Preparation of Stable β-Sultines. Crystal Structure of 2,2-Bis-(*p*-fluorophenyl)-3,3-dimethyl-1,2-oxathietan 2-Oxide

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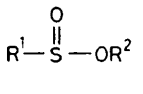
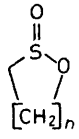
Three 4,4-diaryl-3,3-dimethyl-1,2-oxathietan 2-oxides were prepared by the oxidative cyclisation of 2-hydroxyalkyl t-butyl sulphoxides. They decomposed readily to 1,1-diaryl-2-methylprop-1-enes, but two of them were isolated in crystalline form. The determination of the crystal structure of 4-bis-(*p*-fluorophenyl)-3,3-dimethyl-1,2-oxathietan 2-oxide showed that the oxathietan ring was non-planar, with sulphinyl oxygen pseudo-axially orientated.

OPEN-CHAIN sulphinate esters (1) are easily synthesized[1-3] but their cyclic analogues (2) (sultines) are not so readily available. Before 1967 only one preparation of



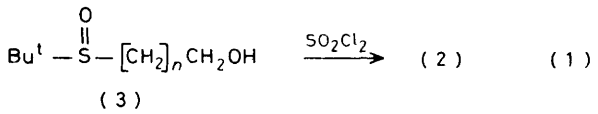
(1)



$n = 2-5$

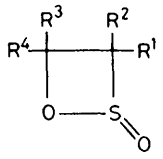
(2)

a sultine had been reported,[4] while in the following years a number of syntheses of particular 5- and 6-membered cyclic sulphinate esters (2; $n = 2$ and 3, respectively)



(3)

have appeared.[5-9] A versatile approach to sultines has been developed in our own laboratories,[10,11] involving the cyclisation of hydroxy-sulphoxide precursors (3), under oxidative conditions, in the presence of sulphuryl chloride or *N*-chlorosuccinimide [equation (1)], and has



(4)

been utilised to investigate the formation of β-sultines (4).

Preliminary studies led to the discovery of an analogue of the Wittig olefin synthesis[12] [equation (2)]. For example, reaction of β-hydroxy-sulphoxides (5) with positive halogen species leads to good yields of alkenes, with concomitant loss of sulphur dioxide and t-butyl halide.

The intermediacy of the β-sultines (6) was suggested; these then undergo thermal extrusion of sulphur dioxide to yield the isolated alkenes, a proposal later supported by the first isolation of a β-sultine[13] produced by a similar route.

Oxidative cyclisation of the β-hydroxy-sulphoxide (7) leads to the formation of a β-sultine (8), which decomposes slowly at room temperature to 2,2-dimethyl-1,1-diphenylethylene [equation (3)].

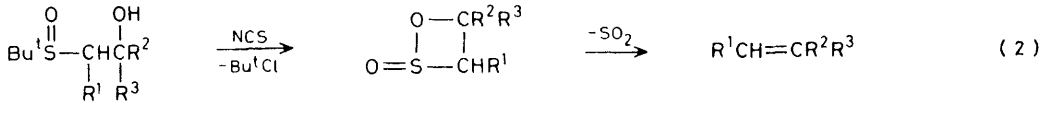
We report here the synthesis and isolation of two further stable β-sultines, and the *X*-ray crystal structure of one of these, 4,4-bis-(*p*-fluorophenyl)-3,3-dimethyl-1,2-oxathietan 2-oxide (11b).

RESULTS AND DISCUSSION

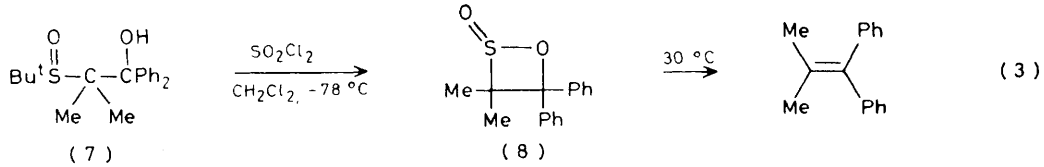
The general route employed to synthesise the tetrasubstituted β-sultines is summarised in Scheme 1.

Reaction of the α-sulphinyl carbanion of sulphoxide (9) with *pp'*-dimethyl- or *pp'*-difluorobenzophenone gave the β-hydroxy-sulphoxides (10a) and (10b) in 51 and 22% yield, respectively.

