and 1140 (SO_2); δ(300 MHz; $CDCl_3$) 1.47–1.60, 1.97–2.22 and 2.46–2.51 [1, 2 and 1 H, m, m, and dm (separation 13), 4- and 5-H_2], 1.97 (3 H, s, 8-Me), 3.39 and 4.07–4.11 [each 1 H, dt (*J* 11.5, 11.5 and 2.5) and dm (separation 12), 3-H_2], 3.46 (3 H, s, $MeSO_2$) and 4.30–4.36 (2 H, m, 1- and 6-H) [irradiation at δ 3.39 caused the signal at δ 1.97–2.22 to simplify and the signal at δ 4.09 to appear as a broad singlet; irradiation at δ 4.09 resulted in a simplification of the signal at δ 1.97–2.22 and in the collapse of the signal at δ 3.39 to a double doublet (*J* 11.5 and 2.5)] (in an NOED spectroscopic experiment, irradiation of the signal at δ 1.97 caused a 13% enhancement of the signal at δ 4.30–4.36; there was no enhancement when the signal at δ 3.46 was irradiated); *m*/*z* (EI) 254 (M^+), 175, 110 and 84 (base peak); *m*/*z* (FAB) 277 (MNa^+, 26%) and 255 (MH^+, 100) (Found: C, 38.0; H, 5.6%).

Reaction of the Bicycle **10a** *with Chloromethyl Methyl Ether*.—An ice-cooled mixture of the bicycle **10a** (0.314 g, 1.30 mmol) and sodium hydride (0.034 g, 1.42 mmol) in dry DMF (6 cm^3) was stirred for 0.5 h and then treated with chloromethyl methyl ether (0.16 cm^3, 0.17 g, 2.1 mmol). The mixture was allowed to warm to room temperature and, after 2 h, it was diluted with diethyl ether (75 cm^3) and washed with brine (3 × 50 cm^3). Evaporation of the dried ($MgSO_4$) organic phase and subjection of the residue to silica gel column chromatography gave two fractions.

The first fraction, eluted with light petroleum–diethyl ether (3:1) and recrystallised from methylene dichloride–carbon tetrachloride, was (1R*,6S*,8R*)-8-*methoxymethyl*-8-*methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*dioxide* **10c** (0.060 g, 16%), m.p. 140–141 °C; ν_{max}(KBr)/cm^{-1} 1330, 1320, 1310, 1285, 1150 and 1120 (SO_2); δ(300 MHz; $CDCl_3$) 1.48–1.56, 1.91–2.16 and 2.39–2.47 [1, 2 and 1 H, m, m and dm (separation 13), 4- and 5-H_2], 3.37 and 3.95–3.99 [each 1 H, dt (*J* 11.5, 11.5 and 2.5) and dm (separation 12), 3-H_2], 3.36 and 3.44 (each 3 H, s, $MeSO_2$ and MeO), 4.05 and 4.35 (each 1 H, d, *J* 11.5, CH_2OMe), 4.68 (1 H, d, *J* 6.5, 1-H) and 4.77 (1 H, br t, separation 6.5, 6-H); *m*/*z* (EI) 284 (M^+), 252, 205 and 189 (base peak) (Found: C, 37.8; H, 5.8; M^+, 284.0398. $C_9H_{16}O_6S_2$ requires C, 38.0; H, 5.65%; *M*, 284.0388).

The second fraction, eluted with light petroleum–diethyl ether (1:1) and recrystallised from methylene dichloride–carbon tetrachloride, was (1R*,6S*,8S*)-8-*methoxymethyl*-8-*methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*dioxide* **11c** (0.220 g, 59%), m.p. 155–156 °C; ν_{max}(KBr)/cm^{-1} 1320 and 1140 (SO_2); δ(300 MHz; $CDCl_3$) 1.51–1.59, 1.92–2.17 and 2.40–2.47 [1, 2 and 1 H, m, m and dm (separation 13), 4- and 5-H_2], 3.40 and 4.06–4.11 [each 1 H, dt (*J* 11.5, 11.5 and 2.5) and dm (separation 12), 3-H_2], 3.457 and 3.463 (each 3 H, s, $MeSO_2$ and MeO), 4.17 and 4.40 (each 1 H, d, *J* 11, CH_2OMe), 4.36–4.43 (1 H, m, 6-H) and 4.69 (1 H, d, *J* 5.5, 1-H); *m*/*z* (EI) 284 (M^+), 205 and 189 (base peak) (Found: C, 37.6; H, 5.6%; M^+, 284.0393).

Preparation of (1R*,6S*,8S*)-8-*Benzyl*-8-*methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*Dioxide* **11d**.—An ice-cooled mixture of the bicycle **10a** (1.00 g, 4.16 mmol) and sodium hydride (0.110 g, 4.6 mmol) in dry DMF (8 cm^3) was stirred for 0.5 h and then treated with benzyl chloride (0.50 cm^3, 0.53 g, 4.6 mmol). The mixture was allowed to warm to room temperature and, after 4 h, it was diluted with diethyl ether (80 cm^3) and washed with brine (3 × 50 cm^3). Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from methylene dichloride–carbon tetrachloride gave the *title com-*

pound **11d** (1.05 g, 76%), m.p. 172–173 °C; ν_{max}(KBr)/cm^{-1} 1310, 1150 and 1135 (SO_2); λ_{max}(EtOH)/nm 209 (ε 9100); δ(300 MHz; $CDCl_3$) 1.38–1.47, 1.64–1.78, 2.00–2.16 and 2.27–2.35 [each 1 H, m, m, m and dm (separation 13), 4- and 5-H_2], 3.24 and 4.00–4.06 [each 1 H, dt (*J* 12, 12 and 2.5) and dm (separation 12), 3-H_2], 3.31 (1 H, br t, separation 6, 6-H), 3.53 (3 H, s, $MeSO_2$), 3.70 and 3.94 (each 1 H, d, *J* 15, CH_2Ph), 4.28 (1 H, d, *J* 5.5, 1-H), and 7.31–7.41 and 7.45–7.50 (3 and 2 H, each m, Ph) [irradiation at δ 4.28 caused the signal at δ 3.31 to appear as a double doublet (*J* 7 and 1)] (in an NOED spectroscopic experiment, irradiation of the signal at δ 3.31 caused a 7.9% enhancement of that at δ 4.28; irradiation of the signal at δ 4.03 enhanced that at δ 3.24 by 13.5%; irradiation of the signal at δ 4.28 resulted in a 7.2% enhancement of that at δ 3.31 and a 3.5% enhancement of the signal at δ 7.45–7.50; no enhancements were observed when the signals at δ 3.53, 3.70 and 3.94 were irradiated); *m/z* (EI) 251 (base peak); *m/z* (FAB) 331 (MH^+, 40%), 159 (68), 137 (44), 109 (57) and 95 (100) (Found: C, 50.7; H, 5.7; S, 19.4. $C_{14}H_{18}O_5S_2$ requires C, 50.9; H, 5.50; S, 19.4%).

