

4,5-Dihydrothiepin 1,1-Dioxide

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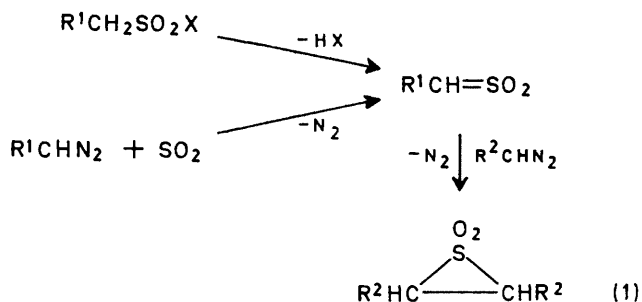
Summary The reaction between sulphur dioxide and two equivalents of vinyldiazomethane yields 4,5-dihydrothiepin 1,1-dioxide: a probable mechanism is discussed.

THE reaction of a diazoalkane with a sulphene¹ (produced either by dehydrohalogenation of a sulphonyl halide or from another diazoalkane molecule and sulphur dioxide) at present provides the only general preparative route to thiepan 1,1-dioxides (equation 1). In the course of searching for new synthetic routes to medium-sized ring sulphones, we have examined the reaction between vinyldiazomethane and sulphur dioxide.

Passage of gaseous sulphur dioxide into an ethereal solution of vinyldiazomethane² results in rapid disappearance of the characteristic red colour of the latter and evolution of N₂. Work-up of the resulting solution by evaporation and chromatography of the residue on silicic acid yields a crystalline sulphone, which, after sublimation (100°/0.1 mm) and recrystallization from benzene-hexane, melts at 111.5–112.5°.

The composition of this new sulphone is C₆H₈SO₂ as shown by elemental analysis and mass spectroscopy. I.r. absorption bands at 7.8 and 9.0 μm establish the presence of the sulphonyl group. Catalytic hydrogenation (Pd-C) results in the uptake of two equivalents of hydrogen and yields thiepan 1,1-dioxide. Treatment of the new substance in benzene under reflux with triethylamine as catalyst, effects quantitative conversion into 2,7-dihydrothiepin 1,1-dioxide,† which has been prepared by 1,6-cycloaddition of

sulphur dioxide to *cis*-hexatriene.³ Hence, the new material is probably an isomeric (and thermodynamically less stable) dihydrothiepin dioxide. Its relatively simple n.m.r. spectrum suggests that it is 4,5-dihydrothiepin 1,1-dioxide (II).



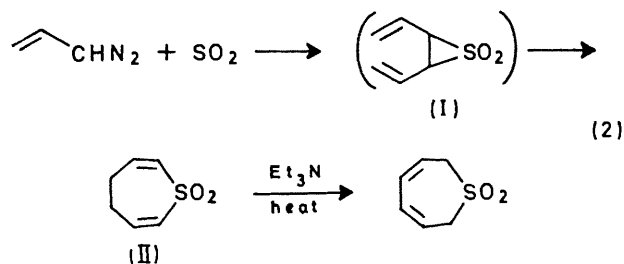
There is a four proton multiplet at δ 2.70, assigned to the γ -methylene groups at positions 4 and 5 shown by decoupling experiments to be adjacent to the high-field pair of a set of four olefinic protons at δ 6.58 and 6.44. These are assigned, respectively, to the α - and β -hydrogens, which appear to be strongly coupled to each other (J 11.0 \pm 0.1 Hz).

A possible mechanism for the formation of the observed product (II) involves the steps of the ordinary diazoalkane-sulphur dioxide reaction (equation 2), producing *cis*-

† When the isomerization is followed by n.m.r. no intermediates can be detected.

divinylthiiran 1,1-dioxide (I) as a transient intermediate.† On the basis of close analogies,⁴ rapid Cope rearrangement to 4,5-dihydrothiepin 1,1-dioxide would be anticipated. Alternative mechanisms involving mesoionic intermediates or various types of conjugate addition cannot be ruled out. If the suggested mechanism is tentatively accepted, a new mode of reactivity is revealed for the highly unstable thiiran dioxide ring, which normally fragments to an olefin and sulphur dioxide.

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† The *trans*-isomer, if formed and if not in equilibrium with the *cis*-isomer, may contribute to the tar which comprises the main reaction product.

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