Treatment of the β-hydroxy-sulphoxides (7), (10a), and (10b) dissolved in dry CH_2Cl_2 at −78 °C with sulphuryl chloride for approximately 30 min, warming to 0 °C, and careful removal of the solvent afforded the crude β-sultines. These were best purified by low-temperature

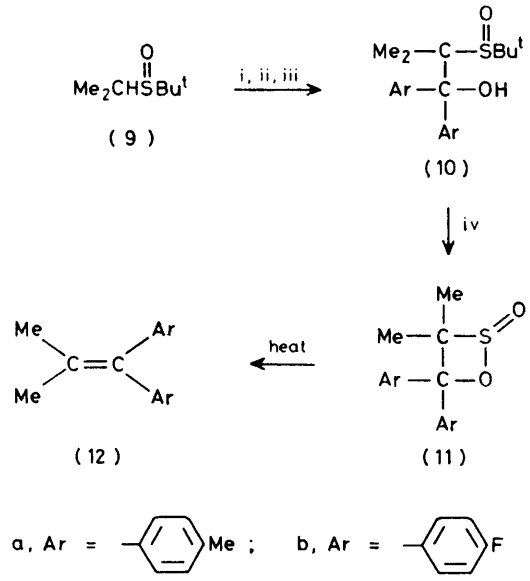


(5) (6) (2)



(7) (8) (3)

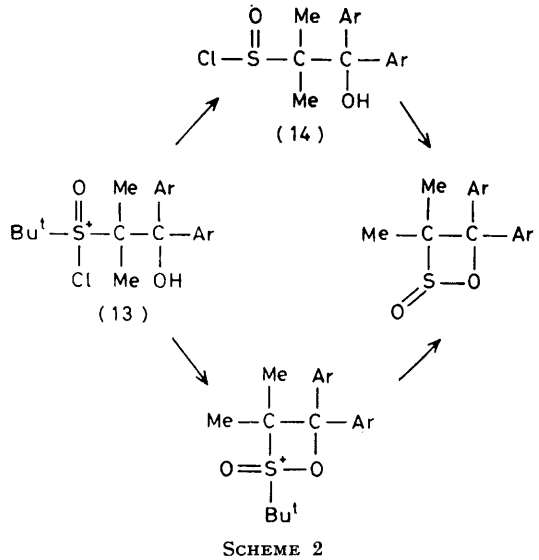
recrystallisation from diethyl ether–hexane. The β-sultines prepared in this manner are colourless, crystalline materials, stable at low temperature but rapidly decomposing on warming. The *pp'*-dimethyl-substituted compound (11a) readily formed 1,1-dimethyl-2,2-bis-(*p*-tolyl)ethylene even at 5 °C and was never obtained



SCHEME 1 *Reagents:* (i) Bu^nLi; (ii) $Ar_2C{=}O$; (iii) H_2O; (iv) SO_2Cl_2

completely free of this contaminant. However, the sultines (8) and (11b) were readily obtained pure.

Two mechanisms have been suggested for the above oxidative cyclisation [11] (Scheme 2), both initially involving addition of a positive halogen species to generate the chloro-oxosulphonium intermediate (13).



SCHEME 2

As can be seen from the Figure, 4,4-bis(*p*-fluorophenyl)-3,3-dimethyl-1,2-oxathietan 2-oxide (and probably all the more stable β-sultines) is non-planar, as has been suggested.[13]

The difference in stability between the tetrasubstituted β-sultines reported here and those bearing fewer substituents, which are unstable at room temperature, may be explained in terms of the interaction of the substituents in both the ground state and in the transition state leading to loss of sulphur dioxide. In the ground state the ring is highly puckered and bulky substituents are accommodated reasonably well. The transition state for the cycloreversion reaction should require shortening of the C–C bond and movement of the carbon substituents into the same plane. This considerably raises the steric interaction between substituents and hence the transition state energy for SO_2 loss, especially when the substituents are large.

As already shown,[12] the loss of sulphur dioxide from β-sultines is a stereospecific *cis* elimination, suggesting that the reaction proceeds in a concerted manner (analogous to the loss of carbon dioxide from β-lactones [14]). The relative insensitivity in the rate of decomposition of (8) to large changes in the dielectric constant of the solvent ($t_{1/2}$ = 24 and 21 h in $CDCl_3$ and CD_3NO_2, respectively) is in agreement with a non-polar transition state, while the stability of (8) and (11) relative to the less substituted sultines argues against a homolytic fission of the C–O bond.