Preparation of tert-*Butyl* (1R*,6S*,8S*)-8-*Methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane*-8-*acetate* 7,7-*Dioxide* **11e**.—An ice-cooled mixture of the bicycle **10a** (1.06 g, 4.40 mmol) and sodium hydride (0.115 g, 4.8 mmol) in dry DMF (10 cm^3) was stirred for 0.5 h and then treated with *tert*-butyl bromoacetate (0.75 cm^3, 0.90 g, 4.6 mmol). The mixture was allowed to warm to room temperature and, after 3 h, it was diluted with diethyl ether (150 cm^3) and washed with brine (4 × 75 cm^3). Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from carbon tetrachloride gave the *title compound* **11e** (as a CCl_4 solvate) (1.60 g, 72%), m.p. 80–84 °C (with gas evolution); ν_{max}(KBr)/cm^{-1} 1740 (ester C=O), 1310, 1150 and 1140 (SO_2); λ_{max}(EtOH)/nm no absorption; δ(300 MHz; $CDCl_3$) 1.48 (9 H, s, Me_3C), 1.52–1.60, 2.03–2.11 and 2.42–2.47 (1, 2 and 1 H, each m, 4- and 5-H_2), 3.21 and 3.44 (each 1 H, d, *J* 16.5, CH_2CO_2), 3.44–3.50 and 4.06–4.10 (each 1 H, m, 3-H_2), 3.51 (3 H, s, $MeSO_2$), 4.60–4.65 (1 H, m, 6-H) and 5.25 (1 H, d, *J* 6, 1-H) [irradiation of the signal at δ 4.63 caused the signals at δ 2.03–2.11 and 2.42–2.47 to simplify and the signal at δ 5.25 to collapse to a singlet; irradiation of the signal at δ 5.25 caused the signal at δ 4.60–4.65 to appear as a double doublet (*J* 6 and 3)] (in an NOED spectroscopic study, irradiation of the signal at δ 3.51 enhanced that at δ 5.25 by 9% and that at δ 4.06–4.10 by 10.5%); δ(300 MHz; C_6D_6) 0.86–1.00 and 1.62–1.72 (each 1 H, m, 5-H_2), 1.43 (9 H, s, Me_3C), 2.51 (1 H, dt, *J* 11, 11 and 3, 3-H), 3.19 (3 H, s, $MeSO_2$), 3.25 and 3.68 (each 1 H, d, *J* 16.5, CH_2CO_2), 3.90–3.97 (1 H, m, 6-H) and 5.01 (1 H, d, *J* 6, 1-H) (the signal at δ 1.43 obscured the signal for 4-H_2 and that at δ 3.19 obscured that for 3-H) [in an NOED spectroscopic experiment, irradiation of the signal at δ 2.51 caused a 6.9% enhancement of that at δ 5.01; irradiation of the signal at δ 3.19 enhanced the signals at δ 2.51 (8.0%), 3.68 (2.9%) and 5.01 (1.5%); irradiation of the signal at δ 3.25 resulted in enhancements of the signals at δ 2.51 (10.7%) and 3.68 (6.2%); when the signal at δ 3.68 was irradiated, that at δ 3.25 was enhanced by 6.6%; irradiation of the signal at δ 3.94 caused enhancements of those at δ 3.25 (5.3%) and 5.01 (10.4%); irradiation of the signal at δ 5.01 effected enhancements of those at δ 2.51 (7.1%), 3.68 (3.3%) and 3.90–3.97 (9.4%)]; *m/z* (EI) 281, 219 (base peak), 201, 198 and 155; *m/z* (FAB) 357 (MH_3^+, 40%), 355 (MH^+, 17), 299 ($MH^+ - C_4H_8$, 100), 281 (64) and 201 (69) (Found: C, 33.2; H, 4.2. $C_{13}H_{22}O_7S_2 \cdot CCl_4$ requires C, 33.1; H, 4.35%).

Preparation of (1R*,6S*,8S*)-8-*Allyl*-8-*methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*Dioxide* **11f**.—An ice-cooled mixture of the bicycle **10a** (13.0 g, 54.0 mmol) and sodium hydride (1.38 g, 56 mmol) in dry DMF (170 cm^3) was stirred for 1 h and then treated with allyl bromide (18.5 cm^3, 26.0 g, 215 mmol). The mixture was allowed to warm to room temperature and, after 18 h, was concentrated. Boiling chloroform (50 cm^3) was added to the residue and the mixture was filtered through Celite. Cooling of the filtrate to −20 °C and filtration gave the *title compound* **11f** (14.0 g, 92%), m.p. 151–152 °C; ν_{max}(KBr)/cm^{-1} 1640 (C=C), 1330, 1305, 1290, 1150 and 1135 (SO_2); λ_{max}(EtOH)/nm no absorption; δ(300 MHz; $CDCl_3$) 1.52–1.60, 1.93–2.20 and 2.43–2.49 [1, 2 and 1 H, m, m, and dm (separation 14), 4- and 5-H_2], 3.06 and 3.34 (each 1 H, dd, *J* 15 and 7.5, CH_2CH:CH_2), 3.38 and 4.06–4.10 [each 1 H, dt, (*J* 11.5, 11.5 and 2) and dm (separation 11.5), 3-H_2], 3.48 (3 H, s, $MeSO_2$), 4.18 (1 H, br t, separation 7, 6-H), 4.44 (1 H, d, *J* 5.5, 1-H), 5.34–5.40 (2 H, m, CH:CH_2) and 5.98–6.12 (1 H, m, C*H*:CH_2) [in an NOED spectroscopic experiment, irradiation of the signal at δ 3.06 caused enhancements of the signals at δ 3.34 (10.3%), 4.18 (2.1%), 4.44 (1.4%), 5.34–5.40 (1.8%) and 5.98–6.12 (3.1%); irradiation of the signal at δ 4.09 caused an 8.8% enhancement of that at δ 3.38; irradiation of the signal at δ 4.18 enhanced those at δ 3.06 (2.8%), 4.44 (5%) and 5.98–6.12 (4.7%); irradiation of the signal at δ 4.44 enhanced the signals at δ 3.38 (2.8%), 4.18 (4.6%), 5.34–5.40 (1.8%) and 5.98–6.12 (3.8%); when the signal at δ 5.34–5.40 was irradiated, enhancements were observed for the signals at δ 4.44 (2.2%) and 5.98–6.12 (6.9%); irradiation of the signal at δ 5.98–6.12 resulted in enhancement of the signals at δ 4.18 (2.7%), 4.44 (1.9%) and 5.34–5.40 (4.9%)]; *m/z* (FAB) 281 (MH^+, 42%), 155 (60), 137 (77), 107 (59) and 89 (100) (Found: C, 42.8; H, 5.6; S, 22.8. $C_{10}H_{16}O_5S_2$ requires C, 42.8; H, 5.75; S, 22.9%).

