Synthesis of Sulphoxides by Intramolecular and Intermolecular Addition of Sulphenic Acids to Olefins and Dienes

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Alkene-ω-sulphenic acids generated by thermolysis of ω-(t-butylsulphinyl)alkenes at 140 °C cyclized regio- and stereo-specifically to *cis*-2-methylthiacycloalkane 1-oxides. Under these conditions *cis*-2-methylthietan 1-oxide equilibrated with its *trans*-isomer, and *cis*-2-methylthiepan 1-oxide underwent ring contraction to *cis*-2-ethylthian 1-oxide. The first examples are provided of the intermolecular addition of simple alkanesulphenic acids to unactivated olefins to give sulphoxides; 2-methylpropane-2-sulphenic acid added regiospecifically and in high yield to terminal acyclic olefins, but in low yield to cyclic olefins. Addition of 2-methylpropane-2-sulphenic acid to cyclo-octa-1,5-diene occurred stereospecifically. Thermolysis of di-t-butyl sulphoxide in hexa-1,5-diene gave a mixture of *cis*-2,5-dimethylthiolan *cis*-1-oxide and *trans*-2,5-dimethylthiolan 1-oxide; thermolysis in cyclo-octa-1,5-diene gave 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide. The constitutions and configurations of the cyclic sulphoxides were predicted from a consideration of the stereoelectronic requirements of the addition of sulphenic acids to olefins.

THE thermal decomposition of sulphoxides bearing a β-hydrogen atom provides a convenient method of making olefins.[1-6] Sulphenic acids are also produced in this reaction,[4] which is reversible[7] and which proceeds by a concerted *syn*-intramolecular mechanism (Scheme).[1] The stereoelectronic requirements of this reversible six-electron sigmatropic rearrangement controlled the stereoselectivity[1,6] and regioselectivity[5] of olefin formation from sulphoxides. We have now exploited these requirements systematically for the stereocontrolled synthesis of sulphoxides from sulphenic acids and olefins. When this work was started[8] there were some reported examples of the addition of simple sulphenic acids to activated (electrophilic) olefins,[4b,9] but examples involving unactivated olefins were confined to intramolecular cyclization of penicillin sulphenic acids,[7a] and to the intermolecular trapping of penicillin sulphenic acids by norbornadiene and keten dimer.[7b]

[1] C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, 1960, **82**, 1810.

[2] C. A. Walling and L. Bollyky, *J. Org. Chem.*, 1964, **29**, 2699; J. L. Kice and J. D. Campbell, *ibid.*, 1967, **32**, 1631; G. A. Russell, E. Sabourin, and G. J. Mikol, *ibid.*, 1966, **31**, 2854; I. D. Entwistle and R. A. W. Johnstone, *Chem. Comm.*, 1965, 29; B. M. Trost and K. K. Leung, *Tetrahedron Letters*, 1975, 4197.

[3] (*a*) D. W. Emerson, A. P. Craig, and I. W. Potts, *J. Org. Chem.*, 1967, **32**, 102; (*b*) D. W. Emerson and T. J. Kornisky, *ibid.*, 1969, **34**, 4115.

[4] (*a*) T. Colclough and J. I. Cunneen, *Chem. and Ind.*, 1960, 626; L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 1962, 3570; (*b*) J. R. Shelton and K. E. Davis, *Internat. J. Sulphur Chem.*, 1973, **8**, 205.

[5] (*a*) D. N. Jones, A. C. F. Edmonds, and S. D. Knox, *J.C.S. Perkin I*, 1976, 459, and references cited therein; (*b*) D. N. Jones, E. Helmy, and A. C. F. Edmonds, *J. Chem. Soc.* (*C*), 1970, 833.

[6] S. I. Goldberg and M. S. Sahli, *J. Org. Chem.*, 1967, **32**, 2659.

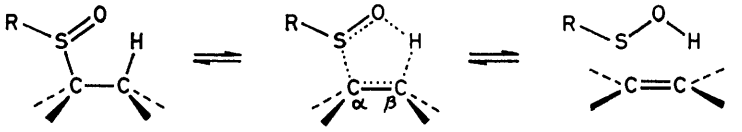
[7] (*a*) D. H. R. Barton, F. Comer, D. J. T. Greig, P. G. Sammes, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *J. Chem. Soc.* (*C*), 1971, 3540; R. D. G. Cooper, *J. Amer. Chem. Soc.*, 1970, **92**, 5010; (*b*) I. Ager, D. H. R. Barton, D. G. T. Greig, G. Lucente, P. G. Sammes, M. V. Taylor, G. Hewitt, B. E. Looker, A. Mowatt, C. A. Robson, and W. G. E. Underwood, *J.C.S. Perkin I*, 1973, 1187.

[8] Preliminary communication, D. N. Jones and D. A. Lewton, *J.C.S. Chem. Comm.*, 1974, 457.

[9] E. Block and J. O'Connor, *J. Amer. Chem. Soc.*, 1974, **96**, 3929.

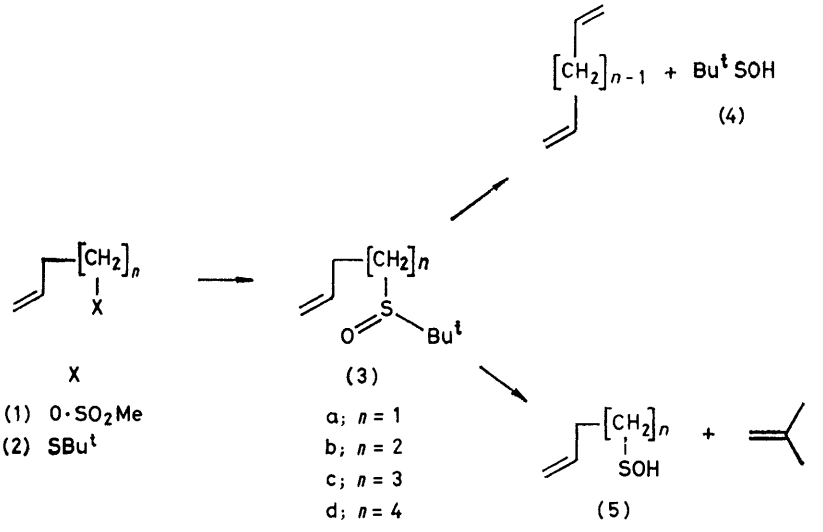
Except for derivatives of anthraquinone,[10] pyrimidine,[11] and penicillin,[12] sulphenic acids are too unstable to be isolated, and in the absence of trapping agents such as electrophilic olefins and acetylenes,[4b,9] trivalent phosphorus derivatives,[13] thiols,[14] sulphinic acids,[15] and trimethylsilyl chloride,[16] they readily undergo intermolecular dehydration to give thiosulphinates.[4a,9] These thiosulphinates themselves decompose thermally to sulphenic acids, thiosulphoxylic acids, thiocarbonyl compounds, and olefins, and they undergo disproportionation to thiosulphonates and disulphides,[9] so that unless the sulphenic acids produced by thermolysis of sulphoxides are efficiently trapped many sulphur-containing products may be formed.

We first investigated the intramolecular reaction of pent-5-ene-1-sulphenic acid (5b), itself generated by thermolysis of 5-t-butylsulphinylpent-1-ene (3b). The sulphoxide (3b) was prepared from pent-5-en-1-ol by sequential treatment with methanesulphonyl chloride to give the methanesulphonate (1b), 2-methylpropane-2-thiolate anions to give the sulphide (2b), and finally peroxydodecanoic acid to oxidize the sulphide. The homologous sulphoxides (3a, c, and d) were prepared by a similar sequence of reactions. The t-butyl sulphoxide (3b) was chosen because it provided nine β-hydrogen atoms, to optimize the formation of the sulphenic acid (5b). If statistical factors alone controlled the regioselectivity of thermolysis of the t-butyl sulphoxide (3b), the sulphenic acids (5b) and (4) should be formed in the ratio 9 : 2, but we expected the ratio to be greater than this because Emerson *et al.*[3a] have shown that in unsymmetrical dialkyl sulphoxides there is an enhanced tendency to thermolytic cleavage of the bond connecting sulphur to the more highly substituted alkyl group.



SCHEME

Thermolysis of 5-t-butylsulphinylpent-1-ene (3b) in xylene at 140 °C for 3 h gave the known[17] *cis*-2-methylthiolan 1-oxide (7) (74%) but none of the *trans*-isomer (8) or thian 1-oxide (12). This result was predictable and rational in terms of the geometry of the transition state for concerted addition, because pent-5-ene-1-sulphenic acid (5b) can readily attain a cyclic array of the five participating atoms in the transition state (*A*) leading to *cis*-2-methylthiolan 1-oxide (7), whereas cyclic transition states are sterically impossible for the transformation



into *trans*-2-methylthiolan 1-oxide (8) and thian 1-oxide (12). Related stereospecific cyclizations of olefinic sulphenic acids have been demonstrated with penicillin derivatives.[7a] In considering these transition states we examined Dreiding models of the cyclic sulphoxides (7), (8), and (12), in order to determine whether the five participating atoms (O, S, C_α, C_β, and H in the Scheme) could be constrained in a cyclic planar array. We think this is reasonable because there is evidence that the transition

[10] T. C. Bruice and P. T. Markiw, *J. Amer. Chem. Soc.*, 1957, **79**, 3150; T. C. Bruice and A. B. Sayih, *ibid.*, 1959, **81**, 3416; K. Fries, *Ber.*, 1912, **45**, 2965; W. Jenny, *Helv. Chim. Acta*, 1958, **41**, 317, 326.

[11] B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *J. Amer. Chem. Soc.*, 1969, **91**, 3634.

[12] T. S. Chou, J. R. Burgtof, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, *J. Amer. Chem. Soc.*, 1974, **96**, 1609.

[13] R. D. G. Cooper and F. L. Jose, *J. Amer. Chem. Soc.*, 1970, **92**, 2575.

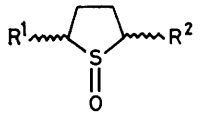
[14] D. H. R. Barton, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, B. E. Looker, and W. G. E. Underwood, *Chem. Comm.*, 1971, 1137.

[15] R. D. Allan, D. H. R. Barton, M. Girijavallabhan, and P. G. Sammes, *J.C.S. Perkin I*, 1974, 1456.

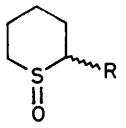
[16] F. A. Davis and A. J. Friedman, *J. Org. Chem.*, 1976, **41**, 897.

[17] J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, 1970, **35**, 3655.

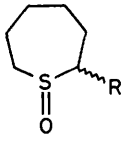
state resembles sulphoxide more than sulphenic acid,[1,5b] and the thermolytic behaviour of steroidal sulphoxides [5] and cyclic sulphoxides [18] indicates that ease of attainment of coplanarity of the five participating atoms influences the energy of the transition state. This tendency towards coplanarity in the cyclic transition state of eliminations proceeding by the *Ei* mechanism is generally



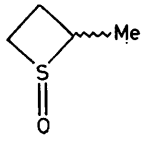
	R^1	R^2
(6)	H	H
(7)	*cis* - Me	H
(8)	*trans* - Me	H
(9)	*cis* - Me	*cis* - Me
(10)	*trans* - Me	*cis* - Me
(11)	*trans* - Me	*trans* - Me



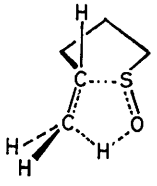
	R
(12)	H
(13)	*cis* - Me
(14)	*trans* - Me
(15)	*cis* - Et
(16)	*trans* - Et



	R
(17)	H
(18)	*cis* - Me
(19)	*trans* - Me



(20)	*cis* - Me
(21)	*trans* - Me



(*A*)

accepted,[19] although deviations from coplanarity can more readily be tolerated when the migrating hydrogen atom is rendered more acidic by an activating group.[20]

Mixtures of *cis*- and *trans*-2-methylthiolan 1-oxide, (7) and (8), have been obtained by oxidation of 2-methylthiolan,[17] but separation of the isomers by chromatography was difficult. Treatment of mixtures of (7) and (8) with sodium hydrogen sulphite has been shown to give pure *trans*-2-methylthiolan 1-oxide (8) because the *cis*-isomer was the more rapidly reduced, but yields were not specified.[21] The thermolysis of the sulphoxide (**3**b) now provides an easy synthesis of *cis*-2-methylthiolan 1-oxide (7), and since stereospecific inversion of configuration in (7) has been achieved,[17,21] both isomers are now accessible by stereospecific methods.

Thermolysis of 6-t-butylsulphinylhex-1-ene (**3**c) in xylene at 140 °C for 3.5 h gave *cis*-2-methylthian 1-oxide (**13**) (88%), and none of the *trans*-isomer (**14**) or thiepan 1-oxide (**17**). The product (**13**) was identical with one of the two sulphoxides (previously of unestablished configuration) obtained by oxidation of 2-methylthian.[22] Initial allocation of configuration followed from the fact that (**13**) may be formed from the sulphenic acid (5c) by way of a cyclic planar transition state [*cf.* (*A*)] according to Dreiding models, whereas a cyclic transition state connecting (5c) and the *trans*-isomer (**14**) is geometrically impossible. Similar transition state arguments were used successfully to predict the stereospecificity and regiospecificity of the cyclization of a steroidal sulphenic acid to a steroidal thian 1-oxide derivative.[23] A cyclic transition state connecting the sulphenic acid (5c) and thiepan 1-oxide (**17**) is not geometrically impossible, but models indicate that it is much more strained than that leading to *cis*-2-methylthian 1-oxide (**13**). However, it seems likely that a more important reason for the absence of thiepan 1-oxide lies in the tendency of sulphenic acids to add to terminal olefins regioselectively in a Markownikoff manner (see later).