Carlsen and Snyder [15] have reported CNDO–MO studies for the [2 + 2] cycloreversion of β-sultines which indicated that a concerted reaction occurs *via* a suprafacial–antarafacial pathway.

Crystal and Molecular Structure of (11b).—Atomic co-ordinates are given in Table 1 and bond angles are in Table 2. 4,4-Bis-(*p*-fluorophenyl)-3,3-dimethyl-1,2-oxathietan 2-oxide in the crystal adopts the conformation shown in the Figure. The four-membered ring is puckered with a dihedral angle of 20.3° between the

TABLE 1

Fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
S	0.097 47(8)	0.474 43(14)	0.068 57(9)
F(1)	0.226 07(17)	0.464 6(3)	0.479 36(16)
F(2)	−0.043 3(2)	−0.210 5(3)	0.154 06(19)
O(1)	0.137 1(2)	0.593 1(3)	0.115 1(2)
O(2)	0.042 18(16)	0.397 0(3)	0.113 44(18)
C(1)	0.103 7(2)	0.298 0(4)	0.159 8(3)
C(2)	0.158 0(3)	0.319 7(4)	0.107 7(3)
C(3)	0.245 5(3)	0.347 1(5)	0.148 2(3)
C(4)	0.140 8(3)	0.222 1(5)	0.038 2(3)
C(5)	0.138 7(3)	0.345 1(4)	0.245 8(3)
C(6)	0.109 1(3)	0.461 3(5)	0.270 2(4)
C(7)	0.137 7(3)	0.500 9(5)	0.348 5(4)
C(8)	0.196 9(3)	0.426 1(5)	0.400 7(4)
C(9)	0.229 4(3)	0.311 8(5)	0.379 7(3)
C(10)	0.198 9(3)	0.272 3(4)	0.301 5(3)
C(11)	0.064 6(3)	0.159 1(4)	0.155 1(3)
C(12)	0.108 4(3)	0.039 6(5)	0.166 6(3)
C(13)	0.072 5(4)	−0.085 8(5)	0.165 5(3)
C(14)	−0.007 3(4)	−0.086 9(6)	0.153 1(3)
C(15)	−0.053 3(3)	0.027 7(6)	0.141 1(3)
C(16)	−0.016 7(3)	0.151 8(5)	0.141 7(3)

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations

S–O(1)	1.466(4)	C(5)–C(6)	1.394(7)
S–O(2)	1.667(4)	C(5)–C(10)	1.386(6)
S–C(2)	1.856(4)	C(6)–C(7)	1.378(8)
O(2)–C(1)	1.487(5)	C(7)–C(8)	1.360(7)
C(1)–C(2)	1.588(8)	C(8)–C(9)	1.379(8)
C(1)–C(5)	1.526(6)	C(9)–C(10)	1.377(7)
C(1)–C(11)	1.523(6)	C(11)–C(12)	1.387(6)
C(2)–C(3)	1.501(6)	C(11)–C(16)	1.390(7)
C(2)–C(4)	1.522(7)	C(12)–C(13)	1.388(7)
C(8)–F(1)	1.381(6)	C(13)–C(14)	1.364(10)
C(14)–F(2)	1.378(7)	C(14)–C(15)	1.367(8)
		C(15)–C(16)	1.383(8)
O(2)–S–O(1)	109.6(0.2)	C(7)–C(6)–C(5)	120.7(0.4)
C(2)–S–O(1)	109.5(0.2)	C(8)–C(7)–C(6)	118.4(0.5)
C(2)–S–O(2)	79.0(0.2)	C(7)–C(8)–F(1)	119.0(0.5)
C(1)–O(2)–S	97.1(0.3)	C(9)–C(8)–F(1)	117.6(0.4)
C(2)–C(1)–O(2)	93.8(0.3)	C(9)–C(8)–C(7)	123.4(0.5)
C(5)–C(1)–O(2)	109.3(0.3)	C(10)–C(9)–C(8)	117.3(0.4)
C(5)–C(1)–C(2)	116.4(0.3)	C(9)–C(10)–C(5)	121.6(0.5)
C(11)–C(1)–O(2)	108.7(0.3)	C(12)–C(11)–C(1)	121.7(0.4)
C(11)–C(1)–C(2)	117.0(0.4)	C(16)–C(11)–C(1)	119.3(0.4)
C(11)–C(1)–C(5)	110.1(0.4)	C(16)–C(11)–C(12)	119.0(0.4)
C(1)–C(2)–S	86.4(0.3)	C(13)–C(12)–C(11)	121.0(0.5)
C(3)–C(2)–S	114.1(0.3)	C(14)–C(13)–C(12)	117.5(0.5)
C(3)–C(2)–C(1)	119.2(0.4)	C(13)–C(14)–F(2)	118.2(0.5)
C(4)–C(2)–S	106.4(0.3)	C(15)–C(14)–F(2)	118.0(0.6)
C(4)–C(2)–C(1)	114.6(0.4)	C(15)–C(14)–C(13)	123.9(0.5)
C(4)–C(2)–C(3)	112.8(0.5)	C(16)–C(15)–C(14)	117.9(0.5)
C(6)–C(5)–C(1)	120.3(0.4)	C(15)–C(16)–C(11)	120.7(0.5)
C(10)–C(5)–C(1)	121.1(0.4)		
C(10)–C(5)–C(6)	118.5(0.4)		