Crystal Data for Compound **11f**.—$C_{10}H_{16}O_5S_2$, *M*, 280.4. Monoclinic, *a* = 12.804(6), *b* = 8.973(5), *c* = 22.834(9) Å, β = 102.62(5)°, *V* = 2560 Å^3 (by least-squares refinement on setting angles of 25 accurately centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (No. 14), *Z* = 8 (2 molecules in the asymmetric unit), D_x = 1.455 g cm^{-3}. Plates. Crystal dimensions: 0.3 × 0.2 × 0.05 mm, μ(Mo-Kα) = 4.04 cm^{-1}.

Data collection and processing. Rigaku AFC6S diffractometer, $\omega/2\theta$ scan mode with ω scan width = 1.37 + 0.30 tanθ and ω scan speed 4 deg min^{-1} {with 2 re-scans of weak reflections [$I < 10\sigma(I)$]}, graphite-monochromated Mo-Kα radiation; 5173 reflections measured ($0 < \theta < 25°$), 4837 unique [merging *R* = 0.047 after absorption correction (max, min transmission factors = 0.80, 1.11)], giving 2369 with $I > 2\sigma(I)$. Intensity standards measured repeatedly during data collection showed negligible decline.

Structure analysis and refinement. Direct methods (MITHRIL)[23] revealed all non-hydrogen atoms including minor disordered sites for the terminal double-bond carbons. Full-matrix least-squares refinement (TEXSAN)[24] with all non-hydrogen atoms anisotropic (except for the disordered carbon atoms which were subjected to isotropic refinement) and hydrogen atoms placed in calculated positions with fixed isotropic vibrational parameters. The weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.03\ F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final *R*- and R_w-values were 0.049, 0.062. Neutral-atom scattering factors[25] were used throughout. All calculations were carried out on a Digital VAX station 3520. Fractional atomic co-ordinates are presented in Table 1, bond lengths in Table 2, and bond angles in Table 3. The molecule, and its atomic labelling, is displayed in Fig. 1. Full lists of the fractional atomic co-ordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data centre.*

* *Supplementary publication* (see section 5.6.3. of 'Instructions for Authors,' Issue 1).

Preparation of Methyl (1R*,6S*,8S*)-8-*Methylsulfonyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane*-8-*acetate* 7,7-*Dioxide* **11g**.—(*a*) Ozone was bubbled for 12 h through a solution of the benzyl derivative **11d** (0.330 g, 1.00 mmol) in acetic acid (25 cm^3). 30% Aq. hydrogen peroxide (5 cm^3) was added to the mixture, which was then stirred overnight and then concentrated. The syrupy residue was dissolved in ethyl acetate (25 cm^3) and the solution was extracted with saturated aq. sodium hydrogen carbonate (2 × 25 cm^3). After acidification, the aqueous phase was extracted with ethyl acetate (2 × 25 cm^3). The extract was washed with water (10 cm^3), dried ($MgSO_4$), and concentrated. Methylene dichloride (25 cm^3) was added to the syrupy residue (0.178 g) and the ice-cooled solution was treated with an excess of diazomethane in diethyl ether. After 5 h, the mixture was concentrated and the residue was subjected to silica gel column chromatography [Et_2O–hexanes (1:1) as eluent] to give the *title compound* **11g** (0.072 g, 23%) as a chromatographically homogeneous syrup which slowly crystallised, m.p. 125–126 °C; ν_{max}(film)/cm^{-1} 1745 (ester C=O), 1315, 1290, 1150 and 1135 (SO_2); λ_{max}(EtOH)/nm 202 (590) and 219 (470); δ(300 MHz; $CDCl_3$) 1.55–1.63, 2.00–2.18 and 2.40–2.48 (1, 2 and 1 H, each m, 4- and 5-H_2), 3.26 and 3.55 (each 1 H, d, *J* 16.5, CH_2CO_2), 3.48 and 4.08–4.14 [each 1 H, dt (*J* 11, 11 and 3) and m, 3-H_2], 3.51 (3 H, s, $MeSO_2$), 3.76 (3 H, s, MeO), 4.57–4.65 (1 H, m, 6-H) and 5.26 (1 H, d, *J* 6, 1-H); *m/z* (FAB) 313 (MH^+, 100%), 201 (31), 154 (26) and 89 (38) (Found: C, 38.8; H, 4.9; S, 20.1. $C_{10}H_{16}O_7S_2$ requires C, 38.5; H, 5.15; S, 20.5%).

(*b*) Ozone was bubbled through a cooled (solid CO_2–Me_2CO) solution of the allyl derivative **11f** (0.200 g, 0.713 mmol) in methylene dichloride (50 cm^3) for 3 h. Formic acid (7 cm^3) and 30% aq. hydrogen peroxide (4 cm^3) were added to the mixture, which was then allowed to warm to room temperature and then concentrated. The residue was dissolved in ethyl acetate (50 cm^3) and the solution was washed with brine (2 × 25 cm^3), dried ($MgSO_4$), and concentrated. An ice-cooled solution of the residue in methylene dichloride (50 cm^3) was treated with an excess of diazomethane in diethyl ether for 6 h. Evaporation and subjection of the residue to silica gel column chromatography [light petroleum–Et_2O (1:1) as eluent] gave a syrup (0.125 g, 56%), which was identified as the title compound **11g** by its 300 MHz ^1H NMR spectrum.

