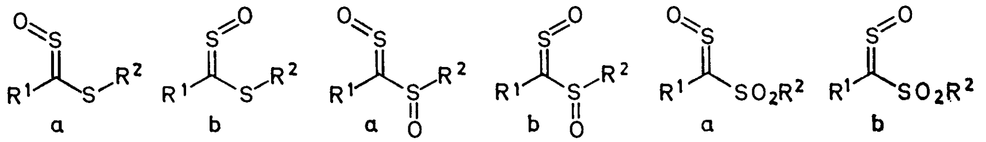
Chemistry of Sulphines. Part XVIII.[1] Electron Impact Induced Rearrangements of Arylthio, Arylsulphinyl, and Arylsulphonyl Substituted Sulphines

By **Albert Tangerman** and **Binne Zwanenburg**,*† Department of Organic Chemistry, University at Nijmegen, Toernooiveld, Nijmegen, The Netherlands † and Department of Organic Chemistry, University of Groningen, Zernikelaan, Groningen, The Netherlands

The mass spectra of aryl arylthio sulphines (I)—(VII), aryl arylsulphinyl sulphines (VIII)—(XIII) and aryl arylsulphonyl sulphines (XIV)—(XVIII) have been rationalized. All three types of sulphines show a rearrangement involving the intermediacy of an oxathiiran. Arylthio sulphines (I)—(VII) show an oxygen migration of the CSO function to the adjacent sulphur atom. The α-thioxo-sulphoxide thus formed undergoes a 1,2-aryl shift from sulphur to oxygen. Arylsulphinyl sulphines (VIII)—(XIII) show a migration of the R^1CSO group to the adjacent sulphoxide oxygen atom. Migration of the aryl (R^2) group to the sulphoxide oxygen atom was not observed. Arylsulphonyl sulphines (XIV)—(XVIII) exhibit almost no loss of the arylsulphonyl group, but migration of the R^1CSO group to the sulphonyl oxygen atom was an important fragmentation route. Specific fragmentation of the diaryl sulphines, *e.g.* loss of O, S, SO, and SOH from the CSO unit are absent in these sulphines.

In recent years a variety of sulphines, a new class of heterocumulenes, has been synthesized by oxidation of thiocarbonyl-containing compounds.[2] An interesting series of substituted sulphines can be obtained by stepwise oxidation of dithiocarboxylates.[3] The mass spectra of these sulphines (I)—(XVIII) were analysed, particularly with the aim of studying the rearrangement and fragmentation processes.



R^1	R^2	a	b	a	b	a	b
Ph	Ph	(I)	(I)	(VIII)	(VIII)	(XIV)	
Mesityl	Ph	(II)	(II)	(IX)	(IX)	(XV)	(XV)
Mesityl	β-Naphthyl	(III)	(III)	(X)	(X)	(XVI)	(XVI)
Mesityl	α-Thienyl	(IV)	(IV)	(XI)	(XI)	(XVII)	(XVII)
Mesityl	Mesityl	(V)	(V)	(XII)		(XVIII)	
Ph	Mesityl	(VI)	(VI)	(XIII)			
α-Thienyl	Mesityl	(VII)					

TABLE 1

Relative abundance of major peaks of aryl arylthio sulphines

Compound / Ion	Relative abundance												
	(Ia)	(Ib)	(IIa)	(IIb)	(IIIa)	(IIIb)	(IVa)	(IVb)	(Va)	(Vb)	(VIa)	(VIb)	(VIIa)
M	8	8	14	13	2	2	3	5	33	10	30	57	55
M − Me			14	14	3	3	4	3	11	5			
M − OH	1	1	30 *	31 *	5	4	6	5	36 *	20 *	12	16	16
M − SH	4 *	6 *	<0·3	<0·3	1	0·5	<0·3	<0·3	<0·3	<0·3	<0·3	<0·3	1
R^1CS_2O			11	11	2	1·5	0·5	0·5	2·5	2·5			
R^1CSO	0·5	0·5	2	1	0·5	0·5	0·5	0·5	2	2·5	0·5	0·5	
R^1CS_2	45	42	45 *	45 *	22	21	100 *	97 *	100	100	38 *	44 *	97 *
R^1CS	100 *	100 *	100 *	100 *	100 *	100 *	27	28	63	61	67	56	70
R^1CO	17	15									16 *	24 *	16
R^2S	7	5	5	3	2	2	1·5	1	1	9	2	1·5	7
R^2O	1	1·5	<0·3	<0·3	0·5	0·5	0·5	0·5	3	14	100 *	100 *	100
R^2	*a*	*a*	17	13	5	3	0·5	6	*a*	*a*	4	2	8

[a] R^2-containing ion identical with corresponding R^1-containing ion.

