

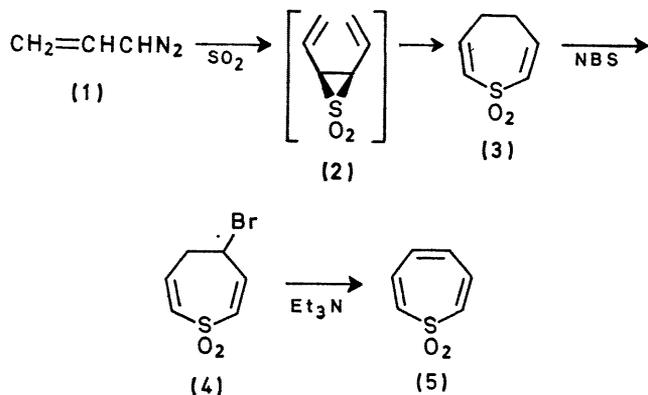
C-C Bond Cleavage Reactions of Episulphones. A Convenient New Synthesis of Thiepin 1,1-Dioxide

By LEO A. PAQUETTE and STEFANO MAIORANA

(Department of Chemistry, The Ohio State University, Columbus, Ohio 43210)

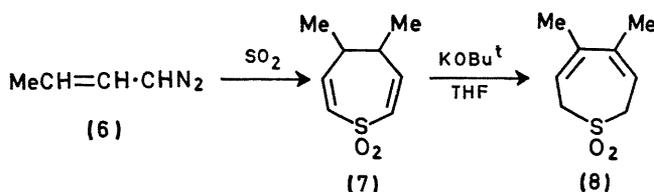
Summary The reaction of vinyl diazomethane and its derivatives with sulphur dioxide and sulphenes yields dihydrothiepin 1,1-dioxides which are useful precursors to thiepin 1,1-dioxides; the probable intermediacy of divinyl episulphones in these reactions is discussed.

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 features⁴ and, in addition, a convenient new synthesis of thiepin 1,1-dioxide has been realized.

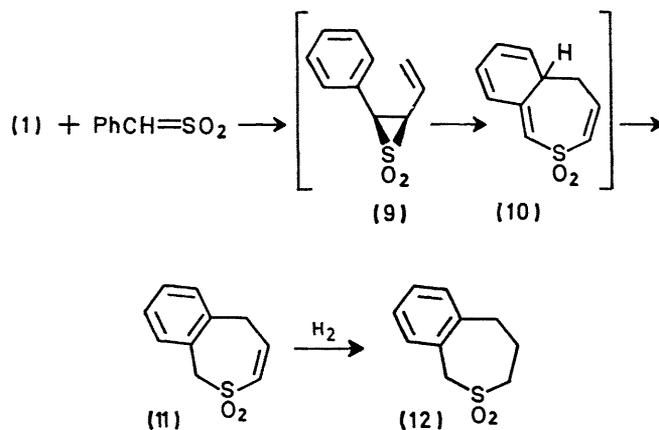


When gaseous sulphur dioxide was introduced slowly into a cold (-20°) ethereal solution of vinyl diazomethane (1)⁵ and the mixture was left at room temperature for 3 h, the burgundy colour of (1) faded, nitrogen was evolved, and a white crystalline sulphone, m.p. 115–115.5°, was obtained (29% yield), 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.].



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 transformations⁹ 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).



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 vinyl diazomethane (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-CH₂), 5.9—6.7 (2H, m, vinyl), and 7.30 (4H, m, aryl) p.p.m.], and catalytic hydrogenation to the known¹² 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 (estimated¹ 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.

(Received, December 14th, 1970; Com. 2152.)

¹ F. G. Bordwell, J. M. Williams, jun., E. B. Hoyt, jun., and B. B. Jarvis, *J. Amer. Chem. Soc.*, 1968, **90**, 429.

² L. A. Paquette in "Mechanisms of Molecular Migrations," vol. 1, ed. B. S. Thyagarajan, Interscience, New York, 1968, pp. 121—156; R. Hoffman, 21st National Organic Symposium, Salt Lake City, Utah, June 1969, Abstracts pp. 109—129.

³ R. Desiderato and R. L. Sass, *Acta Cryst.*, 1967, **23**, 430.

⁴ See W. L. Mock, *Chem. Comm.*, 1970, 1254, for an example of an independent application of this concept which appeared after completion of this work.

⁵ C. D. Hurd and S. C. Lui, *J. Amer. Chem. Soc.*, 1935, **57**, 2656; (b) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 1935, 286; A. Ledwith and D. Parry, *J. Chem. Soc. (B)*, 1967, 41.

⁶ W. L. Mock, *J. Amer. Chem. Soc.*, 1967, **89**, 1281.

⁷ H. Staudinger and F. Pfenninger, *Ber.*, 1916, **49**, 1941; G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, 1957, **90**, 2106; G. Hesse and S. Majmudar, *ibid.*, 1960, **93**, 1129; L. V. Vargha and E. Kovacs, *ibid.*, 1942, **75**, 794; N. P. Neureiter, *J. Amer. Chem. Soc.*, 1966, **88**, 558.

⁸ Many close analogies for this [3,3] sigmatropic shift exist: E. Vogel, *Angew. Chem. Internat. Edn.*, 1962, **1**, 53; 1963, **2**, 1; E. L. Stogryn, M. H. Gianni, and A. J. Passanante, *J. Org. Chem.*, 1964, **29**, 1275; R. A. Braun, *ibid.*, 1963, **28**, 1383 (1963); E. L. Stogryn and S. J. Brois, *ibid.*, **30**, 88 (1965).

⁹ G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem.*, 1965, **77**, 774; *Angew. Chem. internat. Edn.*, 1965, **4**, 752.

¹⁰ D. Y. Curtin and S. M. Gerber, *J. Amer. Chem. Soc.*, 1952, **74**, 4052.

¹¹ G. Opitz and H. Fischer, *Angew. Chem.*, 1965, **77**, 41; *Angew. Chem. Intern. Edn.*, 1965, **4**, 70.

¹² H. Böhme and B. Haack, *Chem. Ber.*, 1968, **101**, 2971.

¹³ E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, 1964, **76**, 432; *Angew. Chem. Intern. Edn. Engl.*, 1964, **3**, 443.