Synthesis of a Stable Cyclic Sulphenate by Thermal Decomposition of a Chlorosulphurane in the Crystalline State

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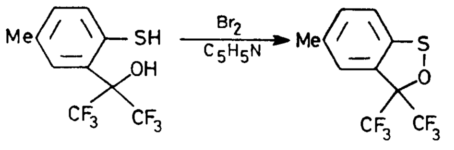
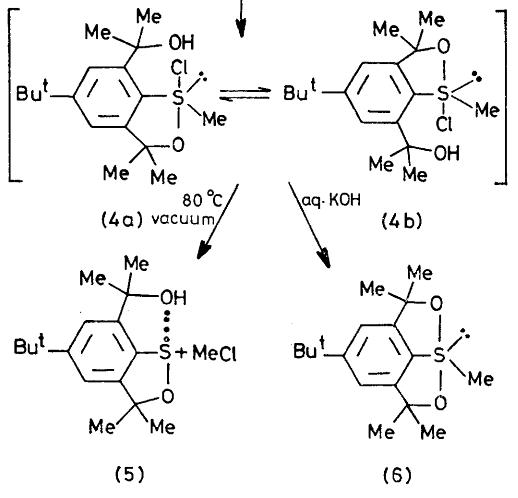
Summary The ready thermal decomposition of crystalline chlorosulphurane (**4**) gives a stable γ-sultene, (**5**), and methyl chloride as the only products.

Cyclic sulphenates, sultenes, have been postulated as reactive intermediates.[1] Recently Astrologes and Martin[2] reported the first isolation of a sultene, (**2**), from the reaction of (**1**) with bromine and pyridine. Compound (**2**) is thermally stable at room temperature but reacts rapidly with water or moist air to give products from disproportionation of the sulphenic acid.



(1) (2)

We here report the synthesis of the first simple alkyl sultene, (**5**), a compound both thermally and hydrolytically stable. The chlorosulphurane (**4**)† was prepared in 75% yield by oxidation of the sulphide diol (**3**) with 1 equiv. of t-butyl hypochlorite. Compound (**4**) is a stable white solid, m.p. 117—119 °C (decomp.) [δ (CDCl$_3$, 220 MHz) 9·03 br (1H, s, OH), 7·44 (1H, d, *J* 1·6 Hz, ArH), 7·35 (1H, d, *J* 1·6 Hz, ArH), 3·65 (3H, s, SMe), 1·91, 1·83, 1·80, and 1·77 (each 3H, s, OCMe), and 1·41 (9H, s, $\mathrm{Bu^t}$)]. The covalent nature of the S–Cl bond is established by comparison of the *S*-methyl shift with those of other model systems.[3,4]



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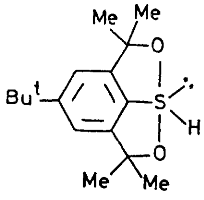
† All compounds gave satisfactory elemental analyses.

Equilibration between (**4a**) and (**4b**) in the presence of D_2O or C_5D_5N is fast on the n.m.r. time scale as evidenced by the coalescence of the aromatic AB pattern to a singlet and the four *gem*-dimethyl singlets to two peaks. Elimination of hydrogen chloride from (**4**) to form the bicyclic alkylaryldialkoxysulphurane (**6**) can be achieved by washing with aq. KOH.‡

Heating a sample of (**4**) at 80 °C (40 °C below its m.p.) *in vacuo* for one day gave a mixture of (**4**) and (**5**) in a ratio of 2 : 3. The volatile material, condensed into a liquid nitrogen trap, was identified as methyl chloride by n.m.r. spectroscopy. The sultene (**5**) was obtained from the mixture by extracting it with pentane from insoluble (**4**). Crystallisation from the pentane filtrate gave (**5**) as a white crystalline solid, m.p. 125·5—127 °C [δ (CCl_4) 6·87 (1H, d, *J* 1·6 Hz, ArH), 6·71 (1H, d, *J* 1·6 Hz, ArH), 1·74 br (1H, s, OH),§ 1·52 (6H, s, OCMe), 1·49 (6H, s, OCMe), and 1·29 (9H, s, Bu^t)].

The sultene (**5**), unlike (**2**), is stable indefinitely towards water at room temperature. The surprising stability of (**5**) may reflect some hypervalent[5] bonding interaction between a lone pair of electrons of the hydroxy oxygen and the sulphur atom. The dotted line drawn in structure (**5**) to reflect this S–O bonding is, at the moment, justified solely on the basis of this observed lack of reactivity of (**5**).



(7)

The non-equivalence of the aromatic protons rules out structures, such as (**7**), with two equivalent S–O bonds.[6]

We thank the National Science Foundation for support and Abbott Laboratories, the Uniroyal Company, and the University of Illinois for fellowships (to P.H.W.L.).

(*Received*, 2*nd May* 1977; *Com.* 420.)

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‡ The synthesis of the sulphide diol (**3**), and the chemical properties of (**6**) and the corresponding sulphurane oxide are reported elsewhere (P. H. W. Lau and J. C. Martin, *J. Amer. Chem. Soc.*, 1977, in the press).

§ The chemical shift of the peak assigned to the O–H proton varies with concentration (δ 1·74 is the smallest observed value). This peak disappears upon addition of D_2O, with no observable changes in the remaining peaks of the spectrum.

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[6] M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *Bull. Soc. chim. France*, 1968, 773, describe an analogous spirophosphorane containing a P-H bond.