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

Aryl Arylthio Sulphines.—The mass spectral features of these types of sulphines are compiled in Table 1. The main fragmentation pattern for the sulphines (I)—(VII) is presented in Scheme 1. The formation of the ions *C* and *D* is most readily explained by assuming an oxygen migration to give ion *A*, followed by a 1,2-aryl shift from sulphur to oxygen.[4] Subsequent S–O bond cleavage in *B* then furnishes the ions *C* and *D*. The further fragmentation of *C* and *D* is in full accordance with the proposed sequence. Only when R^2 is mesityl [(V)—(VII)] is the transition $B \longrightarrow D$ an important one, presumably, because the ion R^2O^+ is stable in that case.

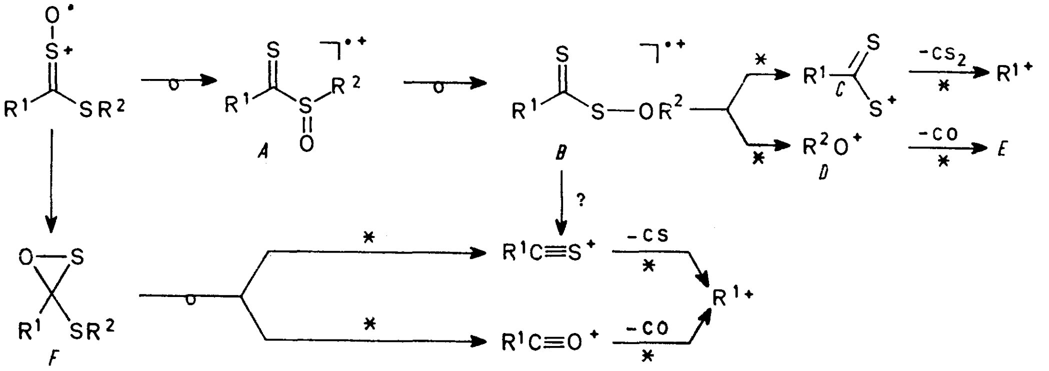
---

[1] Part XVII, A. Tangerman, L. Thijs, A. P. Anker, and B. Zwanenburg, preceding paper.

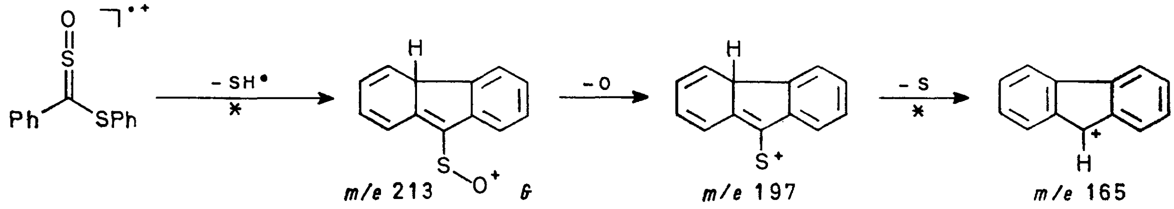
[2] B. Zwanenburg and J. Strating, *Quart. Report Sulfur Chem.*, 1970, **5**, 79; B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1969, 4461.

[3] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1971, **90**, 614.

