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Ring–Chain Tautomerism of the 1,4-Oxathiane *S,S*-Dioxide Anion†

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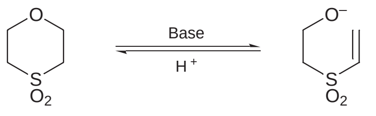
The ring-chain tautomer of the α-sulfonyl anion of 1,4-oxathiane *S,S*-dioxide can be trapped by addition of alkoxides to the vinyl sulfone; the scope of this reaction is explored.

As part of our research into the chemistry of the 1,4-oxathiane *S,S*-dioxide system,[1] we investigated the alkylation of the α-sulfonyl anion as a route to 3-substituted systems. There are some reports of the chemistry of such anions in the literature: for example, the 3-position has been shown to undergo base mediated proton–deuterium exchange in the presence of D_2O,[2] while the halogenation of a more substituted system, as part of a Ramberg–Bäcklund reaction, has also been reported.[3]

We were surprised to find that the anion of 1,4-oxathiane *S,S*-dioxide (generated, *inter alia*, by treatment with Bu^nLi) proved both unreactive (to, for example, alkylation by benzyl bromide) and relatively unstable. This behaviour was more consistent with the incipient α-sulfonyl anion undergoing a ring-fragmentation process to form the labile vinyl sulfone **1**, bearing a relatively unreactive alkoxide moiety, followed by ring closure when a proton source is introduced (Scheme 1). Such behaviour is analogous to that reported of 1,4-oxathiane which, under similar conditions, forms the vinyl sulfide **2**, the oxyanion of which was reported as not reacting with iodomethane, however, in this case reclosure of the ring does not occur (Scheme 2).[4]



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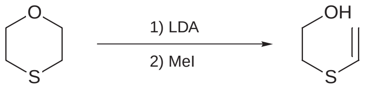
Scheme 1



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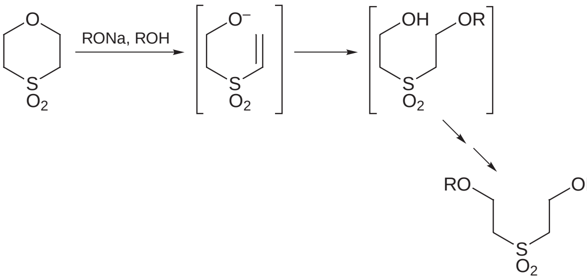
Scheme 2

To test this hypothesis we attempted to trap the ring-opened isomer **1** by a Michael addition reaction. Treatment of 1,4-oxathiane *S,S*-dioxide with diethyl malonate in the presence of sodium ethoxide did not give the anticipated malonate addition product but, more prosaically, yielded the diether **3** (Scheme 3, R = Et). We quickly established that the same product was formed in the absence of malonate. This product is consistent with our proposed ring–chain tautomerism of the oxathiane α-sulfonyl anion giving the vinyl sulfone which is then trapped by ethoxide. A second elimination–addition sequence then takes place and it is interesting to note that we never observed any of the intermediates along the reaction pathway.



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Scheme 3

In addition to supporting our mechanistic idea, this reaction also provided an attractive route to symmetrical, sulfonyl containing diethers and so we decided to explore the scope of this method (Scheme 3 and Table 1). Generally, the reaction proceeded in moderate to good yields with a range of simple alcohols (entries 1–5, 8) although once steric bulk was introduced (entries 7, 9) only decomposition of starting material was observed. Ethylene glycol (entry 6) gave only a gross mixture of polymeric products, even when the reaction temperature was mediated by the addition of THF as a co-solvent.

In summary, we have shown that the ring-chain tautomer of the anion of 1,4-oxathiane *S,S*-dioxide can be trapped by a range of alcohols to give an range of sulfonyl containing ethers which may prove of interest, for example, as chelating agents.

Table 1 Preparation of di-2-alkoxyethylsulfones

Entry	Alcohol (ROH)	Yield of **3**(%)[a]
1	Methanol	89
2	Ethanol	40
3	Butan-1-ol	69
4	Pentan-1-ol	61
5	2-Methoxyethanol	66
6	Ethane-1,2-diol	0[b]
7	2,2-Dimethylpropanol	0[b]
8	Propan-2-ol	57
9	1,1-Dimethylethanol	0[b]

[a]All yields are unoptimized. [b]No recovered starting material was isolated.

Experimental

^1H and ^{13}C NMR spectra were obtained on a Bruker Aspect 3000 spectrometer (at 250 and 63 MHz respectively). Mass spectra were recorded on a Kratos Profile 4V3 spectrometer.

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Di-2-(1′-*methylethoxy*)*ethylsulfone*.—Sodium hydride (0.80 g of 60% dispersion in mineral oil, 0.02 mol) was washed with dry diethyl ether then cooled to 0 °C under nitrogen. Isopropyl alcohol (35 cm^3) was added with great care then, once reaction was complete, 1,4-oxathiane *S,S*-dioxide (0.681 g, 0.005 mol) was added and the mixture brought to reflux for three days. Saturated aqueous ammonium chloride (20 cm^3) was added and the mixture extracted with dichloromethane. Column chromatography on silica gel eluting with dichloromethane–ethyl acetate (3 : 1) gave the title compound as a pale yellow oil (0.68 g, 57%); δ_H ($CDCl_3$) 3.85 (4H, t, *J* 5.7), 3.65 (2H, septet, *J* 6.2), 3.33 (4H, t, *J* 5.7), 1.17 (12H, d, *J* 6.2); δ_C 72.3 (CH), 61.6 (CH_2), 55.2 (CH_2), 21.9 (CH_3); *m/z* 239 $[M + H]^+$

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