

Chemistry of Sulphines. Part XVII.¹ Fragmentation and Rearrangement Processes upon Electron Impact of Aromatic Sulphines

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The mass spectra of the diaryl sulphines (Ia—i) and the fused aromatic sulphines (IIa—d) have been rationalized. The main fragmentation is suggested to proceed *via* an intermediate oxathiiran. The fused sulphines (II) show loss of CO and COH which involves an oxygen transfer from the CSO group to the adjacent aromatic nucleus; this fragmentation is much less pronounced in compounds (I) owing to their non-fused nature. Loss of SO was observed in all cases, which in sulphines (I) leads to the fluorenyl cation upon subsequent loss of H or a substituent.

SULPHINES represent a new class of heterocumulenes which recently became readily available by the peroxy-acid oxidation of the corresponding thiocarbonyl compounds.² This paper deals with a detailed study of the fragmentations and rearrangements in the mass spectra

sulphines show fragmentation and rearrangement processes upon electron impact which are inherent to the CSO system, and hence of diagnostic value.

Diaryl Sulphines.—The main mass spectral features of compounds (Ia—i) are compiled in Table 1. The

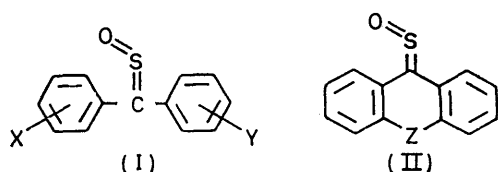
TABLE 1
Relative abundance of major peaks of diaryl sulphines

Compound Ion	Relative abundance								
	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(If)	(Ig)	(Ih)	(Ii)
<i>M</i>	63	58	67	26	27	35	74	12	14
<i>M</i> - H	37*	20*	10*	8*	11*	16*	8*	0.7	0.8
<i>M</i> - O	15*	6	1.4*	1.5	1	3*	5		
<i>M</i> - OH	7	2	2.5	1	1.5	3	11	100*	100*
<i>M</i> - CO	1	2	0.5						
<i>M</i> - COH	12	2	0.5						
<i>M</i> - S	27	16	18	4	5	55	1		
<i>M</i> - SO	2.5	1	9	1	0.3	1	100*	3	3
<i>M</i> - SOH	50**	11	7.5**	6	4	3		4	3
<i>M</i> - (SO + X)		17	24 ^a	42	28		10		
XC ₆ H ₄ CS	24	13.5	6	18	18	11	10	5 ^b	6 ^b
XC ₆ H ₄ CO	100*	100*	100*	100	100	100	84	14 ^c	17 ^c
<i>M</i> - X		21	1	13	40	23	24 ^d	42 ^e	45 ^e
XC ₆ H ₄	35	22	3.5	24	28	25	2	11 ^f	13 ^f

^a *M* - (SO + Me) instead of *M* - (SO + OMe). ^b *m/e* 163 for mesityl-CS⁺. ^c *m/e* 147 for mesityl-CO⁺. ^d *M* - NO instead of *M* - NO₂. ^e *m/e* 241 for *M* - Me. ^f *m/e* 119 for mesityl⁺.

* Metastable observed for the transition from the molecular ion to the indicated fragment ion. ** Metastable observed for (*M* - SO) → (*M* - SOH).

of two types of sulphines, *viz.* the diaryl sulphines (I) and the fused aromatic sulphines (II).



- (I)
a; X = Y = H
b; X = Y = 4-Me
c; X = Y = 4-OMe
d; X = Y = 4-Cl
e; X = Y = 3-Cl
f; X = Y = 3-OMe
g; X = Y = 3-NO₂
h; X = H; Y = 2,4,6-Me₃
i; X = 2,4,6-Me₃; Y = H

- (II)
a; Z = —
b; Z = O
c; Z = S
d; Z = CH=CH

It is well known³ that organosulphur compounds are prone to skeletal rearrangements on electron impact. The results presented here reveal that the aromatic

¹ Part XVI, B. Zwanenburg, A. Wagenaar, L. Thijs, and J. Strating, *J.C.S. Perkin I*, 1973, 73.