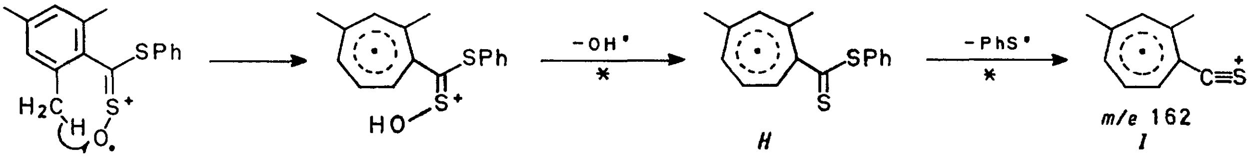
[4] (*a*) J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, 1966, **22**, 3515; (*b*) J. H. Bowie, B. K. Simons, and S.-O. Lawesson, *Rev. Pure Appl. Chem.*, 1969, **19**, 61.



SCHEME 1



SCHEME 2



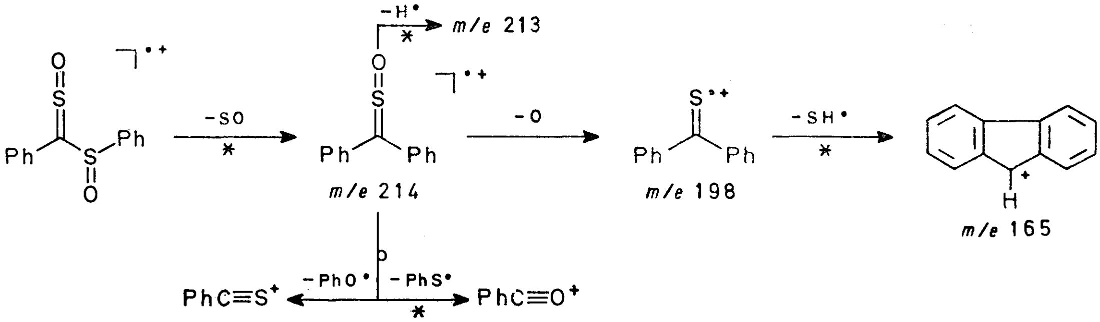
SCHEME 3

TABLE 2

Relative abundance of major peaks of aryl arylsulphinyl sulphines

Compound / Ion	Relative abundance									
	(VIIIa)	(VIIIb)	(IXa)	(IXb)	(Xa)	(Xb)	(XIa)	(XIb)	(XIIa)	(XIIIa)
M	<0·3	<0·3	11	9	2	2	2	1	1	1·5
M − OH			50 *	16 *	10 *	6 *	14 *	5	6	
M − SO	51	24	1·5	1	13	13	20 *	17	5	9
R^1CSO	13	1	26	20	16	8	16	11	6	
R^1CS	82	44	42	54	100	100	45	67	100	100
R^1CO	100	100	100	100	90	88	100	100	54	60
R^2SO_2		6				6	*b*	*b*		
R^2SO	27	32	5	11	12	10	10	11	4	6
R^2S	*a*	*a*	5	6	38	31	22	19	36	19
R^2	*a*	*a*	22	30	24	14	0·5	35	*a*	7

[a] R^2-containing ion identical with corresponding R^1-containing ion. [b] In this case the fragment ion $R^2SO_2^+$ is masked by R^1CO^+.
* Metastable observed for the transition from the molecular ion to the indicated fragment ion.



SCHEME 4

The formation of the ions $R^1C\equiv O^+$ and $R^1C\equiv S^+$ most likely proceeds *via* an intermediate oxathiiran *F*, as suggested for diaryl sulphines.[1] Remarkably, when R^1 was mesityl only fragmentation to $R^1C\equiv S^+$ was observed.

The arylthio sulphines also show minor direct fragmentations to the ions R^1CSO^+, $R^1CS_2O^+$, R^2S^+, and R^{2+}.

A striking difference between the phenyl phenylthio sulphines (I) and the sulphines (II)—(VII) in which the *ortho*-positions of at least one aryl ring are blocked by methyl groups, is the M — SH fragmentation. Since the sulphines (II)—(VII) lack these M — SH fragmentations an *ortho*-effect is suggested. A condensed ion *G* is formed from (Ia) and (Ib), which further fragments to the fluorenyl cation at *m/e* 165 (Scheme 2). The latter ion is also observed for diphenyl sulphine[1] which supports the suggested scheme.