The configuration of *cis*-2-methylthian 1-oxide (**13**) was confirmed in the following manner. Treatment of (**13**) with hydrochloric acid in dioxan [22,24] gave an equilibrium mixture of *cis*- and *trans*-2-methylthian 1-oxide, (**13**) and (**14**), in the ratio 64 : 36, which were separated by chromatography. The n.m.r. characteristics of these isomers in deuteriochloroform (Table) were strikingly similar to those for their 4-t-butyl analogues, (**22**) and (**23**), the configurations of which have been reliably established.[25] Since the conformations of (**22**) and (**23**) are fixed by the t-butyl group, this n.m.r. evidence also suggests that *cis*-2-methylthian 1-oxide (**13**) and *trans*-2-methylthian 1-oxide (**14**) adopt preferentially the depicted conformations (*B*) and (*C*), respectively. This accords with the predictions of conformational analysis. Sulphinyl oxygen in thian 1-oxide [26] and 4-substituted thian 1-oxides [27,28] prefers the axial orientation by about 0.4 kcal mol^{-1}, according to calculation by

[18] D. N. Jones, D. R. Hill, and D. A. Lewton, *Tetrahedron Letters*, 1975, 2235.
[19] D. J. Cram in ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 304; E. L. Eliel, ' Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 232; A. G. W. Baxter and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1976, 366.
[20] A. G. W. Baxter, J. Kitchin, R. J. Stoodley, and R. B. Wilkins, *J.C.S. Chem. Comm.*, 1973, 285; R. J. Stoodley and R. B. Wilkins, *J.C.S. Perkin I*, 1974, 1572.
[21] C. R. Johnson, C. C. Bacon, and J. J. Rigau, *J. Org. Chem.*, 1972, **37**, 919.
[22] L. Sagramora, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, 1972, **55**, 675.
[23] D. N. Jones, D. A. Lewton, J. D. Msonthi, and R. J. K. Taylor, *J.C.S. Perkin I*, 1974, 2637.
[24] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1964, **86**, 1452.
[25] R. Lett, S. Bory, B. Moreau, and A. Marquet, *Bull. Soc. chim. France*, 1973, 2851.
[26] J. B. Lambert and R. G. Keske, *J. Org. Chem.*, 1966, **31**, 3429.
[27] J. C. Martin and J. J. Uebel, *J. Amer. Chem. Soc.*, 1964, **86**, 2936; J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem.*, 1972, **37**, 377.
[28] C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, 1965, **87**, 1109.

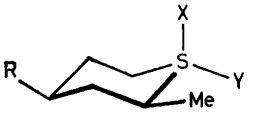
the Westheimer method,[29] and the methyl group in methylcyclohexane, which can be taken as an approximate model for 2-methylthian, exerts a preference for the equatorial orientation of 1.7 kcal mol^{-1}.[30] The conformation (*C*) also derives some stability from the proximity of the sulphinyl oxygen to one of the hydrogen atoms of the methyl group, since the separation of 2.7 Å (from Dreiding models) is identical with that which leads to an attractive interaction of *ca.* 0.4 kcal mol^{-1} between axial sulphinyl oxygen and two *syn*-axial hydrogen atoms in the axial conformer of thian 1-oxide.[28,29] The attractive interaction between the sulphinyl oxygen and the methyl group in (*C*) may therefore be assumed to be *ca.* 0.2 kcal mol^{-1}. Consequently, the diequatorial conformation (*C*) of the *trans*-isomer (14) should be favoured over the diaxial conformation (*D*) by *ca.* 1.5 kcal mol^{-1}, corresponding to a ratio of 93 : 7 at 25 °C, whereas conformation (*B*) of the *cis*-isomer (13) should be more stable than the conformation (*E*) by *ca.* 2.3 kcal mol^{-1}, indicating that conformation (*B*) should be populated to the extent of 98% at 25 °C. Furthermore, this analysis suggests that (*B*) should be more stable than (*C*) by *ca.* 0.2 kcal mol^{-1}, which accords reasonably well with the experimentally observed value of *ca.* 0.3 kcal mol^{-1}. This crude conformation analysis is at least qualitatively correct despite the uncertainty concerning the value of the axial preference of sulphinyl oxygen in thian 1-oxide systems; values estimated from experimental data span the range 0.2—1.3 kcal mol^{-1}.[26,28] The *cis*-isomer (13) (*B*) was chromatographically (t.l.c., g.l.c.) more mobile than the *trans*-isomer (14) (*C*). This supports the allocation of configuration, since there are many examples which indicate that axial thian 1-oxides are chromatographically more mobile than their equatorial isomers.[23,28,31]

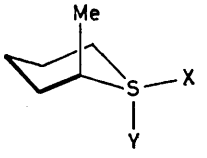
N.m.r. data (τ values) for 2-methylthiacycloalkane 1-oxides*

	Me				2-H		6-H			
	cis		*trans*		*cis*	*trans*	*cis*		*trans*	
	a	b	a	b	a	a	a	b	a	b
(20)	8.47	8.89				6.91				
(21)			8.86	9.54	6.14					
(7)	8.60	8.82				7.32				
(8)			8.77	9.26						
(9)	8.63	8.83				7.00				
(10)	8.62	8.83	8.63	9.09		7.00				
(13)	8.69	8.98				7.53	6.96	7.53		
(14)			8.58	8.88	7.40		7.40		6.69	7.24
(22)	8.70	8.93				7.68	6.92	7.42		
(23)			8.60	8.81	7.44		7.44		6.66	7.07
(15)							6.92	7.50		
(16)									6.71	7.27
(18)	8.62	8.87								
(19)			8.59	8.87						

* a, for $CDCl_3$ solutions; b, for C_6D_6 solutions; *cis* and *trans* refer to the configuration with respect to sulphinyl oxygen.

Thermolysis of 7-t-butylsulphinylhept-1-ene (3d) in xylene at 140 °C for 3.5 h gave a mixture of *cis*-2-methylthiepan 1-oxide (18) and *cis*-2-ethylthian 1-oxide (15)





(22) R = Bu^t, X = O, Y = lone electron pair
(23) R = Bu^t, X = lone electron pair, Y = O
(*B*) R = H, X = O, Y = lone electron pair
(*C*) R = H, X = lone electron pair, Y = O
(*D*) X = lone electron pair, Y = O
(*E*) X = O, Y = lone electron pair

(combined yield 48%) in the ratio 65 : 35 according to g.l.c. We could not separate these sulphoxides on a preparative scale, because (18) isomerized to (15) on preparative g.l.c., and the isomers were chromatographically identical on columns and thin layers of silica. The configuration at sulphur in *cis*-2-methylthiepan 1-oxide follows from its formation by thermolysis of 7-t-butylsulphinylhept-1-ene (3d); the sulphenic acid (5d) formed by thermal decomposition of (3d) can cyclize to *cis*-2-methylthiepan 1-oxide (18) but not to its *trans*-isomer (19) by way of a cyclic transition state. *cis*-2-Ethylthian 1-oxide (15) arises from *cis*-2-methylthiepan 1-oxide (18) by stereospecific ring contraction under the reaction conditions.[18] This easy ring contraction coupled with the chromatographic similarity of (18) and (15) renders the

[29] N. L. Allinger, J. A. Hirsh, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, 1969, **91**, 337.
[30] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965, p. 44.
[31] P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Comm.*, 1967, 550; R. Nagarajan, B. H. Chollar, and R. M. Dodson, *ibid.*, p. 552.

thermolysis of (3d) of little practical utility for the synthesis of *cis*-2-methylthiepan 1-oxide (18).

cis-2-Methylthiepan 1-oxide (18) and *cis*-2-ethylthian 1-oxide (15) were prepared independently as follows. Oxidation of 2-ethylthian, prepared from thian by the method of Tuleen and Bennett,[32] with peroxydodecanoic acid gave a mixture of *cis*- and *trans*-2-ethylthian 1-oxide, (15) and (16), in the ratio 2 : 3. They were separated by chromatography, and allocation of configuration was based on the known stereoselectivity of peroxy-acid oxidation of thian derivatives, and on the established relative chromatographic behaviour of isomeric thian 1-oxide derivatives, which indicate that the less abundant, chromatographically more mobile isomer should have the *cis*-configuration.[23,28,31,33] The similarity of the n.m.r. characteristics (Table) of *cis*- and *trans*-2-ethylthian 1-oxide, respectively, to those of *cis*- and *trans*-2-methylthian 1-oxide substantiated these assignments of configuration. 2-Methylthiepan on oxidation with peroxydodecanoic acid gave a mixture of *cis*- and *trans*-2-methylthiepan 1-oxide, (18) and (19), in the ratio 4 : 96, which was separated into its components by chromatography. The *cis*-isomer (18) was the more mobile, behaviour which finds analogy in the greater chromatographic mobility of *cis*-2-methylthiolan 1-oxide (7) and *cis*-2-methylthian 1-oxide (13) than of their respective *trans*-isomers, (8) and (14). Furthermore, the predominant formation of the *trans*-isomer (19) on oxidation of 2-methylthiepan by peroxy-acid finds analogy in the stereoselectivity of oxidation of 2-methylthian and 2-methylthiolan with the same reagent. Oxidation of 2-methylthiepan with hydrogen peroxide to give two sulphoxides in the ratio 2 : 98 has been described previously,[22] but their configurations were not established.

Thermolysis of 4-t-butylsulphinylbut-1-ene (3a) in xylene at 140 °C for 3.5 h gave *cis*- (20) (24%) and *trans*- (21) 2-methylthietan 1-oxide (7%), after chromatography on silica. As expected, no thiolan 1-oxide (6) was formed, since a cyclic transition state connecting the intermediate sulphenic acid (5a) and thiolan 1-oxide (6) is geometrically impossible. Models reveal that a cyclic transition state, albeit strained, is possible for the conversion of (5a) into *cis*-2-methylthietan 1-oxide (20), and we consider that *trans*-2-methylthietan 1-oxide (21) arises by isomerization of the *cis*-isomer (20). The *cis*- and *trans*-2-methylthietan 1-oxides interconverted at 140 °C in xylene to give a mixture of (20) and (21) in the ratio *ca.* 2 : 1 after 4 h, and the neat sulphoxides interconverted slowly (20 days) even at 20 °C to give a *ca.* 2 : 1 mixture. The greater thermodynamic stability of the *cis*- (20) than of the *trans*-isomer (21) finds analogy in the behaviour of the five- and six-membered counterparts (7) and (8), and (13) and (14). No uncatalysed stereomutation of saturated dialkyl or saturated cyclic sulphoxides at room temperature has been reported hitherto. The stereomutation of sulphoxides, which may proceed by a number of mechanisms,[34] is currently of interest,[35] but evidence relating to the ease of thermal stereomutation of thietan 1-oxide systems is confined to a report that 3-substituted thietan 1-oxides equilibrated in less than 15 min at 170 °C;[36] in contrast, thermal equilibration of diastereoisomeric 4-substituted thian 1-oxides was complete only after 1 h at 190 °C.[28] 2-Methylthietan has been synthesized,[37] but its oxidation to 1-oxides has not been reported.

The configurations of *cis*- and *trans*-2-methylthietan 1-oxides, (20) and (21), were deduced from their n.m.r. spectra (Table) by using the criterion that a methyl group *cis* to sulphinyl oxygen is more deshielded than that *trans* to oxygen. Models constructed in the knowledge that thietan rings are puckered,[36,38,39] and alkyl groups in these systems prefer to adopt a pseudoequatorial orientation,[39] showed this criterion to be reasonable when cognisance was taken of the known features of the anisotropy of the sulphoxide function,[40] in which there is deshielding in the region surrounding an orthogonal plane bisecting the sulphur–oxygen bond, and in which the lone electron pair on sulphur exhibits a shielding effect upon proximate protons on the same side of the ring.[36,39] Additionally, the benzene-induced shifts in the methyl-group resonances were consistent with the predictions of Ledaal's model,[41] in which complexation with benzene should cause a greater shielding of the methyl group in the *trans*- (21) than the *cis*-isomer (20).

