Chemistry of Sulphones. Part XVIII.¹ Electron Impact Induced Re-
arrangements of Arylthio, Arylsulphinyl, and Arylsulphonyl Substituted 
Sulphones

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

By Albert Tangerman and Binne Zwanenburg.

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 a-thioxo-sulphoxide thus formed undergoes a 1,2-aryl shift from sulphur to oxygen. Arylsulphinyl sulphines (VIII)—(XIII) show a migration of the R'CSO group to the adjacent sulphone oxygen atom. Migration of the aryl (R1) group to the sulphone oxygen atom was not observed. Arylsulphonyl sulphines (XIV)—(XVIII) exhibit almost no loss of the arylsulphonyl group, but migration of the R'CSO group to the sulphonyl oxygen atom was an important fragmentation route. Specific fragmentation of the diaryl sulphines, e.g. loss of O, S, or SO2 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. An interesting series of substituted sulphines can be obtained by stepwise oxidation of dithiocarboxylates. The mass spectra 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 R2 is mesityl [(V)–(VII)] is the transition B → D an important one, presumably, because the ion R2O* is stable in that case.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative abundance of major peaks of aryl arylthio sulphines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>Relative abundance</td>
</tr>
<tr>
<td></td>
<td>(Ia) (Ib) (IIa) (IIb) (IIId) (IIIa) (IVa) (IVb) (V) (Vb) (VIa) (VIb) (VIIa)</td>
</tr>
<tr>
<td>M</td>
<td>8 8 14 13 2 2 3 5 33 10 30 67 55</td>
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<tr>
<td>M—Me</td>
<td>1 1 30 31 5 5 4 6 5 36 20 12 16 16</td>
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<tr>
<td>M—OH</td>
<td>4* 6* &lt;0-3 &lt;0-3 1 0-6 &lt;0-3 &lt;0-3 &lt;0-3 &lt;0-3 &lt;0-3 &lt;0-3</td>
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<tr>
<td>R'CSO</td>
<td>11 11 2 1 0-5 0-5 0-5 2 2 2 0-5 0-5</td>
</tr>
<tr>
<td>R'CS</td>
<td>45 42 45* 45* 22 21 100* 97* 100 100 35* 44* 97*</td>
</tr>
<tr>
<td>R'CO</td>
<td>100* 100* 100* 100* 100* 100* 27 28 63 61 67 67 70</td>
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<tr>
<td>R'CO</td>
<td>17 15 18 18* 24* 16</td>
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<tr>
<td>R'S</td>
<td>7 5 5 3 2 2 1 5 1 9 2 1 5 7</td>
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<tr>
<td>R'S</td>
<td>1 1 &lt;0-3 &lt;0-3 0-5 0-5 0-5 3 14 100* 100* 100</td>
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<tr>
<td>R2</td>
<td>a a 17 13 5 3 0-5 6 a a 4 2 8</td>
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</table>

* R2-containing ion identical with corresponding R1-containing ion.
* Metastable observed for the transition from the molecular ion to the indicated fragment ion.
Relative abundance of major peaks of aryl arylsulphinyl sulphones

<table>
<thead>
<tr>
<th>Compound</th>
<th>(VIIIa)</th>
<th>(VIIIb)</th>
<th>(IXa)</th>
<th>(IXb)</th>
<th>(Xa)</th>
<th>(Xb)</th>
<th>(XIa)</th>
<th>(XIb)</th>
<th>(XIIa)</th>
<th>(XIIIa)</th>
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<td>1-5</td>
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<tr>
<td>M-SO</td>
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<td></td>
</tr>
<tr>
<td>R-CS</td>
<td></td>
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<td>13</td>
<td>20</td>
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<td>5</td>
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<td>90</td>
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<td>100</td>
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<td>1</td>
<td>4</td>
<td>6</td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

* R*-containing ion identical with corresponding R*-containing ion. * In this case the fragment ion R*SO*2+ is masked by R*CO*+.
* Metastable observed for the transition from the molecular ion to the indicated fragment ion.

Scheme 1

Scheme 2

Scheme 3

Scheme 4
The formation of the ions \( \text{R}_1\text{C}=\text{O}^+ \) and \( \text{R}_1\text{C}=\text{S}^+ \) most likely proceeds via an intermediate oxathiiran \( \text{P} \), as suggested for diaryl sulphines. Remarkably, when \( \text{R}_1 \) was mesityl only fragmentation to \( \text{R}_1\text{C}=\text{S}^+ \) was observed.

The arylthio sulphines also show minor direct fragmentations to the ions \( \text{R}_1\text{CSO}^+, \text{R}_1\text{CS}_2\text{O}^+, \text{R}_2\text{S}^+, \) and \( \text{R}^+ \).