The M -- OH fragmentation in the sulphines with R^1 = mesityl [(II)—(V)] proceeds in a fashion similar to that described for mesityl phenyl sulphines[1] (Scheme 3). The transition $H \longrightarrow I$ confirms that the H of the OH being split off in Scheme 3 originates from the mesityl and not from the phenyl group.

As suggested in Scheme 3 a *trans*-configuration is necessary for this process. However, the *E*- and *Z*-sulphines (IIa, b)—(Va, b) both show this fragmentation. For the oxygen transfer reaction (Scheme 1) a *cis*-geometry is favourable. Again, the *Z*- as well as *E*-isomers show this migration. It may be concluded that in both cases (Schemes 1 and 3) a thermal or electron impact induced isomerization (*Z* to *E* or *vice versa*) is likely to occur prior to fragmentation.

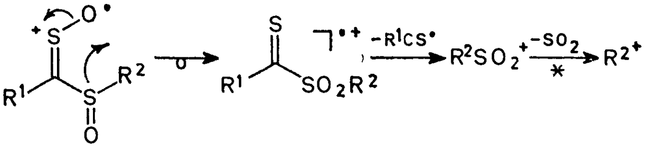
Aryl Arylsulphinyl Sulphines.—The mass spectral features of these types of sulphines are collected in Table 2. The phenyl phenylsulphinyl sulphines (VIIIa) and (VIIIb), which give almost no parent peak, show a prominent M — SO fragmentation at *m/e* 214 which decays further (Scheme 4). The observed cracking pattern of fragment ion *m/e* 214 is characteristic for diphenyl sulphine[1] and can only be reconciled with a mechanism in which the SO which is split off originates from the sulphoxide and not from the CSO function.

The spectrum of the corresponding phenyl phenylsulphonyl sulphine (XIVa), shows the loss of SO_2 to give the same fragment *m/e* 214.

The M — OH fragmentation closely resembles that of the corresponding arylthio sulphines (*cf.* Scheme 3).

An oxygen transfer from the sulphine group to the adjacent sulphoxide function (*cf.* Scheme 1) was observed in two instances (VIIIb) and (Xb) which have the *cis*-geometry necessary for the migration (Scheme 5). The corresponding *trans*-isomers do not show an $R^2SO_2^+$ ion. Apparently, *E*- to *Z*-isomerization does not take place as readily as in the arylthio sulphines.

The main fragmentation pattern of the aryl arylsulphinyl sulphines is presented in Scheme 6. The formation of the ions $R^1C\equiv O^+$ and $R^1C\equiv S^+$ proceeds through an intermediate oxathiiran similar to that suggested in Scheme 1 for the aryl arylthio sulphines. The second process in Scheme 6 involves a migration of the CSO group to the sulphoxide oxygen atom as indicated by the presence of the R^2S^+ ion. The alternative, *i.e.* migration of R^2 to the sulphoxide oxygen atom[4] does not occur since the fragment R^2O^+ expected in this case was not observed. Hence, migration of the CSO group is preferred over that of the aryl group. The ions R^1CSO^+ and R^2SO^+ in Scheme 6 can be explained by either scission of the central C–S bond in the molecular ion or by C–O bond cleavage in the rearranged molecular ion *L*. The formation of the thiabenzenonium ion *K* ($C_5H_5S^+$ for R^2 = Ph) from the fragment ion R^2SO^+ *via* a rearrangement as described by Bowie *et al.*,[4a] has also been observed in the spectra of diaryl sulphoxides,[4a] thiolsulphinates,[5] and thiolsulphonates.[5]



SCHEME 5

Aryl Arylsulphonyl Sulphines.—The mass spectral features of this type of sulphines are summarized in Table 3. Phenyl phenylsulphonyl sulphine (XIVa) shows a prominent M — SO_2 peak at *m/e* 214, as observed for the phenylsulphinyl sulphines (Scheme 4). The arylsulphonyl mesityl sulphines (XV)—(XVIII) show almost no loss of SO_2, but instead small peaks at M — (SO_2 + OH) and M — (SO_2 + Me). In sulphines (XV)—(XVIII) the M — OH fragmentation becomes a very important one; this loss of OH probably proceeds *via* a pathway similar to that suggested for the arylthio mesityl sulphines (*cf.* Scheme 3) and arylsulphinyl mesityl sulphines.

