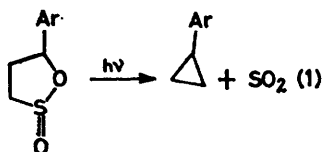


The Flash Thermolysis of γ -Sultines

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The flash thermolysis of 1,2-oxathiolan 2-oxides (1) has been shown to lead to a mixture of cyclopropanes and alkenes. When a stabilising group is present at the 5-position as in (1a) and (1b) only cyclopropanes are obtained.

THE photochemical¹ and thermolytic² breakdown of cyclic sulphones and related compounds have been studied as routes to cyclic compounds. We have recently described the photochemical extrusion of sulphur dioxide from 1,2-oxathiolan 2-oxides leading to cyclopropanes¹ [equation (1)]. However, use of this



process as a synthesis of cyclopropanes is limited because a chromophore is necessary for absorption of energy and good yields are only obtained when an aryl group is at position 5.

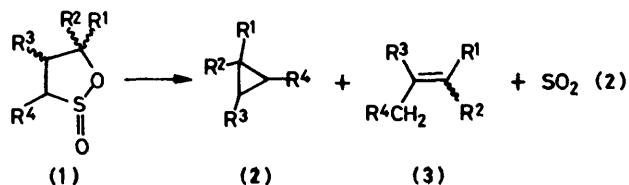
Sulphur dioxide is known to be thermally extruded from sulphones³ and β -sultines⁴ and this paper describes our attempts to increase the scope of this reaction by using flash thermolysis to fragment γ -sultines.

PREPARATION OF γ -SULTINES

All sultines studied have previously been described. The monocyclic γ -sultines were prepared by cyclisation of the appropriate *t*-butyl hydroxyalkyl sulphoxides with sulphinyl chloride⁵ while the benzo-fused sultines were obtained by oxidative cyclisation (sulphuryl chloride in acetic acid) of *o*-hydroxymethylthiophenols.¹

RESULTS AND DISCUSSION

The sultines (1) were thermolysed by vapourising the sample at 0.007 mmHg through a hot silica tube (10 \times 1.2 cm i.d.) heated by a tube furnace. The products



Unless stated all R groups = H

- (a) R¹ = Ph
- (b) R¹ = Ph, R⁴ = Me
- (c) R³ = Me
- (d) R³ = Ph
- (e) R¹ = Me

were collected on a cold finger and analysed by gas liquid chromatography and by ¹H n.m.r. spectroscopy.

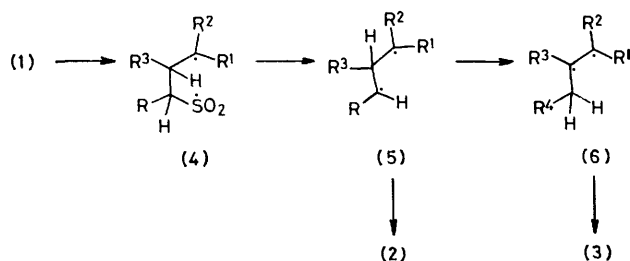
In general, the compounds fragmented as shown [equation (2)] and results at various temperatures are

The thermolysis of γ -sultines (1)

Com- pound	Tempera- ture/ °C	Starting material	Products (%)		
			(2)	(3)	Others
(1a)	550	84	15		
	600	62	37		
	650	24	75		
	750		100		
	850		36	37	allylbenzene, 27
(1b)	750		100		
(1c)	650	87		13	
	700	70		30	
	750		37	62	
(1d)	750	a		a	
(1e)	750		45	35	acetaldehyde, 17

^a Product ratios could not be determined due to overlap of the peaks of α -methylstyrene and starting material in the ¹H n.m.r. spectra.

displayed in the Table. Cyclopropanes (2) are formed but in varying yields, the maximum amount being



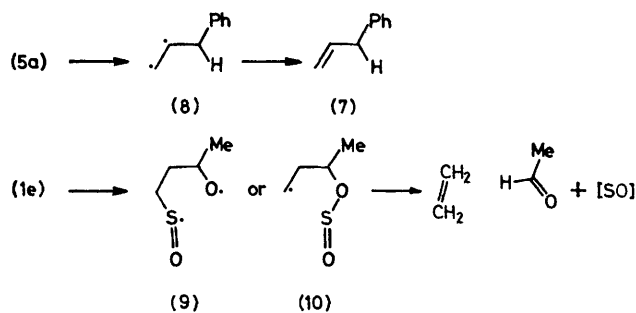
SCHEME 1

obtained at 750 °C. However, it does appear that the thermolyses of (1), as in the photolysis, only give useful yields of cyclopropanes when an aryl group is attached at C-5 [compounds (1a) and (b)]. In the absence of such a group higher temperatures are needed before any worthwhile reaction is observed and any considerable amount of the alkenes (3) formed.

