Cyclization of γδ-Unsaturated Sulphenic Acids to give Thietan 1-Oxide Derivatives. Crystal Structure of *rel*-(1*R*,2*S*,3*R*,4*R*)-3-Hexyl-2-hydroxymethyl-4-methylthietan 1-Oxide

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erythro- and *threo*-2-t-Butylthio-3-vinylnonan-1-ol have been prepared by Claisen rearrangement of the silylketen acetals derived from (*E*)-non-2-enyl t-butylthioacetate followed by reduction with lithium aluminium hydride. The sulphur function influenced the stereoselectivity of formation of the silylketen acetals which, in turn, determined the ratio of diastereoisomeric products obtained in the rearrangement. Thermolysis of *erythro*-2-t-butylsulphinyl-3-vinylnonan-1-ol at 140 °C for 5 min gave *erythro*-1-(hydroxymethyl)-2-vinyloctanesulphenic acid which cyclized spontaneously to a mixture of *rel*-(1*R*,2*R*,3*S*,4*R*)- and *rel*-(1*R*,2*S*,3*R*,4*R*)-3-hexyl-2-(hydroxymethyl)-4-methylthietan 1-oxide. *threo*-2-Butylsulphinyl-3-vinylnonan-1-ol under the same conditions gave a mixture of *rel*-(1*R*,2*R*,3*R*,4*R*)- and *rel*-(1*R*,2*S*,3*S*,4*R*)-3-hexyl-2-(hydroxymethyl)-4-methylthietan 1-oxide. Allocations of configuration to these thietan 1-oxide derivatives based on transition-state considerations have been substantiated by a determination of the crystal structure of the *rel*-(1*R*,2*S*,3*R*,4*R*)-isomer and by n.m.r. spectroscopy, which also led to tentative assignments of conformation.

In connection with a synthesis of prostaglandin analogues containing a thietan ring we required 3-alkyl-2-(hydroxymethyl)-4-methylthietan derivatives of known configuration. Among simple substituted thietans 2-alkyl,[1] 3-alkyl,[2] 2,3-dialkyl,[3] and 2,4-dialkyl derivatives have been described,[4,5] but there are no reports of simple monocyclic 2,3,4-trialkylthietans.† We recognised that synthetic procedures leading to these compounds could take advantage of any oxidation level at sulphur since thietans, their 1-oxides, and 1,1-dioxides are readily interconverted.[2,5,6] For the construction of these trisubstituted thietans from acyclic precursors the common methods [1,7] of ring formation, involving either the reaction of 1,3-dihalides or 1,3-disulphonate esters with sulphide ions, or [2 + 2] cycloaddition of sulphenes to enamines, appeared to be less promising than one in which a sulphenic acid adds intramolecularly to an alkene (Scheme 1). The only example of this process was provided by the cyclization of the unsaturated sulphenic acid (2a) to give *cis*-2-methylthietan 1-oxide (3a).[8] We considered that the moderate yield associated with this cyclization was likely to be compensated for by the advantages resulting from (i) the ease of preparation of the sulphoxide precursors (1b) *via* a Claisen rearrangement of an ester enolate; [9] (ii) the likelihood that this rearrangement would afford some control over the relative stereochemistry of R^1 and R^2 in compound (1b); [10] and (iii) the stereospecificity of the cyclization to the thietan 1-oxide (3b), with respect to the orientation of the methyl group and sulphinyl oxygen.[8] This approach to the synthesis of four diastereoisomers of 3-hexyl-2-(hydroxymethyl)-4-methylthietan 1-oxide is described here, and assignments of stereochemistry discussed.

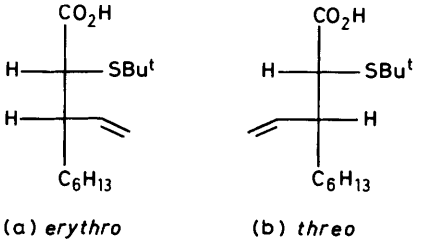
RESULTS AND DISCUSSION

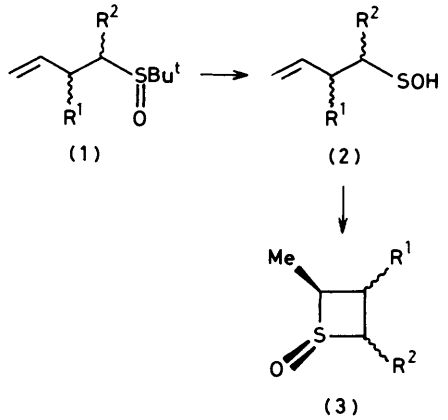
The t-butylthioacetate (4) of (*E*)-non-2-en-1-ol, on sequential treatment with lithium di-isopropylamide and chlorotrimethylsilane at −78 °C in hexane–tetrahydrofuran (THF), gave a mixture of the silylketen acetals (7) and (8), which after 2 h at 60 °C underwent Claisen rearrangement to give the trimethylsilyl esters (9) and (10) (Scheme 2).[9] These were hydrolysed on work-up to give a mixture of *erythro*- and *threo*-2-t-butylthio-3-vinylnonanoic acid, (11) and (12) respectively, in 78% overall yield from compound (4).‡ The conversion was performed without isolation of the silylated intermediates. The diastereoisomeric acids (11) and (12) were chromatographically identical and could not be separated, but reduction of the mixture with lithium aluminium hydride gave a mixture of *erythro*- and *threo*-2-t-butylthio-3-vinylnonan-1-ol, (13) and (14) respectively, in the ratio 3 : 1, which were separated by chromatography.

Configurations were assigned to the hydroxy-sulphides (13) and (14) on the following basis. We expected the ester (4) to furnish, predominantly, the (*E*,*E*)-lithio-

† See ref. 3 for a bicyclic example.

‡ We use the convention that Fischer projection (a) is called *erythro* and (b) is termed *threo*. The usage is arbitrary, because the descriptors should be confined to compounds which bear two pairs of identical substituents on adjacent asymmetric carbon atoms. However, we consider that this convention approximates more closely to the correct usage than that used recently for stereochemically analogous systems. (C. H. Heathcock, C. T. White, J. J. Morrison, and D. VanDerveer, *J. Org. Chem.*, 1981, **46**, 1296.) All the diastereoisomers mentioned in this paper are racemic modifications, but only one enantiomer is depicted throughout.