normals to the three-atom planes meeting at O(2) and C(2) (Table 3). The exocyclic oxygen O(1) adopts an axial position, in contrast to the situation in the *cis*- and *trans*-isomers of 3-*p*-bromophenylthietan 1-oxide [16] where the sulphinyl oxygen is equatorial in both cases. The

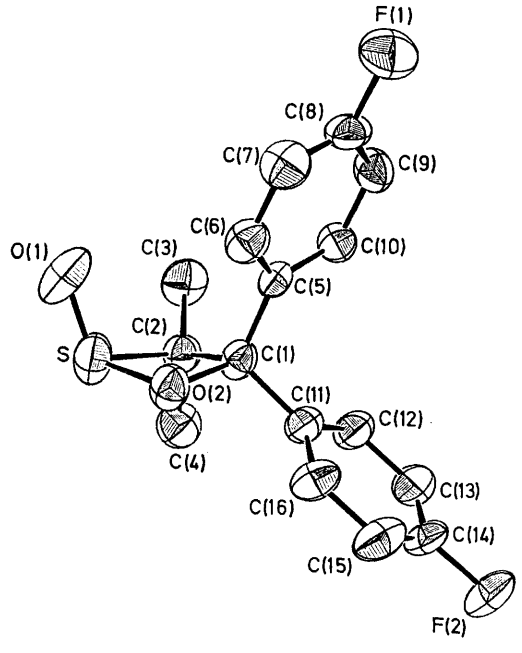


FIGURE The molecular structure of $S(O)OC(Me)_2C(p\text{-}C_6H_4F)_2$ showing the atomic numbering. Hydrogen atoms have been omitted

TABLE 3

Equations of some least-squares planes. Distances (Å) of atoms from these planes are given in square brackets: x,y, and z are fractional co-ordinates

Plane (1): S,O(2),C(2)

$$3.830x + 4.771y + 12.949z = 3.525$$

[O(1) 1.321, C(1) 0.364]

Plane (2): O(2),C(1),C(2)

$$5.243x + 7.221y + 8.446z = 4.048$$

[S 0.469, C(5) 1.252, C(11) −1.248]

Plane (3): C(5)—C(10)

$$-14.404x - 5.542y + 8.289z = -1.878$$

[C(5) 0.005, C(6) −0.011, C(7), C(8), 0.002, C(9) −0.008, C(10) 0.004, F(1) 0.020, C(1) 0.057]

Plane (4): C(11)—C(16)

$$-2.848x + 0.694y + 17.642z = 2.658$$

[C(11) 0.004, C(12) 0.000, C(13) −0.004, C(14) 0.003, C(15) 0.002, C(16) −0.006, F(2) 0.037, C(1) 0.072]

