

## Anionic [1,2]-Rearrangements of 3-Alkyl- and 2,3-Dialkyl-thietan 1-Oxides: Stereospecific Ring Contractions

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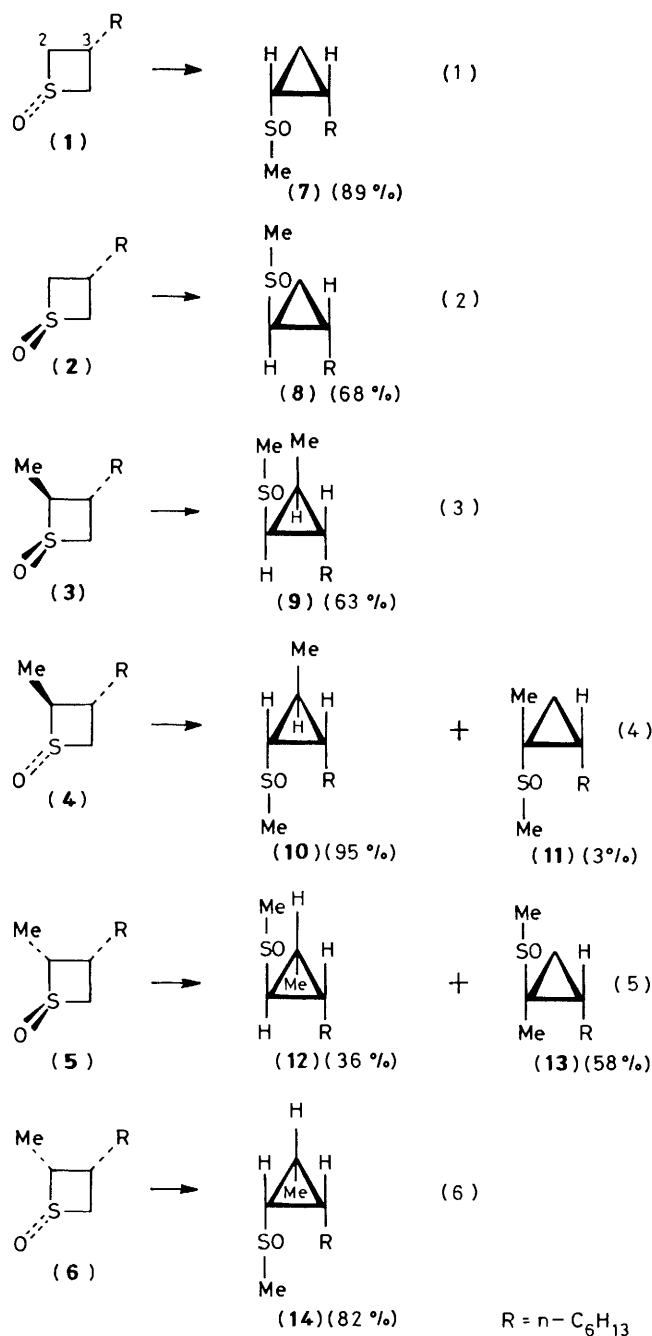
Ring contractions of the lithio-anions of 3-alkyl- and 2,3-dialkyl-thietan 1-oxides to give substituted cyclopropanes occurred stereospecifically with respect to configuration at sulphur, the migrating residue (retention), and the migration terminus (inversion).

Anionic rearrangements, (A) to (B), of sulphonium ylides ( $Y = RS^+$ ) and anions of sulphides ( $Y = S$ ) are well exemplified, but aspects of their mechanism have remained a matter for conjecture.<sup>1</sup> For sulphonium ylides retention of configuration in the migrating group ( $Z$ ) has been observed,<sup>2</sup> but information about the stereochemical outcome at the migration terminus is scant and ambiguous.<sup>3</sup> For sulphoxides ( $Y = SO$ ) examples are rare,<sup>4</sup> and the stereochemical courses for the rearrangements are not well defined. We have found that the base-catalysed ring contractions of 3-alkyl- and 2,3-dialkyl-thietan 1-oxides occur with a stereospecificity which is controlled by the configuration at sulphur, and which throws light on the mechanism.



