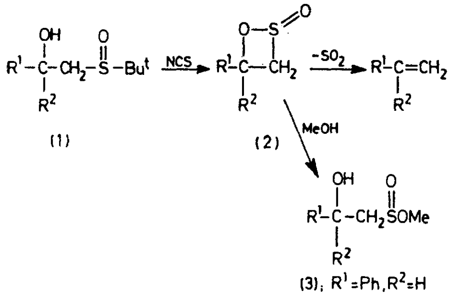
Isolation and Characterization of a Stable 1,2-Oxathietan 2-Oxide (β-Sultine)

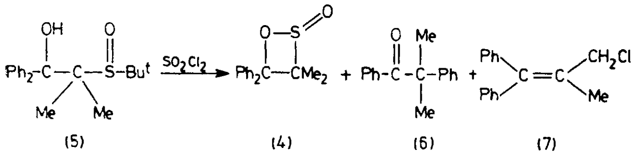
By Tony Durst* and Boris P. Gimbarzevsky

(*Department of Chemistry, University of Ottawa, Ottawa, Canada* K1N 6N5)

Summary Crystalline 3,3-dimethyl-2,2-diphenyl-1,2-oxathietan 2-oxide (**4**) has been obtained from the reaction of the *β*-hydroxy sulphoxide (**5**) with *N*-chlorosuccinimide or SO_2Cl_2; the sultine (**4**) is stable at room temperature for several days but decomposes quantitatively into 1,1-diphenyl-2,2-dimethylethylene and SO_2 when warmed to 30 °C in CH_2Cl_2, the half-life for the decomposition being 24 h.

We recently reported that *β*-hydroxyalkyl t-butyl sulphoxides (**1**) react with *N*-chlorosuccinimide (NCS) or SO_2Cl_2 to give olefins and SO_2 *via* thermally unstable 1,2-oxathietan 2-oxides (*β*-sultines) (**2**)[1] although we were unable to isolate and characterize the intermediate *β*-sultines. In one case (**2**; R^1 = Ph, R^2 = H), we were able to obtain an n.m.r. spectrum which was in agreement with the sultine structure. It was also possible to intercept the same sultine prior to its decomposition into styrene with methanol, to give the sulphinate ester (**3**).[1]





We have now isolated the crystalline β-sultine (**4**), which is thermally remarkably stable compared to the sultines (**2**; R^1 and/or R^2 = alkyl or aryl). Thus, reaction of (**5**), obtained (66%) from the condensation of the lithio salt of isopropyl t-butyl sulphoxide with benzophenone, with NCS in CH_2Cl_2 at room temperature or with SO_2Cl_2 at -70 °C for 30 min, afforded (**4**) (*ca.* 45% isolated, 60% from n.m.r. spectroscopy). In addition, two other products, the ketone (**6**) and the chloro-olefin (**7**) were obtained (*ca.* 15% each).†

The β-sultine (**4**), m.p. 97—99 °C (decomp.), showed a strong i.r. absorption at 1150 cm^{-1} (*cf.* 1100—1120 cm^{-1} for γ- and δ-sultines[2,3]). The n.m.r. spectrum ($CDCl_3$) showed two methyl singlets at δ 1·43 and 1·30 in addition to the aromatic absorption around δ 7·4.

The sultine (**4**) when warmed in CH_2Cl_2, $CDCl_3$, or CD_3NO_2 to 30 °C, decomposed quantitatively into 1,1-diphenyl-2,2-dimethylethylene and SO_2, the half-life being 24, 24, and 21 h respectively in the three solvents. The relative insensitivity of the rate of decomposition of (**4**) to large changes in the dielectric constant of the solvent is in agreement with a non-polar transition state. The observation that (**4**) is significantly more stable than (**2**; R^1 = Ph, R^2 = H) argues against the formation of a biradical intermediate, obtained by homolytic scission of the C–O bond, in the rate determining step of the SO_2 extrusion. At this point, we feel that the SO_2 extrusion from β-sultines is a concerted process similar to the CO_2 loss from β-lactones.[4] The SO_2 loss from β-sultines has been shown to be a stereospecific *cis* elimination.[1]

We suggest that the stability of (**4**) relative to the other sultines, *e.g.* (**2**; R^1 = Ph, R^2 = H), is due to an increase in adverse steric interactions in going from the ground state of (**4**) to the transition state for decomposition. The conformation of (**5**) is probably non-planar‡ with the substituents on C(3) and C(4) as far apart as possible. During the olefin formation, the C–C bond is shortened considerably and the substituents at C(3) and C(4) would tend to move into the same plane, thereby considerably increasing the steric interactions and raising the transition state energy.

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† The ketone (**6**) had n.m.r. peaks at δ 1·55 (s, 6H) and 7·3 (m, 10H), and an i.r. band at 1675 cm^{-1}. The chloride (**7**) is unstable and has been only tentatively identified based on its n.m.r. spectrum, δ 1·91 (s, 3H), 4·13 (s, 2H), and 7·0 (s, 10H); and a positive halogen test.

‡ X-Ray structure determinations of 4-membered ring sulphoxides (G. L. Hardgrove, Jr., J. S. Bracholdt, and M. M. Lien, *J. Org. Chem.*, 1974, **39**, 246; J. H. Barlow, C. R. Hall, D. R. Russell, and D. J. H. Smith, *J.C.S. Chem Comm.*, 1975, **133**; S. Allemark, *Arkiv. Kemi*, 1967, **26**, 73) and sulphones (M. L. Ziegler, J. Weiss, H. Schildknecht, N. Grund, and H.-E. Sasse, *Annalen*, 1973, 1702) indicate considerable ring puckering.

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