Interestingly, almost no fragmentation to $R^2SO_2^+$ was observed, but instead the formation of R^2SO^+ ions was of considerable importance. A 1,2-shift of the sp^2-hybridized carbon atom of the sulphine group from sulphur to the sulphone oxygen atom can explain this observation (see Scheme 7). The presence of the ions *O*, arising from S–O bond scission in ion *N*, substantiates the suggested fragmentation. The alternative shift of the R^2 group to the sulphone oxygen atom[4,6] was not observed. This migration closely resembles that of aryl arylsulphinyl sulphines presented in Scheme 6. In addition to this process, fragmentation *via* an oxathiiran intermediate was found to play an important role.

In conclusion, the three types of sulphines derived from dithiocarboxylates undergo well defined skeletal rearrangements under electron impact. In all three cases fragmentation *via* an intermediate oxathiiran was observed. A rearrangement involving the 1,2-shift of the sulphine function (R^1CSO) in preference to that of

---

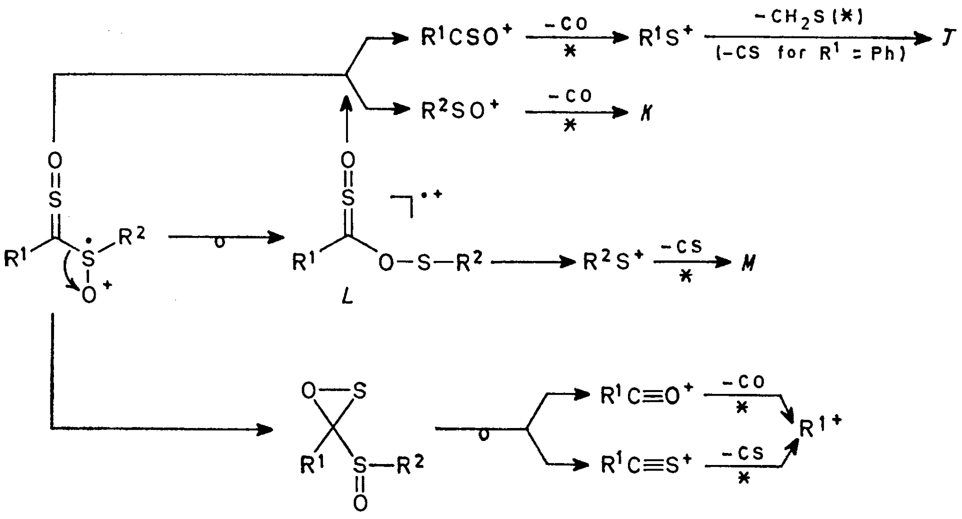
[5] S. Kozuka, H. Takahash, and S. Oae, *Bull. Chem. Soc. Japan*, 1970, **43**, 129.

[6] S. Meyerson, H. Drews, and E. K. Fields, *Analyt. Chem.*, 1964, **36**, 1294.

an aryl (phenyl, β-naphthyl, α-thienyl, mesityl) group forms a characteristic feature of arylsulphinyl and arylsulphonyl sulphines. Specific fragmentations of the diaryl sulphines, *i.e.* loss of O, S, SO, and SOH from the CSO unit in the molecular ion[1] were not observed for these sulphines.

