

# FAB-Induced Deprotonation, Elimination and Decomposition of 1,3-Dithiolane S-Oxides.

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The gas-phase unimolecular decomposition of  $[M-H]^-$  of 1,3-dithiolane S-oxides has been studied using Fast Atom Bombardment (FAB) for anion generation. A comparison with the reactivity in solution is made and some differences or similarities with the chemistry in the gas-phase are discussed. The decomposition pathways of the molecules under investigation are function of the substituents.

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## Introduction.

One of the most studied aspects of the condensed-phase chemistry of 1,3-dithiolanes is the ease that they undergo a variety of reactions, upon treatment with strong bases, such as deprotonation, cycloreversion and elimination, depending on the experimental conditions adopted [1].

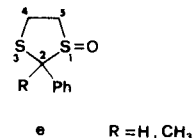
The general mechanism proposed for these reactions is reported in Scheme 1:

These are deprotonation at C-2 carbon followed by cycloelimination to give the dithiocarboxylate anion and ethylene (Equation 1), or attack by the base at C-4 and subsequent fragmentation to the corresponding thiocarbonyl compound **c**, which may undergo reduction, S-addition, C-addition or double addition by further reaction with base (Equation 2) [1]. As an example the reaction of 4,4,5,5-tetraphenyl-1,3-dithiolane with base gives the corresponding alkene [2,3] while 2-hexyl-1,3-dithiolane decomposes to the corresponding thiocarbonyl compound [3]. In other words the selection of pathways 1 and/or 2 is dependent either on the reaction conditions or on the stability of the products.

The gas-phase negative ion-molecule chemistry of

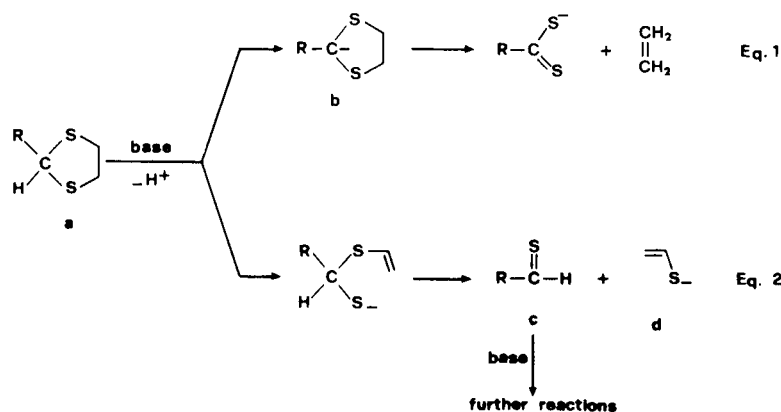
1,3-dithiolanes **a**, as obtained by ICR experiments, is slightly different from that in solution [4]. For example no deprotonation products **b** are observed, because cycloreversion to  $RCS_2^-$  and ethylene occurs. This competes with the second pathway of Scheme 1 (Equation 2), and the thioacetaldehyde anion **d** is often the major product observed [4].

Recently we have reported data on the electron impact mass spectrometric behaviour of 1,3-dithiolane S-oxides **e** proving, whenever possible, the occurrence of some decomposition pathways with the aid of B/E and MIKE scans, collisional spectroscopy and labelling experiments [5].



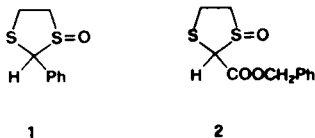
The aim of the present investigation is to examine the same compounds, 1,3-dithiolane S-oxides, in order to determine if oxidation at sulfur affected either the regioselectivity of deprotonation or the stability of the resulting carbanion toward fragmentation.

Scheme 1



## Results and Discussion.

Two model substrates were chosen for this study. These are **1** and **2** below. In particular compound **2** bears a typical electron-withdrawing group such as  $-\text{COOCH}_2\text{Ph}$ , that should be able, in principle, to better stabilize, by resonance, the hydrogen abstraction at C-2.