² B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577; B. Zwanenburg and J. Strating, *Quart. Reports Sulfur Chem.*, 1970, **5**, 79.

sulphines (Ia—g) show prominent *M* - 1 peaks which are almost absent in the spectrum of (Ih) and (Ii) which have the *ortho*-positions of one phenyl ring blocked by methyl groups. Because of this difference we suggest a ring fusion process typical for diphenyl compounds.⁴

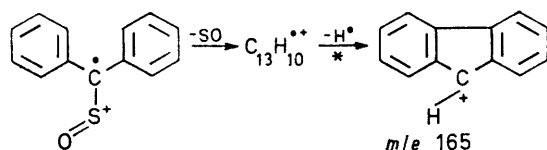
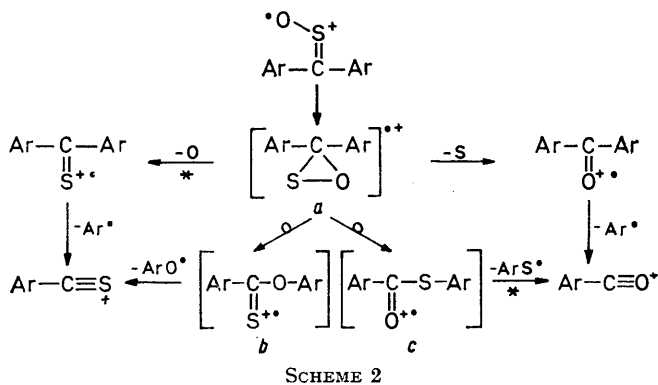
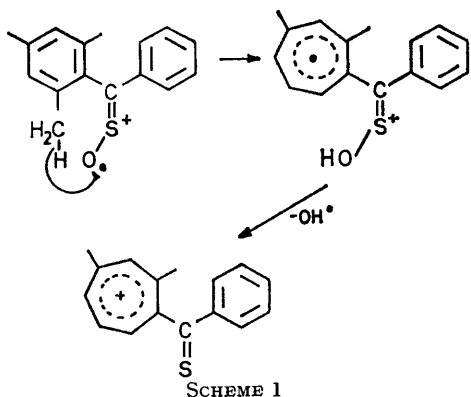
While the *M* - OH fragmentation is a minor one in the sulphines (Ia—g), it becomes the predominant one in (Ih) and (Ii). As shown in Scheme 1, in the latter sulphines loss of OH can produce stable ions of the tropylium type. Such a fragmentation would be facilitated by a *cis*-relationship between the mesityl and the sulphine groups. However, *cis*- and *trans*-mesityl phenyl sulphine show this fragmentation to an equal extent. Thus, a thermal or electron impact induced isomerization must have taken place prior to the cyclization to the seven-membered ring.

The loss of S, O, ArO[•], and ArS[•] from the molecular ion most probably proceeds through an intermediate oxathiiran *a*. The intermediate *a* then splits off either S or O, to give the diaryl ketone and diaryl thioketone

³ J. H. Bowie, B. K. Simons, and S.-O. Lawesson, *Rev. Pure Appl. Chem.*, 1969, **19**, 61.

⁴ J. H. D. Eland and C. J. Danby, *J. Chem. Soc.*, 1965, 5935.

fragment, respectively. Alternatively, *a* can undergo a phenyl migration to give either species *b* or *c*. Loss of



ArO^\bullet or ArS^\bullet , respectively, gives then the observed fragments $\text{ArC}\equiv\text{S}^+$ and $\text{ArC}\equiv\text{O}^+$ (Scheme 2). The

known⁶ to give a fragmentation to the fluorenyl cation (m/e 165). This ion is coupled with a doubly charged ion at m/e 82.5.⁴ The spectrum of diphenyl sulphine (Ia) also shows these characteristic peaks which may arise from the parent ion by loss of SO and subsequent loss of H (Scheme 3) (m/e 82.5; 7%).

The sulphines (Ib–g) give basically the same fragmentation as (Ia). In addition they show a decomposition of the daughter ions. For instance, loss of SO and subsequent loss of the substituent (see Table 1) instead of H (*cf.* Scheme 3), or the reverse, also gives a fluorenyl cation,⁶ characteristically accompanied by a prominent doubly charged ion (2–6%). This significant fragmentation of (Ia–g) to a fluorenyl cation is absent in the spectra of the sulphines (Ih) and (Ii) because the *ortho*-positions of one phenyl ring are blocked by methyl groups.

