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

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Chemistry of Sulphines. Part XVIII.\textsuperscript{1} Electron Impact Induced Rearrangements of Arylthio, Arylsulphinyl, and Arylsulphonyl Substituted Sulphines

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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'CSO group to the adjacent sulphoxide oxygen atom. Migration of the aryl (Ra) 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'CSO 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.\textsuperscript{2} An interesting oxygen migration to give ion A, followed by a 1,2-aryl shift from sulphur to oxygen.\textsuperscript{4} Subsequent S=O bond cleavage in B then furnishes the ions C and D.

\[ \text{R}^1 \text{S} \rightarrow \text{R}^1 \text{SO} \]

\[ \text{R}^2 \text{S} \rightarrow \text{R}^2 \text{SO} \]

\[ \text{R}^1 \text{N} \rightarrow \text{R}^1 \text{NO} \]

\[ \text{R}^2 \text{N} \rightarrow \text{R}^2 \text{NO} \]

of these sulphines (I)—(XVIII) were analysed, particularly with the aim of studying the rearrangement and fragmentation processes.

Aryl Arylthio Sulphines.—The mass spectral features of these types of sulphines are compiled in Table 1. The main fragmentation pattern for the sulphines

\[ \text{R}^1 \text{S} \rightarrow \text{R}^1 \text{SO} \]

\[ \text{R}^2 \text{S} \rightarrow \text{R}^2 \text{SO} \]

\[ \text{R}^1 \text{N} \rightarrow \text{R}^1 \text{NO} \]

\[ \text{R}^2 \text{N} \rightarrow \text{R}^2 \text{NO} \]

The further fragmentation of C and D is in full accordance with the proposed sequence. Only when R\textsuperscript{2} is mesityl [(V)—(VII)] is the transition B \rightarrow D an important one, presumably, because the ion R\textsuperscript{2}O\textsuperscript{+} is stable in that case.


Scheme 1

Scheme 2

Scheme 3

Scheme 4

Table 2

Relative abundance of major peaks of aryl arylsulphinyl sulphones

<table>
<thead>
<tr>
<th>Compound</th>
<th>(VIIa)</th>
<th>(VIIb)</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>
</tr>
</thead>
<tbody>
<tr>
<td>Ion M</td>
<td>0.3</td>
<td>0.3</td>
<td>1</td>
<td>9</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1-5</td>
<td></td>
</tr>
<tr>
<td>M - OH</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M - SO</td>
<td>61</td>
<td>24</td>
<td>1</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>RCSO</td>
<td>13</td>
<td>6</td>
<td>6</td>
<td>22</td>
<td>11</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>RCS</td>
<td>82</td>
<td>44</td>
<td>42</td>
<td>54</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>RCO</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>88</td>
<td>88</td>
<td>88</td>
<td>88</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>RSO</td>
<td>8</td>
<td>6</td>
<td>1</td>
<td>11</td>
<td>17</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>RS</td>
<td>27</td>
<td>32</td>
<td>5</td>
<td>11</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>R⁴</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td></td>
</tr>
</tbody>
</table>

* R⁴-containing ion identical with corresponding R¹-containing ion.  * In this case the fragment ion R⁵SO⁺ is masked by R⁴CO⁺.

* Metastable observed for the transition from the molecular ion to the indicated fragment ion.
The formation of the ions R\(^1\)C=O\(^+\) and R\(^1\)C=S\(^+\) most likely proceeds via an intermediate oxathiiran \(P\), as suggested for diaryl sulphines.\(^1\) Remarkably, when R\(^1\) was mesityl only fragmentation to R\(^1\)C=S\(^+\) was observed.

The arylthio sulphines also show minor direct fragmentations to the ions R\(^1\)CSO\(^+\), R\(^1\)CS\(_2\)O\(^+\), R\(^2\)SO\(^+\), and R\(^2\)R\(^2\)SO\(^+\).

A striking difference between the phenyl phenylthio sulphines (I) and the sulphones (II)—(VII) in which the ortho-positions of at least one aryl ring are blocked by methyl groups, is the \(M - OH\) fragmentation. Since the sulphones (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 sulphone\(^1\) which supports the suggested scheme.

The \(M - OH\) fragmentation in the sulphones with R\(^1\) = mesityl [(II)—(V)] proceeds in a fashion similar to that described for mesityl phenyl sulphones\(^1\) (Scheme 3). The transition H \(\rightarrow\) 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 \(Z\)-sulphones (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 \((Z \leftrightarrow E or vice versa)\) is likely to occur prior to fragmentation.

\textit{Aryl Arylsulphonyl Sulphines.—}The mass spectral features of these types of sulphines are summarized in Table 3. Phenyl phenylsulphonyl sulphone (XIVa) shows a prominent \(M - SO_3\) peak at \(m/e\) 214, as observed for the phenylsulphonyl 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 sulphones (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 arylsulphonyl mesityl sulphines.

Interestingly, almost no fragmentation to R\(^2\)SO\(_3\)\(^+\) was observed, but instead the formation of R\(^2\)SO\(^+\) ions was of considerable importance. A \(1,2\)-shift of the \(sp^2\)-hybridized carbon atom of the sulphone 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 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 (RC=SO\(^+\)) in preference to that of


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

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^1CS^1 and R^1CSO^1 in Tables 1—3 was made by means of the isotopic abundance of ^16O (0·2%) and ^34S (4·2%).

The sulphines (I), (II), (VIII), (IX), (XIV), and (XV) were prepared as described previously. 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. The yields (%) and m.p.s (°C) of the sulphines are (IIIa), 52, m.p. 102—104; (IIIb), 27, m.p. 117—118; (Xa), 59, m.p. 131—132; (Xb), 60, m.p. 132—134; (XVIa), 51, m.p. 155—156; (XVIb), 77, m.p. 178—180; (IVa), 46, m.p. 27—28; (IVb), 48, m.p. 124—125; (Xla), 32, m.p. 78—81; (Xlb), 20, m.p. 111—112; (VIIa), 81, m.p. 105—105; (VIIb), 65, m.p. 165—169; (Va), 80, m.p. 129—130; (Vb), 1, m.p. 197—199; (XIIa), 47, m.p. 144—145; (XIIa), 56, m.p. 166—167; (Vla), 60, m.p. 62—63; (VIIb), 16, m.p. 101—103; (XIIa), 14, m.p. 77—79; and (VIIa), 84, m.p. 107—108. Correct combustion analyses were obtained for all sulphines. Analytically pure samples were used for mass spectrometric analyses.

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