

Skeletal Rearrangement Processes of Organic Sulphur Compounds on Electron Impact¹

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ARYL SULPHONES,^{2,3} sulphoxides,^{2a,3} sulphides,⁴ di-
sulphides,⁵ sulphinylamines,⁶ sulphonylhydrazones,⁷

aliphatic thioesters,⁸ mercaptoesters,⁹ and aryl-
sulphonamides¹⁰ undergo a series of skeletal

TABLE

| Compound | Rearrangement process | Relative abundance of rearrangement ion (%) | |
|--|---|---|-----------|
| R·CS·CH ₂ ·COPh | | | |
| (I) R = Me | M—CO | 3 | |
| (II) R = Ph | M [*] —CO | 3 | |
| R·C ₆ H ₄ ·SO ₂ Cl | | | |
| (III) R = H | M—SO ₂ | 3 | |
| (IV) R = <i>p</i> -Me | M—SO ₂ | 5 | |
| (V) R = <i>o</i> -NO ₂ | { M—SO ₂ M—SO ₂ —NO ₂ | { 2 14 | |
| R·SO ₂ ·NHR ¹ | | | |
| R | R ¹ | | |
| (VI) Ph | H | M [*] —SO ₂ | 37 |
| (VII) <i>p</i> -tolyl | H | M [*] —SO ₂ | 15 |
| (VIII) Ph | <i>o</i> -tolyl | M [*] —SO ₂ | 3 |
| (IX) Ph | SO ₂ Ph | { M [*] —SO ₂ M [*] —SO ₂ —SO ₂ | { 25 3 |
| R·CS·CH ₂ ·CO ₂ R ¹ | Formation of MeO ⁺ | | |
| R | R ¹ | | |
| (X) Me | Et | MeO ⁺ | 64 |
| (XI) Me | Pr ^a | MeO ⁺ | 100 |
| (XII) Me | Bu ^a | MeO ⁺ | 38 |
| (XIII) Ph | Et | MeO ⁺ | 82 |
| (XIV) MeCS·CH-(CO ₂ Et) ₂ | MeO ⁺ | | 100 |
| (XV) S = C(CH ₂ ·CO ₂ Et) ₂ | MeO ⁺ | | 100 |

rearrangement processes on electron impact. As a continuation we have investigated the skeletal rearrangement processes which are observed in the mass spectra of some further sulphur compounds, including sulphonyl chlorides, β -thioketo-esters, and some simple arylsulphonamides. These processes are summarised in the Table. The compositions of all rearrangement ions have been established by exact mass measurements and the presence of an appropriate metastable ion for a process is indicated by an asterisk.

The losses of carbon monoxide from the molecular ions of (I) and (II) were not expected, as the analogous β -diketones do not contain M—CO ions.¹¹ This is a further illustration of the role sulphur may play in rearrangement processes. The loss of SO₂ from the molecular ions of the sulphonyl chlorides (III—V) and the sulphonamides (VI—IX) exactly parallel the M—SO₂ processes in the spectra of aryl sulphones^{2,3} and sulphonylhydrazones.⁷

The MeO⁺ ions [*m/e* 31, base peak in the spectra of (XI), (XIV), and (XV)] produced by the β -thioketo-esters on electron impact, must owe their genesis to participation between the C=S and the ester groups, as similar ions are not generally observed in the spectra of β -ketoesters^{9,12} (an exception is the spectrum of allyl-acetoacetate⁸ where the MeO⁺ peak constitutes 24% of the base peak). Labelling studies are in progress to examine the formation of the MeO⁺ ion.

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¹ Part XX in the series "Electron Impact Studies". Part XIX, cf. ref. 9b.

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