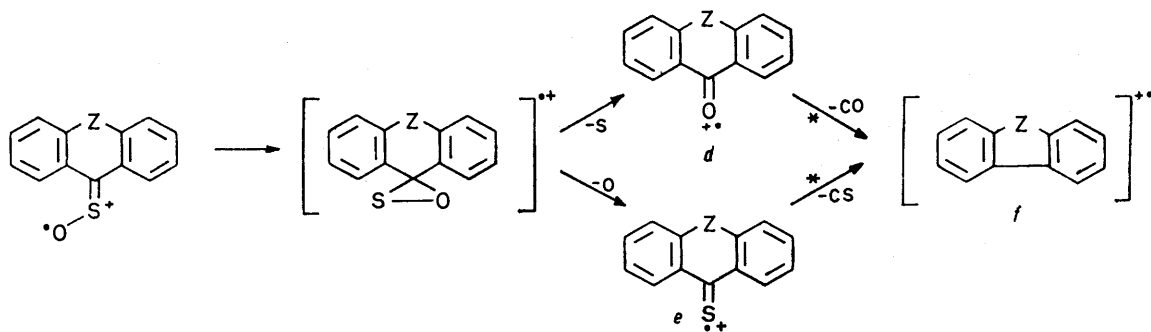
Fused Aromatic Sulphines.—The main spectral features of the fused aromatic sulphines (II) are compiled in Table 2. The $M - S$ and $M - O$ fragments probably

TABLE 2
Relative abundance of major peaks of the fused aromatic sulphines

Compound Ion	Relative abundance			
	(IIa)	(IIb)	(IIc)	(IId)
<i>M</i>	100	100	100	100
<i>M</i> - H	2 *	30 *	51 *	73 *
<i>M</i> - O	8	10	4	<0.3
<i>M</i> - OH	5	5	9	9
<i>M</i> - CO	69 *	11 *	5 *	4
<i>M</i> - COH	5	1	1	10
<i>M</i> - S	40	10	6	3
<i>M</i> - SO	8	44	35	21
<i>M</i> - SOH	24 *	9	23	94
<i>M</i> - CSO	31	10	8	7
<i>M</i> - (SO + CZ)		20	39	

* Metastable observed for the transition from the molecular ion to the indicated fragment.

arise from the parent ion *via* a three-membered ring intermediate as suggested for the sulphines (I). However, migration of the aromatic nucleus (*cf.* Scheme 2) is



fragmentation of nitrones, which are isoelectronic with sulphines, is suggested⁵ as proceeding *via* a three-membered heterocyclic intermediate, *i.e.* an oxaziridine.

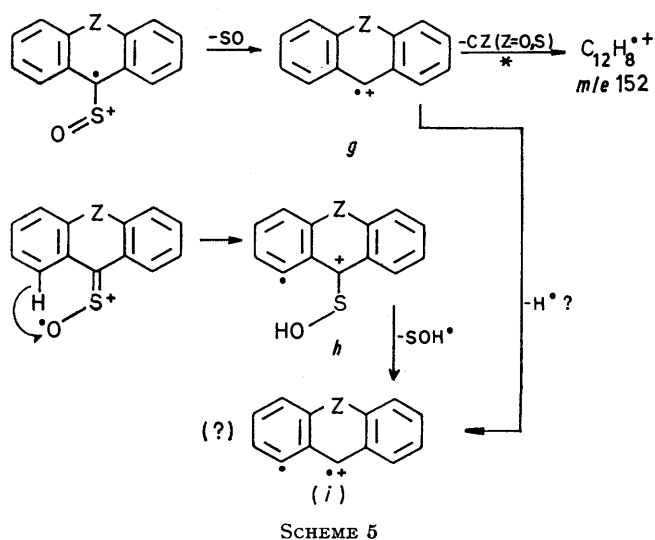
Thiobenzophenones and diphenyldiazomethane are

⁵ B. Sogaard Larsen, G. Schroll, S.-O. Lawesson, J. H. Bowie, and R. G. Cooks, *Chem. and Ind.*, 1968, 321.

prohibited in these cases because of the rigidity of the system. The daughter ions *d* and *e* being identical with the molecular ions of the corresponding ketones or thio-ketones,⁶ then lose CO or CS, respectively, to produce the

⁶ D. Schumann, E. Frese, and A. Schönberg, *Chem. Ber.*, 1969, 102, 3192.

ion *f* (Scheme 4). Ion *f* may also arise by direct extrusion of CSO.