(*c*) A solution of the *tert*-butyl ester **11e** (as a CCl_4 solvate) (0.120 g, 0.236 mmol) in deuteriochloroform (1 cm^3) was treated with TFA (0.2 cm^3) and the reaction was monitored by ^1H NMR spectroscopy. After 1 h, when the reaction was complete, the solution was concentrated and the residue was dissolved in methylene dichloride (15 cm^3). An excess of diazomethane in diethyl ether was added to the ice-cooled solution which, after 6 h, was concentrated. Subjection of the residue to silica-gel chromatography (Et_2O as eluent) gave a syrup (0.060 g, 81%), which was identified as the title compound **11g** on the basis of its 300 MHz ^1H NMR spectrum.

Preparation of (2R*)-2-(*Methylsulfonylmethyl*)*tetrahydropyran* **14**.—A stirred mixture of the bicycle **10a** (0.480 g, 2.00 mmol), Raney nickel[26] (~5.0 g) and ethanol (100 cm^3) was heated under reflux for 18 h. The mixture was then filtered through Celite and the filtrate was concentrated. Subjection of the residue (0.216 g) to silica gel column chromatography (Et_2O as eluent) gave two fractions.

The first eluted material (0.076 g, 21%) was the *title compound* **14**. After trituration with diethyl ether, it was obtained as a solid with m.p. 103–104 °C; ν_{max}(KBr)/cm^{-1} 1290 and 1140 (SO_2); λ_{max}(EtOH)/nm 203 (510), 224 (180) and 274 (20); δ(300 MHz; $CDCl_3$) 1.32–1.44, 1.48–1.64 and 1.83–1.92 (1, 4 and 1 H, each m, 3-, 4- and 5-H_2), 2.90 (1 H, dq, *J* 15 and 1, C*H*HSO_2), 3.00 (3 H, d, *J* 1, $MeSO_2$), 3.22 (1 H, dd, *J* 15 and 10, CH*H*SO_2), 3.44–3.54 (1 H, m, 2-H) and 3.86–4.00 (2 H, m, 6-H_2); *m/z* (FAB) 391 (100%), 179 (MH^+, 12) and 149 (60) (Found: C, 47.4; H, 8.3; 17.6. $C_7H_{14}O_3S$ requires C, 47.2; H, 7.90; S, 18.0%).

The second eluted material (0.068 g, 14% recovery), isolated as a solid, was the starting material **10a** on the basis of 300 MHz ^1H NMR spectroscopy.

Preparation of (1R*,6S*,8S*)-8-*Methylsulfonyl*-8-*propyl*-2-*oxa*-7-*thiabicyclo*[4.2.0]*octane* 7,7-*Dioxide* **11h**.—A stirred mixture of the allyl derivative **11f** (0.050 g, 0.18 mmol), Raney nickel[26] (~0.4 g) and ethanol (20 cm^3) was heated under reflux for 16 h, cooled, and filtered through Celite. Concentration of the filtrate and crystallisation of the residue from methylene dichloride–carbon tetrachloride gave the *title compound* **11h** (0.041 g, 81%), m.p. 163–164 °C; ν_{max}(KBr)/cm^{-1} 1330, 1305, 1150 and 1130 (SO_2); λ_{max}(EtOH)/nm 201 (230); δ(300 MHz; $CDCl_3$) 1.02 (3 H, t, *J* 7.5, *Me*CH_2), 1.53–2.21 and 2.45–2.62 (6 and 2 H, each m, CH_2CH_2Me, and 4- and 5-H_2), 3.39 and 4.08–4.13 [each 1 H, dt (*J* 11.5, 11.5 and 2.5) and dm (separation 11.5), 3-H_2], 3.45 (3 H, s, $MeSO_2$), 4.26–4.30 (1 H, m, 6-H) and 4.50 (1 H, d, *J* 5.5, 1-H); *m/z* (EI) 189, 149, 109 and 91; *m/z* (FAB) 587 (M_2Na^+, 20%), 565 (M_2H^+, 6), 305 (MNa^+, 100) and 283 (MH^+, 100) (Found: C, 42.2; H, 6.7; S, 22.8. $C_{10}H_{18}O_5S_2$ requires C, 42.5; H, 6.45; S, 22.7%).

Preparation of Methyl (2S*,3S*)-2-(*Methylsulfonylmethyl*)-*tetrahydropyran*-3-*sulfonate* **15a**.—(*a*) An ice-cooled mixture of the bicycle **10a** (0.100 g, 0.416 mmol) and 3% sodium amalgam[27] (~0.5 g) in dry methanol (3 cm^3) was stirred for 2 h and then allowed to warm to room temperature. After 16 h, methanol (5 cm^3) was added to the mixture, which was then stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin until acidic. Filtration and evaporation of the filtrate left a residue, which was dissolved in chloroform (15 cm^3). An excess of diazomethane in diethyl ether was added to the ice-cooled solution which, after 16 h, was concentrated. Subjection of the residue to silica gel column chromatography [Et_2O–MeOH (18:1) as eluent] gave the *title compound* **15a** (0.079 g, 70%). After crystallisation from methylene dichloride–carbon tetrachloride, the sample showed m.p. 114 °C; ν_{max}(KBr)/cm^{-1} 1355, 1315, 1300, 1280, 1165 and 1140 (SO_2); δ(300 MHz; $CDCl_3$) 1.48–1.59, 2.02–2.25 and 2.50–2.57 (1, 2 and 1 H, each m, 4- and 5-H_2), 3.02 (3 H, d, *J* 1, $MeSO_2$), 3.27 and 3.80 [each 1 H, br d (separation 15.5) and dd (*J* 15.5 and 10.5), CH_2SO_2Me], 3.34–3.47 (1 H, m, 3-H), 3.65 and 4.09–4.16 [each 1 H, dt (*J* 11.5, 11.5 and 3) and dm (separation 11.5), 6-H_2], 3.94 (3 H, s, MeO) and 4.40 (1 H, dt, *J* 10.5, 2 and 2, 2-H) [irradiation at δ 3.27 caused the signal at δ 3.02 to collapse to a singlet, that at δ 3.80 to collapse to a doublet (*J* 10.5) and that at δ 4.40 to collapse to a double doublet (*J* 10.5 and 2); irradiation at δ 3.40 caused a simplification of the signal at δ 2.02–2.25 and the collapse of the signal at δ 4.40 to a double doublet (*J* 10.5 and 2); irradiation at δ 3.80 caused the signal at δ 3.27 to appear as a broad singlet and that at δ 4.40 to appear as a triplet (*J* 2); irradiation at δ 4.40 resulted in a sharpening of the signals at δ 3.27 and 3.34–3.47 and the collapse of the signal at δ 3.80 to a doublet (*J* 15.5)]; *m/z* (EI) 193 ($M^+ - CH_3O_2S$) and 97 (base peak) (Found: C, 35.4; H, 5.8. $C_8H_{16}O_6S_2$ requires C, 35.3; H, 5.90%).

