

SYNTHESIS OF CYCLIC SULFINATE ESTERS (SULTINES) VIA
t-BUTYL HYDROXYALKYL SULFOXIDES

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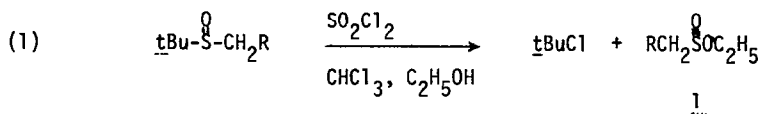
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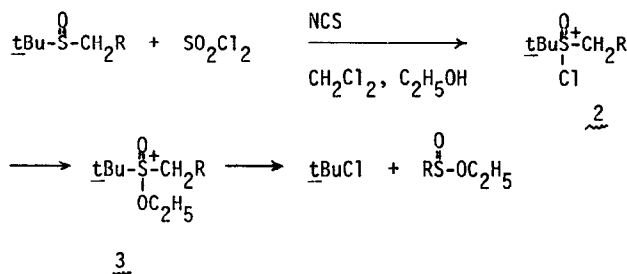
Relatively few examples of cyclic sulfinate esters (sultines) have been described in the literature¹ and the methods used to prepare these compounds are not applicable to the synthesis of sultines of different ring size bearing a variety of substituents. In this communication we would like to report a general synthesis of sultines which does allow for variations in ring size and substitution pattern.

We have recently reported that t-butyl alkyl sulfoxides undergo carbon-sulfur bond cleavage upon treatment with N-bromo- or N-chlorosuccinimide or SO₂Cl₂ in CHCl₃-C₂H₅OH to give t-butyl chloride and ethyl esters of sulfinic acids^{2,3}.

The mechanism of the cleavage reaction has been discussed²

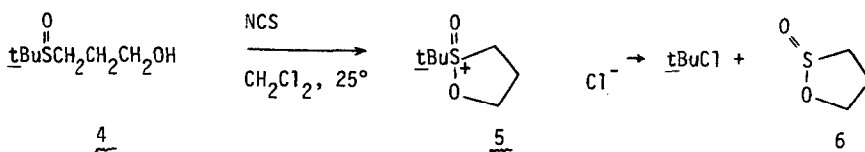


and evidence has been presented to show that chloro-oxosulfonium ions 2 and probably alkoxyoxosulfonium ions 3 are involved. Scheme 1.



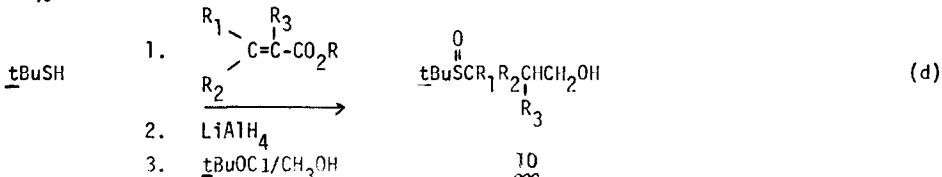
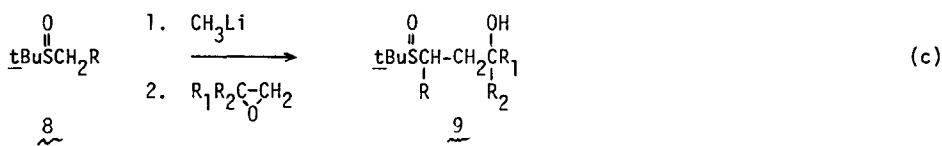
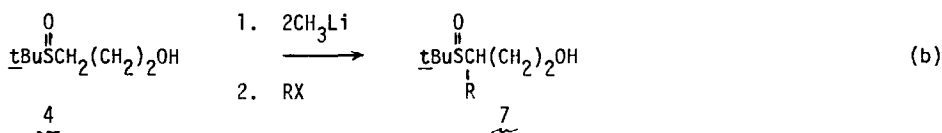
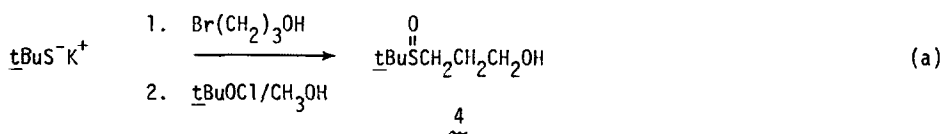
Scheme 1

Reaction of a variety of t-butyl- γ -hydroxysulfoxides with NCS or SO₂Cl₂ in CH₂Cl₂ led, in generally good to excellent yields, to γ sultines (1,2-oxathiolane-2-oxides). Again, initial formation of a chloro-oxosulfonium salt, followed by cyclization to a cyclic alkoxyoxosulfonium salt 5⁴ and subsequent fragmentation of the t-butyl carbon-sulfur bond would account for the product formation. Scheme 2.