The Table shows that methyl groups at C-2 *cis* to sulphinyl oxygen in the four- and five-membered cyclic sulphoxides are more deshielded than those in their *trans*-isomers, whereas in the six- and seven-membered sulphoxides the converse is true. Furthermore, for deuteriochloroform solutions the methyl group in the *cis*-isomers (13), (7), and (20) becomes increasingly more deshielded with decreasing ring size, whereas for the *trans*-isomers (14), (8), and (21), the methyl group becomes increasingly more shielded. These trends are rational in terms of the progressive flattening of the rings with decreasing size, which decreases the torsion angle [about the S–C(2) bond] between the methyl group and sulphinyl oxygen in the *cis*-isomers, and decreases the

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[36] C. R. Johnson and W. O. Siegl, *J. Amer. Chem. Soc.*, 1969, **91**, 2796.
[37] L. A. Paquette and J. P. Freeman, *J. Org. Chem.*, 1970, **35**, 2249.
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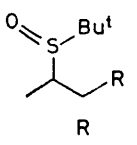
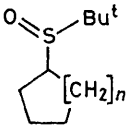
[39] R. M. Dodson, E. H. Jankis, and G. Klose, *J. Org. Chem.*, 1970, **35**, 2520; W. O. Siegl and C. R. Johnson, *ibid.*, p. 3657; *Tetrahedron*, 1971, **27**, 341; B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, *J. Amer. Chem. Soc.*, 1971, **93**, 676; W. Wucherpfennig, *Tetrahedron Letters*, 1970, 765.
[40] R. D. G. Cooper, P. V. DeMarco, J. C. Cheng, and N. D. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 1408, and references cited therein.
[41] T. Ledaal, *Tetrahedron Letters*, 1968, 1683.

torsion angle between the methyl group and the lone electron pair on sulphur in the *trans*-isomers.

The ease of the intramolecular additions of sulphenic acids to unactivated olefins encouraged us to investigate some intermolecular reactions. There had been reports that such reactions do not occur in simple systems,[4b,9] but on the other hand sulphenic acids derived from penicillins had been trapped by unactivated olefins.[7b] Thermolysis of di-t-butyl sulphoxide in pentene at 140 °C for 8 min and in boiling octene for 4 min gave 2-t-butylsulphinylpentane (24) (83%) and 2-t-butylsulphinyloctane (25) (74%), respectively. These results are consistent with the thermal decomposition of di-t-butyl sulphoxide to 2-methylpropane-2-sulphenic acid, which in turn added regiospecifically to the olefin. The regiospecificity of addition accords with the suggestion that





(24) Et
(25) $[CH_2]_4 \cdot CH_3$
(26) $CH_2 \cdot CH{:}CH_2$

(27) $n = 1$
(28) $n = 2$
(29) $n = 4$

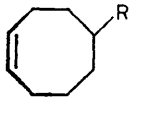
the partial carbon–sulphur bond in the transition state for the reversible sigmatropic reaction (Scheme) is polarized in such a manner that the carbon atom has some cationic character.[3,4b] Addition in the Markownikoff manner should therefore be facilitated.

Cyclopentene, cyclohexene, and cyclo-octene also added 2-methylpropane-2-sulphenic acid, generated by thermolysis of di-t-butyl sulphoxide, to give the t-butyl cycloalkyl sulphoxides (27) (28%), (28) (8%), and (29) (12%), respectively. For both acylic and cyclic olefins the efficiency of intermolecular addition of 2-methylpropane-2-sulphenic acid depended markedly on the mode of purification of the di-t-butyl sulphoxide. Best results were obtained when it was sublimed and stored under reduced pressure. Use of material purified by crystallization or stored in air after sublimation resulted in much less efficient addition.

The successful intermolecular addition of 2-methylpropane-2-sulphenic acid to olefins provided the basis for the easy synthesis of thiolan 1-oxide derivatives from 1,5-dienes. Thermolysis of di-t-butyl sulphoxide in hexa-1,5-diene at 130 °C for 5 min gave 5-t-butylsulphinylhex-1-ene (26) (84%). Further thermolysis of the sulphoxide (26) at 120 °C for 4 h in light petroleum gave an approximately equimolecular mixture of *cis*-2,5-dimethylthiolan *cis*-1-oxide (9) and *trans*-2,5-dimethylthiolan 1-oxide (10) (51% combined yield). Thermolysis of di-t-butyl sulphoxide in hexa-1,5-diene for 20 min at 130 °C furnished a mixture of (26) (21%), (9) (23%), and (10) (11%) after chromatography.

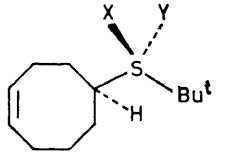
The sulphoxides (9) and (10) were separated by chromatography, and their constitutions and configurations were deduced from their n.m.r. spectra (Table) by use of the criteria described earlier in the text.[17] In accord with the configurational assignments the *cis,cis*-isomer (9) in which sulphinyl oxygen is sterically hindered by two methyl groups was chromatographically more mobile than the *cis,trans*-isomer (10) in which oxygen is encumbered by only one methyl group. The oxidation by hydrogen peroxide of *trans*-2,5-dimethylthiolan to its 1-oxide (10) and of *cis*-2,5-dimethylthiolan to a sulphoxide has been reported,[42] but configuration at sulphur in the latter sulphoxide was not mentioned. We consider this compound to be *cis*-2,5-dimethylthiolan *trans*-1-oxide (11) since its reported n.m.r. characteristics in deuterium oxide (C-2 and C-5 proton signals at τ 6.82) differed from those of *cis*-2,5-dimethylthiolan *cis*-1-oxide (9), in which the C-2 and C-5 protons resonated at τ 6.54. This assignment concurs with the general observation that hydrogen peroxide oxidizes thiolan derivatives from the less hindered side.[17,33]

The foregoing reactions suggested a convenient synthesis of 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37). The parent bicyclic sulphide (36) was previously accessible only by a cumbersome five-step synthesis from cyclo-octa-1,3-diene in 3% overall yield.[43] It was possible to predict that the sulphenic acid (33) generated by pyrolysis of the cyclo-octenyl t-butyl sulphoxides (34)

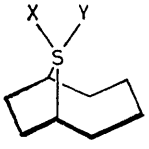


R

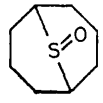
(30) $O \cdot SO_2Me$
(31) SBu^t
(32) SO_2Bu^t
(33) SOH



(34) X = O, Y = lone electron pair
(35) X = lone electron pair, Y = O
(One enantiomer shown in each case)



(36) X = Y = lone electron pair
(37) X = lone electron pair, Y = O
(38) X = O, Y = lone electron pair
(39) X = Y = O



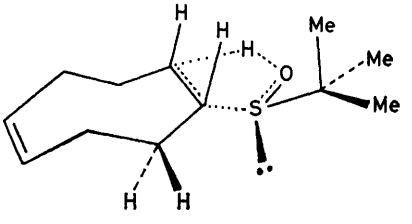
(40)

and (35) would cyclize to 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) and not to the isomeric *exo*-oxide (38) or 9-thiabicyclo[3.3.1]nonane 9-oxide (40), since models reveal that a cyclic transition state which approaches (but does not achieve) coplanarity can be obtained for the intramolecular addition of the sulphenic acid to the olefin in (33) to give (37), whereas in the transition states leading to the *exo*-oxide (38) and the oxide (40) the five

[42] A. R. Jones, *Chem. Comm.*, 1971, 1042.

[43] E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, 1966, **31**, 1669.

participating atoms deviate markedly from coplanarity. Accordingly, thermolysis of di-t-butyl sulphoxide in cyclo-octa-1,5-diene at 148 °C for 1.5 h gave 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (36%) as the only bicyclic sulphoxide obtained after chromatography and sublimation. The constitution of the sulphoxide (37) was established by its reduction with phosphorus trichloride to give the known bicyclic sulphide (36), and by its oxidation to the known sulphone (39).[43] The *endo*-configuration of the sulphoxide (37) predicted by the transition state arguments was substantiated by the fact that an isomeric sulphoxide (38) was obtained exclusively on oxidation of the bicyclic sulphide (36) with peroxydodecanoic acid in light petroleum, and by the observation that the sulphoxide (38) was chromatographically



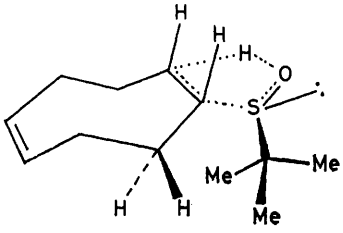
(F)

less mobile than the sulphoxide (37). This behaviour was consistent with the allocated configurations, since models show that the *endo*-face of the sulphur bridge in (36) is more sterically crowded than the *exo*-face (see before). Independent syntheses of the sulphoxides (37) and (38),[35] reported since this work was completed,[8] confirm these assignments of configuration.

The convenience of this synthesis of the *endo*-oxide (37) from cyclo-octa-1,5-diene was emphasized by the fact that it was difficult to obtain from the bicyclic sulphide (36). Oxidation of (36) with ozone or with periodate gave the *exo*-oxide (38) exclusively, whereas t-butyl hypochlorite or *N*-chlorobenzotriazole [44] in aqueous methanol gave mixtures of the *exo*- and *endo*-sulphoxides (87 : 13 and 93 : 7, respectively) in which the *exo*-isomer (38) markedly predominated.

In order to elucidate some of the details of the conversion of cyclo-octa-1,5-diene into the bicyclic sulphoxide (37) we prepared the diastereoisomeric cyclo-octenyl t-butyl sulphoxides (34) and (35). Treatment of cyclo-oct-4-en-1-ol with methanesulphonyl chloride gave the methanesulphonate (30), which on reaction with 2-methylpropan-2-thiolate ions in propan-2-ol furnished 5-t-butylthiocyclo-octene (31). Oxidation of the sulphide (31) with peroxydodecanoic acid in light petroleum gave a mixture of (*RS,SR*)-5-t-butylsulphinylcyclo-octene (34) and (*RS,RS*)-5-t-butylsulphinylcyclo-octene (35), which were separated by chromatography. These sulphoxides differed only in configuration at sulphur: oxidation of each isomer separately gave the same sulphone (32).

Thermolysis of (34) and (35) separately in xylene at 140 °C for 30 min gave 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (12 and 19%, respectively). Quenching a mixture of cyclo-octadiene and di-t-butyl sulphoxide after 2 min at 140 °C gave the (*RS,SR*)-isomer (34) in 36% yield; under these conditions none of the diastereoisomeric sulphoxide (35) nor the bicyclic sulphoxide (37) was obtained. This provided the first example of a stereospecific intermolecular addition of a sulphenic acid to an olefin. The stereospecificity is rational in terms of the cyclic, concerted mechanism of addition, since the transition state (*F*) for conversion of cyclo-octa-1,5-diene into (34) is much less sterically compressed than the transition state (*G*) leading to (35), by virtue of the greater non-bonded interactions between the t-butyl group and the ring in (*G*) than in (*F*). The configuration of (34) followed from this rationale, which is identical in principle with that used previously for the allocation of



(G)

configuration to steroidal sulphoxides on the basis of their relative rates of thermolysis.[5]

The low yield (12%) obtained for the thermolytic conversion of (34) into the *endo*-oxide (37) in boiling xylene contrasted with the 42% yield of (37) obtained by thermolysis of di-t-butyl sulphoxide in cyclo-octa-1,5-diene. However, thermolysis of the sulphoxide (34) in boiling cyclo-octa-1,5-diene gave the bicyclic sulphoxide (37) in 44% yield, decomposition of (34) taking 1.5 h to complete under these conditions whereas in boiling xylene (140 °C) it was complete after 30 min. Therefore it appeared that the sulphoxide (34) gave the sulphenic acid (33) and 2-methylpropane-2-sulphenic acid (4), and that in cyclo-octa-1,5-diene the sulphenic acid (4) recombined with the solvent to give (33), which thereby maintained its concentration sufficiently to optimise its conversion *via* the sulphenic acid (34) into the bicyclic sulphoxide (37). This interpretation was substantiated by the behaviour of the (*RS,RS*)-isomer (35) on thermolysis in cyclo-octa-1,5-diene at 148 °C; after 15 min (35) had completely decomposed to give the isomeric (*RS,SR*)-sulphoxide (34) and the bicyclic sulphoxide (37). Evidently the sulphoxide (35) was also decomposing to both 2-methylpropane-2-sulphenic acid (4) and cyclo-oct-4-ene-1-sulphenic acid (33), and whereas the latter (33) cyclized in part to the *endo*-sulphoxide (37), the former (4) added in part to the solvent to give only (34) in accord with the transition states arguments presented earlier. The marked extent of elimination into the cyclo-octene ring on thermolysis of (34) and (35) indicated that the statistical and electronic factors [3] which normally favour elimination into the t-butyl group are not

[44] W. D. Kingsbury and C. R. Johnson, *Chem. Comm.*, 1969, 365.

predominant, and we tentatively consider that, in analogy with the behaviour of steroidal t-butyl sulphoxides,[5b] relief of steric compression associated with the decomposition of these sulphoxides into cyclo-octadiene and 2-methylpropane-2-sulphenic acid is important in determining the regioselectivity of elimination.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined with either a Perkin-Elmer 457 or 180 spectrophotometer, u.v. spectra for solutions in ethanol with a Cary 14 spectrophotometer, mass spectra with an A.E.I. MS9 or MS12 instrument, and n.m.r. spectra with a Varian HA-100 spectrometer for solutions in deuteriochloroform, unless otherwise indicated. Analytical g.l.c. was performed on a Perkin-Elmer F11 gas chromatograph, utilizing a flame ionization detector. Glass columns (6 ft, with 3 mm int. diam.) were used with a gas flow rate of 35 ml min^{-1}. The column packings employed were 5% FFAP on Chromosorb G,AW-DMCS (80—100 mesh); 2.5% OV 17 on Chromosorb G,AW-DMCS (80—100 mesh); 15% Carbowax 20M on Chromosorb W (80—100 mesh); 15% n-hexadecane on Chromosorb P (80—100 mesh); and 10% PEGA on Chromosorb W NAW (80—100 mesh). Preparative g.l.c. was performed on a Pye 105 automatic preparative chromatograph. Glass columns (7 ft, with 9 mm int. diam.) were used with a gas flow rate of 80 ml min^{-1}. The column packing was 30% OV 17 on Chromosorb W NAW (60—80 mesh). Preparative thin-layer chromatography (p.l.c.) was performed with a 1 mm layer of silica gel G (Merck). Light petroleum refers to the fraction b.p. 40—60 °C.