The negative FAB spectra of **1** and **2** are reported in Table 1. Unexpectedly the peaks corresponding to deprotonation products are quite small (entry 1). Their presence, however, is to emphasize. As already pointed out in the introduction, the ICR data on 1,3-dithiolanes never show this anionic species [4]. Their observation, in the present investigation, may be due mainly to two different reasons: i) the sulfoxide moiety better stabilizes the anion formed, ii) the narrower time-window ( $10^{-7}$  present case *vs*  $10^{-3}$  ICR) allows the detection of such short lived anions. In order to establish the operativity of point i) and/or ii) we undertook the study of the FAB mass spectrometric behaviour of **3**. As shown in Table 2, **3** also exhibits an abundant  $[\text{M-H}]^-$  species, proving the lack of influence of the oxidation of the sulfur atom on  $[\text{M-H}]^-$  production. Hence we are forced to propose point ii) as the responsible  $[\text{M-H}]^-$  detection. Once more mass spectrometry proves its validity in the structure characterization of elusive moieties [7].



Loss of ethylene is present for compounds **1** and **2** as well as for **3**. This process could occur either in the con-

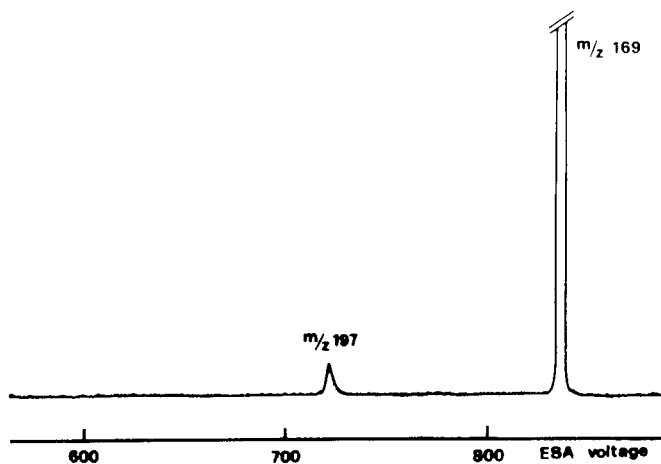
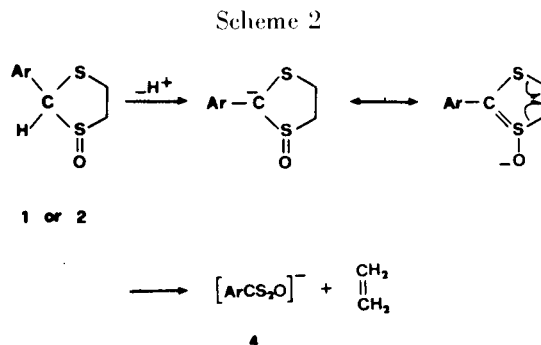


Figure 1.  $\text{B}^2/\text{E}$  linked scan spectrum of  $m/z$  169 ion originating from  $[\text{M-H}]^-$  of compound **1**.

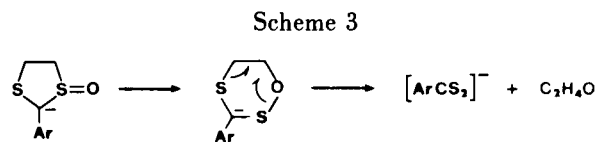
densed phase *i.e.* in the matrix, or in the gas-phase through unimolecular decomposition of  $[\text{M-H}]^-$ . The  $\text{B}^2/\text{E}$  spectrum of the ion  $[(\text{M-H})-\text{C}_2\text{H}_4]^-$ ,  $m/z$  169 for **1**, shown in Figure 1, proves unequivocally that the only precursor of this species is the corresponding deprotonated molecular ion. Hence the occurrence of a gas-phase unimolecular ethylene loss is proven, also the presence of an analogous decomposition pathway in the matrix can not be excluded. For the unimolecular loss of ethylene a mechanistic pathway similar to that shown in Scheme 1, Equation 1 may be proposed:



Ion **4** can be structured in different ways. Its  $\text{B}/\text{E}$  spectrum shows only one decomposition leading to a ionic species at  $m/z$  137, for **1**, reasonably due to loss of the sulfur atom. Its MIKE spectrum is evidence for the same ionic species. A kinetic release of 115 meV is associated with the process. In addition to this, ionic species at  $m/z$  64, corresponding to  $\text{S}_2$  moiety is present in the MIKE spectrum. These data are in agreement with the formation of C-O and S-S bonds, which forced us to propose a four-membered ring species for **4** [5].