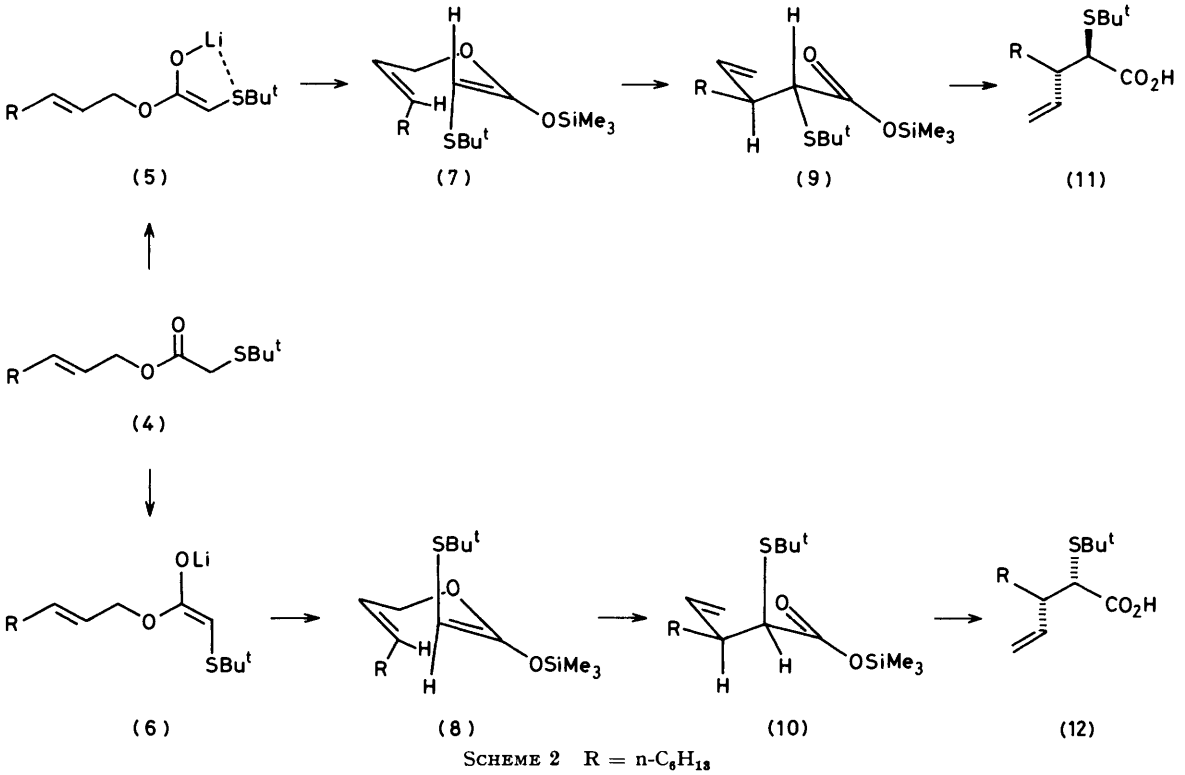
a; $R^1 = R^2 = H$
b; $R^1 = n\text{-}C_6H_{13}$, $R^2 = CH_2OH$

SCHEME 1

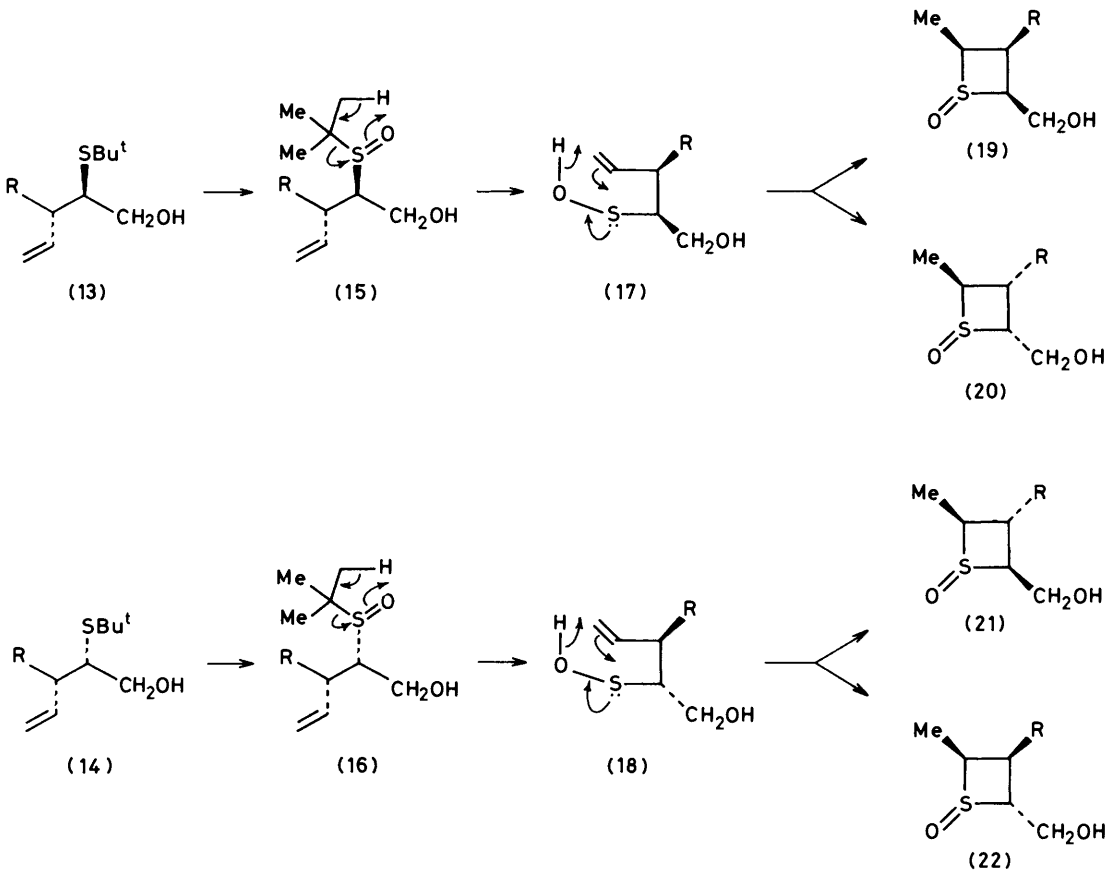
enolate (5), because of stabilizing chelation involving lithium and sulphur, present in this isomer but absent in the (*E*,*Z*)-isomer (6).[11] In propanoates [as compound (4), Me instead of SBu^t] it has been shown that enolization using lithium di-isopropylamide in THF gives, predominantly, lithium enolates which are analogous to the (*E*,*Z*)-isomer (6).[10] Trapping of the enolates (5) and (6) by chlorotrimethylsilane furnishes a mixture of the silylketen acetals (7) and (8) in which the (*E*,*Z*)-isomer (7) predominates. The ratio of the isomers (7) to (8) is reflected in the ratio of *erythro*- to *threo*-γδ-unsaturated acids (11) and (12), respectively, since ester enolate rearrangements proceed specifically by way of chair-like transition states, unless there are usually strong steric effects.[10,12]