Poor combustion analytical data were obtained for many of the sulphoxides because they were very hygroscopic, but satisfactory data were obtained for the sulphones derived by oxidation of these compounds.

Preparation of the Methanesulphonates (1a—d).—(*a*) Methanesulphonyl chloride (26 ml, 0.33 mol) was cooled to 0 °C and added slowly to a cold stirred solution of but-3-en-1-ol (8.0 g, 0.11 mol) in dry pyridine (20 ml), with the temperature kept below 5 °C. The mixture was allowed to warm to room temperature and stirred for 1 h before pouring onto ice. Acidification with 18% hydrochloric acid followed by a normal work-up with ether gave *but-3-enyl methanesulphonate* (1a) (12.7 g, 76%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 360, 1 342, and 1 174 (SO_2·O), and 3 058, 1 643, and 909 cm^{-1} (H_2C=CH), τ 4.21 (1 H, m, =CH–), 4.86 (2 H, m, H_2C=), 5.76 (2 H, t, J 6.5 Hz, CH_2·O·SO_2), 7.01 (3 H, s, CH_3·SO_2·O), and 7.51 (2 H, q, J 6.5 Hz, CH_2) (Found: C, 40.2; H, 6.8; S, 21.2. $C_5H_{10}O_3S$ requires C, 40.0; H, 6.7; S, 21.35%).

(*b*) Treatment of pent-4-en-1-ol (36 g, 0.42 mol) with methanesulphonyl chloride (100 ml, 1.3 mol) as above gave *pent-4-enyl methanesulphonate* (1b) (63 g, 92%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 359, 1 339, and 1 175 (SO_2·O), and 3 080 and 1 645 cm^{-1} (H_2C=CH), τ 4.22 (1 H, m, =CH–), 4.98 (2 H, m, H_2C=), 5.79 (2 H, t, J 6.5 Hz, CH_2·O·SO_2), 7.02 (3 H, s, CH_3·SO_2·O), 7.82 (2 H, q, J 7 Hz, 3-H_2), and 8.16 (2 H, quint, J 7 Hz, 2-H_2) (Found: C, 44.1; H, 7.15; S, 19.2. $C_6H_{12}O_3S$ requires C, 43.9; H, 7.4; S, 19.5%).

(*c*) Treatment of hex-5-en-1-ol (12 g, 0.12mol) with methanesulphonyl chloride (28 ml, 0.36 mol) as above gave *hex-5-enyl methanesulphonate* (1c) (20.9 g, 98%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 358, 1 338, and 1 174 (SO_2·O), and 3 081 and 1 642 cm^{-1} (H_2C=CH), τ 4.23 (1 H, m, =CH–), 5.03 (2 H, m, H_2C), 5.79 (2 H, t, J 6.5 Hz, CH_2·O·SO_2), 7.02 (3 H, s, CH_3·SO_2·O), and 7.90 (2 H, q, J 6.5 Hz, 4-H_2) (Found: C, 47.35; H, 7.7; S, 18.1. $C_7H_{14}O_3S$ requires C, 47.2; H, 7.9; S, 18.0%).

(*d*) Treatment of hept-6-en-1-ol (7.5 g, 0.07 mol) with methanesulphonyl chloride (10 ml, 0.13 mol) as above gave *hept-6-enyl methanesulphonate* (1d) (12.7 g, 100%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 358, 1 337, and 1 173 (SO_2·O), and 3 071, 1 641, and 917 cm^{-1} (H_2C=CH–), τ 4.22 (1 H, m, =CH–), 5.04 (2 H, m, H_2C=), 5.80 (2 H, t, J 6.5 Hz, CH_2·O·SO_2), 7.02 (3 H, s, CH_3·SO_2·O), and 7.93 (2 H, q, J 6.5 Hz, 5-H_2) (Found: C, 50.2; H, 8.3; S, 16.8. $C_8H_{16}O_3S$ requires C, 50.0; H, 8.4; S, 16.7%).

Preparation of the Sulphides (2a—d).—(*a*) 2-Methylpropane-2-thiol (45 ml, 0.4 mol) was added to a solution of sodium isopropoxide [from sodium (18.4 g, 0.8 mol)] in propan-2-ol (500 ml). After the addition of the methanesulphonate (1a) (12 g, 0.08 mol) in propan-2-ol (120 ml) the solution was boiled under nitrogen for 5 min, poured onto ice, and extracted with ether. The extract was washed with 5% potassium hydroxide solution, then with water, dried (Na_2SO_4), and evaporated. Distillation of the residue under reduced pressure yielded *4-t-butylthiobut-1-ene* (2a) (7.8 g, 68%), b.p. 57—61° at 14 mmHg, $\nu_{max.}$ ($CHCl_3$) 3 082, 1 641, 995, and 919 cm^{-1} (H_2C=CH–), τ 4.18 (1 H, m, =CH–), 4.98 (2 H, m, H_2C=), 7.41 (2 H, m, CH_2·S), 7.69 (2 H, q, J 7 Hz, 3-H_2), and 8.68 (9 H, s, Me_3C·S), *m/e* 144 (Found: C, 66.9; H, 11.4; S, 22.3. $C_8H_{16}S$ requires C, 66.6; H, 11.2; S, 22.2%).

(*b*) The methanesulphonate (1b) (2.1 g, 0.013 mol) was treated with 2-methylpropane-2-thiolate anions as above to give *5-t-butylthiopent-1-ene* (2b) (1.7 g, 84%), b.p. 74° at 18 mmHg, $\nu_{max.}$ ($CHCl_3$) 3 079, 1 640, 989, and 916 cm^{-1} (H_2C=CH–), τ 4.23 (1 H, m, =CH–), 5.03 (2 H, m, H_2C=), 7.48 (2 H, t, J 7 Hz, CH_2·S), 7.84 (2 H, q, J 7 Hz, 3-H_2), 8.32 (2 H, quint, J 7 Hz, 4-H_2), and 8.71 (9 H, s, Me_3C·S), *m/e* 158 (Found: C, 67.8; H, 11.3; S, 20.1. $C_9H_{18}S$ requires C, 68.3; H, 11.5; S, 20.25%).

(*c*) Treatment of the methanesulphonate (1c) (4.8 g, 0.027 mol) as above gave *6-t-butylthiohex-1-ene* (2c) (4.0 g, 86%), b.p. 84—85° at 12 mmHg, $\nu_{max.}$ ($CHCl_3$) 3 080, 1 645, 990, and 910 cm^{-1} (H_2C=CH–), τ 4.23 (1 H, m, =CH–), 5.06 (2 H, m, H_2C=), 7.49 (2 H, t, J 6.5 Hz, CH_2·S), 7.95 (2 H, q, J 6.5 Hz, 3-H_2), and 8.71 (9 H, s, Me_3C·S) (Found: M^+, 172.129 1. $C_{10}H_{20}S$ requires M, 172.128 6).

(*d*) The methanesulphonate (1d) (12.5 g, 0.065 mol) on treatment with 2-methylpropane-2-thiolate as above gave *7-t-butylthiohept-1-ene* (2d) (10.6 g, 88%), b.p. 112—116° at 19 mmHg, $\nu_{max.}$ ($CHCl_3$) 3 079, 1 641, 995, and 913 cm^{-1} (H_2C=C–), τ 4.21 (1 H, m, =CH–), 5.06 (2 H, m, H_2C=), 7.49 (2 H, t, J 6.5 Hz, CH_2·S), 7.95 (2 H, q, J 6.5 Hz, 3-H_2), and 8.69 (9 H, s, Me_3C·S), *m/e* 186 (Found: C, 70.9; H, 11.9; S, 7.05. $C_{11}H_{22}S$ requires C, 70.9; H, 11.9; S, 17.2%).

Preparation of the Sulphoxides (3a—d).—(*a*) A stirred solution of 4-t-butylthiobut-1-ene (2a) (6.9 g, 0.048 mol) in light petroleum (90 ml) was cooled to 0 °C and peroxydodecanoic acid (87% pure; 11.9 g, 0.048 mol) was slowly added. After 15 min the solution was evaporated and the residue chromatographed on a column of alumina (200 g) prepared in ether. Elution with ether gave *4-t-butylsulphinylbut-1-ene* (3a) (7.4 g, 97%), $\nu_{max.}$ ($CHCl_3$) 1 029 and 1 015 (>SO), and 3 085, 1 643, 995, and 924 cm^{-1} (H_2C=CH–), τ 4.14 (1 H, m, =CH–), 4.91 (2 H, m, H_2C=), 7.45 (4 H, 3- and 4-H_2), and 8.75 (9 H, s, Me_3C·SO), τ(C_6D_6) 4.24 (1 H, m, =CH–), 4.99 (2 H, m, H_2C=), 7.54 (2 H, m, CH_2·SO), 7.78

(2 H, m, 3-H_2), and 9.01 (9 H, s, Me_3C·SO), *m/e* 160 (Found: C, 60.1; H, 10.2; S, 19.8. $C_8H_{16}OS$ requires C, 59.95; H, 10.1; S, 20.0%).

(*b*) Oxidation of 5-t-butylthiopent-1-ene (2b) (1.03 g, 6.5 mmol) as above gave *5-t-butylsulphinylpent-1-ene* (3b) (0.93 g, 82%), $\nu_{max.}$ ($CHCl_3$) 1 028 and 1 014 (>SO), and 3 082, 1 642, 990, and 920 cm^{-1} (H_2C=CH–), τ 4.23 (1 H, m, =CH–), 4.99 (2 H, m, H_2C=), 7.54 (2 H, m, CH_2·SO), 7.75 (2 H, q, *J* 7 Hz, 3-H_2), and 8.76 (9 H, s, Me_3C·SO), τ(C_6D_6) 4.40 (1 H, m, =CH–), 5.08 (2 H, m, H_2C=), and 9.06 (9 H, s, Me_3C·SO) (Found: M^+, 174.107 0. $C_9H_{18}OS$ requires *M*, 174.107 8).

(*c*) 6-t-Butylthiohex-1-ene (2c) (5.7 g, 0.033 mol) was treated with peroxydodecanoic acid as above to furnish *6-t-butylsulphinylhex-1-ene* (3c) (5.4 g, 87%), $\nu_{max.}$ ($CHCl_3$) 1 025 and 1 013 (>SO), and 3 081, 1 641, and 917 cm^{-1} (H_2C=CH–), τ 4.22 (1 H, m, =CH–), 5.04 (2 H, m, H_2C=), 7.54 (2 H, m, CH_2·SO), 7.89 (2 H, q, *J* 7 Hz, 3-H_2), and 8.77 (9 H, s, Me_3C·SO), τ (C_6D_6) 4.30 (1 H, m, =CH–), 5.05 (2 H, m, H_2C=), and 9.01 (9 H, s, Me_3C·SO) (Found: M^+, 188.124 7. $C_{10}H_{20}OS$ requires *M*, 188.123 5).

(*d*) Oxidation of 7-t-butylthiohept-1-ene (2d) (10.0 g, 0.054 mol) as above gave the oily *7-t-butylsulphinylhept-1-ene* (3d) (10.1 g, 93%), $\nu_{max.}$ ($CHCl_3$) 1 023 and 1 012 (>SO), and 3 080, 1 642, and 915 cm^{-1} (H_2C=CH–), τ 4.22 (1 H, m, =CH–), 5.05 (2 H, m, H_2C=), 7.55 (2 H, m, CH_2·SO), 7.93 (2 H, q, *J* 6.5 Hz, 3-H_2), and 8.76 (9 H, s, Me_3C·SO), τ(C_6D_6) 4.26 (1 H, m, =CH–), 5.01 (2 H, m, H_2C=), and 9.05 (9 H, s, Me_3C·SO), *m/e* 202 (Found: C, 65.1; H, 11.0; S, 15.6. $C_{11}H_{22}OS$ requires C, 65.3; H, 11.0; S, 15.8%).

Oxidation of the Sulphoxides (3a—d) *to Sulphones.*—4-t-Butylsulphinylbut-1-ene (3a) (100 mg, 0.62 mmol) in light petroleum (4 ml) was treated with peroxydodecanoic acid (87% pure; 170 mg, 0.68 mmol). After 15 min the mixture was poured onto a column of alumina (5 g); elution with ether gave *4-t-butylsulphonylbut-1-ene* (90 mg, 82%), m.p. 39—40° (with sublimation), $\nu_{max.}$ ($CHCl_3$) 1 304 and 1 116 (>SO_2), and 3 087, 1 643, 992, and 917 cm^{-1} (H_2C=CH–), τ 4.13 (1 H, m, =CH–), 4.88 (2 H, m, H_2C=), 7.03 (2 H, m, CH_2·SO_2), 7.37 (2 H, m, 3-H_2), and 8.58 (9 H, s, Me_3C·SO_2), τ(C_6D_6) 4.41 (1 H, m, =CH–), 5.13 (2 H, m, H_2C=), and 8.96 (9 H, s, Me_3C·SO_2) (Found: C, 54.7; H, 9.4; S, 18.1. $C_8H_{16}O_2S$ requires C, 54.5; H, 9.15; S, 18.2%).