A striking difference between the phenyl phenylthio sulphinyl sulphines (I) and the sulphines (II)–(VII) in which the \( \text{H}^- \) positions of at least one aryl ring are blocked by methyl groups, is the \( \text{M}^- \) SH fragmentation. Since the sulphines (II)–(VII) lack these \( \text{M}^- \) SH fragmentations an \( \text{ortho}^- \) effect is suggested. A condensed ion \( \text{G} \) 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 \( \text{M}^- \) OH fragmentation in the sulphines with \( \text{R}_1 = \text{mesityl} \) \( [\text{II}^-
(\text{VI}) \) proceeds in a fashion similar to that described for mesityl phenyl sulphines \(^1 \) (Scheme 3). The transition \( \text{H}^- \rightarrow \text{I}^+ \) confirms that the \( \text{H}^- \) of the OH being split off from 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 \( \text{E}^- \) and \( \text{Z}^- \) sulphines (IIa, b)–(Va, b) both show this fragmentation. For the oxygen transfer reaction (Scheme 1) a cis-geometry is favourable. Again, the \( \text{Z}^- \) as well as \( \text{E}^- \) isomers show this migration. It may be concluded that in both cases (Schemes 1 and 3) a thermal or electron impact induced isomerization \( \text{Z} \rightarrow \text{E} \) or \( \text{vice versa} \) is likely to occur prior to fragmentation.

Aryl Arylsulphinyl Sulphines.—The mass spectral features of these types of sulphines are summarized in Table 2. The phenyl phenylsulphinyl sulphines (VIIa) and (VIIb), which give almost no parent peak, show a prominent \( \text{M}^- \) 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 sulphone and not from the CSO function.

The spectrum of the corresponding phenyl phenylsulphonyl sulphine (XIVa), shows the loss of \( \text{SO}_2 \) to give the same fragment \( m/e \) 214.

The \( \text{M}^- \) OH fragmentation closely resembles that of the corresponding arylthio sulphines (cf. Scheme 3).

An oxygen transfer from the sulphine group to the adjacent sulphone function (cf. Scheme 1) was observed in two instances (VIIib) and (Xb) which have the cis-geometry necessary for the migration (Scheme 6). The corresponding trans-isomers do not show an \( \text{R}_2\text{SO}^+ \) ion. Apparently, \( \text{E}^- \) to \( \text{Z}^- \) isomerization does not take place as readily as in the arylthio sulphines.

The main fragmentation pattern of the aryl arylsulphynyl sulphines is presented in Scheme 6. The formation of the ions \( \text{R}_1\text{C}=\text{O}^+ \) and \( \text{R}_1\text{C}=\text{S}^+ \) 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 sulphone oxygen atom as indicated by the presence of the \( \text{R}_2\text{S}^+ \) ion. The alternative, i.e. migration of \( \text{R}_2 \) to the sulphone oxygen atom \(^4 \) does not occur since the fragment \( \text{R}_2\text{SO}^+ \) expected in this case was not observed. Hence, migration of the CSO group is preferred over that of the aryl group. The ions \( \text{R}_1\text{CSO}^+ \) and \( \text{R}_1\text{SO}^+ \) 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 \( \text{L} \). The formation of the thiabenzenonium ion \( \text{K} \) \( (\text{C}_9\text{H}_6\text{S}^+ \) for \( \text{R}_2 = \text{Ph}) \) from the fragment ion \( \text{R}_1\text{SO}^+ \) via a rearrangement as described by Bowie et al., \(^4 \) has also been observed in the spectra of diaryl sulphenoxides, \(^4 \) thiolsulphinates, \(^5 \) and thiolsulphonates.

Aryl Arylsulphonyl Sulphines.—The mass spectral features of this type of sulphines are summarized in Table 3. Phenyl phenysulphonyl sulphine (XIVA) shows a prominent \( \text{M}^- \) SO peak at \( m/e \) 214, as observed for the phenylsulphonyl sulphines (Scheme 4). The aryksulphonyl mesityl sulphines (XV)–(XVIII) show almost no loss of \( \text{SO}_2 \) but instead small peaks at \( \text{M}^- \) \( (\text{SO}_2 + \text{OH}) \) and \( \text{M}^- \) \( (\text{SO}_2 + \text{Me}) \). In sulphines (XV)–(XVIII) the \( \text{M}^- \) 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 aryksulphonyl mesityl sulphines.

Interestingly, almost no fragmentation to \( \text{R}_2\text{SO}^+ \) was observed, but instead the formation of \( \text{R}_2\text{SO}^+ \) ions was of considerable importance. A 1,2-shift of the \( \text{sp}^2 \) 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 \( \text{O}, \) arising from 1,2 shift of the sulphone oxygen atom \(^4 \) was not observed. This migration closely resembles that of aryksulphinyl 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 sulphone function (R/C=SO) in preference to that of

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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 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
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\(^{13}\)CS\(_{2}\) and R\(^{13}\)CSO\(_{2}\) 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.\(^7\) The other sulphines were prepared by stepwise oxidation of the corresponding dithiocarboxylates R"C(=S)SR. 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;
- (Xla), 32, m.p. 78—81.5;
- (Xlb), 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;
- (XVIIb), 16, m.p. 101.5—103;
- (VIIa), 60, m.p. 62—63;
- (VIIb), 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.

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