Oxidation of the hydroxy-sulphides (13) and (14) separately with peroxydodecanoic acid gave the corresponding sulphoxides (15) and (16) (Scheme 3). Thermolysis of the *erythro*-isomer (15) for 5 min in boiling xylene (140 °C) furnished a mixture of *rel*-(1*R*,2*R*,3*S*,4*R*)-3-hexyl-2-(hydroxymethyl)-4-methylthietan 1-oxide (19) and the *rel*-(1*R*,2*S*,3*R*,4*R*)-isomer (20) in the ratio 1 : 3 (22% combined yield), whilst the *threo*-isomer (16) under the same conditions gave a mixture of the *rel*-(1*R*,2*R*,-3*R*,4*R*)- and *rel*-(1*R*,2*S*,3*S*,4*R*)-isomers, (21) and (22) respectively, in the ratio 3 : 1 (44% combined yield). These cyclic products were readily separated by chromatography, but other, less polar products were difficult to separate and were not investigated.

The formation of the thietan 1-oxides (19)—(22) may be rationalized, and their configurations assigned, in the following manner (Scheme 3). Thermolysis of the t-butyl sulphoxide (15) furnished the sulphenic acid (17) by *syn*-elimination of 2-methylpropene.[8] The sulphenic acid then added intramolecularly to both diastereotopic faces of the olefin to give the isomeric thietan 1-oxide derivatives (19) and (20). Because the intramolecular addition is a concerted process proceeding *via* a cyclic five-membered transition state, the methyl groups at C-4 are *cis* to the sulphinyl oxygen.[8] Of the two diastereoisomeric transition states, the one, (A), which leads to compound (19) is more sterically compressed than that,

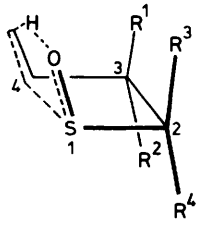


SCHEME 2 R = $n\text{-}C_6H_{13}$



SCHEME 3 R = n-C_6H_{13}

(B), which leads to compound (20), by virtue of the all-*cis* arrangement of substituents on the developing thietan ring in (A), and hence the isomer (20) is the predominant product. A similar rationale accounts for the formation of compounds (21) and (22) from the precursor (16), *via* compound (18), but in this case the steric effects in the



	R^1	R^2	R^3	R^4
(A)	C_6H_{13}	H	CH_2OH	H
(B)	H	C_6H_{13}	H	CH_2OH
(C)	H	C_6H_{13}	CH_2OH	H
(D)	C_6H_{13}	H	H	CH_2OH

diastereoisomeric transition states (C) and (D) require further comment. We consider the dominant repulsive non-bonded interaction to be that occurring between the hexyl group at C-3 and the developing methyl group at C-4 in (D), because the closest distance between these groups (*ca.* 1.2 Å) is appreciably smaller, according to models, than that (*ca.* 3.2 Å) between the nascent C-4 methyl group and the C-2 hydroxymethyl group in (C). Steric compression between the hydroxymethyl group and the sulphinyl oxygen in (C) (*ca.* 2.4 Å separation from models) is rendered less important by virtue of the greater C–S than C–C bond length (1.833 as opposed to 1.54 Å).[13] Hence we consider transition state (C) to be less sterically compressed than (D), and the predominant product was accordingly assigned the configuration depicted in structure (21).

A number of competing reactions may be invoked to account for the moderate yields of the cyclic products (19)—(22). Statistical and other factors usually markedly favour the elimination of 2-methylpropene from alkyl t-butyl sulphoxides.[14] However the thermolytic elimination of compounds (15) and (16) to give 2-methylpropene and the sulphenic acids (17) and (18), respectively, may be accompanied by much elimination to 2-methylpropane-2-sulphenic acid and 3-vinylnon-2-en-1-ol, since it is known that sulphoxide eliminations are also facilitated when they produce conjugated systems.[15] Thermal decomposition of the sulphoxide (15) at 126 °C in octane, monitored continuously by t.l.c., was complete after 100 min, but only traces of thietan 1-oxides were produced at any stage, whereas at 165 °C in mesitylene the thietan 1-oxides (19) and (20) were produced in 19% combined yield after 1.5 min. This is understandable if the activation energy for the undesired elimination is lower than for the required one. The reaction is further

complicated by the thermal instability of the thietan 1-oxides, which is probably due to the reversibility of the reaction paths leading to the sulphenic acids (17) and (18), respectively.[16] In addition, the angle strain introduced into the bicyclic transition states (A)—(D) by the presence of the incipient four-membered ring should retard the intramolecular sulphenic acid–olefin additions. The sulphenic acids (17) and (18) would, therefore, have greater opportunity to undergo intermolecular additions to the olefins,[8] and intermolecular dehydration to give thiosulphinates. Most sulphenic acids undergo the last reaction so readily that they cannot be isolated.[17] In order to minimise these competing reactions the thermolyses were performed in dilute solution. Optimum yield of the thietan 1-oxides (19)—(22) were obtained when the sulphoxides (15) (and 16) were thermolysed at 140 °C for 5 min in xylene; some starting material remained. It may be noted that intramolecular addition of sulphenic acids to olefins to form five- and six-membered rings proceeds efficiently.[8]

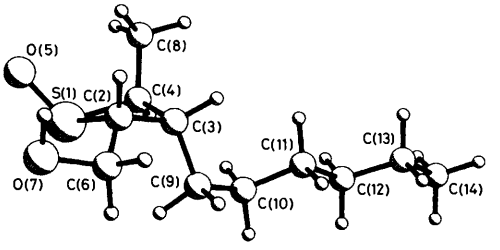


FIGURE 1 General view of the molecule of compound (20), indicating the crystallographic numbering system