Treatment of *cis*- and *trans*-3-hexylthietan 1-oxide, (1) and (2), separately with lithium cyclohexylisopropylamide (1.1 mol. equiv.) in tetrahydrofuran at  $-20^\circ\text{C}$  for 15 min followed by addition of methyl iodide gave respectively *cis*- and *trans*-2-hexyl-1-(methylsulphinyl)cyclopropane, (7) (89%) and (8) (68%) (Scheme 1). Under similar conditions the four diastereoisomers of 3-hexyl-2-methylthietan 1-oxide, (3)—(6), underwent ring contraction stereospecifically, and, for the isomers (3) and (6), regiospecifically. In each case the product sulphoxides (7)—(14) were mixtures diastereoisomeric at sulphur, and in order to facilitate the assignment of structures by n.m.r. methods (at 400 MHz) the sulphoxides were oxidised to the corresponding sulphones. The sulphoxides (1)—(6) were prepared by peroxyacid oxidation of the corresponding substituted thietans, and their configurations were determined by established chemical and spectroscopic methods.<sup>5</sup>

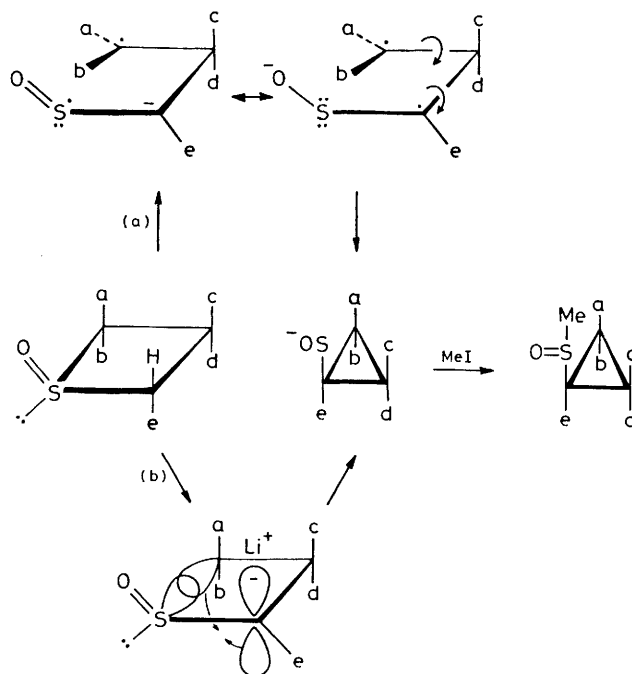
The anions of the thietan 1-oxides evidently rearranged to cyclopropylsulphenate anions,<sup>4</sup> which were trapped by methyl iodide (Scheme 2).<sup>6</sup> The stereochemical features of the ring contractions may be summarized as follows. The sul-



Scheme 1†

phenyl oxygen atom in a given thietan 1-oxide and the methylsulphonyl group in the product are in the same orientation with respect to the other ring substituents [equations (1)—

† The sulphoxides (7)—(10) were isolated and fully characterized, as were the corresponding sulphones. The sulphoxides (11)—(14) were characterized as their sulphones, isolated by preparative g.l.c. Yields in equations (1)—(3) refer to isolated yields of sulphoxides, and in equations (4)—(6) to yields based on g.l.c. analysis of the sulphones. The stereospecificity of the rearrangements was established by g.l.c. investigation of the crude product mixtures, after oxidation to the sulphones. All the sulphones showed different g.l.c. retention times (OV225, 2.5% on Chromosorb G).



Scheme 2

(6)], the configuration at the migrating carbon atom is retained [equations (3)—(6)] while the configuration at the migration terminus is inverted [see the formation of (11) and (13)], and regiospecific ring contraction occurs only if the sulphonyl oxygen atom is *cis* to a 2-methyl group in the thietan 1-oxide [compare equations (3) and (4), and equations (5) and (6)].

These stereochemical consequences accord with those expected for a concerted process,<sup>7</sup> initiated by the preferential abstraction of an  $\alpha$ -proton *cis* to the sulphonyl oxygen atom [Scheme 2, pathway (b)].<sup>‡</sup> Concertedness may be facilitated by the lithium cation,<sup>7</sup> and by the geometrical constraints of the four-membered ring. Such concerted mechanisms in general are geometrically unfavourable,<sup>7</sup> and for ylides radical pairs are involved.<sup>2,8</sup> A homolysis-recombination mechanism for these ring contractions would involve a conrotatory ring closure of a diradical,<sup>9</sup> the direction of which is controlled by the geometry of the sulphenate anion and which proceeds faster than the loss of stereochemical integrity at the migrating group, the migration terminus, and at sulphur [Scheme 2, pathway (a)]. Evidence that closure of 1,3-diradicals is fast compared with bond rotation, and that partial stereospecificity pertains in the closure of other diradicals supports the feasibility of this mechanism.<sup>10</sup>

The evidence available does not distinguish between the two mechanisms, but the conclusions to be drawn are nevertheless significant: *either* these ring contractions provide the only examples of stereochemically characterized 'allowed' concerted anionic [1,2]-sigmatropic rearrangements, *or* they illustrate that a radical mechanism for the rearrangements is associated with a stereospecificity which accords with that expected for sigmatropy with conservation of orbital symmetry.

‡ Speculation as to the precise geometry of the initial anion is unwarranted (the parent thietan 1-oxide rings are puckered, see ref. 5) and the rings have been depicted as planar for convenience.

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