(*b*) A solution of the bicycle **10a** (0.050 g, 0.21 mmol) and sodium methoxide (0.033 g, 0.61 mmol) in dry methanol (3 cm^3) was stirred for 16 h. The mixture was diluted with methanol (5 cm^3) and stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin until acidic. Filtration and evaporation of the filtrate left a residue, which was dissolved in chloroform (15 cm^3). An excess of diazomethane in diethyl ether was added to the ice-cooled solution which, after 16 h, was concentrated. Subjection of the residue to silica gel column chromatography [Et_2O–MeOH (18:1) as eluent] and crystallisation of the

chromatographed material from methylene dichloride–carbon tetrachloride gave a material (0.046 g, 81%), m.p. 113–114 °C, which was identified as the title compound **15a** by 300 MHz ^{1}H NMR spectroscopy.

Preparation of Methyl (2R*,3S*)-2-(*Methylsulfonylmethyl*)-*tetrahydropyran-3-sulfonate* **17a**.—(*a*) A solution of the bicycle **10a** (2.00 g, 8.32 mmol) and sodium hydroxide (2 mol dm^{-3}; 15 cm^3, 30 mmol) in THF (30 cm^3) was heated under reflux for 3 h. The mixture was ice-cooled, stirred with an excess of Amberlite IR-120 (H^+) ion-exchange resin until acidic, and filtered. Evaporation of the filtrate left a residue, which was dissolved in chloroform (50 cm^3). An excess of diazomethane in diethyl ether was added to the ice-cooled solution which, after 16 h, was concentrated. Subjection of the residue to silica gel column chromatography (CH_2Cl_2 as eluent) gave the *title compound* **17a** (1.42 g, 63%). After crystallisation from methylene dichloride, the sample showed m.p. 131–132 °C; ν_{max}(KBr)/cm^{-1} 1340, 1300, 1160, 1140 and 1115 (SO_2); δ(300 MHz; $CDCl_3$) 1.64–2.00 and 2.42–2.47 [3 and 1 H, m, and dm (separation 13), 4- and 5-H_2], 3.02 (3 H, s, $MeSO_2$), 3.35–3.55 (3 H, m, C*H*HSO_2Me, 3- and 6-H), 3.75 (1 H, dd, *J* 15.5 and 1.5, CH*H*SO_2Me), 3.95 (3 H, s, MeO), 4.01–4.06 (1 H, dm, separation 11, 6-H) and 4.15 (1 H, dt, *J* 8, 8 and 2, 2-H) [irradiation at δ 3.75 caused the signal at δ 3.35–3.55 to simplify and that at δ 4.15 to collapse to a triplet (*J* 8); irradiation at δ 4.04 caused the signals at δ 1.64–2.00, 2.42–2.47 and 3.35–3.55 to simplify; irradiation at δ 4.15 resulted in a simplification of the signal at δ 3.35–3.55 and the collapse of the signal at δ 3.75 to a doublet (*J* 15.5)]; *m/z* (EI) 193 ($M^+ - CH_3O_2S$), 186, 150, 123, 113 and 97 (base peak) (Found: C, 35.1; H, 5.8; S, 23.1 $C_8H_{16}O_6S_2$ requires C, 35.3; H, 5.90; S, 23.55%).

(*b*) A solution of the *cis*-sulfonate **15a** (0.100 g, 0.37 mmol) and sodium hydroxide (2 mol dm^{-3}; 1 cm^3, 2 mmol) in THF (2 cm^3) was heated under reflux for 3 h. Work-up, treatment of the product with diazomethane, chromatography, and recrystallisation of the chromatographed product as before gave the *trans*-sulfonate **17a** (0.083 g, 83%), m.p. 131 °C, identified by its 300 MHz ^{1}H NMR spectrum.

Preparation of Methyl (2S*,3S*)-2-[(1′R*)-1′-(*Methylsulfonyl*)*but-3′-enyl*]*tetrahydropyran-3-sulfonate* **21a**.—(*a*) An ice-cooled mixture of the bicycle **11f** (0.050 g, 0.18 mmol) and 3% sodium amalgam[27] (~0.2 g) in dry methanol (2 cm^3) was stirred for 2 h and then allowed to warm to room temperature. After 16 h, methanol (5 cm^3) was added to the mixture which was then stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin until an acidic solution resulted (pH paper). Filtration and evaporation of the filtrate left a residue, which was dissolved in chloroform (10 cm^3). An excess of diazomethane in diethyl ether was added to the ice-cooled solution which, after 16 h, was concentrated. Subjection of the residue to silica gel column chromatography (Et_2O as eluent) gave the title compound **21a** (0.042 g, 75%) as a syrup. The 300 MHz ^{1}H NMR spectrum of the sample matched that of the product obtained in the following experiment.

(*b*) A mixture of the bicycle **11f** (0.350 g, 1.25 mmol), sodium hydroxide (2 mol dm^{-3}; 5 cm^3, 10 mmol) and THF (10 cm^3) was heated under reflux for 3 h. After having been cooled, the mixture was diluted with THF (25 cm^3) and stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin for 1 h. The resin was filtered and the filtrate was concentrated to leave a residue, which was dissolved in chloroform (100 cm^3). An excess of diazomethane in diethyl ether was added to the ice-cooled solution which, after 16 h, was concentrated. Subjection of the residue to silica gel column chromatography (Et_2O as eluent) gave the *title compound* **21a** (0.168 g, 43%) as a chromatographically homogeneous syrup; ν_{max}(film)/cm^{-1} 1640 (C=C), 1350, 1295, 1165 and 1135 (SO_2); λ_{max}(EtOH)/nm 201 (500) and 230 (200); δ(300 MHz; $CDCl_3$) 1.47–1.53, 1.93–2.05, 2.25–2.38 and 2.50–2.56 [each 1 H, dm (separation 12), m, m, and dm (separation 12), 4- and 5-H_2], 2.64 and 3.08–3.18 [each 1 H, ddd (*J* 16, 10 and 5.5) and m, CH_2CH:CH_2], 3.08 (3 H, s, $MeSO_2$), 3.49–3.53 (1 H, m, 3-H), 3.64 and 4.17 [each 1 H, ddd, (*J* 13, 11.5 and 3) and br dd (*J* 11.5 and 5.5), 6-H_2], 3.73 (1 H, ddd, *J* 11, 5.5 and 3, C*H*SO_2Me), 3.95 (3 H, s, MeO), 4.02 (1 H, dd, *J* 11 and 2, 2-H), 5.09–5.17 (2 H, m, CH:CH_2) and 5.93–6.07 (1 H, m, C*H*:CH_2); *m/z* (FAB) 625 (M_2H^+, 11%) and 313 (MH^+, 100) (Found: C, 42.6; H, 6.7; S, 20.1. $C_{11}H_{20}O_6S_2$ requires C, 42.3; H, 6.45; S, 20.5%).