Angles (°) between normals to the planes

(1)–(2)	20.3	(2)–(3)	122.4
(1)–(3)	106.7	(2)–(4)	52.6
(1)–(4)	33.4	(3)–(4)	74.2

dihedral angles in the thietan 1-oxide isomers are larger however, **33** and 32° for *cis* and *trans* respectively, so the distinction between axial and equatorial positions is more marked. Torsion angles (Table 4) O(1)–S–O(2)–

TABLE 4

Selected torsion angles (°) [a]

O(1)–S–O(2)–C(1)	−92.7	S–O(2)–C(1)–C(11)	−136.6
C(2)–S–O(2)–C(1)	14.3	O(2)–C(1)–C(2)–S	14.7
O(1)–S–C(2)–C(1)	93.8	O(2)–C(1)–C(2)–C(3)	130.3
O(1)–S–C(2)–C(3)	−26.7	O(2)–C(1)–C(2)–C(4)	−91.7
O(1)–S–C(2)–C(4)	−151.7	C(5)–C(1)–C(2)–S	−99.1
O(2)–S–C(2)–C(1)	−13.3	C(5)–C(1)–C(2)–C(3)	16.6
O(2)–S–C(2)–C(3)	−133.7	C(5)–C(1)–C(2)–C(4)	154.6
O(2)–S–C(2)–C(4)	101.3	C(11)–C(1)–C(2)–S	127.8
S–O(2)–C(1)–C(2)	−16.5	C(11)–C(1)–C(2)–C(3)	−116.5
S–O(2)–C(1)–C(5)	103.2	C(11)–C(1)–C(2)–C(4)	21.5

[a] As defined by R. H. Stanford and J. Waser, *Acta Crystallogr., Sect. A*, 1972, **28**, 213.

C(1) and O(1)–S–C(2)–C(1) have an average magnitude of 93.3°, which also illustrates the axial nature of the O(1); the corresponding torsion angle averages in the *cis*- and *trans*-thietan 1-oxides [16] are 129.8 and 131.0°. In a planar four-membered ring this torsion angle would be near to 120°. A possible explanation of the change in preference to axial from the exocyclic oxygen is to invoke an anomeric effect [17] caused by inclusion of the oxygen atom into the four-membered ring. The S–O(1) bond length is shorter than in the thietan 1-oxides [1.482(13) and 1.492(19) Å for *cis* and *trans*, respectively] which reflects the increased electronegativity of the sulphur atom in the β-sultine.

Bond lengths in the *p*-fluorophenyl rings show a trend towards a shortening of the ring C–C bond lengths involving the F-substituted carbon atom. The mean of the four chemically equivalent bonds to C(7)–C(8) is 1.368 ± 0.008, whereas the four bonds including C(6)–C(7) average 1.382 ± 0.005 Å and those including C(5)–

C(6) average 1.389 ± 0.004 Å. The internal ring angle at the F-substituted position is significantly greater than 120°, the average being 123.6°. To test whether this trend is general to *p*-fluorophenyl rings, a search was made using the Cambridge Crystallographic Data Files.[18] A total of 73 rings from 32 structure determinations was found, after eliminating structures where constraints had been applied to the ring-atom refinement, this was reduced to a set of 44 *p*-fluorophenyl rings. The averages of the three internal C–C distances are (F)C–C (*ortho* to F), 1.365 ± 0.022, C(*o*)–C(*m*) 1.387 ± 0.020, and C(*m*)–C(*p*) 1.389 ± 0.021, the internal ring angle at the F-substituted position averages to 124.1 ± 2°, showing that the trends observed in this structure are general.

The two *p*-fluorophenyl rings in (11b) are equally disposed above and below the O(2)–C(1)–C(2) plane. The relative orientations of the ring planes may be referred to an 'ideal' geometry in which each ring is at right angles to the plane defined by atoms C(1), C(5), and C(11). Ring C(11)–C(16) is almost in this orientation, the rotation about bond C(1)–C(11) being only 5°, whereas ring C(5)–C(10) is rotated 27° about C(1)–C(5) to avoid close contacts with hydrogen atoms on C(3). There are no particularly short intramolecular contacts, the shortest being H(12) · · · H(42) at 2.25 and H(10) · · · H(33) at 2.43 Å. Intermolecular contacts are similarly unremarkable, the shortest being between F(2) and H(7) at 2.29 Å.