Scheme 2

A variety of *t*-butyl γ -hydroxysulfoxides are readily prepared by a number of general routes outlined in equations a-d. The combined sequence involving the preparation of the γ -hydroxysulfoxides and the cleavage reactions allows the preparation of γ -sultines having a variety of substituents at specific positions in the heterocyclic ring. Table 1.



To illustrate the versatility of the method we have synthesized the three possible mono-methylated isomers 11, 12 and 13 by combining equations b, d and c with the cleavage reaction respectively. Thus reaction of 4 with 2 equivalents of CH_3Li , followed by alkylation with CH_3I gave 7⁵ ($\text{R} = \text{CH}_3$) in 82% isolated yield. The latter compound on treatment with NCS in CH_2Cl_2 afforded 3-methyl-1,2-oxathiolane 2-oxide (11) in 72% yield. The 5-methyl isomer 13 was prepared by reaction of the lithio derivative of 8 ($\text{R} = \text{H}$) with propylene oxide (88%) followed by cyclization (70%)⁶. Finally, the 4-methyl isomer 12 was obtained in 75% yield from 10 ($\text{R}_1 = \text{R}_2 = \text{H}$, $\text{R}_3 = \text{CH}_3$), which in turn had been prepared by Michael addition of *t*-butylmercap-

tan to α -methylmethacrylate followed by LiAlH_4 reduction and *t*-butylhypochlorite oxidation⁷. In each case the sultines were obtained as diastereomeric mixtures. Their n.m.r. spectra were rather complex as expected but in general agreement with the gross structures. The $S = 0$ stretching frequencies in the infrared occurred at $\sim 1100 - 1120 \text{ cm}^{-1}$. The isomers were further characterized by oxidation with MCPBA to the known sultones⁸.

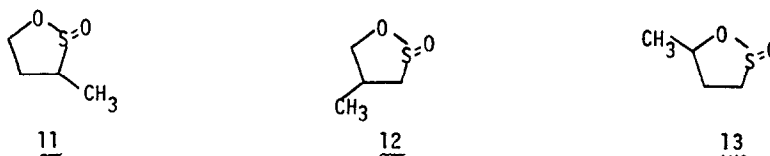
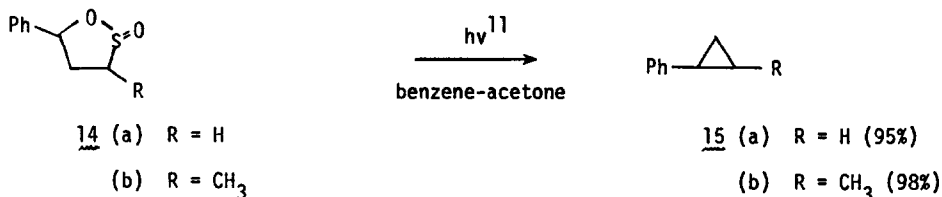


Table 1. Synthesis of 1,2-Oxathiolane-2-oxides (γ -Sultines)

Method of Preparation of Hydroxysulfoxide	Substituents				Yield of Sultine (%)
	R	R ₁	R ₂	R ₃	
a	H	H	H	H	83
b	CH ₃	H	H	H	75
c	H	H	CH ₃	H	70
c	H	H	Ph	H	96
c	CH ₃	H	CH ₃	H	98
c	CH ₃	H	Ph	H	90
d	H	H	H	CH ₃	72

The method described for the synthesis of the γ -sultines is also applicable to the synthesis of larger ring homologs⁹. A route analogous to equation (a) followed by NCS treatment of the appropriate hydroxysulfoxides allowed the preparation of the 6,7 and 8 membered ring sultines in 75, 58 and 53% yield respectively. The preparation of other substituted members of these sultines thus depends only on the availability of the appropriate *t*-butyl hydroxyalkyl sulfoxides.

In preliminary experiments we have found that several γ -sultines are photochemically labile. Of particular interest is the photochemical transformation of sultines such as 14 into cyclopropanes and SO_2 ¹⁰. Further studies on the photochemistry of sultines are in progress.



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2. F. Jung and T. Durst, Chem. Commun., 4 (1973).
3. F. Jung, N.K. Sharma and T. Durst, J. Amer. Chem. Soc., 95, in press.
4. T. Durst and K.C. Tin, Can. J. Chem., 49, 2374 (1971).
5. All new compounds were adequately characterized by their spectroscopic properties and for analytic data.
6. The reactions of lithio sulfoxides derived from 8 with epoxides gave γ -hydroxy sulfoxides in greater than 85% yield.
7. Carl R. Johnson and David McCants, Jr., J. Amer. Chem. Soc., 37, 1109 (1965).
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9. The attempted synthesis of β -sultines has also been studied. These compounds are thermally unstable and decompose to olefins and SO_2 (ref. 3).
10. The corresponding γ -lactones show qualitatively similar photochemical behavior. R.S. Givens and W.F. Oettle, J. Org. Chem., 36, 4325 (1972).
11. The irradiation was carried out using a 450 watt Hanovia Hg lamp.