Oxidation of the sulphoxides (3b—d) as above gave, respectively, the following oily sulphones: *5-t-butylsulphonylpent-1-ene* (88%), $\nu_{max.}$ ($CHCl_3$) 1 291 and 1 116 (>SO_2), and 3 086, 1 642, 992, and 922 cm^{-1} (H_2C=CH–), τ 4.24 (1 H, m, =CH–), 4.96 (2 H, m, H_2C=), 7.10 (2 H, m, CH_2·SO), 7.76 (2 H, q, *J* 7 Hz, 3-H_2), and 8.60 (9 H, s, Me_3C·SO_2), τ(C_6D_6) 4.45 (1 H, m, =CH–), 5.10 (2 H, m, H_2C=), 7.48 (2 H, m, CH_2·SO_2), and 8.90 (9 H, s, Me_3C·SO_2) (Found: C, 57.0; H, 9.3; S, 16.7. $C_9H_{18}O_2S$ requires C, 56.8; H, 9.5; S, 16.85%); *6-t-butylsulphonylhex-1-ene* (90%), $\nu_{max.}$ ($CHCl_3$) 1 284 and 1 116 (>SO_2), and 3 080, 1 642, 993, and 919 cm^{-1} (H_2C=CH–), τ 4.22 (1 H, m, =CH–), 5.02 (2 H, m, H_2C=), 7.09 (2 H, m, CH_2·SO_2), and 8.59 (9 H, s, Me_3C·SO_2), τ(C_6D_6) 4.35 (1 H, m, =CH–), 5.08 (2 H, m, H_2C=), 7.50 (2 H, m, CH_2·SO_2), 8.89 (9 H, s, Me_3C·SO_2) (Found: C, 59.0; H, 9.7; S, 15.8. $C_{10}H_{20}O_2S$ requires C, 58.8; H, 9.9; S, 15.7%); and *7-t-butylsulphonylhept-1-ene* (88%), $\nu_{max.}$ ($CHCl_3$) 1 291 and 1 117 (>SO_2), and 3 080, 1 641, 995, and 916 cm^{-1} (H_2C=CH–), τ 4.23 (1 H, m, =CH–), 5.05 (2 H, m, H_2C=), 7.11 (2 H, m, CH_2·SO_2), and 8.60 (9 H, s, Me_3C·SO_2) (Found: C, 60.25; H, 10.2; S, 14.8. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.2; S, 14.7%).

Thermolysis of the Sulphoxides (3a—d).—(*a*) 4-t-Butylsulphinylbut-1-ene (3a) (5 g) was kept under nitrogen in refluxing xylene (120 ml) for 3.5 h. The solution was poured onto a column of alumina (150 g), which was eluted with light petroleum to remove the xylene. Elution with ether gave material which was rechromatographed on a column of silica (100 g) (ether as eluant). The first isomer eluted was cis-2-*methylthietan* 1-*oxide* (20) (0.79 g, 24%), $\nu_{max.}$ ($CHCl_3$) 1 065 cm^{-1} (>SO), τ 6.39 (1 H, m, 4-H *cis* to O), 6.66 (1 H, m, 4-H *trans* to O), 6.91 (1 H, m, 2-H), 7.13—7.72 (2 H, m, 3-H_2), and 8.47 (3 H, d, *J* 6.5 Hz, CH_3), τ(C_6D_6) 7.01 (1 H, m, 4-H *cis* to O) and 8.89 (3 H, d, *J* 6.5 Hz, CH_3) (Found: M^+, 104.030 4. C_4H_8OS requires *M*, 104.029 6). Further elution gave trans-2-*methylthietan* 1-*oxide* (21) (0.22 g, 7%), $\nu_{max.}$ ($CHCl_3$) 1 065 cm^{-1}, τ 6.14 (1 H, m, 2-H), 6.33 (1 H, m, 4-H *cis* to O), 6.63 (1 H, m, 4-H *trans* to O), 6.83—7.63 (2 H, m, 3-H_2), and 8.86 (3 H, d, *J* 7 Hz, CH_3), τ(C_6D_6) 6.77 (1 H, m, 2-H), and 9.54 (3 H, d, *J* 7 Hz, CH_3) (Found: M^+, 104.030 4. C_4H_8OS requires *M*, 104.029 6).

(*b*) A solution of 5-t-butylsulphinylpent-1-ene (3b) (0.5 g) in xylene (10 ml) was boiled under nitrogen for 3 h. It was then poured onto a column of neutral alumina (50 g), which was eluted with light petroleum (50 ml) to remove the xylene. Elution with ether–methanol (9 : 1) gave *cis*-2-methylthiolan 1-oxide (7) (0.25 g, 74%), $\nu_{max.}$ ($CHCl_3$) 1 018 cm^{-1} (>SO), τ 6.83 (1 H, m, 5-H *cis* to O), 7.18 (1 H, m, 5-H *trans* to O), 7.32 (1 H, m, 2-H), and 8.60 (3 H, d, *J* 6.5 Hz, CH_3), τ(C_6D_6) 8.82 (3 H, d, *J* 6.5 Hz, CH_3) [lit.,[17] τ 8.60 (3 H, d, *J* 6.5 Hz, CH_3), τ(C_6D_6) 8.82 (3 H, d, *J* 6.2 Hz, CH_3)] (Found: M^+, 118.045 7. Calc. for $C_5H_{10}OS$: *M*, 118.045 4).

(*c*) 6-t-Butylsulphinylhex-1-ene (3c) (4.57 g) in boiling xylene (90 ml) was kept under nitrogen for 3.5 h and the cooled solution poured onto a column of alumina (200 g). The column was eluted first with light petroleum to remove the xylene and then with ether–methanol (9 : 1) to give cis-2-*methylthian* 1-*oxide* (13) (2.82 g, 88%), $\nu_{max.}$ ($CHCl_3$) 1 053, 1 009, and 985 cm^{-1} (>SO), τ 6.96 (1 H, m, 6-H *cis* to O), 7.53 (1 H, m, 2-H), and 8.69 (3 H, d, *J* 6.5 Hz, CH_3), τ(C_6D_6) 7.53 (1 H, m, 6-H *cis* to O) and 8.98 (3 H, d, *J* 6.5 Hz, CH_3) (Found: M^+, 132.062 0. $C_6H_{12}OS$ requires *M*, 132.061 0).

(*d*) 7-t-Butylsulphinylhept-1-ene (3d) (9.3 g) was kept under nitrogen in refluxing xylene (190 ml) for 3.5 h. The mixture was then poured onto a column of alumina (300 g), which was eluted with light petroleum to remove the xylene. Elution with ether–methanol (19 : 1) gave a mixture (3.0 g, 45%) of *cis*-2-methylthiepan 1-oxide (18) and *cis*-2-ethylthian 1-oxide (15) in the ratio 65 : 35 (g.l.c. analysis; OV17 column), *m/e* 146 (Found: C, 57.6; H, 9.75; S, 22.2. Calc. for $C_7H_{14}OS$: C, 57.5; H, 9.65; S, 21.9%). During the longer times required for preparative g.l.c. only *cis*-2-ethylthian 1-oxide (15) was obtained, since *cis*-2-methylthiepan 1-oxide (18) rearranges thermally to *cis*-2-ethylthian 1-oxide (15).[18] To confirm the ratio of sulphoxides obtained initially, the mixture was converted into thermally stable sulphides and sulphones.

A portion (0.3 g, 1.4 mmol) of the foregoing mixture of (18) and (15) in dichloromethane (3 ml) was treated with phosphorus trichloride (0.24 ml, 2.8 mmol). After 5 min at room temperature the mixture was poured onto ice and extracted with ether. The extract was washed with water, saturated sodium hydrogen carbonate solution, and water again, and was dried (Na_2SO_4). Evaporation through a 12 cm × 1.2 cm column containing glass helices gave 2-methylthiepan and 2-ethylthian (0.17 g, 95%) in the ratio 62 : 38

(g.l.c. analysis; OV17 column). Separation by preparative g.l.c. (FFAP column) gave 2-methylthiepan and 2-ethylthian, identical with the authentic compounds.

The mixture (108 mg, 0.74 mmol) of *cis*-2-methylthiepan 1-oxide and *cis*-2-ethylthian 1-oxide in light petroleum (1.5 ml) and ether (1.5 ml) was treated with peroxydodecanoic acid (85% pure; 210 mg, 0.83 mmol). After 15 min the mixture was poured onto a column of alumina (5 g) prepared in ether. Elution with ether gave a mixture of 2-methylthiepan 1,1-dioxide and 2-ethylthian 1,1-dioxide (105 mg, 88%) in the ratio 65 : 35 (g.l.c. analysis; FFAP column), *m/e* 162 (Found: C, 51.7; H, 8.6; S, 19.8. Calc. for $C_7H_{14}O_2S$: C, 51.8; H, 8.7; S, 19.8%).

Equilibration of cis- *and* trans-2-*Methylthietan* 1-*Oxides* (20) *and* (21).—(*a*) A solution of *cis*-2-methylthietan 1-oxide (20) (50 mg) in xylene (2 ml) was boiled (140 °C) under nitrogen. According to t.l.c. equilibration was complete after 4 h, and the solution was poured onto a column of alumina (2 g). Elution with light petroleum removed the xylene, and elution with ether gave a mixture of *cis*- and *trans*-thietan 1-oxides, (20) and (21), in the ratio 66 : 34 (methyl n.m.r. signals). The n.m.r. spectrum confirmed t.l.c. evidence that there were no other products. Treatment of *trans*-2-methylthietan 1-oxide (21) in the above manner for 6 h gave a mixture of the *cis*- and *trans*-isomers, (20) and (21), in the ratio 63 : 37 (n.m.r.).

(*b*) A sample of each of the 2-methylthietan 1-oxides, (20) and (21), was kept in a Pyrex vessel at room temperature (20 °C). After 20 days each vessel contained only a mixture of *cis*- and *trans*-2-methylthietan 1-oxides, (20) and (21), according to n.m.r., in the ratio 68 : 32 (from the *cis*-isomer) or 61 : 39 (from the *trans*-isomer).

2-*Methylthiolan* 1,1-*Dioxide*.—A solution of peroxydodecanoic acid (89% pure; 240 mg, 0.99 mmol) and *cis*-2-methylthiolan 1-oxide (7) (104 mg, 0.88 mmol) in light petroleum (4 ml) and ether (1 ml) was kept at room temperature for 15 min and poured onto a column of alumina (5 g). Elution with ether gave 2-*methylthiolan* 1,1-*dioxide* (100 mg, 85%), $\nu_{max.}$ ($CHCl_3$) 1 310, 1 143, and 1 114 cm^{-1} (>SO_2), τ 6.72—7.23 (3 H, m, CH·SO_2 and CH_2·SO_2) and 8.67 (3 H, d, *J* 7 Hz, CH_3), τ(C_6D_6) 7.25—7.76 (3 H, m, CH·SO_2 and CH_2·SO_2) and 9.00 (3 H, d, *J* 7 Hz, CH_3) [lit.,[17] τ(C_6D_6) 8.96 (3 H, d, *J* 7 Hz, CH_3)], *m/e* 134 (Found: C, 44.5; H, 7.2; S, 23.7. $C_5H_{10}O_2S$ requires C, 44.75; H, 7.5; S, 23.9%).

cis- *and* trans-2-*Methylthian* 1-*Oxides*, (13) *and* (14).—Peroxydodecanoic acid (96% pure, 0.48 g) was added to 2-methylthian (0.24 g) in light petroleum (3 ml). After 2 h the solution was poured onto a silica column (20 g). Elution with ether–methanol (19 : 1) gave a mixture of the sulphoxides (13) and (14) (0.253 g, 93%) in the ratio 37 : 63 (g.l.c.; FFAP column). Preparative g.l.c. (FFAP column) afforded first *cis*-2-methylthian 1-oxide (13), identical with the sample obtained previously, and then trans-2-*methylthian* 1-*oxide* (14), $\nu_{max.}$ ($CHCl_3$) 1 030 cm^{-1} (>SO), τ 6.69 (1 H, m, 6-H *trans* to O), 7.40 (2 H, m, 2-H and 6-H *cis* to O), 7.63—8.75 (6 H, m, three CH_2), and 8.58 (3 H, d, *J* 7 Hz, CH_3), τ(C_6D_6) 7.24 (1 H, m, 6-H *trans* to O), 7.54—7.92 (2 H, m, 2-H and 6-H *cis* to O), and 8.88 (3 H, d, *J* 7 Hz, CH_3) (Found: M^+, 132.062 0. $C_6H_{12}OS$ requires M^+, 132.061 0).

cis-2-Methylthian 1-oxide (13) (20 mg) in dioxan–concentrated hydrochloric acid (2 : 1; 1 ml) was left for 2 h at room temperature. Extraction with dichloromethane gave a mixture of *cis*- and *trans*-2-methylthian 1-oxides, (13) and (14) (13 mg, 65%), in the ratio 65 : 35 (g.l.c.; FFAP column). Treatment of the *trans*-isomer (14) in the same way gave a similar mixture.