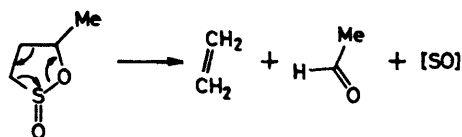
These reactions can be best described as depicted in Scheme 1. The loss of sulphur dioxide from β -sultines is concerted⁴ but such a process is not possible here and the reaction is probably stepwise. Initial cleavage would give a diradical (4). Loss of sulphur dioxide would give (5) from which the observed products can be derived. Ring closure of (5) will give the cyclopropanes (2), while hydrogen atom transfer leads to alkenes (3). Indeed, thermolysis of compound (1d) gave α -methylstyrene as the only observed product. The amount of phenylcyclopropane formed from (1a) increased with temperature up to 750 °C. Above this temperature, *cis*-

and *trans*- β -methylstyrene are formed together with allylbenzene (7), which must arise from further rearrangement of (5a) to (8).

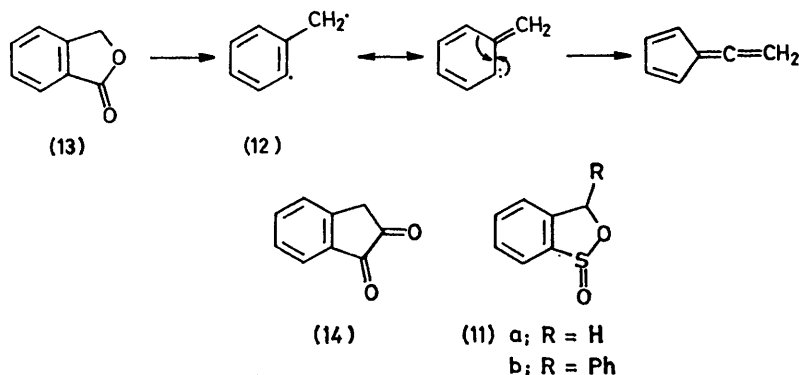
The thermolysis of γ -sultine (1e) is more interesting since at least some of the product appears to be due to loss of sulphur monoxide. Such reactions are known to occur⁶ but are uncommon. The formation of acetaldehyde from (1e) can be visualised as occurring by loss of sulphur monoxide from the diradical (9) or (10) followed by carbon-carbon bond cleavage (Scheme 2). It is



interesting that the production of acetaldehyde may be the consequence of a concerted process (Scheme 3). We



intend to investigate this possibility further. Ethylene, which would have been formed in either process, was



Thermolysis of (11a) below 700 °C gave only recovered starting material while at higher temperatures a multitude of unidentified products were obtained. T.l.c. of the product from a typical experiment at 750 °C showed the presence of at least 6 compounds. Flash vacuum thermolysis of (11b) at 750 °C gave fluorene as the only product, with no starting material remaining. This probably arises by rearrangement of the initial diradical

(Scheme 4). Fluorene was also established to be the major product in the photolysis of (11b).¹

EXPERIMENTAL

M.p.s were determined using a Kofler heating stage. I.r. spectra were recorded with Perkin-Elmer 257 and 580 instruments and n.m.r. spectra were recorded at 60 MHz with a Varian T-60 or at 100 MHz with a JEOL JNM-PS-100 instrument. G.l.c. analyses were performed on a Pye 104 flame-ionisation chromatograph fitted with a 1.5 m \times 4 mm i.d. glass column packed with 3% silicon OV17 on silanised

not trapped under the conditions of the experiment and sulphur monoxide disproportionates into sulphur dioxide and sulphur.

Flash vacuum thermolysis of the benzo-fused sultines (11) might be a route to the diradical (12) which has been formed from the flash vacuum thermolysis of phthalide (13)⁷ and also implicated in the flash thermolysis of indane-1,2-dione (14).⁸ Products from these reactions are mainly fulvenallene⁷ and benzocyclopropene⁸ and it was hoped that the use of (11) would be a new route to these materials.

100–120 mesh Diatomite. G.l.c.–mass spectral analysis was carried out using a V.G. Micromass 16B instrument at 70 eV. Isobutylene was obtained from Matheson and phenylcyclopropane from Aldrich. The ¹H n.m.r. spectra of α -methylstyrene, β -methylstyrene, and allylbenzene are described in the Varian catalogue, and that of 1-methyl-1-phenylcyclopropane by Gilbert and Seyden-Penne.⁹ A sample of methylcyclopropane for comparison was prepared by dehalogenation of 1,3-dibromo-2-methylpropane with zinc.¹⁰

General Procedure for Thermolysis.—The sultine (150 mg) in a small flask was vapourised through the furnace, set at

various temperatures as described in the Table, using a Kugelrohr Oven. The product was collected on a cold-finger filled with acetone-solid CO₂ and washed with deuteriochloroform into the n.m.r. tube. The products were identified by ¹H n.m.r. spectroscopy and g.l.c.-mass spectral analysis. Product ratios were calculated from careful integration of the 100 MHz spectra and the results are presented in the Table.

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