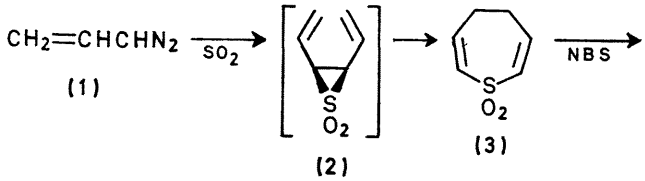
C–C Bond Cleavage Reactions of Episulphones. A Convenient New Synthesis of Thiepin 1,1-Dioxide

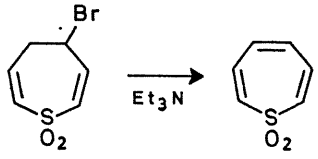
By LEO A. PAQUETTE and STEFANO MAIORANA
(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

Summary The reaction of vinyldiazomethane and its derivatives with sulphur dioxide and sulphenes yields dihydrothiepin 1,1-dioxides which are useful precursors to thiepin 1,1-dioxides; the probable intermediacy of divinyl episulphones in these reactions is discussed.

EPISULPHONES (thi-iran 1,1-dioxides) commonly readily decompose at 25—50° (E_{act} = *ca.* 17—21 kcal/mole)[1] with expulsion of sulphur dioxide and formation of alkenes with retained stereochemistry. Although the mechanism of this highly stereospecific reaction is undecided,[1,2] the marked kinetic bias for C–S bond cleavage is certain. A recent *X*-ray crystal structure analysis of *cis*-but-2-ene episulphone revealed, however, that this strained three-membered heterocycle does possess an exceptionally long C–C bond (1·60 Å).[3] The purpose of the present study was to cause C–C bond cleavage of episulphones to become kinetically dominant. This has been accomplished by modification of certain structural features[4] and, in addition, a convenient new synthesis of thiepin 1,1-dioxide has been realized.

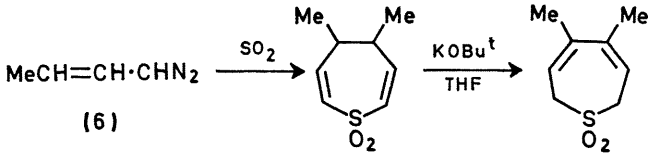


(1) (2) (3)



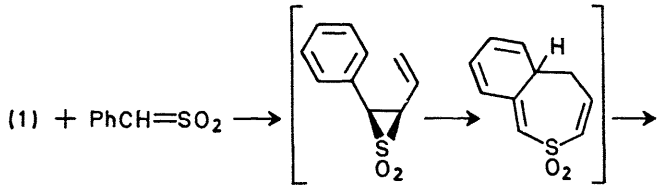
(4) (5)

When gaseous sulphur dioxide was introduced slowly into a cold (−20°) ethereal solution of vinyldiazomethane (**1**)[5] and the mixture was left at room temperature for 3 h, the burgundy colour of (**1**) faded, nitrogen was evolved, and a white crystalline sulphone, m.p. 115—115·5°, was obtained (29% yield), identified as 4,5-dihydrothiepin 1,1-dioxide (**3**) on the basis of (a) its n.m.r. spectrum : δ($CDCl_3$) 2·70 (4H, m, γ-methylene) 6·44 (2H, β-H), and 6·58 (2H, α-H) p.p.m.; (b) ready catalytic hydrogenation to thiepan 1,1-dioxide, m.p. 70—71°;[6] (c) essentially quantitative isomerization (Bu^tOK–tetrahydrofuran) to 2,7-dihydrothiepin 1,1-dioxide, m.p. 107—108°, and ultimate conversion into thiepin 1,1-dioxide (**5**).[6] The latter transformation was accomplished by allylic bromination of (**3**) followed by triethylamine-promoted dehydrobromination of (**4**) whose non-rearranged structure was established by spin-decoupling experiments at 100 MHz [δ ($CDCl_3$; Me_4Si) 2·86—3·38 (1H, m allyl), 3·64—4·06 (1H, m, allyl), 5·08 (1H, m, >CHBr), and 6·17—7·10 (4H, m, vinyl) p.p.m.].

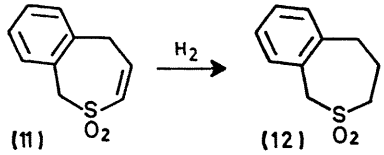


(6) (7) (8)

The conversion of (**1**) into (**3**), similar to the synthesis of episulphones from diazoalkanes and SO_2,[7] is probably due to the transient formation of the *cis*-divinyl episulphone (**2**) which is subject to rapid Cope rearrangement.[8]† This sigmatropic change (C–C bond cleavage), as expected from energy considerations (the activation energy for related transformations[9] is *ca.* 12 kcal mol^{-1}), can compete effectively with the customarily observed fragmentation pathway (C–S bond rupture). Moreover, the reaction appears to be of general synthetic utility for the synthesis of medium-sized cyclic unsaturated sulphones. For example, exposure of 1-diazobut-2-ene (**6**)[10] to gaseous SO_2 afforded sulphone (**7**) in good (43%) yield. Base-catalysed isomerization of (**7**) led to (**8**), m.p. 119—120·5°, λ_{max} (EtOH) 225 nm (ε 5300).



(9) (10)



(11) (12)

Since episulphones can also be readily obtained by reaction of sulphenes with diazoalkanes,[11] the scope of the method is enhanced; *e.g.*, addition of vinyldiazomethane (**1**) to benzylidene sulphone (from phenylmethanesulphonyl chloride and triethylamine) furnished sulphone (**11**), m.p. 157—158°. Structural assignment to (**11**) was based on its u.v. [λ_{max} (EtOH) 261 (ε 240) and 272 nm (185)] and n.m.r. spectra [δ ($CDCl_3$; Me_4Si): 3·62 (2H, d, *J* 5·5 Hz, C-5-CH_2),

† We have no evidence concerning the concertedness or non-concertedness of this step.

4·52 (2H, d, J 1·8 Hz, C-2-CH_2), 5·9—6·7 (2H, m, vinyl), and 7·30 (4H,m, aryl) p.p.m.], and catalytic hydrogenation to the known[12] dihydro-derivative (12), m.p. 179—180°.

A reasonable mechanism for the formation of (**11**) involves the expected intervention of episulphone (**9**) which rearranges to (**10**) despite the need for temporary disruption of aromaticity in the benzene ring. To regain aromatic stabilization, (**10**) is required to undergo a [1,7] hydrogen shift. We presume in the case of (**9**) that the competition between Cope rearrangement (estimated [13] E_{act} *ca.* 19—20 kcal mol^{-1}) and its thermal fragmentation (estimated[1] E_{act} *ca.* 19—21 kcal mol^{-1}) is nearly evenly balanced.

Further studies on this reaction and the chemistry of the medium-ring sulphones will be reported later.

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