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PHOTOLYSIS OF UNSATURATED CYCLIC SULPHONES

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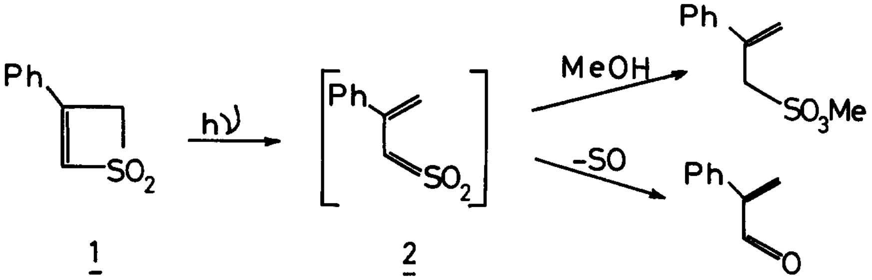
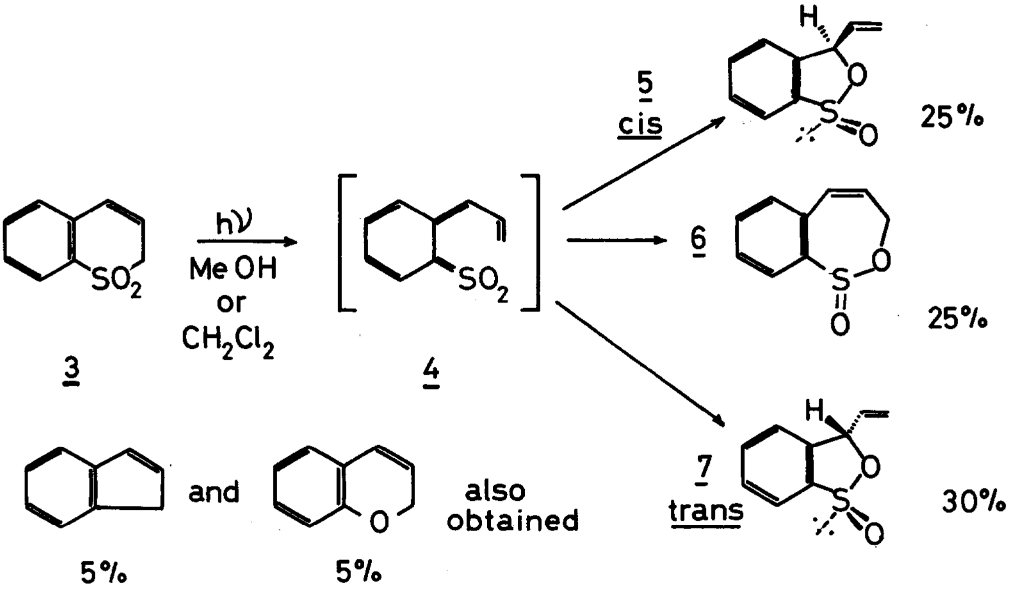
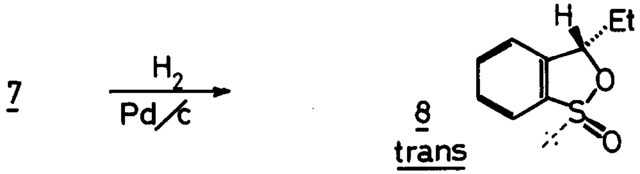
The generation of sulphene intermediates has attracted considerable attention over the last few years.[1] Such intermediates have been suggested in the thermolytic[2] and photolytic[3,4] fragmentation of cyclic sulphones. Trapping experiments indicate[3] that vinyl sulphenes (2) are involved in the photolysis of thiete sulphone derivatives, e.g. (1). In the absence of methanol, loss of sulphur monoxide occurs.



Photolysis of 2H-1-benzothiopyran-1,1-dioxide[5] (3) in dichloromethane or methanol with light of 254 nm wavelength gave a mixture of cyclic sulphinate esters (sultines).

Indene, 2H-1-benzopyran, and the cis sultine (5)[6] b.p. 122°/0.1 mm, τ(100 MHz, C_6D_6), 2.72 - 3.30 (4H, m), 3.89 (1H, d *J* 7.3 Hz), 4.54 (1H, ddd, *J* 16.6, 9.3 and 7.3 Hz), 4.90 (1H, dd, *J* 16.6 and 1.9 Hz), and 5.00 (1H, dd, *J* 9.3 and 1.9 Hz)[7], ν_{max}($CHCl_3$) 1600, 1435 (broad), and 1130 (s) cm^{-1}, were obtained pure by chromatography on silica.[8] The remaining mixture of (6) and (7) defied direct separation, but hydrogenation of the mixture using a 10% palladium-charcoal catalyst followed by chromatography on silica[8] gave (6) as an oil τ ($CDCl_3$) 2.20-2.90 (4H, m), 3.53 (1H, broad d, *J* 12 Hz), 4.10 (1H, dt, *J* 12 and 3 Hz), and 5.13(2H, t, *J* 3 Hz), ν_{max}($CHCl_3$) 1148 (s), 1120, and 1045 cm^{-1}, and the trans ethyl-substituted sultine (8), τ($CDCl_3$) 2.00-2.30 (1H, m), 2.45-2.83 (3H, m), 5.77-6.50 (1H, m), 7.98-8.43 (2H, m), and 8.45 (3H, t, *J* 7 Hz), ν_{max}($CHCl_3$) 1467, 1440, 1262, 1122 (s), and 1008 cm^{-1}.

