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SKELETAL REARRANGEMENT REACTIONS IN SULPHIDES, DISULPHIDES, SULPHOXIDES AND SULPHONES UPON ELECTRON IMPACT

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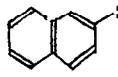
In order to facilitate structure elucidation by mass spectrometry, it is necessary that skeletal rearrangement processes which occur on electron impact be well documented. Recently, such rearrangement processes have been demonstrated to occur in some ketones (1,2), esters (2-5), thioesters (6) and carbamates (7). We now report the occurrence of some skeletal rearrangement reactions in sulphides, disulphides, sulphoxides and sulphones upon electron impact.

The rearrangement reactions which occur in the sulphides (I-V), the disulphides (VI, VII), the sulphoxide (VIII) and the sulphone (IX) are summarised in the table. The compositions of all rearrangement ions have been established by exact mass measurements.

Rearrangement Ions in the Mass Spectra of Some Sulphides, Disulphides, Sulphoxides and Sulphones

Compound	Rearrangement Ion	R.A.‡
$C_6H_5SCH_3$ (I)	M-HS (*)	26
 (II)	M-HS (*)	13
$C_6H_5SC_6H_5$ (III)	M-S	4
	M-HS	6
	M-H_2S	9
$C_6H_5CH_2SC_6H_5$ (IV)	M-H_3S	4
$C_6H_5CH_2SCH_2C_6H_5$ (V)	M-S	2
$C_6H_5SSC_6H_5$ (VI)	M-S (*)	16
	M-HS (*)	15
	M-2S	11
$C_6H_5CH_2SSCH_2C_6H_5$ (VII)	M-S	19
	M-2S	12
	M-CH_2S	10
$C_6H_5CH_2\overset{\overset{O}{\|}}{S}CH_2C_6H_5$ (VIII)	M-SO	30
$C_6H_5-\overset{\overset{O}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}-C_6H_5$ (IX)	M-SO_2	5

‡ R.A. = Relative Abundance as % of the base peak.

Those cases in which the rearrangement fragment is formed in a one-step process from the molecular ion, as indicated by an appropriate metastable peak, are indicated in the table by an asterisk (*). Generally speaking, the sulphides or disulphides may eliminate a sulphur atom (with or without additional hydrogen atoms) and the terminal groups then combine. The sulphoxide (VIII) and the sulphone (IX) behave analogously.

Additional exact mass measurements establish that rearrangement fragments occur at lower masses, and these may be decomposition products of the primary rearrangement ions, e.g., m/e 152 (8%, $C_{12}H_8^+$) and m/e 153 (7%, $C_{12}H_9^+$) from IX.

Although some sulphones are known to rearrange thermally with elimination of sulphur dioxide at relatively high temperatures,[8] the possibility of thermal rearrangement has been excluded in the case of IX by obtaining the spectrum by the direct inlet procedure at approximately 60°C.

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