2-*Methylthian* 1,1-*Dioxide*.—A solution of peroxydodecanoic acid (87% pure; 206 mg, 0.83 mmol) and *cis*-2-methylthian 1-oxide (13) 100 mg, 0.76 mmol) in light petroleum (2 ml) and ether (2 ml) was kept at room temperature for 15 min, and poured onto a column of alumina (5 g). Elution with ether gave 2-methylthian 1,1-dioxide (100 mg, 89%), m.p. 66—67° (with sublimation) (lit.,[45] 65—66°), $\nu_{max.}$ ($CHCl_3$) 1 322, 1 296, 1 281, and 1 128 cm^{-1} (>SO_2), τ 6.77—7.31 (3 H, m, CH·SO_2 and CH_2·SO_2–) and 8.67 (3 H, d, *J* 7 Hz, CH_3), *m/e* 148 (Found: C, 48.6; H, 7.9; S, 21.9. Calc. for $C_6H_{12}O_2S$: C, 48.6; H, 8.2; S, 21.6%).

2-*Ethylthian*.—*N*-Chlorosuccinimide (2.88 g, 0.021 mol) was added in portions over 15 min to a solution of thian (2.0 g, 0.02 mol) in dry benzene (25 ml). The temperature was maintained at 20—25 °C by intermittent external cooling. After stirring for 1 h, the mixture was filtered and the filtrate added dropwise to an ice-cold solution of ethylmagnesium bromide in ether (0.2 g ml^{-1}; 60 ml, 0.09 mol). The mixture was allowed to warm to room temperature and stirred for 15 h before pouring onto ice-cold 20% sulphuric acid. Work-up with ether then gave 2-*ethylthian* (1.17 g, 46%), τ 7.16—7.56 (3 H, m, CH·S and CH_2·S), 8.50 (2 H, quint, *J* 7 Hz, CH_2Me), and 9.03 (3 H, t, *J* 7 Hz, CH_3), *m/e* 130 (Found: C, 64.8; H, 10.7; S, 24.6. $C_7H_{14}S$ requires C, 64.55; H, 10.8; S, 24.6%).

cis- *and* trans-2-*Ethylthian* 1-*Oxides*, (15) *and* (16).—Peroxydodecanoic acid (96% pure; 1.3 g, 5.7 mmol) was added to a stirred solution of 2-ethylthian (0.75 g, 5.7 mmol) in light petroleum (60 ml). After 15 min the mixture was poured onto a column of alumina (40 g); elution with ether–methanol (9 : 1) afforded a mixture of *cis*- and *trans*-2-ethylthian 1-oxide (15) and (16) (0.74 g, 88%) in the ratio 2 : 3 (g.l.c.; OV17 column). Chromatography on a silica column (50 g) [elution with ether–methanol (19 : 1)] gave first cis-2-*ethylthian* 1-*oxide* (15) (0.18 g), $\nu_{max.}$ ($CHCl_3$) 1 029 and 992 cm^{-1} (>SO), τ 6.92 (1 H, m, 6-H *cis* to O) and 8.94 (3 H, t, *J* 7 Hz, CH_3), τ(C_6D_6) 7.50 (1 H, m, 6-H *cis* to O) and 9.18 (3 H, t, *J* 7 Hz, CH_3), *m/e* 146, followed by a mixture of isomers. Further elution gave trans-2-*ethylthian* 1-*oxide* (16) (0.28 g), $\nu_{max.}$ ($CHCl_3$) 1 030 and 1 001 cm^{-1} (>SO), τ 6.71 (1 H, m, 6-H *trans* to O) and 8.96 (3 H, t, *J* 7 Hz, CH_3), τ(C_6D_6) 7.27 (1 H, m, 6-H *trans* to O) and 9.21 (3 H, t, *J* 7 Hz, CH_3), *m/e* 146.

2-*Ethylthian* 1,1-*Dioxide*.—A solution of *cis*- and *trans*-2-ethylthian 1-oxides, (15) and (16) (in the ratio 2 : 3) (0.1 g), in benzene (3 ml) was treated with peroxydodecanoic acid (96% pure; 0.2 g). After stirring for 1 h at room temperature the solution was evaporated and the product was chromatographed (p.l.c.) with ether–light petroleum (4 : 1) as eluant. Extraction of the band at R_F 0.6 afforded 2-*ethylthian* 1,1-*dioxide* (95 mg, 85%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 316, 1 288, and 1 128 cm^{-1} (>SO_2), τ 6.8—7.43 (3 H, m, CH_2·SO_2·CH), 8.13—8.70 (8 H, m, four CH_2), and 8.94 (3 H, t, *J* 8 Hz, CH_3); *m/e* 162 (Found: C, 51.7; H, 8.6; S, 19.7. $C_7H_{14}O_2S$ requires C, 51.8; H, 8.7; S, 19.8%).

cis- *and* trans-2-*Methylthiepan* 1-*Oxides*, (18) *and* (19).—2-Methylthiepan (50 mg, 0.38 mmol) in light petroleum (3 ml) was treated with peroxydodecanoic acid (96% pure; 87 mg, 0.38 mmol) and after 15 min at room temperature the solution was poured onto a column of alumina (4 g). Elution with ether gave a mixture of *cis*- and *trans*-2-

[45] E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3632.

methylthiepan 1-oxides (52 mg, 92%) in the ratio 4 : 96 (g.l.c.; OV17 column). The mixture was chromatographed on silica (p.l.c.) eluted with ether–methanol (9 : 1). Extraction of the bands at R_F 0.5 and 0.4 gave, respectively, cis-2-*methylthiepan* 1-*oxide* (18) (2 mg, 3%), $\nu_{max.}$ ($CHCl_3$) 1 044, 1 021, and 998 cm^{-1} (>SO), τ 6.82—7.12 (1 H, m), 7.18—7.49 (2 H, m), 7.64—8.52 (8 H, m), and 8.62 (3 H, d, *J* 7 Hz, CH_3), τ(C_6D_6) 7.47 (1 H, m) and 8.87 (3 H, d, *J* 7 Hz, CH_3), *m/e* 146; and trans-2-*methylthiepan* 1-*oxide* (19) (50 mg, 89%), $\nu_{max.}$ ($CHCl_3$) 1 020 cm^{-1} (>SO), τ 6.84—7.05 (2 H, m), 7.06—7.40 (1 H, m,) and 8.62 (3 H, d, *J* 7 Hz, CH_3), *m/e* 146 (Found: C, 57.7; H, 9.8; S, 22.2. $C_7H_{14}OS$ requires C, 57.5; H, 9.65; S, 21.9%).

2-*Methylthiepan* 1,1-*Dioxide*.—Peroxydodecanoic acid (96% pure; 0.4 g) was added to a stirred solution of *cis*- and *trans*-2-methylthiepan 1-oxides, (18) and (19) (0.2 g), in ether–light petroleum (1 : 1; 10 ml). After 30 min the mixture was poured onto a column of alumina (12 g). Elution with ether gave an oil which was rechromatographed on silica (p.l.c.) eluted with ether–light petroleum (17 : 3). Extraction of the band at R_F 0.6 gave 2-*methylthiepan* 1,1-*dioxide* (0.205 g, 93%), m.p. 48°, $\nu_{max.}$ ($CHCl_3$) 1 314, 1 291, 1 130, and 1 116 cm^{-1} (>SO_2), τ 6.76—7.11 (3 H, m, CH_2·SO·CH), 7.88—8.49 (8 H, m), and 8.60 (3 H, d, *J* 7 Hz, CH_3), *m/e* 162 (Found: C, 52.0; H, 8.6; S, 19.8. $C_7H_{14}O_2S$ requires C, 51.8; H, 8.7; S, 19.8%).

2-*t-Butylsulphinylpentane* (24).—Di-t-butyl sulphoxide (0.2 g, 1.2 mmol) in pent-1-ene (1.4 ml, 12 mmol) was heated at 140 °C under nitrogen in a sealed tube for 8 min. The pentene was evaporated off and the residue chromatographed on silica (p.l.c.; ether). Extraction of the band at R_F 0.5 gave the *product* (24) (0.18 g, 83%), $\nu_{max.}$ ($CHCl_3$) 1 026 cm^{-1} (>SO), $\nu_{max.}$ (EtOH) 221 nm (ε 870), τ 7.25 (1 H, sext, *J* 6.5 Hz, CH·SO), 8.75 (9 H, s, Me_3C·SO), 8.82 (3 H, d, *J* 6.5 Hz, CH·CH_3), and 9.06 (3 H, t, *J* 6.5 Hz, CH_2·CH_3), *m/e* 176 (Found: C, 61.3; H, 11.3; S, 18.4. $C_9H_{20}OS$ requires C, 61.3; H, 11.4; S, 18.2%).

2-*t-Butylsulphinyloctane* (25).—Di-t-butyl sulphoxide (1.1 g) in oct-1-ene (16 ml) was boiled under nitrogen for 4 min, cooled by immersion in ice, and poured onto a column of alumina. Elution with light petroleum removed the octene; elution with ether gave the oily *product* (25) (1.0 g, 74%), $\nu_{max.}$ ($CHCl_3$) 1 015 cm^{-1} (>SO), τ 7.41 (1 H, m, CH·SO), 8.77 (9 H, s, Me_3C·SO), 8.83 (3 H, d, *J* 7 Hz, CH·CH_3), and 9.13 (3 H, t, CH_2·CH_3), *m/e* 218.

t-Butylsulphinylcyclopentane (27).—Di-t-butyl sulphoxide (0.2 g) in cyclopentene (3 ml) was heated under nitrogen at 143 °C in a sealed tube for 5 min. The cyclopentene was evaporated off and the residue chromatographed on silica (p.l.c.; ether). Extraction of the band at R_F 0.5 gave the *product* (27) (60 mg, 28%), $\nu_{max.}$ ($CHCl_3$) 1 010 cm^{-1} (>SO), τ 6.96 (1 H, m, CH·SO), 7.75—8.51 (8 H, m, four CH_2), and 8.87 (9 H, s, Me_3C·SO), *m/e* 174.

t-Butylsulphinylcyclohexane (28).—Di-t-butyl sulphoxide (5 g) in cyclohexene (40 ml) was boiled under nitrogen for 6.5 h, cooled, and poured onto a column of alumina (100 g). The cyclohexene was removed by elution with light petroleum; elution with ether gave a mixture which was rechromatographed on silica (p.l.c.; ether). Extraction of the band at R_F 0.5 gave the *product* (28) (230 mg, 8%), $\nu_{max.}$ ($CHCl_3$) 1 015 cm^{-1} (>SO), τ 7.35 (1 H, m, CH·SO), 7.94—8.64 (10 H, m, five CH_2), and 8.74 (9 H, s, Me_3C·SO) (Found: M^+, 188.123 6. $C_{10}H_{20}SO$ requires *M*, 188.123 5).

t-Butylsulphinylcyclo-octane (29).—Di-t-butyl sulphoxide (0.5 g) in cyclo-octene (4 ml) was kept under nitrogen at 140 °C for 2 min, then the cooled solution was poured onto a column of alumina (20 g). Elution with light petroleum removed the cyclo-octene; elution with ether gave the *product* (29) (80 mg, 12%), $\nu_{max.}$ ($CHCl_3$) 1 015 cm^{-1} (>SO), τ 7.24 (1 H, m, CH·SO), 7.86—8.6 (14 H, m, seven CH_2), and 8.76 (9 H, s, Me_3C·SO), *m/e* 216 (Found: C, 66.4; H, 10.9; S, 14.9. $C_{12}H_{24}OS$ requires C, 66.6; H, 11.1; S, 14.8%).

2-*t-Butylsulphonylpentane*.— 2-t-Butylsulphinylpentane (24) (60 mg, 0.34 mmol) in light petroleum (3 ml) was treated with peroxydodecanoic acid (96% pure; 83 mg, 0.37 mmol). After 15 min the mixture was poured onto a column of alumina (4 g); elution with ether gave the oily 2-*t-butylsulphonylpentane* (55 mg, 84%), $\nu_{max.}$ ($CHCl_3$) 1 284 and 1 113 cm^{-1} (>SO_2), τ 6.81 (1 H, m, CH·SO_2), 8.57 (9 H, s, Me_3C·SO_2), 8.61 (3 H, d, *J* 7 Hz, CH·CH_3), and 9.04 (3 H, t, *J* 7 Hz, CH_2·CH_3) (Found: C, 56.5; H, 10.3; S, 16.8. $C_9H_{20}O_2S$ requires C, 56.2; H, 10.5; S, 16.7%).