X-Ray crystallographic data for the thietan (20) confirmed the allocated configuration (Figure 1) and revealed that in the crystalline state the ring adopted the conformation (20a). The thietan ring is folded about the two α-C atoms by 151°, which compares with the values, derived from crystallographic data, of 153°, 148°, and 145° reported respectively for 3,3-dimethylthietan 1-oxide,[18] *trans*-3-*p*-bromophenylthietan 1-oxide,[19] and *trans*-3-carboxythietan 1-oxide.[20] The hexyl substituent had an extended conformation, except for a synclinal arrangement about C(9)—C(10). Molecules of compound (20) existed as hydrogen-bonded pairs in the crystal, joined by two hydrogen bonds between the hydroxy-oxygen of one molecule and the sulphinyl oxygen of its enantiomer (Figure 2). The hydrogen atoms of the hydroxy-groups were not located in the *X*-ray analysis, and their locations in Figure 2 were derived only by assuming reasonable bond lengths and angles. The length of the depicted hydrogen bond was 2.71 Å, whereas the distance of 3.65 Å between the hydroxy-oxygen and sulphinyl oxygen within the same molecule was too long for hydrogen bonding. Intermolecular hydrogen bonds persisted in dilute solutions of the thietan 1-oxides (19)—(22) in carbon tetrachloride and, to a lesser extent, in dilute chloroform solutions according to i.r. spectroscopic studies and osmometric measurements (see Experimental section). This phenomenon must be borne in mind when considering the n.m.r. data and the conformations of the molecules for deuteriochloroform solutions (see later).

The determination of the configuration of the thietan 1-oxide (20) also established the configuration of the isomer (19) and verified the mechanistic rationalisation

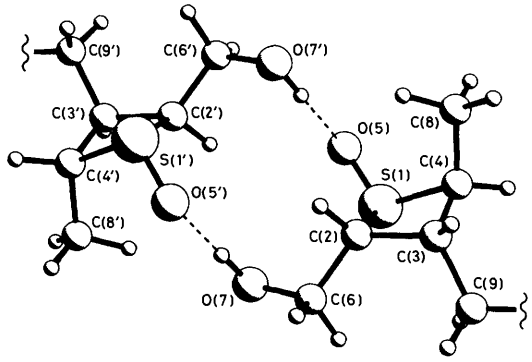


FIGURE 2 View of the molecule indicating possible intermolecular hydrogen bonding by means of dotted lines

which led to the initial assignments of configuration. This, in turn, lent further confidence to the assignments of configuration for compounds (21) and (22), and subsequent chemical transformations (see following paper) confirmed their structure. N.m.r. spectral data, in particular those related to aromatic solvent-induced shifts (ASIS),[21] also substantiated these assignments (Table 1). Protons on the opposite side of the ring to the sulphinyl oxygen in thietan 1-oxides undergo larger ASIS than those on the same side of the ring,[2b,7,8] so that ASIS data for compounds (19)—(22) are in accord with the depicted configurations.

TABLE 1

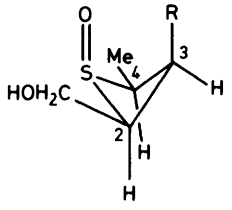
N.m.r. data for the thietan 1-oxide derivatives (19)—(22) †

	2-H	3-H	4-H	Me
(19)	3.77	2.88	3.77	1.39
	(−0.35)	(−0.68)	(−0.76)	(−0.28)
(20)	3.59	2.69	3.34	1.45
	(0.09)	(−0.44)	(−0.56)	(−0.17)
(21)	2.97	2.97	2.97	1.30
	(−0.30)	(−0.36)	(−0.71)	(−0.26)
(22)	3.31	2.27	3.68	1.39
	(0.04)	(−0.40)	(−0.57)	(−0.16)

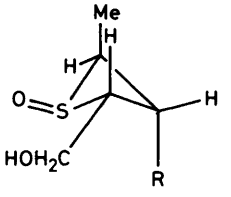
† Values for $CDCl_3$ solutions; $\Delta(\delta(C_6D_6) - \delta(CDCl_3))$ values in parentheses.

The correlations of n.m.r. data with configuration are valid regardless of the conformations of the molecules, but the striking similarity of ASIS data for the thietan 1-oxides (19) and (21) (for the methyl group and H-4), and (20) and (22) suggests that compounds (19) and (21) adopt the same ring conformation, and that another conformation is assumed by compounds (20) and (22). The conformations (19a)—(22a) may be tentatively assigned to the isomers in solution; structures (21a) and (22a) contain one pseudoxial and three pseudoequatorial substituents. It is known that substituents in thietan rings and the sulphinyl oxygen in thietan 1-oxides prefer the

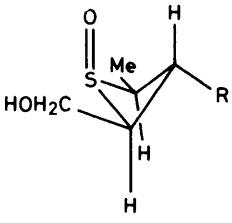
pseudoequatorial orientation;[2,4a] although the relative magnitudes of these conformational preferences have not been determined some evidence suggests that the preference of the sulphinyl oxygen for the pseudoequatorial orientation may be greater than that of a C-3 aryl or alkyl group.[6,19] In complexes with lanthanoids it is



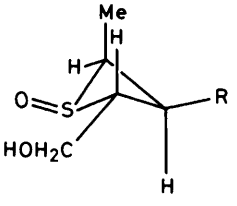
(19a)



(20a)



(21a)



(22a)

R = n-C_6H_{13}

greater by 1.0 kcal mol^{-1} * than that of a methyl group,[6] and we may take this to be a maximum value for an uncomplexed sulphinyl oxygen. The conformational preference of a methyl group in cyclohexyl systems is 1.8 kcal mol^{-1}, and for other n-alkyl groups it is *ca.* 2.1 kcal mol^{-1}.[22] Direct application of these values to thietan systems is not valid, but it is reasonable to expect that the conformational preference of the sulphinyl oxygen in compound (21a) would not outweigh that of two alkyl groups and a hydroxymethyl group. These considerations also led to allocations of conformation to compounds (22a) and (20a), which also exist in the crystalline state. For compound (19a) we considered the additional factor that the separation between pseudoaxial substituents at S-1 and C-3 is greater than that between pseudoaxial substituents at C-2 and C-4 by virtue of the greater C–S than C–C bond length. No account has been taken of the possible influence of intermolecular hydrogen bonding upon the conformations of the rings, so that this qualitative conformational analysis must be regarded with circumspection.

Some support for these conformational assignments is provided by the n.m.r. data, since 3-H in compound (21a) is deshielded relative to that in structure (19a), and in compound (22a) it is markedly shielded relative to that in the stereoisomer (20a). This accords with the known anisotropy of the sulphinyl bond, for which protons near a plane orthogonally bisecting the bond are deshielded, whilst those lying near the extrapolated O–S axis are shielded.[23] The n.m.r. spectra were not sufficiently well resolved to permit the derivation of all the coupling constants for the ring protons, so that these parameters could not be employed to further elucidate the conformations.

