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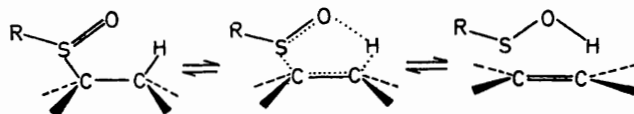
Stereospecific Synthesis of Thiolan 1-Oxide Derivatives by Intramolecular Addition of Sulphenic Acids to Olefins

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Summary Pyrolysis of derivatives of 5-t-butylsulphinylpentene, which may be prepared by reaction of t-butylsulphenic acid with 1,5-dienes, provides a method for the stereospecific synthesis of thiolan 1-oxide derivatives.

THE thermal decomposition of dialkyl sulphoxides to alkenes and alkanesulphenic acids, which proceeds by a concerted *syn*-intramolecular mechanism (Scheme),¹ was recently shown to be reversible.^{2,3} We have exploited the stereoelectronic requirements of this reversible six-electron sigmatropic rearrangement to synthesise cyclic and bicyclic sulphoxides stereospecifically. Products of addition of simple alkanesulphenic acids to unactivated olefins have not been reported hitherto, although sulphenic acids derived from penicillins have been trapped by norbornadiene,³ and the addition of t-butylsulphenic acid to electrophilic olefins has been described.^{4,5}

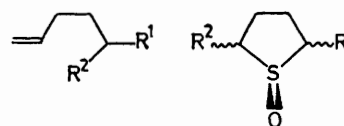


(A)

SCHEME

5-t-Butylsulphinylpentene (**1**), prepared in 64% yield from pent-4-en-1-ol by sequential treatment with methanesulphonyl chloride, t-butylthiolate ions, and peroxydecanoic acid, gave *cis*-2-methylthiolan 1-oxide⁶ (**2**) (74%) on pyrolysis (light petroleum, 160°).† No *trans*-2-methyl-

thiolan 1-oxide (**3**) or thian 1-oxide was formed. This result was rational in terms of the decomposition of (**1**) into the sulphenic acid (**4**) and 2-methylpropene, followed by intramolecular addition of the sulphenic acid to the double

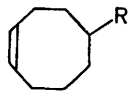


- | | |
|--|--|
| (1) R ¹ = H, R ² = Bu ^t S(O) | (2) R ¹ = H, R ² = <i>cis</i> -Me |
| (4) R ¹ = H, R ² = SOH | (3) R ¹ = H, R ² = <i>trans</i> -Me |
| (5) R ¹ = Me, R ² = Bu ^t S(O) | (6) R ¹ = R ² = <i>cis</i> -Me |
| (8) R ¹ = Me, R ² = SOH | (7) R ¹ = <i>trans</i> -Me, R ² = <i>cis</i> -Me
(<i>cis</i> , <i>trans</i> with reference to O) |

bond *via* a cyclic transition state, as (A), the stereoelectronic requirements of which preclude the formation of the *trans*-sulphoxide (**3**) and thian 1-oxide. Similarly, pyrolysis of 5-t-butylsulphinylhexene (**5**) (120°, light petroleum) gave (**6**) (25%) and (**7**) (26%) which were separated chromatographically; no 2-methylthian 1-oxide or *cis*-2,5-dimethylthiolan *trans*-1-oxide were formed. The configurations of (**6**) and (**7**) followed from their n.m.r. spectra, using the criterion that a methyl group *cis* to sulphanyl oxygen is deshielded relative to that *trans* to oxygen, the relative deshielding being greater in C₆D₆ than in CDCl₃.⁶ The cyclization of the sulphenic acid (**8**) [formed from (**5**)] to (**6**) and (**7**) occurred in *ca.* 80% yield, if the regioselectivity of the elimination of the sulphoxide (**5**) is governed predominantly by statistical factors related to the number of available β-hydrogens.⁷ This provides a convenient synthesis of (**7**),⁸ and a stereospecific synthesis of (**6**). The

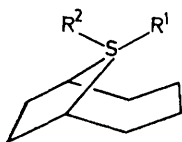
† Satisfactory analytical and i.r., n.m.r., and mass spectral data were obtained for all the compounds, with the exception of the very hygroscopic sulphoxides, for which poor combustion analytical data were obtained.

oxidation of *cis*-2,5-dimethylthiolan has been described without mention of configuration at sulphur in the resulting sulphoxide.⁸ Reaction of hexa-1,5-diene with *t*-butylsulphenic acid, generated *in situ* by pyrolysis of di-*t*-butyl sulphoxide,⁴ gave (5) (21%), (6) (23%), and (7) (11%),



(9) R = SOH

(10) R = Bu^tS(O)



(11) R¹ = O, R² = lone electron pair

(12) R¹ = lone electron pair, R² = O

(13) R¹ = R² = lone electron pair

(14) R¹ = R² = O

which were separated chromatographically. Addition of *t*-butylsulphenic acid to the diene was regiospecific, no 6-*t*-butylsulphinylnonane being formed.

The transition state considerations adumbrated above led to the prediction that the sulphenic acid (9), generated by pyrolysis of the sulphoxide (10) would cyclize to 9-thiabicyclo[4,2,1]nonane *endo*-9-oxide (11), and not to the isomeric *exo*-oxide (12) or 9-thiabicyclo[3,3,1]nonane 9-oxide. Accordingly, addition of di-*t*-butyl sulphoxide to boiling *cis,cis*-cyclo-octa-1,5-diene over 30 min gave (11) (42%) as the only bicyclic sulphoxide, after chromatography and sublimation. Reduction of (11) with phosphorus trichloride in dichloromethane gave 9-thiabicyclo[4,2,1]nonane (13),⁹ which on oxidation with peroxydecanoic acid gave exclusively the *exo*-oxide (12); it is established that peroxy-acids oxidise bicyclic sulphides preferentially from the less hindered side.¹⁰ Oxidation of the sulphoxides (11) and (12) gave the sulphone (14).⁹ Models reveal that sulphanyl oxygen is sterically more accessible in (12) than (11), and accordingly (11) displayed the greater mobility during chromatography on silica (t.l.c.); this provided additional evidence for the configurations depicted.

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

² D. H. R. Barton, F. Comer, D. G. 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.

³ D. H. R. Barton, D. G. T. Greig, G. Lucente, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *Chem. Comm.*, 1970, 1683.

⁴ J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 718.

⁵ E. Block, *J. Amer. Chem. Soc.*, 1972, **94**, 642.

⁶ J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, 1970, **35**, 3655; C. R. Johnson, C. C. Bacon, and J. J. Rigau, *ibid.*, 1972, **37**, 919.

⁷ D. W. Emerson, A. P. Craig, and I. W. Potts, *J. Org. Chem.*, 1967, **32**, 102.

⁸ A. R. Jones, *Chem. Comm.*, 1971, 1042.

⁹ E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, 1966, **31**, 1669.

¹⁰ M. Kishi and T. Komeno, *Tetrahedron Letters*, 1971, 2641.