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



SCHEME 6

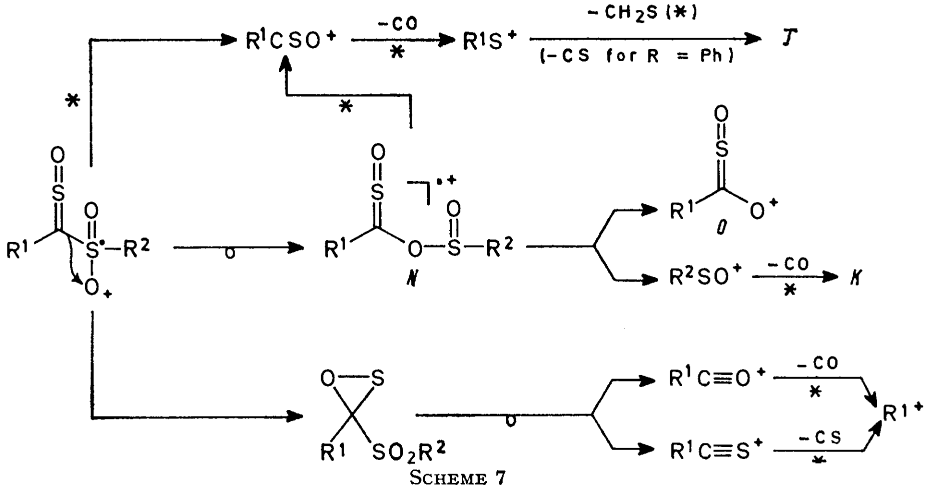
TABLE 3

Relative abundance of major peaks of aryl arylsulphonyl sulphines

Compound / Ion	Relative abundance							
	(XIVa)	(XVa)	(XVb)	(XVIa)	(XVIb)	(XVIIa)	(XVIIb)	(XVIIIa)
M	11	35	20	3	39	43	20	7
M – Me		48	30	6	39	56	48	17
M – OH		100 *	74 *	9 *	100 *	100 *	100 *	10 *
M – SO_2	20			0·5	1·5	1·5	3	<0·3
R^1CSO_2	1	17	18	5	11	8	19	42
R^1CSO	61	34	30	7 *	25 *	19	37	29
R^1CS	100	27	53	23	56	24	83	100
R^1CO	93	33	57	32	31	34	83	35
R^2SO_2	<0·3	<0·3	<0·3	2	1	*b*	*b*	<0·3
R^2SO	76	44	70	23	58	37	74	22
R^2	*a*	32	76	100	24	0·5	3	*a*

[a] R^2-containing ion identical with R^1-containing ion. [b] In this case the fragment ion $R^2SO_2^+$ is masked by R^1CO^+.

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



SCHEME 7

system was used in all cases. The source temperatures ranged from 100 to 140 °C. All intensities were corrected for isotopic abundance. A distinction between the fragments R^1CS_2 and R^1CSO_2 in Tables 1—3 was made by means of the isotopic abundance of ^{18}O (0·2%) and ^{34}S (4·2%).

The sulphines (I), (II), (VIII), (IX), (XIV), and (XV) were prepared as described previously.[3] The other sulphines were prepared by stepwise oxidation of the corresponding dithiocarboxylates $R^1C(=S)SR^2$. The latter were synthesized according to Mayer *et al.*[7] The yields (%) and m.p.s (°C) of the sulphines are (IIIa), 52, m.p. 102·5—104; (IIIb), 27, m.p. 117—118; (Xa), 59, m.p. 131—132·5; (Xb), 60, m.p. 132—134; (XVIa), 51, m.p. 155—156; (XVIb), 77, m.p. 178—180·5; (IVa), 46, m.p. 27—28·5; (IVb), 48, m.p. 124—125; (XIa), 32, m.p. 78—81·5; (XIb), 20, m.p. 111—112; (XVIIa), 81, m.p. 105—105·5; (XVIIb), 65, m.p. 165—169; (Va), 80, m.p. 129—130; (Vb), 1, m.p. 197—199; (XIIa), 47, m.p. 144·5—145·5; (XVIIIa), 56, m.p. 166·5—167·5; (VIa), 60, m.p. 62—63; (VIb), 16, m.p. 101·5—103; (XIIIa), 14, m.p. 77—79·5; and (VIIa), 84, m.p. 107·5—108. Correct combustion analyses were obtained for all sulphines. Analytically pure samples were used for mass spectrometric analyses.

We thank Mr. A. Kieviet (University of Groningen) for measuring the mass spectra, Mr. W. M. Hazenberg and his staff (University of Groningen) for performing the elemental analyses, and the Netherlands Organization for Pure Research (SON/ZWO) for a grant for the mass spectrometer (University of Groningen).

[2/2036 *Received*, 30*th August*, 1972]

---

[7] H. Viola, S. Scheithauer, and R. Mayer, *Chem. Ber.*, 1968, **101**, 3517.