* 1 kcal is 4.184 kJ.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined with either a Perkin-Elmer 157G or 180 spectrophotometer, mass spectra with an A.E.I. MS12 instrument, and n.m.r. spectra with a Perkin-Elmer R34 spectrometer for solutions in deuteriochloroform, unless otherwise indicated. Signal allocations in n.m.r. spectra were established by appropriate spin-decoupling experiments. Chromatography refers to separation on columns of silica (Whatman SO t.l.c.) using the short-path technique at *ca.* 60 mmHg above atmospheric pressure, or alumina (Camag, basic) at atmospheric pressure. Light petroleum refers to the fraction with b.p. 40—60 °C.

(E)-*Non-2-enyl t-Butylthioacetate* (4).—Treatment of (*E*)-non-2-en-1-ol (40.9 g, 230 mmol) in pyridine (400 ml) with t-butylthioacetyl chloride (48 g, 230 mmol) at room temperature for 18 h gave, after chromatography on silica (500 g) (diethyl ether–light petroleum, 1 : 19, as eluant), the *product* (4) (57.3 g, 73%), $\nu_{max.}$ (liq. film) 1 743 (CO) and 962 cm^{-1} (CH=CH); δ 5.76 (1 H, quin, *J* 7 Hz, =C*H*CH_2O), 5.52 (1 H, quin, *J* 7 Hz, CH_2CH=), 4.41 (2 H, d, *J* 7 Hz, =CHCH_2), 3.23 (2 H, s, CH_2S), 2.00 (2 H, m, CH_2CH=), 1.30 (9 H, s, Me_3CS), 1.24 (8 H, m, $[CH_2]_4$), and 0.83 (3 H, t, *J* 7 Hz, Me); *m/e* 272 (M^+) (Found: C, 66.3; H, 10.3; S, 11.8. $C_{15}H_{28}O_2S$ requires C, 66.1; H, 10.4; S, 11.8%).

erythro- *and* threo-2-*t-Butylthio*-3-*vinylnonanoic Acid* (11) *and* (12).—n-Butyl-lithium (222 mmol) in hexane (231 ml) was added to di-isopropylamine (32.7 ml, 232 mmol) in tetrahydrofuran (THF) (150 ml) with stirring at −10 °C under nitrogen. The solution was cooled to −78 °C, and a solution of (*E*)-non-2-enyl t-butylthioacetate (4) (57.3 g, 211 mmol) in THF (180 ml) was added during 20 min with stirring. After a further 30 min, chlorotrimethylsilane (27.5 ml, 218 mmol) was added dropwise. The mixture was allowed to warm to room temperature, and then heated at 60 °C for 2 h. After cooling, diethyl ether (1.2 l) was added and the solution was washed with 2N-hydrochloric acid (2 × 200 ml). The aqueous washings were extracted with diethyl ether (2 × 200 ml) and the combined ether extracts were dried ($MgSO_4$) and evaporated. Chromatography of the residue on silica (400 g), (diethyl ether–light petroleum, 1 : 9 and then diethyl ether as eluants) gave a mixture of erythro- and threo-2-*t-butylthio*-3-*vinylnonanoic acid* (11) and (12) (44.7 g, 78%), $\nu_{max.}$ 2 900br and 1 712 (CO_2H), 1 640, 987 and 912 cm^{-1} (CH=CH_2); δ 9.20 (1 H, br, CO_2H), 5.60 (1 H, m, =CH), 5.07 (2 H, m, =CH_2), 3.28 (1 H, d, *J* 8 Hz, CHS in minor diastereoisomer), 3.19 (1 H, d, *J* 8 Hz, CHS in major diastereoisomer), 2.44 (1 H, m, =CHC*H* in minor diastereoisomer), 2.29 (1 H, m, =CHC*H* in major diastereoisomer), 1.84 (1 H, m, C-4 C*H*H'), 1.31 (9 H, s, Me_3CS), 1.23 (9 H, m, $[CH_2]_4$ and C-4 CH*H'*), and 0.84 (3 H, t, *J* 7 Hz, Me); *m/e* 272 (M^+) (Found: C, 66.1; H, 10.45; S, 11.9. $C_{15}H_{28}O_2S$ requires C, 66.1; H, 10.4; S, 11.8%).

erythro- *and* threo-2-*t-Butylthio*-3-*vinylnonan*-1-*ol* (13) *and* (14).—A mixture of *erythro*- and *threo*-2-t-butylthio-3-

vinylnonanoic acid (11) and (12) (44.4 g, 163 mmol) in diethyl ether (150 ml) was added dropwise with stirring to lithium aluminium hydride (6.8 g, 180 mmol) in diethyl ether (1 l). After boiling for 6 h, and subsequent careful addition of wet diethyl ether and water to the suspension, the solids were filtered off and the diethyl ether evaporated. Chromatography of the residue on silica (500 g) (diethyl ether–light petroleum, 1 : 9 as eluant) gave erythro-2-*t-butylthio*-3-*vinylnonan*-1-*ol* (13) (12.2 g), $\nu_{max.}$ (liq. film) 3 430 (OH), 1 640, 992, and 910 cm^{-1} ($CH{=}CH_2$); δ 5.68 (1 H, m, =CH), 5.05 (2 H, m, $=CH_2$), 3.70 (1 H, m, C*H*H'OH), 3.48 (1 H, m, CH*H'*OH), 2.70 (1 H, q, *J* 7 Hz, CHS), 2.37 (1 H, m, OH), 2.22 (1 H, m, =CHC*H*), 1.69 (1 H, m, C-4 C*H*H'), 1.31 (9 H, s, Me_3CS), 1.24 (9 H, m, $[CH_2]_4$ and C-4 (CH*H'*), and 0.85 (3 H, t, *J* 7 Hz, Me); δ ($CDCl_3$–D_2O) 3.70 (1 H, dd, J_{AB} 11 Hz, J_{AX} 6 Hz, C*H*H'OH), and 3.48 (1 H, dd, J_{AB} 11 Hz, J_{BX} 7 Hz, CH*H'*OH); *m/e* 258 (M^+) (Found: C, 70.1; H, 11.5; S, 12.65. $C_{15}H_{30}OS$ requires C, 69.8; H, 11.6; S, 12.4%).