EXPERIMENTAL

Isopropyl t-Butyl Sulphoxide (9).—2-Bromopropane (12.3 g, 0.1 mol) was added dropwise, at room temperature, to a stirred methanolic solution of t-butylmercaptan (9.0 g, 0.1 mol) and potassium hydroxide (6.0 g, 0.11 mol). The mixture was heated under reflux overnight, then cooled, and any solid potassium bromide removed by filtration. The bulk of the solvent was removed and the residue diluted with water. Extraction with dichloromethane, drying of the organic extract, and removal of solvent gave crude isopropyl t-butyl sulphide, which was further purified by distillation, collecting the fraction boiling at 120 °C at atmospheric pressure.

The purified sulphide was dissolved in ethyl acetate, and stirred at 0 °C while *m*-chloroperbenzoic acid (1 mol. equiv.) was added. After stirring at room temperature for 2 days, the solvent was removed and the residue distilled under reduced pressure, yielding isopropyl t-butyl sulphoxide (5.20 g, 35%), b.p. 60 °C at 0.5 mmHg.

2-*Hydroxy*-1,1-*dimethyl*-2,2-*diphenylethyl t-Butyl Sulphoxide* (7).—Isopropyl t-butyl sulphoxide (3.22 g, 21.7 mmol) was dissolved in tetrahydrofuran (THF) (100 ml) at 0 °C under N_2. Methyl-lithium (12 ml; 1.8 M) was added dropwise over 10 min, followed by benzophenone (3.84 g, 20 mmol). The mixture was then stirred for an additional 10 min, quenched with water, and extracted (× 5) with CH_2Cl_2 (each 50 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated off. The crude product was recrystallised from CH_2Cl_2–diethyl ether–hexane, to yield the *sulphoxide* (7) (3.21 g, 49%), m.p. 100–102 °C, δ($CDCl_3$) 8.0—7.7 (m, 2 H), 7.6—7.1 (m, 8 H), 6.5 (OH), 1.63 (s, 6 H), and 1.37 (s, 9 H), ν($CHCl_3$) 3 250, 2 080, 2 000, 1 450, 1 050, 1 040, 1 010, and 990 cm^{-1} (Found: C, 72.85; H, 8.15. $C_{20}H_{26}O_2S$ requires C, 72.69; H, 7.94%).

3,3-*Dimethyl*-4,4-*diphenyl*-1,2-*oxathietan* 2-*Oxide* (8).—The β-hydroxy-sulphoxide (7) (0.181 g, 0.55 mmol) was dissolved in CH_2Cl_2 (100 ml) and cooled to −78 °C. Sulphuryl chloride (0.077 g, 0.57 mmol) was added and the mixture stirred for 30 min. Removal of solvent and recrystallisation from diethyl ether–pentane at −78 °C gave the β-*sultine* (8) (0.070 g, 50%), m.p. 97—99 °C (decomp.), δ($CDCl_3$) 7.4 (m, 10 H), 1.43 (s, 3 H), and 1.30 (s, 3 H); ν($CHCl_3$) 1 150 cm^{-1} (Found: C, 70.7; H, 5.85; S, 11.5. $C_{16}H_{16}SO_2$ requires C, 70.56; H, 5.92; S, 11.75%).

2-*Hydroxy*-2,2-*bis*-(p-*fluorophenyl*)-1,1-*dimethylethyl t-Butyl Sulphoxide* (10b).—Isopropyl t-butyl sulphoxide (1 g, 6.7 mmol) was dissolved in THF (20 ml) and cooled to −78 °C under an inert atmosphere. The solution was stirred vigorously while a solution of n-butyl-lithium (1.1 mol. equiv.) in hexane was added by syringe. Stirring was maintained for a further 5 min, and then a solution of *p*-difluorobenzophenone (1.46 g, 6.7 mmol) in THF (10 ml) was added over 30 min.

The reaction was quenched after a further 1 h by addition of THF–H_2O (10 : 1 v/v) at −78 °C. After warming to room temperature, the organic layer was separated, and the aqueous layer was extracted with ether. The extracts were combined, dried, and the solvent removed to give a light yellow oil (1.2 g), which crystallised on standing. Recrystallisation from dichloromethane–hexane gave the *sulphoxide* (10b) (0.5 g, 22%), m.p. 102—105 °C, δ($CDCl_3$) 7.9—6.8 (m, 8 H), 6.5br (s, 1 H), 1.55 (s, 3 H), 1.51 (s, 3 H), and 1.35 (s, 9 H); $\nu_{max.}$ (KBr) 3 200, 2 980, 1 593, 1 500, 1 220, 1 160, 1 040, 1 005, 975, and 830 cm^{-1} (Found: C, 65.1; H, 6.7; S, 8.8%. $C_{20}H_{24}F_2O_2S$ requires C, 65.54; H, 6.60; S, 8.75%).