(*c*) A mixture of the bicycle **11f** (0.168 g, 0.60 mmol), sodium hydroxide (2 mol dm^{-3}; 3 cm^3, 6 mmol) and THF (5 cm^3) was heated under reflux for 3 h. Evaporation of the solvent left a residue, which was dissolved in dry methanol (10 cm^3) and stirred with 3% sodium amalgam[27] (~6.0 g) at 0 °C for 2 h and then at room temperature overnight. The mixture was diluted with methanol (20 cm^3), stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin for 1 h, and filtered through Celite. Evaporation of the solvent left an orange syrup, which was dissolved in chloroform (50 cm^3). The ice-cooled solution was left overnight with an excess of diazomethane in diethyl ether. Evaporation of the solvent left a pale-orange syrup (0.176 g) which was mainly the title compound **21a** on the basis of 300 MHz ^{1}H NMR spectroscopy.

Preparation of Methyl (2R*,3S*)-2-{(1′R*)-1′-([$^2H_3$]*Methylsulfonyl*)[1-^{2}H]*but-3′-enyl*}*tetrahydropyran-3-sulfonate* **23**.—A mixture of the bicycle **11f** (0.168 g, 0.60 mmol), sodium hydroxide (2 mol dm^{-3}; 3 cm^3, 6 mmol) and THF (5 cm^3) was heated under reflux for 3 h. After having been cooled, the mixture was diluted with THF (10 cm^3) and stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin for 1 h. Filtration and evaporation of the filtrate gave a residue, which was dissolved in a mixture of THF (5 cm^3) and sodium deuterioxide (2 mol dm^{-3}; 3 cm^3, 6 mmol). The solution was heated under reflux for 3 h, cooled, diluted with THF (10 cm^3) and stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin for 1 h. Filtration and evaporation of the filtrate gave a residue (0.152 g), which was dissolved in chloroform (75 cm^3). The ice-cooled solution was left overnight with an excess of diazomethane in diethyl ether. Evaporation, and subjection of the residue to silica gel column chromatography (Et_2O as eluent), gave the title compound **23** (0.062 g, 33%) as a syrup; δ(300 MHz; $CDCl_3$) 1.46–1.53, 1.91–2.05, 2.22–2.40 and 2.49–2.57 [each 1 H, dm (separation 12), m, m, and dm (separation 12), 4- and 5-H_2], 2.64 and 3.08–3.18 [each 1 H, dd, (*J* 16 and 10) and dm (separation 16), CH_2CH:CH_2], 3.49–3.53 (1 H, m, 3-H), 3.64 and 4.17 [each 1 H, ddd (*J* 13, 11.5 and 3) and br dd (*J* 11.5 and 5.5), 6-H_2], 3.95 (3 H, s, MeO), 4.02 (1 H, br s, 2-H), 5.09–5.17 (2 H, m, CH:CH_2) and 5.95–6.08 (1 H, m, C*H*:CH_2).

Preparation of (2S*,3S*)-3-*Methylsulfonyl*-2-(*methylsulfonylmethyl*)*tetrahydropyran* **15d**.—A mixture of thiophenol (1.50 cm^3, 1.58 g, 14.3 mmol) and sodium hydride (0.172 g, 7.2 mmol) in dry THF (50 cm^3) was stirred for 0.5 h and then treated with the bicycle **10a** (0.865 g, 3.60 mmol). The mixture was heated under reflux overnight and then concentrated. The residue was dissolved in 80% aq. methanol (120 cm^3) and stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin. After 1 h, the mixture was filtered and the filtrate was stirred with sodium hydrogen carbonate (3.00 g, 36 mmol). Evaporation, after 1 h, left a residue, which was dissolved in dry DMF (30 cm^3) and treated with methyl iodide (4.0 cm^3, 9.1 g, 64 mmol). After 4 h, the mixture was concentrated and the residue was subjected to silica gel column chromatography to give two homogeneous fractions.

The first fraction (0.096 g, 6%) eluted with hexanes, was identified as diphenyl disulfide on the basis of its m.p. of 58–59 °C (lit.,[28] 60–61 °C) and its ^{1}H NMR spectrum [δ(300 MHz; $CDCl_3$) 7.13–7.28 and 7.40–7.48 (6 and 4 H, each m, 2 × Ph)]. [When the filtered ion-exchange resin was stirred with $CHCl_3$ (50 cm^3), the mixture filtered, and the filtrate dried ($MgSO_4$) and concentrated, a further quantity of PhSSPh (1.022 g, 65%), m.p. 58–59 °C, was isolated].