Further elution gave a mixture of the diastereoisomers (13) and (14) (22.5 g) followed by threo-2-*t-butylthio*-3-*vinylnonan*-1-*ol* (14) (3.0 g), $\nu_{max.}$ (liq. film) 3 390 (OH), 1 640, 992, and 910 cm^{-1} ($CH{=}CH_2$); δ 5.61 (1 H, m, =CH), 5.04 (2 H, m, $=CH_2$), 3.64 (1 H, dd, J_{AB} 11 Hz, J_{AX} 7 Hz, C*H*H'OH), 3.50 (1 H, dd, J_{AB} 11 Hz, J_{BX} 7 Hz, CH*H'*OH), 2.76 (1 H, dt, *J* 7 Hz, *J'* 3 Hz, CHS), 2.38 (1 H, m, =CHC*H*), 2.19 (1 H, s, OH), 1.48 (2 H, m, C-4 CH_2), 1.31 (9 H, s, Me_3CS), 1.24 (8 H, m, $[CH_2]_4$), and 0.85 (3 H, t, *J* 7 Hz, Me); *m/e* 258 (M^+) (Found: C, 69.7; H, 11.6; S, 12.4. $C_{15}H_{30}OS$ requires C, 69.8; H, 11.6; S, 12.4%).

Further chromatography of the mixed fraction effected complete separation of the isomers, the total recovery of which was 37.7 g (90%); the ratio of (13) : (14) was 72 : 27.

erythro-2-*t-Butylsulphinyl*-3-*vinylnonan*-1-*ol* (15).—Peroxydodecanoic acid (12.2 g, 95% pure, 56.6 mmol) was slowly added to a stirred solution of *erthro*-2-t-butylthio-3-vinylnonan-1-ol (13) (14.6 g, 56.6 mmol) in light petroleum (500 ml) at 0 °C. After 15 min the solvent was evaporated and the residue chromatographed on alumina (260 g). Elution with diethyl ether gave the *product* (15) (15.2 g, 98%), m.p. 58 °C (from diethyl ether–light petroleum), $\nu_{max.}$ ($CHCl_3$) 3 420 (OH), 1 638, 992, and 916 ($CH{=}CH_2$), and 1 039 cm^{-1} (SO); δ 5.55 (1 H, m, =CH), 5.13 (2 H, m, $=CH_2$), 4.05 (1 H, m, C*H*H'OH), 3.90 (1 H, m, CH*H'*OH), 3.65 (1 H, dd, *J* 5 Hz, *J'* 9 Hz, CHH'O*H*), 2.94 (1 H, m, CHS), 2.21 (1 H, m, =CHC*H*), 1.28 (9 H, s, Me_3CS), 1.24 (10 H, m, $[CH_2]_5$), and 0.84 (3 H, t, *J* 7 Hz, Me); δ ($CDCl_3$–D_2O) 4.13 (1 H, dd, J_{AB} 13 Hz, J_{AX} 8 Hz, C*H*H'OH), and 3.90 (1 H, dd, J_{AB} 13 Hz, J_{BX} 3 Hz, CH*H'*OH); *m/e* 274 (M^+) (Found: C, 65.4; H, 10.9; S, 11.95. $C_{15}H_{30}O_2S$ requires C, 65.6; H, 11.0; S, 11.7%).

threo-2-*t-Butylsulphinyl*-3-*vinylnonan*-1-*ol* (16).—Oxidation of *threo*-2-t-butylthio-3-vinylnonan-1-ol (14) (7.15 g) with peroxydodecanoic acid as for the *erythro*-isomer gave the *product* (16) (7.59 g, 99%), m.p. 51 °C (from diethyl ether–light petroleum), $\nu_{max.}$ ($CHCl_3$) 3 340 (OH), 1 638, 1 000, and 910 ($CH{=}CH_2$), and 1 030 cm^{-1} (SO); δ 5.63 (1 H, m, =CH), 5.10 (2 H, m, $=CH_2$), 4.13 (1 H, m, C*H*H'OH), 3.91 (1 H, m, CH*H'*OH), 3.56 (1 H, dd, *J* 5 Hz, *J'* 10 Hz, CHH'O*H*), 2.97 (1 H, m, CHS), 2.20 (1 H, m, =CHC*H*), 1.70 (1 H, m, C-4 C*H*H'), 1.28 (9 H, s, Me_3CS), 1.26 (9 H, m, $[CH_2]_4$ and C-4 CH*H'*), and 0.84 (3 H, t, *J* 7 Hz, Me); δ ($CDCl_3$–D_2O) 4.13 (1 H, dd, J_{AB} 14 Hz, J_{AX} 10 Hz, C*H*H'OH), 3.91 (1 H, dd, J_{AB} 14 Hz, J_{BX} 3 Hz, CH*H'*OH); *m/e* 274 (M^+) (Found: C, 65.5; H, 10.9; S, 11.8. $C_{15}H_{30}O_2S$ requires C, 65.6; H, 11.0; S, 11.7%).

rel-(1R,2R,3S,4R)- *and* rel-(1R,2S,3R,4R)-3-*Hexyl*-2-(*hydroxymethyl*)-4-*methylthietan* 1-*Oxide* (19) *and* (20).—*erythro*-2-t-Butylsulphinyl-3-vinylnonan-1-ol (17) (1.02 g, 3.72 mmol) in xylene (5 ml) was added quickly to boiling xylene (100 ml) under nitrogen. After 5 min the solution was poured onto solid xylene (50 ml, cooled in a bath of liquid nitrogen). Evaporation of the solvent under reduced pressure at 40 °C and chromatography of the residue on silica (20 g) (diethyl ether–light petroleum, 1 : 1 and then diethyl ether as eluants) gave the starting material (17) (611 mg). Further elution with diethyl ether gave rel-(1R,2R,3S,4R)-3-*hexyl*-2-(*hydroxymethyl*)-4-*methylthietan* 1-*oxide* (19) (18 mg) as an oil, $\nu_{max.}$ (CCl_4) 3 420 (OH), and 1 050 cm^{-1} (SO); δ (see Table 1) 4.46 (1 H, m, C*H*H'OH), 3.95 (1 H, m, CH*H'*OH), 3.42 (1 H, m, OH), 1.50 (2 H, m, 9-CH_2). 1.25 (8 H, m, $[CH_2]_4$), and 0.87 (3 H, t, *J* 7 Hz, terminal Me); δ ($CDCl_3$–D_2O) 4.46 (2 H, dd, J_{AB} 12 Hz, J_{AX} 10 Hz, C*H*H'OH), and 3.95 (2 H, dd, J_{AB} 12 Hz, J_{BX} 4 Hz, CH*H'*-OH); *m/e* 218 (M^+) (Found: C, 60.2; H, 10.2; S, 14.8. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.2; S, 14.7%). Further elution gave rel-(1R,2S,3R,4R)-3-*hexyl*-2-(*hydroxymethyl*)-4-*methylthietan* 1-*oxide* (20) (54 mg), m.p. 44 °C (from diethyl ether–light petroleum), $\nu_{max.}$ (CCl_4) 3 350 (OH), and 1050 cm^{-1} (SO); δ (see Table 1) 4.32 (1 H, t, *J* 5 Hz, OH), 3.98 (2 H, m, CH_2OH), 1.25 (10 H, m, $[CH_2]_5$), and 0.87 (3 H, t, *J* 7 Hz, terminal Me); *m/e* 218 (M^+) (Found: C, 60.8; H, 10.3; S, 14.85. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.2; S, 14.7%). Conversion of the compound (17) into the thietans (19) and (20) was achieved in a yield of 9%; the combined yield was 22%, based on starting material consumed.