4,4-*Bis*-(p-*fluorophenyl*)-3,3-*dimethyl*-1,2-*oxathietan* 2-*Oxide* (11b).—The β-hydroxy-sulphoxide (10b) (0.079 g, 0.22 mmol) in dry dichloromethane (2.5 ml) was cooled to −78 °C under an inert atmosphere. The solution was vigorously stirred while sulphuryl chloride (0.035 g, 20 μl, 0.25 mmol) in dichloromethane was added dropwise. The reaction was stirred at low temperature for a further 1 h, then warmed to 0 °C for 30 min. After removal of solvent *in vacuo* at 0 °C yielding a clear viscous oil, recrystallisation from ether–hexane gave the S-*oxide* (11b) (0.016 g, 24%) m.p. 102—104 °C (decomp.), δ($CDCl_3$) 7.6—6.8 (m, 8 H), 1.45 (s, 3 H), and 1.27 (s, 3 H), $\nu_{max.}$ (CH_2Cl_2) 1 580, 1 495, 1 220, 1 153, 980, and 845 cm^{-1} (Found: C, 62.25; H, 4.7; S, 10.4. $C_{16}H_{14}F_2O_2S$ requires C, 62.32, H, 4.58, S, 10.40%).

2-*Hydroxy*-1,1-*dimethyl*-2,2-*bis*-(p-*tolyl*)*ethyl t-Butyl Sulphoxide* (10a).—Isopropyl t-butyl sulphoxide (0.5 g, 3.3 mmol) was dissolved in THF (20 ml) and cooled, with stirring under an inert atmosphere, to −78 °C. A solution of n-butyl-lithium (1.1 mol. equiv.) was slowly added by syringe. After 5 min 4,4′-dimethylbenzophenone (0.7 g, 3.3 mmol) in THF (20 ml) was slowly added, and the resultant mixture stirred at −78 °C for 5 min. The reaction was then quenched by addition of THF–H_2O, and allowed to warm to room temperature. Separation of the organic layer, extraction of the aqueous layer with diethyl ether, drying, and removal of solvent from the combined organic layers gave a pale yellow oil. Recrystallisation from chloroform–hexane gave the *sulphoxide* (10a) (0.6 g, 51%), m.p. 113—115 °C, δ($CDCl_3$) 7.8—6.9 (m, 8 H), 2.29 (s, 3 H), 2.25 (s, 3 H),

1.57 (s, 3 H), 1.55 (s, 3 H), and 1.33 (s, 9 H), $\nu_{max.}$ (KBr) 3 240, 3 000—2 900, 1 515, 1 510, 1 450, 1 190, 1 170, 1 140, 1 060, 1 030, 990, 937, 905, 795, and 790 cm^{-1} (Found: C, 73.4; H, 8.7; S, 8.7. $C_{22}H_{30}O_2S$ requires C, 73.69; H, 8.34; S, 8.94%).

3,3-Dimethyl-4,4-bis-(p-tolyl)-1,2-oxathietan 2-Oxide (11a).—The β-hydroxy-sulphoxide (10a) (0.5 g, 1.4 mmol) in dichloromethane was cooled to −78 °C, and a solution of sulphuryl chloride (0.21 g, 0.124 ml, 1.54 mmol) in dichloromethane (3 ml) slowly added, with vigorous stirring. After 30 min at −78 °C, the reaction was warmed to 0 °C and the solvent removed *in vacuo*, taking care not to allow the temperature to rise above 10 °C. Recrystallisation of the resulting oil from diethyl ether–hexane at low temperature yielded white crystals (0.099 g, 0.3%). The ^1H n.m.r. spectrum showed the product to be the β-sultine (11a) (80%), contaminated by a decomposition product [1,1-dimethyl-2,2-bis-(*p*-tolyl)ethylene]. Despite careful low-temperature recrystallisations, this impurity could not entirely be eliminated. Consequently, elemental analysis was not attempted. The product had δ($CDCl_3$) 7.5—7.0 (m, 8 H), 2.32 (s, 3 H), 2.30 (s, 3 H), 1.44 (s, 3 H), and 1.28 (s, 3 H), [superimposed upon this is the spectrum of the corresponding alkene (see below)], $\nu_{max.}$ ($CHCl_2$) 3 100—2 950, 1 520, 1 470, 1 155, 980, 960, and 820 cm^{-1}.