The second fraction (0.348 g, 38%), eluted with diethyl ether–ethyl acetate (1:1) and obtained as a solid, was the *title compound* **15d**, m.p. 146–148 °C; ν_{max}(KBr)/cm^{-1} 1300, 1275, 1140 and 1125; λ_{max}(EtOH)/nm 203 (540) and 219 (970); δ(300 MHz; $CDCl_3$) 1.58–1.68, 2.02–2.20 and 2.38–2.50 (1, 2 and 1 H, each m, 4- and 5-H_2), 3.00 and 3.02 [each 3 H, d (*J* 1) and s, 2 × $MeSO_2$], 3.10–3.16 (1 H, m, 3-H), 3.43 and 3.84 [each 1 H, dq (*J* 15.5 and 1) and dd (*J* 15.5 and 10.5), CH_2SO$_2$Me], 3.66–3.76 and 4.07–4.15 (each 1 H, m, 6-H_2) and 4.50 (1 H, ddd, *J* 10.5, 3 and 2, 2-H) [in a 2D-COSY experiment, the following connectivities were established: δ 4.50 to 3.84 to 3.43 to 3.00; δ 4.50 to 3.43; δ 4.50 to 3.10–3.16 to 2.38–2.50 to 2.02–2.20 to 1.58–1.68; δ 4.07–4.15 to 3.66–3.76 to 2.02–2.20; δ 4.07–4.15 to 2.02–2.20; δ 4.07–4.15 to 1.58–1.68; δ 3.66–3.76 to 1.58–1.68; δ 3.10–3.16 to 2.02–2.20; δ 2.38–2.50 to 1.58–1.68]; *m*/*z* (FAB) 279 (MNa^+, 66%), 257 (MH^+, 100), 176 (67) and 97 (29) (Found: C, 37.8; H, 6.4; S, 25.4. $C_8H_{16}O_5S_2$ requires C, 37.5; H, 6.30; S, 25.0%).

Preparation of (2R*,3S*)-3-*Methylsulfonyl*-2-[(1′R*)-1′-(*methylsulfonyl*)*but*-3′-*enyl*]*tetrahydropyran* **21d**.—A mixture of thiophenol (0.75 cm^3, 0.79 g, 7.2 mmol) and sodium hydride (0.086 g, 3.6 mmol) in dry THF (25 cm^3) was stirred for 0.5 h and then treated with the bicycle **11f** (0.505 g, 1.80 mmol). The mixture was heated under reflux overnight and then concentrated. The residue was dissolved in 80% aq. methanol (60 cm^3) and stirred with an excess of Amberlite IR-120 (H^+) ion-exchange resin. After 1 h, the mixture was filtered and the filtrate was stirred with sodium hydrogen carbonate (1.50 g, 18 mmol). Concentration, after 1 h, left a residue, which was dissolved in dry DMF (15 cm^3) and treated with methyl iodide (2 cm^3, 4.6 g, 32 mmol). After 4 h the mixture was concentrated and the residue was subjected to silica gel column chromatography to give two fractions.

The first fraction (0.056 g, 7%), eluted with hexanes, was identified as diphenyl disulfide on the basis of its m.p. (57–58 °C) and its 300 MHz ^{1}H NMR spectrum. [When the filtered ion-exchange resin was stirred with $CHCl_3$ (25 cm^3), the mixture filtered, and the filtrate dried ($MgSO_4$) and concentrated, a further quantity of PhSSPh (0.522 g, 67%), m.p. 58–59 °C, was isolated.]

The second fraction (0.352 g, 66%), eluted with diethyl ether and isolated as a solid, was the *title compound* **21d**. After recrystallisation from methylene dichloride–carbon tetrachloride, the sample showed m.p. 170–171 °C; ν_{max}(KBr)/cm^{-1} 1640 (C=C), 1290, 1135, 1130 and 1120 (SO_2); λ_{max}(EtOH)/nm 202 (480) and 250 (70); δ(300 MHz; $CDCl_3$) 1.54–1.62, 2.00–2.16, 2.17–2.33 and 2.48–2.56 [each 1 H, dm (separation 12), m, m and dm (separation 12), 4- and 5-H_2], 2.76 and 3.07–3.17 [each 1 H, ddd (*J* 16, 10 and 5) and m, CH_2CH:CH$_2$], 3.04 and 3.07 (each 3 H, s, 2 × $MeSO_2$), 3.24–3.28 (1 H, m, 3-H), 3.70 and 4.20 [each 1 H, dt (*J* 12, 12 and 3) and dd (*J* 12 and 5), 6-H_2], 3.81–3.89 (1 H, m, C*H*CH$_2$CH:CH$_2$), 4.06 (1 H, dd, *J* 11 and 2, 2-H), 5.11–5.17 (2 H, m, CH_2:CH) and 5.92–6.06 (1 H, m, C*H*:CH$_2$) [in a 2D-COSY experiment, the following connectivities were established: δ 5.92–6.06 to 5.11–5.17 to 3.07–3.17 to 2.75; δ 5.92–6.06 to 3.07–3.17; δ 5.92–6.06 to 2.76; δ 5.11–5.17 to 3.07–3.17; δ 5.11–5.17 to 2.76; δ 4.20 to 3.70 to 2.17–2.33 to 1.54–1.62; δ 4.20 to 2.17–2.33; δ 4.20 to 1.54–1.62; δ 4.06 to 3.81–3.89 to 3.07–3.17; δ 4.06 to 3.24–3.28 to 2.48–2.56 to 2.17–2.33; δ 3.81–3.89 to 3.07–3.17; δ 3.81–3.89 to 2.76; δ 3.70 to 2.17–2.33; δ 3.70 to 1.54–1.62; δ 3.24–3.28 to 2.48–2.56; δ 3.24–3.28 to 2.00–2.16 to 1.54–1.62; δ 2.48–2.56 to 2.00–2.16; δ 2.48–2.56 to 1.54–1.62]; *m*/*z* (FAB) 297 (MH^+, 100%) and 155 (32) (Found: C, 44.7; H, 6.7; S, 22.0. $C_{11}H_{20}O_5S_2$ requires C, 44.55; H, 6.80; S, 21.65%).

Crystal Data for Compound **21d**.—$C_{11}H_{20}O_5S_2$, *M*, 296.4. Orthorhombic, *a* = 8201(2), *b* = 10.277(3), *c* = 17.164(7) Å, *V* = 1447 Å^3 (by least-squares refinement on setting angles of 25 accurately centred reflections, λ = 0.710 69 Å), space group $P2_12_12_1$ (No. 19), *Z* = 4, D_x = 1.361 g cm^{-3}. Blocks. Crystal dimensions: 0.2 × 0.2 × 0.15 mm, μ(Mo-Kα) = 3.61 cm^{-1}.

Data collection and processing. Enraf–Nonius CAD-4 diffractometer, $\omega/2\theta$ scan mode with ω scan width = 0.80 + 0.35 tanθ and ω scan speed ranging from 0.5 to 5 deg min^{-1} depending on intensity gathered in a pre-scan, graphite-monochromated Mo-Kα radiation; 2709 reflections measured ($0 < \theta < 24°$), 1363 unique [merging R = 0.041 giving 893 with $I > 3\sigma(I)$]. Intensity standards measured repeatedly during data collection showed no decline.

