

Short Communication

Flash Vacuum Pyrolysis of 1,3-Dithiolane 1-Oxides

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Flash vacuum pyrolysis has in recent years gained interest as a useful method for the preparation of very reactive compounds.^{1,2} We were interested in methods of generation of reactive thiocarbonyl compounds such as thioaldehydes³ and thioketenes.³

Thiocarbonyl compounds have previously been generated from 1,3-dithiolanes by: 1, 1,3-anionic cyclo-reversion of 1,3-dithiolane-derived anions, which can give thioketones, thioaldehydes, thioketenes, dithiocarboxylic acids or thioesters depending on the derivative and the conditions;⁴ 2, recently by flash vacuum pyrolysis of 1,3-dithiolane 1,1-dioxides.⁵

Our attention was drawn to the pyrolysis of 1,3-dithiolane 1-oxides, because a study of the pyrolysis of benzothiophenes and derivatives by Davis *et al.*⁶ showed that the sulfoxides were more reactive than the corresponding sulfides or sulfones. This is also in complete agreement with the bond dissociation energies for the process, eqn. (1), where the stability of the $RS(O)_n-R \rightarrow RS(O)_n \cdot + R \cdot$, $n=0, 1, 2$

carbon–sulfur bond increases in the series $RSO- < RS- < RSO_2$ according to data from Benson.⁷

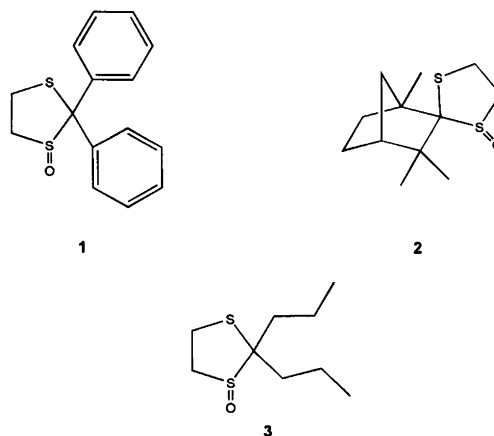
The pyrolysis of 1,3-dithiolane sulfoxides has earlier been investigated by Chen⁸ and by Hoffmann *et al.*,⁹ but the formation of thiocarbonyl compounds has not been observed.

We decided to look at some 1,3-dithiolane sulfoxides, where the corresponding thiocarbonyl compounds were known and reasonably stable. The sulfoxides studied are shown in Scheme 1.

Results and discussion

Only in two cases were we able to detect the formation of thiocarbonyl compounds: 2,2-diphenyl-1,3-dithiolane

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Scheme 1.

1-oxide (1) starts to pyrolyse at 400 °C and 0.01 mmHg to give thiobenzophenone¹⁰ and sulfur. The yield of thiobenzophenone¹⁴ as function of the temperature is shown in Table 1. Spiro{1,3,3-trimethylbicyclo[2.2.1]heptane-2,2'-(1',3'-dithiolane 1'-oxide)} (2) gave thiofenchone.^{11,12} However, a higher temperature was needed as shown in Table 2.

2,2-Dipropyl-1,3-dithiolane 1-oxide (3) failed to give any 4-heptanethione.¹³ We suggest a stepwise homolytic cleavage as shown in Scheme 2.

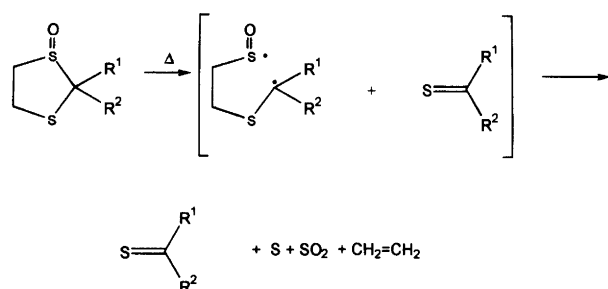
Support for this mechanism comes from the results

Table 1. Formation of thiobenzophenone by pyrolysis of 1.

$T/^\circ\text{C}$	Isolated yield (%)
400	3
500	16
550	54
600	25
650	14

Table 2. Formation of thiofenone by pyrolysis of 2.

$T/^\circ\text{C}$	Isolated yield (%)
700	50
750	54
800	63
850	25



Scheme 2.

with the sulfoxides **1** and **2**, where the higher temperature needed for pyrolysis of **2** compared with **1** can be ascribed to the easier formation of a benzhydryl radical compared with a tertiary alkyl radical. Additional support comes from work by Kondo *et al.*¹⁴ on the mechanism of the pyrolytic extrusion of sulfur monoxide from diphenylthiirane oxide in solution. They were able to trap the intermediate diradical by performing the reaction in the presence of 4,4'-dimethoxythioacetophenone, which gave 1,3-dithiolane 1-oxide. Furthermore sulfur monoxide is known to be highly reactive, disproportionating to sulfur and sulfur dioxide.¹⁵

Conclusion

We have shown that flash vacuum pyrolysis of 1,3-dithiolane 1-oxides can lead to thiocarbonyl compounds. However, the full scope and limitations of this reaction remain to be clarified.

Experimental

The set-up used for the flash pyrolysis has been described by Brown.¹⁶ The pyrolysis was done at a pressure of

0.01 mmHg, and the products were trapped on a cold finger cooled with liquid N_2 . The thiones were identified by comparison with authentic samples prepared according to the literature.

2,2-Diphenyl-1,3-dithiolane 1-oxide (**1**) was prepared according to Kuhn and Neugebauer.¹⁷

Spiro{1,3,3-trimethylbicyclo[2.2.1]heptane-2,2'-(1',3'-dithiolane 1'-oxide)} (**2**) and 2,2-dipropyl-1,3-dithiolane 1-oxide (**3**) were prepared from spiro[1,3,3-trimethylbicyclo[2.2.1]heptane-2,2'-(1',3'-dithiolane)}¹⁸ and 2,2-dipropyl-1,3-dithiolane¹⁹ by oxidation with 3-chloroperbenzoic acid in CH_2Cl_2 .

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