Thermal Decomposition of 3,4-Oxathiabicyclo[4.1.0]heptane 4-Oxides into Sulphur Dioxide and a 1,4-Diene. A Novel $\pi_2^s + \pi_{2s} + \pi_{2s}$ Cycloreversion

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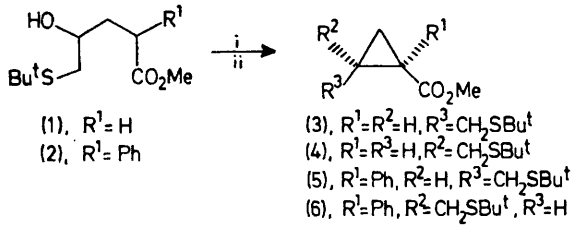
Summary The thermolysis of the bicyclic sultines (**12**), (**13**), and (**14**) gives, smoothly and stereospecifically, a 1,4-diene and SO_2 *via* a novel concerted cycloreversion.

WE have recently shown that the thermal decomposition of 3,6-dihydro-1,2-oxathiin 2-oxides[1] and of β-sultines[2] are stereospecific, possibly concerted, cycloreversions. An interesting aspect of these reactions is the remarkable ease with which the SO_2 extrusion occurs. In the case of the 1,2-oxathiin 2-oxides, decomposition into 1,3-dienes and SO_2 occurred at temperatures below 0 °C.[1] This contrasts with the temperatures of *ca.* 125 °C required for the decomposition of the isomeric 2,5-dihydrothiophen 1,1-dioxides to the same products *via* the cheletropic extrusion pathway.[3]

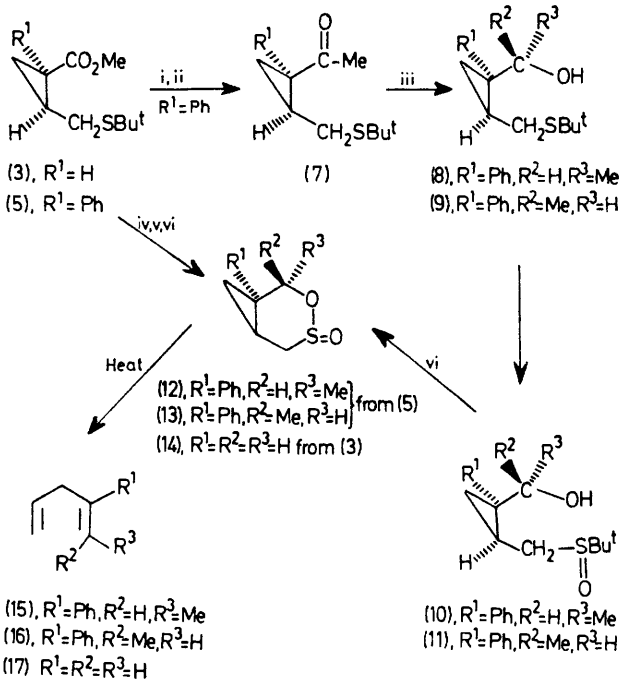


SCHEME 1. i, $MeSO_2Cl$; ii, MeO^-Na^+.

We now report that 3,4-oxathiabicyclo[4.1.0]heptane 4-oxides fragment stereospecifically into 1,4-dienes and SO_2 *via* a probable $\pi_{2s} + \pi_{2s} + \pi_{2s}$ cycloreversion. Again the SO_2 extrusion from the sulphinate ester occurs at a temperature *ca.* 100 °C below that required for the decomposition of the isomeric 3-thiabicyclo[3.1.0]hexane 3,3-dioxides.[4] This constitutes the third example of a new family of symmetry-allowed cycloreversions.[1,2]

The *cis*-methoxycarbonyl sulphides (**3**), precursor of (**14**), and (**5**), precursor of (**12**) and (**13**), were easily obtained *via* a solvent-influenced stereoselective cyclization of (**1**) and (**2**) (Scheme 1).‡ Thus when hexamethylphosphoric triamide was used as solvent, (**1**) gave (**3**) and (**2**) gave (**5**) (87 and 83% stereoisomeric purity, respectively). In tetrahydrofuran, however, the *trans*-isomer was the sole product from (**1**), whereas (**2**) gave (**5**) and (**6**) in the ratio of 1 : 3. This is in contrast to the base-induced cyclization of 2-halogenomethyl glutarates, in which these solvents have the opposite effect on the product stereochemistry.[5]