Structure analysis and refinement. Direct methods (MULTAN-80)[29] revealed all non-hydrogen atoms. Full-matrix least-squares refinement (SHELX-76)[30] with all non-hydrogen atoms anisotropic and hydrogen atoms placed in calculated positions with fixed isotropic vibrational parameters. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.03\ F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R- and R_w-values were 0.056, 0.043. Neutral-atom scattering factors[25] were used throughout. All calculations were carried out on the University of Manchester Computing Centre Amdahl 5760 computer. Fractional atomic co-ordinates are presented in Table 4, bond lengths in Table 5, and bond angles in Table 6. The molecule and its atomic labelling is displayed in Fig. 2. Full lists of the fractional atomic co-ordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Preparation of Methyl (2R*,3S*)-2-[(1′R*)-1′-(*Methylsulfonyl*)*but*-3′-*enyl*]*tetrahydropyran*-3-*sulfinate* **27b**.—(*a*) Sodium hydride (0.086 g, 3.6 mmol) was added to a stirred solution of thiophenol (0.75 cm^3, 0.79 g, 7.2 mmol) in dry THF (25 cm^3) followed, after 0.5 h, by the bicycle **11f** (0.505 g, 1.80 mmol). The mixture was heated under reflux overnight, cooled, diluted with 50% aq. THF (25 cm^3) and then stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin. After 1 h, the mixture was filtered through Celite and the filtrate was concentrated. The yellow residue was dissolved in chloroform (100 cm^3) and the ice-cooled solution was left overnight with an excess of diazomethane in diethyl ether. Evaporation of the solvent and subjection of the residue to silica gel column chromatography gave three fractions.

The first fraction (0.622 g, 79%), eluted with hexanes and isolated as a solid, was identified as diphenyl disulfide on the basis of its m.p. (56–57 °C) and its 300 MHz ^{1}H NMR spectrum.

The second fraction (0.176 g, 33%), eluted with diethyl ether, was *isomer* A of the *title compound* **27b**. After trituration with diethyl ether, it was obtained as a solid (0.144 g, 27%) with m.p. 115–116 °C; ν_{max}(KBr)/cm^{-1} 1645 (C=C), 1290, 1130, 1120 and 1100 (SO_2); λ_{max}(EtOH)/nm 204 (840) and 221 (1400); δ(300 MHz; $CDCl_3$) 1.55–1.61, 1.86–2.02 and 2.25–2.32 (1, 2 and 1 H, each m, 4- and 5-H_2), 2.78 (1 H, ddd, *J* 16, 10 and 5.5, C*H*HCH:CH$_2$), 3.04 (3 H, s, $MeSO_2$), 3.04–3.10 (2 H, m,

* *Supplementary publication* (see section 5.6.3 of 'Instructions for Authors', Issue 1).

CH*H*CH:CH and 3-H), 3.72 and 4.15–4.21 [each 1 H, dt (*J* 12, 12 and 3) and m, 6-H_2], 3.81–3.88 (1 H, m, C*H*SO_2Me), 3.85 (3 H, s, MeO), 4.10 (1 H, dd, *J* 11 and 1.5, 2-H), 5.10–5.18 (2 H, m, CH:CH_2) and 5.86–6.00 (1 H, m, C*H*:CH_2); *m/z* (FAB) 593 (M_2H^+, 12%), 297 (MH^+, 100), 265 ($C_{10}H_{17}O_4S_2^+$, 43) and 217 ($C_{10}H_{17}O_3S^+$, 24) (Found: C, 44.4; H, 7.0; S, 21.2. $C_{11}H_{20}O_5S_2$ requires C, 44.55; H, 6.80; S, 21.65%).

The third fraction (0.166 g, 31%), eluted with diethyl ether, was *isomer* B of the *title compound* **27b**. After trituration with diethyl ether, it was obtained as a solid (0.134 g, 25%) with m.p. 114–115 °C; ν_{max}(KBr)/cm^{-1} 1645 (C=C), 1290 and 1120 (SO_2); λ_{max}(EtOH)/nm 204 (920) and 222 (1530); δ(300 MHz; $CDCl_3$) 1.50–1.56, 1.77–2.03 and 2.55–2.66 [1, 2 and 2 H, br d (separation 12), m and m, 4- and 5-H_2 and C*H*HCH:CH_2], 2.94–3.00 (1 H, dm, separation 16, CH*H*CH:CH_2), 3.08 (4 H, s, $MeSO_2$ and 3-H), 3.24 (1 H, ddd, *J* 11, 6 and 3, C*H*SO_2Me), 3.67 and 4.15 [each 1 H, dt, (*J* 11.5, 11.5 and 2.5) and br dd (*J* 11.5 and 5.5), 6-H_2], 3.84 (3 H, s, MeO), 4.08 (1 H, dd, *J* 11 and 1.5, 2-H), 5.08–5.15 (2 H, m, CH:CH_2) and 5.88–6.02 (1 H, m, C*H*:CH_2); *m/z* (FAB) 593 (M_2H^+, 20%), 297 (MH^+, 100), 265 ($C_{10}H_{17}O_4S_2^+$, 62) and 217 ($C_{10}H_{17}O_3S^+$, 13) (Found: C, 44.4; H, 6.5; S, 22.0%).

(*b*) A mixture of the bicycle **11f** (0.505 g, 1.80 mmol), 3% sodium amalgam[27] (~18.0 g) and anhydrous methanol (20 cm^3) was stirred at 0 °C for 2 h and at room temperature overnight. The mixture was diluted with methanol (50 cm^3) and stirred with an excess of Amberlite IR-120(H^+) ion-exchange resin for 1 h. After having been filtered through Celite, the mixture was concentrated and the residue was dissolved in chloroform (100 cm^3). The ice-cooled solution was left overnight with an excess of diazomethane in diethyl ether. Evaporation, and subjection of the residue to silica gel chromatography (Et_2O as eluent), gave two fractions.

The first eluted material (0.196 g) was triturated with diethyl ether to give isomer *A* of the title compound **27b** (0.166 g, 31%), m.p. 115–116 °C. The 300 MHz ^{1}H NMR spectrum of the material matched that of the sample obtained in the previous experiment.

The second eluted material (0.188 g) was triturated with diethyl ether to give isomer *B* of the title compound **27b** (0.158 g, 30%), m.p. 114–115 °C. The 300 MHz ^{1}H NMR spectrum of the material matched that of the sample obtained in the previous experiment.

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