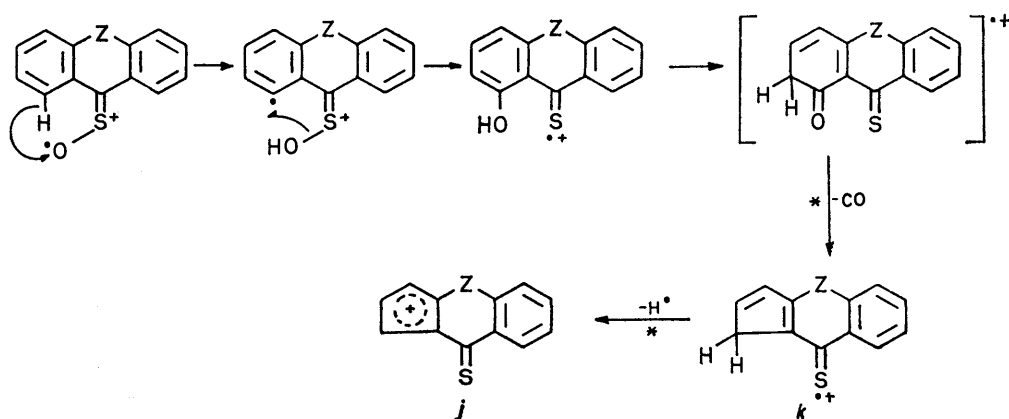
Loss of SO and SOH from the molecular ion gives the fragments *g* and *i* (Scheme 5). A metastable peak

suggested by Job⁸ and recently confirmed by Siegel.⁹ Phenols are known to lose CO and COH fragments on electron impact.^{7,10} The fragmentations shown in Scheme 6 play a more important role in the fused sulphines (II) than in (I), which is most likely caused by the rigidity of sulphines (II).

EXPERIMENTAL

All mass spectra were determined on an AEI MS 9 double focusing mass spectrometer operating at an ionizing potential of 70 eV and an accelerating voltage of 8 kV. The metastable transitions examined occurred in the second field-free region of the spectrometer. The direct inlet system was used in all cases. The source temperatures were (Ia), 100; (Ib), 120; (Ic), 100; (Id), 125; (Ie), 160; (If), 130; (Ig), 180; (Ih), 110; (Ii), 100; (IIa), 120; (IIb), 130; (IIc), 130; and (IId), 90 °C. All intensities were corrected for isotopic abundance.

The sulphines (Ia–d) and (IIa–d) were prepared as described previously.¹¹ The sulphines (Ie–g) were prepared by peroxyacid oxidation of the corresponding thio-ketones [(Ie) 70%, m.p. 62–64°; (If) oil, contaminated with some (ca. 10%) ketone; and (Ig) 79%, m.p. 162–164°]. The isomeric sulphines (Ih) and (Ii) were obtained by peroxyacid oxidation of mesityl phenyl thio-ketone.



confirms the $M \rightarrow M - \text{SOH}$ transition in the case of (IIa); the formation of *i* can also be envisaged by loss of H^\bullet from *g*. In the sulphines (IIb) and (IIc), where CZ is a stable species (CO or CS), elimination of CZ from ion *g* takes place to give a fragment $\text{C}_{12}\text{H}_8^+$, m/e 152. Such an elimination resembles the loss of CO from diphenyl ether.⁷

The $M - \text{H}$ and $M - \text{OH}$ fragmentations can be envisaged as occurring from the rearranged ion *h*.

The $M - \text{CO}$ and $M - \text{COH}$ fragmentations can be rationalized as shown in Scheme 6. This part of the cracking pattern bears some resemblance with that of the heterocumulene *N*-sulphinylaniline ($\text{C}_6\text{H}_5\text{N}=\text{S}=\text{O}$) as

⁷ J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Chem. Phys.*, 1959, **63**, 1861.

⁸ B. E. Job, *Chem. Comm.*, 1967, 44.

The mixture of *Z*- and *E*-isomers was separated by thick layer chromatography on silica gel with CH_2Cl_2 as developing solvent [(Ih) 19%, m.p. 58–59° and (Ii) 53%, m.p. 101.5–104°]. From all these sulphines [except (If)] correct combustion analyses were obtained. Analytically pure samples were used for the mass spectrometric analyses.

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⁹ A. S. Siegel, *Org. Mass Spectrometry*, 1970, **3**, 875.

¹⁰ T. Aczel and H. E. Lumpkin, *Analyt. Chem.*, 1960, **32**, 1819.

¹¹ B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, 1971, **27**, 1731.