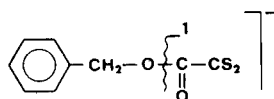
Comparing the two compounds under examination, the loss of ethylene is much more important for **1** than for **2** (100% *vs* 6%). This result is consistent with data in solution referring to 1,3-dithiolanes having typical electron withdrawing groups, such as carbonyl or cyano, bounded at C-2 carbon [3]. Also in solution, it is a fact that the anionic species **b** which was formed is shown in Scheme 1 and is stable toward cycloreversion.

Loss of  $\text{C}_2\text{H}_4\text{O}$  is preeminent in both cases and gives rise to the most abundant ion for **2**. It may be related to a rearrangement of the molecule to a six-membered oxygen-containing ring typical of sulfoxides [8] followed by decomposition, as proposed in Scheme 3:



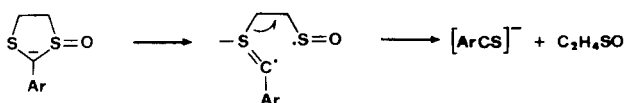
The presence of the same decomposition process for **1** rules out the possibility of a concurrent loss of  $\text{CO}_2$  from **2**. The product ion  $[\text{ArCS}_2]^-$  so formed shows, in the case of

compound **2** MIKE spectrum evidencing the losses of CO and C<sub>2</sub>OS<sub>2</sub>, corresponding to the cleavage as indicated at point 1 shown below:

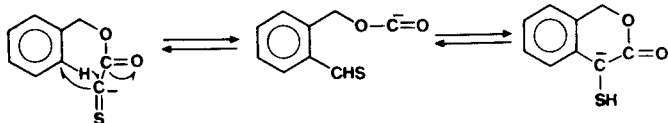


Compounds **1** and **2** both expel C<sub>2</sub>H<sub>4</sub>SO from their molecular ions. This decomposition is in agreement with the preferential cleavage of the carbon-sulfoxide bond, as already observed in the positive ion EI mass spectrometry of the same compounds. For this loss the mechanism described in Scheme 4 may be proposed:

Scheme 4



While the [ArCS]<sup>-</sup> moiety, for **1**, further decomposes through [CS] loss, for compound **2** concurrent losses of [CS] and [CO] suggest the presence of a ionic species differently structured, originated through a [CS] transfer in the *ortho*-position of the benzene ring [9]:



All the decompositions discussed up to now are related to the removal of the hydrogen from the C-2 carbon. There are at least two other possibilities:

Scheme 5

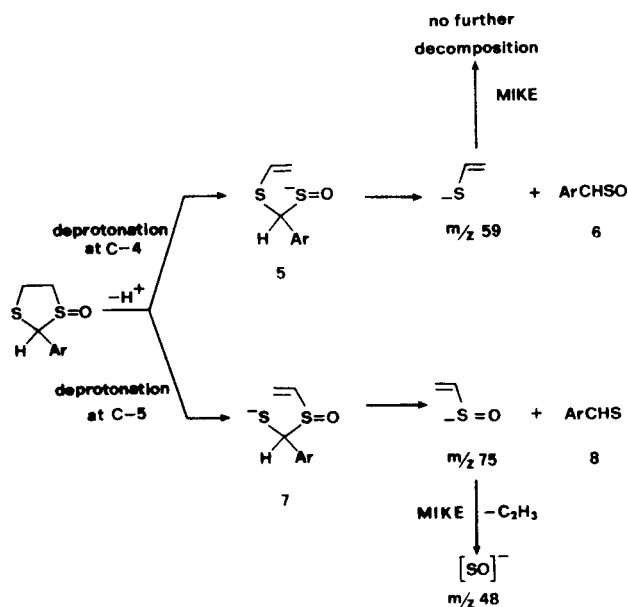


Table 1

Negative Fast Atom Bombardment Spectra of **1** and **2** in a Glycerol Matrix [a]

	entry	m/z	%	m/z	%
[M-H] <sup>-</sup>	1	197	10	255	1
[(M-H)-C <sub>2</sub> H <sub>4</sub> ] <sup>-</sup>	2	169	100	227	6
[(M-H)-C <sub>2</sub> H <sub>4</sub> O] <sup>-</sup>	3	153	75	221	100
[(M-H)-C <sub>2</sub> H <sub>4</sub> SO] <sup>-</sup>	4	121	19	179	4
[(M-H)-ArCHS] <sup>-</sup> [b]	5	75	65	75	2
[(M-H)-ArCHSO] <sup>-</sup> [b]	6	59	37 [c]	59	- [c]

[a] The data % refer to an average of three scans. [b] Ar=Ph or COOCH<sub>2</sub>Ph. [c] Contribution of glycerol decomposition has been subtracted from the overall peak.