2-*t-Butylsulphonyloctane*.—Oxidation of 2-t-butylsulphinyloctane (25) (400 mg) in light petroleum (4 ml) with peroxydodecanoic acid (88% pure; 460 mg) as above gave 2-*t-butylsulphonyloctane* (410 mg, 95%), m.p. 39—41°, $\nu_{max.}$ ($CHCl_3$) 1 276 and 1 105 cm^{-1} (>SO_2), τ 6.83 (1 H, m, CH·SO_2), 8.59 (9 H, s, Me_3C·SO_2), 8.69 (3 H, d, *J* 7 Hz, CH·CH_3), and 9.15 (3 H, t, *J* 6 Hz, CH·CH_3) (Found: C, 61.7; H, 11.1; S, 13.75. $C_{12}H_{26}O_2S$ requires C, 61.5; H, 11.2; S, 13.7%).

t-Butylsulphonylcyclopentane.— t-Butylsulphinylcyclopentane (27) (280 mg) in light petroleum (4 ml) was treated with peroxydodecanoic acid (88% pure; 420 mg) as above to give *t-butylsulphonylcyclopentane* (300 mg, 99%), m.p. 80—82°, $\nu_{max.}$ ($CHCl_3$) 1 275 and 1 104 cm^{-1} (>SO_2), τ 6.47 (1 H, m, CH·SO), 7.76—8.46 (8 H, m, four CH_2), and 8.60 (9 H, s, Me_3C·SO_2) (Found: C, 56.55; H, 9.4; S, 16.8. $C_9H_{18}O_2S$ requires C, 56.8; H, 9.5; S, 16.8%).

Thermolysis of Di-t-butyl Sulphoxide in Hexa-1,5-diene.—(*a*) Di-t-butyl sulphoxide (0.1 g, 0.63 mmol) in hexa-1,5-diene (0.52 g, 6.3 mmol) was heated in a sealed tube at 130 °C for 5 min. The excess of hexa-1,5-diene was then evaporated off and the residue chromatographed on silica (p.l.c.) eluted with ether. Extraction of the band at R_F 0.5 gave 5-*t-butylsulphinylhex*-1-*ene* (26) (0.1 g, 84%), $\nu_{max.}$ ($CHCl_3$) 1 028 (>SO), and 3 080, 1 641, and 918 cm^{-1} (H_2C=CH–), $\lambda_{max.}$ (EtOH) 222 nm (ε 810), τ 4.24 (1 H, m, =CH–), 4.99 (2 H, m, H_2C=), 7.22 (1 H, sext, *J* 7 Hz, CH·SO), 7.79 (2 H, q, *J* 7 Hz, 3-H_2), 8.22 (2 H, m, 4-CH_2), 8.76 (9 H, s, Me_3C·SO), and 8.82 (3 H, d, *J* 7 Hz, 6-H_3), τ(C_6D_6) 4.38 (1 H, m, =CH–), 5.08 (2 H, m, H_2C=), 7.56 (1 H, sext, *J* 7 Hz, CH·SO), 8.00 (2 H, q, *J* 7 Hz, 3-H_2), 8.92 (3 H, d, *J* 7 Hz, 6-H_3), and 9.02 (9 H, s, Me_3C·SO) (Found: M^+, 188.123 8. $C_{10}H_{20}OS$ requires *M*, 188.123 5).

(*b*) Di-t-butyl sulphoxide (1.3 g, 8 mmol) in hexa-1,5-diene (8.8 ml, 80 mmol) was heated in a sealed tube at 130 °C for 20 min. The excess of hexa-1,5-diene was then evaporated off and the residue chromatographed on a column of silica (60 g) prepared in ether. Elution with ether gave 5-t-butylsulphinylhex-1-ene (26) (0.32 g, 21%) followed by cis-2,5-*dimethylthiolan* cis-1-*oxide* (9) (0.24 g, 23%), $\nu_{max.}$ ($CHCl_3$) 1 059, 1 022, 1 003, and 983 cm^{-1} (>SO), τ 7.00 (2 H, m, two CH·SO), 7.88 (4 H, m, two CH_2), and 8.63 (6 H, d, *J* 7 Hz, two CH_3), τ(C_6D_6) 7.51 (2 H, m, two CH·SO), 8.28 (4 H, m, two CH_2), and 8.83 (6 H, d, *J* 7 Hz, two CH_3), τ(D_2O) 6.54 (2 H, m, two CH·SO), 7.35—8.10 (4 H, m, two CH_2), and 8.48 (6 H, d, *J* 7 Hz, two CH_3) (Found: M^+, 132.061 2. $C_6H_{12}OS$ requires *M*, 132.060 9). Further elution with ether–methanol (97 : 3) gave trans-2,5-*dimethyl*-

thiolan 1-*oxide* (10) (0.12 g, 11%), $\nu_{max.}$ ($CHCl_3$ 1 051, 1 021, 1 001, and 985 cm^{-1} (>SO), τ 7.00 (1 H, m, CH·SO *cis* to O), 8.62 (3 H, d, *J* 6.5 Hz, CH_3 *cis* to O), and 8.63 (3 H, d, *J* 7.5 Hz, CH_3 *trans* to O), τ(C_6D_6) 7.18 (1 H, m, CH·SO *cis* to O), 7.72 (1 H, m, CH·SO *trans* to O), 8.83 (3 H, d, *J* 6.5 Hz, CH_3 *cis* to O), and 9.09 (3 H, d, *J* 7.5 Hz, CH_3 *trans* to O) (Found: M^+, 132.061 2).

Thermolysis of 5-*t-Butylsulphinylhex*-1-*ene* (26).—A solution of 5-t-butylsulphinylhex-1-ene (78 mg) in light petroleum was heated in a sealed tube at 120 °C for 4 h, then evaporated, and the residue was chromatographed on silica (p.l.c.) [ether–chloroform (2 : 1) as eluant]. Extraction of the band at R_F 0.1 gave a mixture (28 mg, 51%) of *cis*-2,5-dimethylthiolan *cis*-1-oxide (9) and *trans*-2,5-dimethylthiolan 1-oxide (10) in the ratio 9 : 10 (from n.m.r. methyl signals in [$^2H_6$]benzene).

cis-2,5-*Dimethylthiolan* 1,1-*Dioxide*.—A solution of peroxydodecanoic acid (91% pure; 162 mg, 0.68 mmol) and *cis*-2,5-dimethylthiolan *cis*-1-oxide (9) (82 mg, 0.62 mmol) in light petroleum (2 ml) and ether (2 ml) was kept at room temperature for 15 min, poured onto a column of alumina (5 g), and eluted with ether to give cis-2,5-*dimethylthiolan* 1,1-*dioxide* (80 mg, 87%), $\nu_{max.}$ ($CHCl_3$) 1 310, 1 131, and 1 116 cm^{-1} (>SO_2), τ 6.91 (2 H, m, two CH·SO_2) and 8.68 (6 H, d, *J* 7 Hz, two CH_3), τ(C_6D_6) 7.41 (2 H, m, two CH·SO_2) and 9.01 (6 H, d, *J* 7 Hz, two CH_3), *m/e* 148 (Found: C, 48.5; H, 7.9; S, 21.6. $C_6H_{12}O_2S$ requires C, 48.6; H, 8.2; S, 21.6%).

trans-2,5-*Dimethylthiolan* 1,1-*Dioxide*.—*trans*-2,5-Dimethylthiolan 1-oxide (10) (70 mg, 0.53 mmol) in light petroleum (2 ml) and ether (2 ml) was treated with peroxydodecanoic acid (91% pure; 138 mg, 0.58 mmol). After 15 min, the mixture was poured onto a column of alumina (5 g). Elution with ether gave trans-2,5-*dimethylthiolan* 1,1-*dioxide* (65 mg, 83%), $\nu_{max.}$ ($CHCl_3$) 1 307, 1 136, and 1 117 cm^{-1} (>SO_2), τ 7.01 (2 H, m, two CH·SO_2), 8.63 (6 H, d, *J* 7 Hz, two CH_3), τ(C_6D_6) 7.52 (2 H, m, two CH·SO_2) and 8.97 (6 H, d, *J* 7 Hz, two CH_3), *m/e* 148 (Found: C, 48.7; H, 8.15; S, 21.4%).

5-*t-Butylsulphonylhex*-1-*ene*.— 5-t-Butylsulphinylhex-1-ene (26) (107 mg, 0.57 mmol) in light petroleum (5 ml) was treated with peroxydodecanoic acid (89% pure; 152 mg, 0.62 mmol). After 15 min the mixture was poured onto a column of alumina (5 g); elution with ether gave 5-*t-butylsulphonylhex*-1-*ene* (100 mg, 86%), $\nu_{max.}$ ($CHCl_3$) 1 287 and 1 112 (>SO_2), and 3 082, 1 643, 996, and 921 cm^{-1} (H_2C=CH–), τ 4.24 (1 H, m, =CH–), 4.97 (2 H, m, H_2C=), 6.75 (1 H, m, CH·SO_2), 8.59 (9 H, s, Me_3C·SO_2), and 8.61 (3 H, d, *J* 7 Hz, 6-H_3), τ(C_6D_6) 4.42 (1 H, m, =CH–), 5.08 (2 H, m, H_2C=), 7.08 (1 H, m, CH·SO_2), 8.85 (3 H, d, *J* 7 Hz, 6-H_3), and 8.87 (9 H, s, Me_3C·SO_2) (Found: C, 58.7; H, 9.7; S, 15.8. $C_{10}H_{20}O_2S$ requires C, 58.8; H, 9.9; S, 15.7%).

(Z)-*Cyclo-oct*-4-*enyl Methanesulphonate* (30).—Methanesulphonyl chloride (13 ml, 0.17 mol) was added to a stirred solution of (*Z*)-cyclo-oct-4-enol [46] (14 g, 0.11 mol) in dry pyridine (120 ml) at 0 °C. The solution was allowed to warm to room temperature, stirred for 1 h, and acidified with 18% hydrochloric acid. Work-up with ether gave the *product* (30) (22.6 g, 100%), $\nu_{max.}$ ($CHCl_3$) 1 354, 1 332, and 1 171 (SO_2·O), and 1 649w (*cis*-CH=CH–), τ 4.35 (2 H, m, –CH=CH–), 5.23 (1 H, m, $J_{1,2a}$ 9.5, $J_{1,2b}$ 4.5, $J_{1,8a}$ 9.5, $J_{1,8b}$ 0 Hz, CH·O·SO_2), and 7.05 (3 H, s, CH_3·SO_2·O) (Found: C, 52.6; H, 8.0; S, 15.7. $C_9H_{16}O_3S$ requires C, 52.9; H, 7.9; S, 15.7%).

(Z)-5-*t-Butylthiocyclo-octene* (31).—The methanesulphonate (30) (22.6 g, 0.11 mol) in propane-2-ol (150 ml) was added with stirring to a solution of sodium isopropoxide [from sodium (12.8 g, 0.55 mol) and 2-methylpropane-2-thiol (63 ml, 0.55 mol)] in propan-2-ol (600 ml). The mixture was boiled under nitrogen for 1 h, poured onto ice, and extracted with ether. The extract was washed with 5% potassium hydroxide solution and water, and dried (Na_2SO_4). Evaporation, and distillation of the residue under reduced pressure gave the *product* (31) (14.8 g, 67%), b.p. 131—133° at 19 mmHg, $\nu_{max.}$ ($CHCl_3$) 1 649w cm^{-1} (*cis*-CH=CH–), τ 4.37 (2 H, m, CH=CH), 7.17 (1 H, m, CH·S), and 8.69 (9 H, s, Me_3C·S), τ(C_6D_6) 4.40 (2 H, m, CH=CH), 7.17 (1 H, m, CH·S), and 8.75 (9 H, s, Me_3C·S), *m/e* 198 (Found: C, 72.6; H, 11.1; S, 16.3. $C_{12}H_{22}S$ requires C, 72.7; H, 11.2; S, 16.2%).

(RS,SR)(Z)- (34) and (RS,RS)(Z)-5-*t-Butylsulphinylcyclo-octene* (35).—(*a*) Peroxydodecanoic acid (88% pure; 15.3 g, 0.062 mol) was added in portions to a stirred solution of (*Z*)-5-t-butylthiocyclo-octene (31) (12.3 g, 0.062 mol) in light petroleum (120 ml) at 0 °C. After 15 min the solution was evaporated and the residue poured onto a column of alumina (300 g). Elution with ether gave the products (34) and (35) (12.8 g, 96%), which were separated on a column of silica (700 g) [ether–light petroleum (1 : 1) as eluant]. Eluted first was the (RS,SR)-*isomer* (34) (4.6 g, 35%), m.p. 63—65°, $\nu_{max.}$ ($CHCl_3$) 1 029 (>SO) and 1 647w cm^{-1} (*cis*-CH=CH–), $\lambda_{max.}$ (EtOH) 222 nm (ε 940), τ 4.33 (2 H, m, CH=CH), 7.30 (1 H, m, CH·SO), 8.41—8.70 (1 H, m), and 8.81 (9 H, s, Me_3C·SO), τ(C_6D_6) 4.51 (2 H, m, CH=CH), 7.34 (1 H, m, CH·SO), and 9.03 (9 H, s, Me_3C·SO), *m/e* 214 (Found: C, 67.4; H, 10.3; S, 15.0. $C_{12}H_{22}OS$ requires C, 67.2; H, 10.3; S, 15.0%). Further elution gave a mixture of isomers (5.1 g, 38%) followed by the (RS,RS)-*isomer* (35) (1.9 g, 14%), m.p. 55—56°, $\nu_{max.}$ ($CHCl_3$) 1 029 (>SO) and 1 648w cm^{-1} (*cis*-CH=CH), $\lambda_{max.}$ (EtOH) 220 nm (ε 1 070), τ 4.33 (2 H, m, CH=CH), 7.27 (1 H, m, CH·SO), 8.34—8.67 (2 H, m), and 8.77 (9 H, s, Me_3C·SO), τ(C_6D_6) 4.50 (2 H, m, CH=CH), 7.46 (1 H, m, CH·SO), and 8.98 (9 H, s, Me_3C·SO), *m/e* 214 (Found: C, 67.4; H, 10.25; S, 14.9. $C_{12}H_{22}OS$ requires C, 67.2; H, 10.3; S, 15.0%).