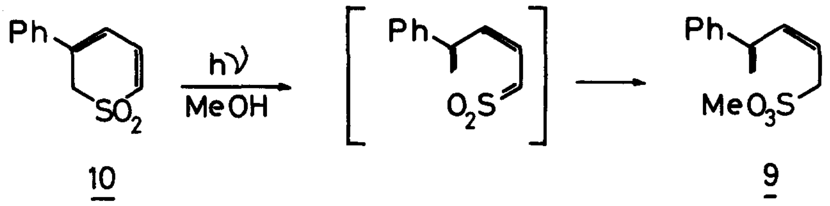




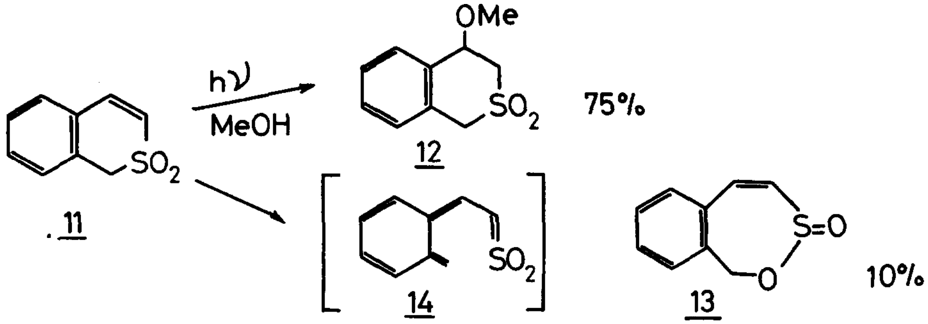
The assignment of stereochemistry of the 5-membered sultines is based upon the relative chemical shifts of the methine protons in each molecule.[9]

Although the photolysis was followed to completion by GLC small amounts of starting material (∿ 10%) were always obtained on chromatography of the products.

Preliminary quenching experiments and emission spectroscopy indicates that the reaction is occurring from both the singlet and triplet states. It is important to note that the sulphene (4) is not trapped when the irradiation is carried out in methanol. We also have not been able to intercept any intermediates with reactive dienophiles. This may be because a sulphene is not involved in the reaction or that the sulphene, once formed, rapidly cyclises back to aromaticity. We prefer the latter explanation because King and Lewars have shown[10] that a sulphonate ester (9) is obtained from photolysis in methanol of the sulphone (10). In this case the intermediate sulphene obviously has a longer lifetime.



Photolysis of 1H-2-benzothiopyran-2,2-dioxide[5] (11) in methanol at 254 nm did produce an addition product. The major product obtained is 4-methoxy-isothiochroman-2,2-dioxide (12), b.p. 145°/0.005 mm, τ(C_6D_6) 7.16 (3H, s), 7.00 (1H, ddd, *J*, 14, 5 and 1.2 Hz), 6.67 (1H, dd, *J* 14 and 5 Hz), 6.27 (1H, d, *J* 15 Hz), 5.93 (1H, t, *J* 5 Hz), 5.56 (1H, d, *J* 15 Hz), and 3.18 - 2.48 (4H, m), ν_{max}(CH_2Cl_2) 1314 (s), 1200, 1144, 1119 (s), and 1086 (s) cm^{-1}, which is formally derived from ionic addition of methanol to the double bond.[11] This material is identical with that obtained by methylation of 4-hydroxy-isothiochroman-2,2-dioxide. The n.m.r. spectrum indicates that there is a small coupling (1.2 Hz) between one pair of 1,3 hydrogens in a W-conformation, through the sulphone group.[12]



The sultine (13) may be derived from the conjugated sulphene (14) by ring closure on oxygen.

The minor products indene and 2H-1-benzopyran obtained from the photolysis of (3) have also been obtained in larger amounts from flash thermolysis of this compound.[13] It is probable that the benzopyran at least is derived from a sultine precursor whereas indene may be formed by a more direct extrusion of sulphur dioxide. Further studies of the photolysis and thermolysis of sultines are in progress.

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References and Footnotes

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7. The spectrum was analysed using INDOR spectroscopy.
8. Column chromatography separations were carried out on Kieselgel 60 PF_{254}, supplied by E. Merck for layer chromatography, using a slight positive pressure.
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11. This reaction may occur by photoprotonation of the double bond. See P.J. Kropp, Photochemistry of Alkenes in Solution, in Photochemistry **3**, p. 585, International Symposium St. Moritz, 1970, Butterworth and Co., London, for a discussion of similar reactions.
12. Similar coupling has been noted elsewhere. L.A. Paquette and R.W. Begland, *J. Org. Chem.*, 1969, **34**, 2896.
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