Table 2

Negative Fast Atom Bombardment Spectrum of **3** in a Glycerol Matrix [a]

	m/z	%
[M-H] <sup>-</sup>	181	20
[(M-H)-C <sub>2</sub> H <sub>4</sub> ] <sup>-</sup>	153	100
[(M-H)-PhCHS] <sup>-</sup>	59	90 [b]

[a] The data % refer to an average of three scans. [b] Contribution of glycerol decomposition has been subtracted from the overall peak.

From data of Table 1 (entries 5 and 6) deprotonation at C-5 is favoured and this should be mainly related to the intrinsic thermodynamic stability of the neutral species expelled. In fact the less stable anion (m/z 75) is formed, but the more stable neutral **8** is lost. It is noteworthy that also in this case for the ion at m/z 75 a preferential cleavage of the C-S(O) bond is observed.

In summary, the decomposition pathways of the anions under investigation are dominated by the nature of the substituents that is reflected, in turn, on the stability of the anion formed and, consequently, on the deprotonation site. The data of Table 1 show that when Ar=Ph deprotonation and elimination are present in a 2:1 ratio (entries 2 + 3 + 4 vs 5 + 6) whereas in the presence of an electron-withdrawing group, deprotonation at C-2 carbon, and related decompositions, are the only reactions observed.

## EXPERIMENTAL

1,3-Dithiolane S-oxides are easily synthesized from the corresponding aldehydes or ketones by reaction with 1,2-ethane dithiol followed by oxidation, usually with *meta*-chloroperbenzoic acid [5].

All the examined compounds were analytically pure samples, purified by standard procedures.

Mass spectrometric measurements were obtained using a VG ZAB2F mass spectrometer operating in Fast Atom Bombardment (FAB) mode, using 8 keV Xe atoms bombarding glycerol solutions of the compounds under examination.

Metastable transitions were detected either by B/E and B<sup>2</sup>/E [6a] linked scans or by MIKE [6b] spectra.

#### REFERENCES AND NOTES

- [1a] S. R. Wilson, G. M. Georgiadis, H. N. Khatri and J. E. Bartmess, *J. Am. Chem. Soc.*, **102**, 3577 (1980); [b] F. A. Carey and O. D. Dailey, Jr., *Phosphorus Sulfur* **10**, 169 (1981); [c] T. Oida, S. Tanimoto, H. Terao and M. Okano, *J. Chem. Soc., Perkin Trans. I*, 1715 (1986).
- [2] S. Schonberg, D. Cernik and W. Urban, *Ber.*, **64**, 2577 (1931).
- [3] S. Tanimoto, H. Terao, T. Oida and H. Ikehira, *Bull. Inst. Chem. Res. Kyoto Univ.*, **62**, 54 (1984).
- [4] J. E. Bartmess, R. L. Hays, H. N. Khatri, R. N. Misra and S. R. Wilson, *J. Am. Chem. Soc.*, **103**, 4746 (1981).
- [5] O. Bortolini, G. Licini and P. Traldi, *Org. Mass. Spectrom.*, **23**, 841 (1988).
- [6a] A. P. Bruins, K. R. Jennings and S. Evans, *Int. J. Mass. Spectrom. Ion Phys.*, **26**, 395 (1978); [b] R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
- [7] A. Turco, A. Morvillo, U. Vettori and P. Traldi, *Inorg. Chem.*, **24**, 1123 (1985).
- [8a] J. H. Bowie, D. H. Williams, S. O. Lawesson, J. O. Madsen, C. Nolde and G. Schroll, *Tetrahedron*, **22**, 3515 (1966); [b] I. D. Entwistle, R. A. W. Johnstone and B. J. Millard, *J. Chem. Soc. (C)*, 302 (1967).
- [9] H. Kuschel and H. F. Grutzmacher, *Org. Mass. Spectrom.*, **9**, 408 (1974).