(*b*) A solution of di-t-butyl sulphoxide (1.0 g) in (*Z,Z*)-cyclo-octa-1,5-diene (7.6 ml) was added quickly, with stirring, to boiling (*Z,Z*)-cyclo-oct-1,5-diene (7.6 ml). After 2 min the reaction flask was quenched in an ice-bath and the cooled solution poured onto a column of alumina (40 g). The column was first eluted with light petroleum to remove the excess of diene, and then with ether to give (*RS,SR*)(*Z*)-5-t-butylsulphinylcyclo-octene (0.49 g, 37%), identical with the characterized product.

(Z)-5-*t-Butylsulphonylcyclo-octene*.—(*a*) Peroxydodecanoic acid (86% pure; 270 mg, 1.1 mmol) was added to a solution of (*Z*)-5-t-butylthiocyclo-octene (31) (100 mg, 0.5 mmol) in light petroleum (4 ml). After 15 min the mixture was poured onto a column of alumina (5 g). Elution with ether gave (Z)-5-*t-butylsulphonylcyclo-octene* (105 mg, 90%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 280, 1 119, and 1 107 (>SO_2), and 1 648w cm^{-1} (*cis*-CH=CH–), τ 4.31 (2 H, m, CH=CH), 6.77 (1 H, m, CH·SO_2), and 8.61 (9 H, s, Me_3C·SO_2), τ(C_6D_6) 4.57 (2 H, m, vinyl), 6.94 (1 H, m, CH·SO_2), and 8.83 (9 H, s, Me_3C·SO_2), *m/e* 230 (Found: C, 62.6; H, 9.8; S, 13.8. $C_{12}H_{22}O_2S$ requires C, 62.6; H, 9.6; S, 13.9%).

(*b*) Oxidation of (*RS,SR*)(*Z*)-5-t-butylsulphinylcyclo-octene (102 mg, 0.48 mmol) with peroxydodecanoic acid (86% pure; 132 mg, 0.52 mmol) in light petroleum (4 ml)

as in (*a*) gave (*Z*)-5-t-butylsulphonylcyclo-octene (100 mg, 91%), identical with the characterized product. Similarly, oxidation of (*RS,RS*)(*Z*)-5-t-butylsulphinylcyclo-octene (51 mg, 0.24 mmol) with peroxydodecanoic acid (86% pure; 66 mg, 0.26 mmol) in light petroleum (2 ml) gave (*Z*)-5-t-butylsulphonylcyclo-octene (50 mg, 91%).

9-*Thiabicyclo*[4.2.1]*nonane* endo-9-*Oxide* (37).—(*a*) Di-t-butyl sulphoxide (2.0 g) was kept under nitrogen in boiling (*Z,Z*)-cyclo-octa-1,5-diene (75 ml) for 1.5 h. The cooled solution was poured onto a column of alumina (30 g) and eluted with light petroleum to remove the excess of diene. Elution with ether–methanol (19 : 1) gave material which was chromatographed on a column of silica (50 g). Elution with ether–methanol (98 : 2) gave 9-*thiabicyclo*[4.2.1]*nonane* endo-9-*oxide* (0.7 g, 36%), m.p. 191° (with sublimation), $\nu_{max.}$ ($CHCl_3$) 1 038 cm^{-1} (>SO), $\lambda_{max.}$ (EtOH) 226 nm (ε 330), τ 6.44 (2 H, m, two CH·SO), 7.72 (2 H, m, 7-H-*exo* and 8-H-*exo*), and 7.80—8.57 (10 H, m), τ(C_6D_6) 6.99 (2 H, m, two CH·SO), 7.61—8.26 (4 H, m), and 8.40—8.93 (8 H, m) (Found: M^+ 158.076 2. $C_8H_{14}OS$ requires *M*, 158.076 5).

(*b*) (*RS,SR*)(*Z*)-5-t-Butylsulphinylcyclo-octene (34) (300 mg) in boiling xylene (9 ml) was kept for 30 min under nitrogen. The cooled solution was poured onto a column of alumina (15 g) and eluted with light petroleum to remove the xylene. Elution with ether–methanol (19 : 1) gave material which was rechromatographed on silica (p.l.c.; ether). Extraction of the band at R_F 0.3 gave 9-thiabicyclo-[4.2.1]nonane *endo*-9-oxide (37) (26 mg, 12%).

(*c*) Thermolysis of (*RS,RS*)(*Z*)-5-t-butylsulphinylcyclo-octene (35) (300 mg) in xylene (9 ml) for 30 min with work-up as in (*a*) gave 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (43 mg, 19%).

(*d*) (*RS,SR*)(*Z*)-5-t-Butylsulphinylcyclo-octene (34) (200 mg) was kept under nitrogen in boiling (*Z,Z*)-cyclo-octa-1,5-diene (6 ml) for 1.5 h. The cooled solution was poured onto a column of alumina (15 g) and eluted with light petroleum to remove the excess of diene. Elution with ether–methanol (19 : 1) gave material which was rechromatographed on silica (p.l.c.; ether). Extraction of the band at R_F 0.3 gave 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (65 mg, 44%).

(*e*) Thermolysis of (*RS,RS*)(*Z*)-5-t-butylsulphinylcyclo-octene (35) (200 mg) in (*Z,Z*)-cyclo-octa-1,5-diene (6 ml) for 1.5 h with work-up as in (*d*) gave 9-thiabicyclo[4.2.1]-nonane *endo*-9-oxide (37) (70 mg, 47%). Another reaction on the same scale, but for 15 min, gave after work-up as in (*d*) (*RS,SR*)(*Z*)-5-t-butylsulphinylcyclo-octene (34) (101 mg, 50%) and 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (23 mg, 16%).

9-*Thiabicyclo*[4.2.1.]*nonane* (36).—(*a*) Phosphorus trichloride (1.75 ml, 0.02 mol) was added dropwise to a stirred solution of 9-thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (1.6 g, 0.01 mol) in dichloromethane (30 ml). After 1 min the mixture was poured onto ice and extracted with ether, and the extract was washed with water, saturated sodium hydrogen carbonate solution, and water again. After drying (Na_2SO_4) the solution was evaporated through a 12 cm × 1 cm column containing glass helices. The waxy residue crystallized from methanol to give 9-thiabicyclo[4.2.1]-nonane (36) (1.3 g, 90%), m.p. 127—128° (lit.,[43] 127—128°), τ 6.34 (2 H, m, two CH·S), 7.73 (2 H, m, 7-H-*exo* and 8-H-*exo*), and 7.87—8.81 (10 H, m), τ(C_6D_6) 6.55 (2 H, m, two CH·S), 7.94 (2 H, m, 7-H-*exo* and 8-H-*exo*), and 8.05—8.96 (10 H, m) (Found: C, 67.3; H, 9.9; S, 22.5. Calc. for $C_8H_{14}S$: C, 67.5; H, 9.9; S, 22.5%).

(*b*) Reduction of 9-thiabicyclo[4.2.1]nonane *exo*-9-oxide (38) (75 mg, 0.47 mol) with phosphorus trichloride (0.21 ml, 2.4 mmol) in dichloromethane (10 ml) as in (*a*) gave 9-thiabicyclo[4.2.1]nonane (36) (20 mg, 30%), identical with the characterized product. The losses during purification were substantial because of the high camphor-like volatility of the sulphide.

Oxidation of 9-*Thiabicyclo*[4.2.1]*nonane* (36).—(*a*) Peroxydodecanoic acid (91% pure; 0.69 g, 2.9 mmol) was added to a solution of 9-thiabicyclo[4.2.1]nonane (36) (0.41 g, 2.9 mmol) in light petroleum (20 ml). After 15 min the mixture was poured onto a column of alumina (15 g); elution with ether gave 9-*thiabicyclo*[4.2.1]*nonane* exo-9-*oxide* (38) (0.44 g, 97%), m.p. 180° [after sublimation at 100° and 0.1 mmHg], $\nu_{max.}$ ($CHCl_3$) 1 014 cm^{-1} (>SO), τ 6.39 (2 H, m, two CH·SO), 7.13 (2 H, m, 7-H-*exo* and 8-H-*exo*), and 7.75—8.64 (10 H, m), τ(C_6D_6) 6.74 (2 H, m, two CH·SO), 7.32 (2 H, m, 7-H-*exo* and 8-H-*exo*), and 8.23—9.23 (10 H, m), *m/e* 158 (Found: C, 60.5; H, 9.0; S, 20.0. $C_8H_{14}OS$ requires C, 60.7; H, 8.9; S, 20.3%).

(*b*) 9-Thiabicyclo[4.2.1]nonane (36) (0.2 g, 1.4 mmol) in methanol (3 ml) was added to a stirred solution of sodium periodate (0.3 g, 1.4 mmol) in water (3 ml) at 0 °C. The mixture was allowed to warm to room temperature and after stirring for 3 h the white slurry was shaken with chloroform and filtered through glass wool. The organic layer of the filtrate was dried (Na_2SO_4) and evaporated to give 9-thiabicyclo[4.2.1]nonane *exo*-9-oxide (38) (0.21 g, 94%).

(*c*) Ozone was bubbled through a solution of 9-thiabicyclo[4.2.1]nonane (36) (0.2 g) in dichloromethane (40 ml) at −78 °C until the reaction was complete (t.l.c.). Nitrogen was then passed through the solution for 30 min before allowing it to warm to room temperature. Evaporation gave 9-thiabicyclo[4.2.1]nonane *exo*-9-oxide (38) (0.2 g, 90%).

(*d*) A solution of 9-thiabicyclo[4.2.1]nonane (36) (50 mg, 0.35 mmol) in methanol (2 ml) was cooled to −78 °C and t-butyl hypochlorite (40 mg, 0.37 mmol) in methanol (1 ml) was added dropwise. After stirring at −78 °C in the dark for 1 h, the mixture was warmed to −40 °C and anhydrous sodium carbonate added. Filtration, and concentration of the filtrate gave a mixture of 9-thiabicyclo[4.2.1]nonane *exo*- and *endo*-9-oxides, (38) and (37), in the ratio 87 : 13 (g.l.c.; FFAP column).

(*e*) 1-Chlorobenzotriazole (54 mg, 0.35 mmol) in methanol (1 ml) was added dropwise to a stirred solution of 9-thiabicyclo[4.2.1]nonane (36) (50 mg, 0.35 mmol) in methanol (2 ml) at −78 °C. After stirring for 1 h the mixture was warmed to room temperature, poured into 3% sodium hydroxide solution (5 ml), and extracted with dichloromethane. After drying (Na_2SO_4), evaporation of solvent left a mixture of 9-thiabicyclo[4.2.1]nonane *exo*-9-oxide (38) and *endo*-9-oxide (37) (51 mg, 92%) in the ratio 93 : 7 (g.l.c.; FFAP column).

9-*Thiabicyclo*[4.2.1]*nonane* 9,9-*Dioxide* (39).—(*a*) 9-Thiabicyclo[4.2.1]nonane *endo*-9-oxide (37) (100 mg, 0.63 mmol) in light petroleum (8 ml) was treated with peroxydodecanoic acid (96% pure; 157 mg, 0.70 mmol). After 15 min, the mixture was poured onto a column of alumina (5 g); elution with ether gave 9-thiabicyclo[4.2.1]nonane 9,9-dioxide (39) (100 mg, 91%), m.p. 241° (lit.,[43] 235—237°), $\nu_{max.}$ ($CHCl_3$) 1 293 and 1 113 cm^{-1} (>SO_2), τ 6.83 (2 H, m, two CH·SO_2), 7.51 (2 H, m, 7-H-*exo* and 8-H-*exo*), and 7.76—8.66 (10 H, m), τ(C_6D_6) 7.27 (2 H, m, two CH·SO_2), 7.93 (2 H, m, 7-H-

exo and 8-H-*exo*), and 8.08—9.22 (10 H, m) (Found: C, 55.0; H, 8.2; S, 18.6. Calc. for $C_8H_{14}OS$: C, 55.1; H, 8.1; S, 18.4%).

(*b*) A solution of 9-thiabicyclo[4.2.1]nonane *exo*-9-oxide (**38**) (74 mg, 0.47 mmol) and peroxydodecanoic acid (91% pure; 246 mg, 1.0 mmol) in light petroleum (12 ml) was kept at room temperature for 2 h. Work-up as in (*a*) gave 9-thiabicyclo[4.2.1]nonane 9,9-dioxide (**39**) (75 mg, 92%), identical with the characterised product.

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