rel(1R,2R,3R,4R)- *and* rel-(1R,2S,3S,4R)-3-*Hexyl*-2-(*hydroxymethyl*)-4-*methylthietan* 1-*Oxide* (21) *and* (22).—Treatment of *threo*-2-t-butylsulphinyl-3-vinylnonan-1-ol (16) (4.29 g) in the same way gave (in order of elution from silica with diethyl ether) starting material (16) (2.54 g), rel-(1R,2R,3R,4R)-2-3-*hexyl*-2-(*hydroxymethyl*)-4-*methylthietan* 1-*oxide* (21) (450 mg, 33% based on starting material consumed), m.p. 68 °C (from diethyl ether–light petroleum), $\nu_{max.}$ (CCl_4) 3 390 (OH) and 1 045 cm^{-1} (SO); δ (see Table 1) 4.19 (1 H, dd, *J* 7 Hz, *J'* 6 Hz, OH), 4.04 (1 H, m, C*H*H'OH), 3.82 (1 H, m, CH*H'*OH), 1.50 (2 H, m, 9-CH_2), 1.25 (8 H, m, $[CH_2]_4$), and 0.85 (3 H, t, *J* 7 Hz, terminal Me); δ ($CDCl_3$–D_2O) 4.04 (1 H, dd, J_{AB} 12 Hz, J_{AX} 8 Hz, C*H*H'OH), and 3.82 (1 H, dd, J_{AB} 12 Hz, J_{BX} 3 Hz, CH*H'*OH); *m/e* 218 (M^+) (Found: C, 60.8; H, 10.1; S, 14.6. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.2; S, 14.7%), and rel-(1R,2S,3S,4R)-3-*hexyl*-2-(*hydroxymethyl*)-4-*methylthietan* 1-*oxide* (22) (150 mg, 11% based on starting material consumed), m.p. 38—41 °C (from diethyl ether–light petroleum), $\nu_{max.}$ (CCl_4) 3 360 (OH) and 1 045 cm^{-1} (SO); δ (see Table 1) 4.27 (1 H, m, OH), 4.02 (1 H, m, C*H*H'OH), 3.77 (1 H, m, CH*H'*OH), 1.47 (2 H, m, 9-CH_2), 1.25 (8 H, m, $[CH_2]_4$), and 0.87 (3 H, t, *J* 7 Hz, terminal Me); δ (CDCl–D_2O) 4.02 (1 H, dd, J_{AB} 12 Hz, J_{AX} 4 Hz, C*H*H'OH), and 3.77 (1 H, d, J_{AB} 12 Hz, J_{BX} 6 Hz, CH*H'*OH); *m/e* 218 (M^+) (Found: C, 60.3; H, 10.1; S, 14.5. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.2; S, 14.7%).

I.r. and Osmometric Measurements for the Hydroxy-sulphoxides (19)—(22).—The compounds (19)—(22) in carbon tetrachloride each exhibited only one hydroxy-absorption band (see above) at wavenumbers typical of hydrogen-bonded hydroxy-groups. The molecular extinction coefficients for these bands, using peak heights as a measure of optical density, were very similar at five different concen-

trations, each of which differed by a factor of two within the range 135—6.9 mmol l^{-1} for each compound. The extinction coefficients were: 43 ± 4 for (19); 83 ± 8 for (20); 59 ± 6 for (21); and 82 ± 5 for (22). Intermolecular association of these hydroxy-sulphoxides (M, 218) in carbon tetrachloride and chloroform was revealed by their apparent molecular weights in solution, determined by use of a Mechrolab vapour phase osmometer. For carbon tetrachloride solutions these were (concentrations, in mmol l^{-1}, in parentheses): 472 for (19) (165.7); 468 for (20) (58.2); 355 for (21) (98.6); and 533 for (22) (95.4). For chloroform solutions they were: 257 for (19) (60.3); 272 for (20) (68.6); 233 for (21) (74.5); and 272 for (22) (62.8).

TABLE 2

Fractional atomic co-ordinates with standard deviations in parentheses: values multiplied by 10^4

	x/a	y/b	z/c
C(2)	−1 339(5)	4 787(9)	3 455(5)
H(2A)	−0 840(5)	5 718(9)	3 756(5)
C(3)	−1 652(5)	4 662(9)	2 121(5)
H(3A)	−1 605(5)	5 642(9)	1 612(5)
C(4)	−0 824(5)	3 412(8)	1 974(5)
H(4A)	−1 019(5)	2 631(8)	1 283(5)
C(6)	−2 199(5)	5 125(11)	4 278(5)
H(6A)	−2 905(5)	4 415(11)	4 082(5)
H(6B)	−2 460(5)	6 248(11)	4 167(5)
C(8)	0 314(6)	3 928(10)	1 740(6)
H(8A)	0 837(6)	2 994(10)	1 650(6)
H(8B)	0 676(6)	4 596(10)	2 454(6)
H(8C)	0 236(6)	4 562(10)	0 950(6)
C(9)	−2 865(5)	4 193(10)	1 767(5)
H(9A)	−3 398(5)	5 045(10)	2 021(5)
H(9B)	−3 011(5)	3 199(10)	2 224(5)
C(10)	−3 162(6)	3 914(11)	0 455(6)
H(10A)	−3 959(6)	3 384(11)	0 321(6)
H(10B)	−2 543(6)	3 199(11)	0 174(6)
C(11)	−3 218(7)	5 271(11)	−0 280(6)
H(11A)	−3 757(7)	6 058(11)	0 055(6)
H(11B)	−2 399(7)	5 730(11)	−0 259(6)
C(12)	−3 677(7)	4 883(11)	−1 551(6)
H(12A)	−4 460(7)	4 331(11)	−1 550(6)
H(12B)	−3 098(7)	4 163(11)	−1 898(6)
C(13)	−3 849(9)	6 200(14)	−2 316(7)
H(13A)	−4 417(9)	6 933(14)	−1 965(7)
H(13B)	−3 065(9)	6 742(14)	−2 338(7)
C(14)	−4 325(7)	5 776(12)	−3 553(6)
H(14A)	−4 440(7)	6 746(12)	−4 082(6)
H(14B)	−5 112(7)	5 237(12)	−3 538(6)
H(14C)	−3 760(7)	5 046(12)	−3 910(6)
O(5)	0 342(3)	2 790(6)	4 140(3)
O(7)	−1 722(3)	4 897(6)	5 447(3)
S(1)	−0 813(1)	2 911(3)	3 522(1)