Decomposition of 4,4-Bis-(p-fluorophenyl)-3,3-dimethyl-1,2-oxathietan 2-Oxide (11b).—A sample of the β-sultine (11b) was dissolved in $CDCl_3$ and maintained at 30°. When decomposition was shown (n.m.r.) to be complete ($t_{\frac{1}{2}}$ 23 h), the solvent was removed, and the residue was vacuum-distilled in a Kugel apparatus, b.p. 130 °C at 0.01 mmHg. The clear oil thus obtained crystallised on cooling to give *1,1-bis-(p-fluorophenyl)-2-methylprop-1-ene* (12b), m.p. 42—50 °C, δ($CDCl_3$) 7.4—6.8 (m, 8 H), and 1.80 (s, 6 H) $\nu_{max.}$ (neat) 1 603, 1 508, 1 225, 1 155, and 833 cm^{-1} (Found: C, 77.95; H, 5.7. $C_{16}H_{14}F_2$ requires C, 78.67, H, 5.78%).

Decomposition of 3,3-Dimethyl-4,4-bis-(p-tolyl)-1,2-oxathietan 2-Oxide (11a).—A sample of crude β-sultine (11a) was dissolved in $CDCl_3$ and maintained at 12 ± 2 °C while the decomposition was followed by ^1H n.m.r. After 15 h the conversion into 2-methyl-1,1-bis-(*p*-tolyl)prop-1-ene (12a) was complete. The product showed δ($CDCl_3$) 7.5—6.8 (m, 8 H), 2.3 (s, 6 H), and 1.8 (s, 6 H).

X-Ray Structure Determination of (11b).—Suitable crystals were obtained from diethyl ether–hexane and were mounted in sealed Lindemann glass capillary tubes. Preliminary Weissenberg and precession photographs established the unit cell to be C-centred monoclinic.

Crystal Data. $C_{16}H_{14}F_2O_2S$, M = 308.3. Monoclinic, a = 17.905(15), b = 9.829(8), c = 18.05(2) Å, β = 110.7(1)°, U = 2 973 Å^3, Z = 8, D_c = 1.38, F(000) = 1 280, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 1.94 cm^{-1}. Space group $C2/c$ assumed.

Intensity data were collected using a STADI-2 Stoe Weissenberg diffractometer with graphite-monochromated Mo-K_α radiation. The crystal chosen for data collection (dimensions 0.15 × 0.20 × 0.2 mm) could not be aligned about any of the principal cell axes, accordingly data was collected about [1,0,2] which yields an F-centered triclinic cell. Sufficient Weissenberg layers were collected to measure all unique reflections $0.09 < \sin\theta/\lambda < 0.60$ (2 659 measurements), and after correction for Lorentz and polarisation effects, re-indexing, and merging common reflections, 1184 reflection intensities with $I > 3\sigma(I)$ were obtained. The structure was solved using the direct-methods program EEES in the SHELX-76 system [18] which was also used for the subsequent least-squares refinement. All non-hydrogen atoms appeared on the E-map with the second highest probability based on the M(abs) test. In the final cycles of least-squares refinement all non-hydrogen atoms had anisotropic thermal parameters, phenyl hydrogen atoms were included in calculated positions (C–H = 1.08 Å) with individual isotropic thermal parameters, and methyl hydrogens were refined in rigid groups with C–H fixed at 1.08 Å and a common isotropic thermal parameter. The final R-factor was 0.0497 (R' = 0.0469) using a weighting scheme with $w \propto 1/[\sigma^2(F) + 0.004\,F^2]$. Atomic positional parameters are in Table 1. Observed and calculated structure factors, thermal parameters, and hydrogen atom co-ordinates are listed in Supplementary Publication No. SUP 23016 (9 pp.).*

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* For details see Notices to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

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