Reaction of the *cis*-hydroxy sulphoxide (**10**) with sulphuryl chloride in methylene chloride at −78 °C[6] gave the sultine (**12**) [δ ($CDCl_3$) 1·15 (3H, d) and 4·05 (1H, q)] as a mixture of the two possible diastereoisomers§ varying only in the stereochemistry at the sulphinyl sulphur. Similarly, (**11**) gave (**13**) [δ ($CDCl_3$) 1·3 (3H, d) and 4.85 (1H, q)]. The sultines (**12**) and (**13**) are fairly stable at room temperature.



SCHEME 2. i, $MeSOCH_2^-Na^+$; ii, Zn and AcOH; iii, $NaBH_4$; iv, $LiAlH_4$; v, [O]; vi, SO_2Cl_2 at −78 °C.

The configuration at C-2 has been tentatively assigned on the basis of their physical properties and the method of preparation (Scheme 2).¶ On thermolysis in chloroform at reflux, (**12**) gave *cis*-4-phenylhexa-1,4-diene (**15**)[7] in quantitative yield and >99·5% isomeric purity, while (**13**) afforded the isomeric *trans*-diene (**16**) in a similar yield and purity.[7] The half-lives for decomposition of (**12**) and

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‡ Compound (**2**) was obtained from methyl phenylacetate *via* anion condensation with allyl bromide to give methyl 2-phenylpent-4-enoate, followed by epoxidation and reaction with Bu^tSNa, saponification, and esterification (58% overall yield). Compound (**1**) was prepared similarly.

§ Cyclization of each separated isomer of (**10**) gave the same diastereoisomeric mixture of (**12**). The same result was obtained with (**11**). This shows that such a cyclization is not stereospecific at the sulphinyl group.[1] Satisfactory microanalyses were obtained for all new compounds.

¶ Reduction of (**7**) with $LiAlH_4$ or $NaBH_4$ in Pr^iOH at room temperature gives mainly one of the two possible diastereoisomers, (**8**), in >90% yield. The stereoselectivity and the stereochemistry of the reduction can be explained by the influence of the neighbouring sulphide group. For discussion, see H. O. House, 'Modern Synthetic Reactions', Benjamin, New York, 1972, pp. 54–70 and references cited.

(**13**) under these conditions were 1·3 and 10 h respectively. The decomposition reactions were monitored by n.m.r. spectroscopy.

The small influence of the solvent on the reaction rate ($t_{\frac{1}{2}}$, $CDCl_3$–[$^2H_6$]-Me_2SO = 1 : 3·5) is not in agreement with a dipolar or a diradical intermediate resulting from an initial C–O bond cleavage. The strong non-bonding interactions in the transition state of the intermediate leading to (**16**), as compared to (**15**), as well as a possible difference in the stereochemistry at the sulphinyl group (see below), could account for the differences in the rate of decomposition between (**12**) and (**13**) [$t_{\frac{1}{2}}$, (**12**) : (**13**) = 1·3 : 10].[1] These results are consistent with a concerted cycloreversion, the favoured allowed disrotatory process being the one in which SO_2 departs *anti* to the methylene group of the cyclopropane ring.[8] A similar stereochemical control of cyclopropanes[9a] and aziridines[9b] in $\pi_{2s} + \pi_{2s} + \pi_{2s}$ cycloreversions has been observed.

The stereochemistry of the sulphinyl group has been shown to have no influence on the direction of bond rotation[1,2] but can influence the rate of decomposition. Thus, the two isomers of the parent sultine (**14**) decompose quantitatively without any apparent interconversion into the 1,4-pentadiene (**17**), at a relative rate of 1 : 4·5. We have not yet determined unambiguously the stereochemistry of the sulphinyl group.

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