Crystallographic Analysis of the Compound (20).—*Crystal data*. $C_{11}H_{22}O_2S$, M_r = 218.4, Monoclinic, space group, $P2_1/c$, a = 12.19(4), b = 9.16(5), c = 11.62(4) Å, β = 97.16(3)° from diffractometer measurements (Mo-K_α radiation), V = 1 287.2 Å^3, Z = 4, $F(000)$ = 480, μ = 1.89 cm^{-1}.

The compound (20) was crystallized from light petroleum (b.p. 40—60 °C). Systematic absences (from precession photographs) $h0l$ with l odd and $0k0$ with k odd indicated space group $P2_1/c$. Data were collected for $h0$—$6l$ with $\theta_{max.}$ = 27.5° on a Stoe STADI-2 2-circle diffractometer (graphite monochromated Mo-K_α radiation). This gave 2 174 sets of data of which 1 002 unique reflexions with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The structure was solved by direct phasing methods with the SHELX-76 system of programmes,[24] which was used for all calculations. Complex neutral atomic scattering factors were taken from International Tables for X-Ray Crystallography.[25] Hydrogen atoms (except those on the hydroxy-group which could not be reliably located) were placed in calculated positions and refined with isotropic temperature factors and constrained C–H bond lengths. Weighted full-matrix least-squares refinement converged at R = 0.081 for 1 002 observed reflexions ($R = \Sigma||F_o| - |/\Sigma|F_o|$); R_w = 0.067 ($R_w = \Sigma(||F_o| - |F_c||\cdot w^{\frac{1}{2}})/\Sigma(|F_o|\cdot w)^{\frac{1}{2}}$, $w = 9.84/\sigma^2(F_o) + 1.6 \times 10^{-4}F_o^2$). The crystal began to decompose part-way through data collection. Layer scale factors partially corrected for this, but R remains rather high. In the final refinement cycle all shifts in parameters were less than their standard deviations. Positional parameters are given in Table 2, bond distances and bond angles in Table 3, and torsion angles in Table 4. Structure factors and thermal parameters are listed in Supplementary Publication No. 23267 (9 pp.).*

TABLE 3

Interatomic distances and bond angles in compound (20) with estimates of standard deviations in parentheses

(a) Bond lengths/Å

C(2)–C(3)	1.555(7)	C(6)–O(7)	1.425(6)
C(2)–C(6)	1.536(8)	C(9)–C(10)	1.544(8)
C(2)–S(1)	1.832(8)	C(10)–C(11)	1.504(10)
C(3)–C(4)	1.549(9)	C(11)–C(12)	1.555(9)
C(3)–C(9)	1.545(8)	C(12)–C(13)	1.497(11)
C(4)–C(8)	1.521(8)	C(13)–C(14)	1.532(10)
C(4)–S(1)	1.856(6)	O(5)–S(1)	1.502(4)

(b) Bond angles/°

C(6)–C(2)–C(3)	122.3(5)	O(7)–C(6)–C(2)	109.6(5)
S(1)–C(2)–C(3)	90.8(5)	C(10)–C(9)–C(3)	114.0(6)
S(1)–C(2)–C(6)	115.1(6)	C(11)–C(10)–C(9)	114.4(7)
C(4)–C(3)–C(2)	94.7(5)	C(12)–C(11)–C(10)	109.7(7)
C(9)–C(3)–C(2)	113.2(5)	C(13)–C(12)–C(11)	112.8(8)
C(9)–C(3)–C(4)	112.4(6)	C(14)–C(13)–C(12)	111.2(9)
C(8)–C(4)–C(3)	114.3(6)	C(4)–S(1)–C(2)	76.5(3)
S(1)–C(4)–C(3)	90.1(4)	O(5)–S(1)–C(2)	113.0(3)
S(1)–C(4)–C(8)	110.7(4)	O(5)–S(1)–C(4)	112.0(3)

TABLE 4

Torsion angles (°) in the compound (20); estimated standard deviations *ca.* 0.5°

C(6)–C(2)–C(3)–C(4)	−143.7
C(6)–C(2)–C(3)–C(9)	−27.0
S(1)–C(2)–C(3)–C(4)	−22.7
S(1)–C(2)–C(3)–C(9)	93.9
C(3)–C(2)–C(6)–O(7)	169.0
S(1)–C(2)–C(6)–O(7)	60.3
C(3)–C(2)–S(1)–C(4)	19.3
C(3)–C(2)–S(1)–O(5)	127.7
C(6)–C(2)–S(1)–C(4)	146.2
C(6)–C(2)–S(1)–O(5)	−105.3
C(2)–C(3)–C(4)–C(8)	−90.4
C(2)–C(3)–C(4)–S(1)	22.4
C(9)–C(3)–C(4)–C(8)	152.2
C(9)–C(3)–C(4)–S(1)	−94.8
C(2)–C(3)–C(9)–C(10)	−174.2
C(4)–C(3)–C(9)–C(10)	−68.5
C(3)–C(4)–S(1)–C(2)	−19.3
C(3)–C(4)–S(1)–O(5)	−129.1
C(8)–C(4)–S(1)–C(2)	96.7
C(8)–C(4)–S(1)–O(5)	−13.0
C(3)–C(9)–C(10)–C(11)	−70.8
C(9)–C(10)–C(11)–C(12)	−172.2
C(10)–C(11)–C(12)–C(13)	175.0
C(11)–C(12)–C(13)–C(14)	−178.8

* For details of Supplementary publication scheme see Notice to Authors, No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

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