Skeletal-rearrangement Fragments in the Mass Spectra of β-(Alkylthio)propionic Acids and Esters[1]

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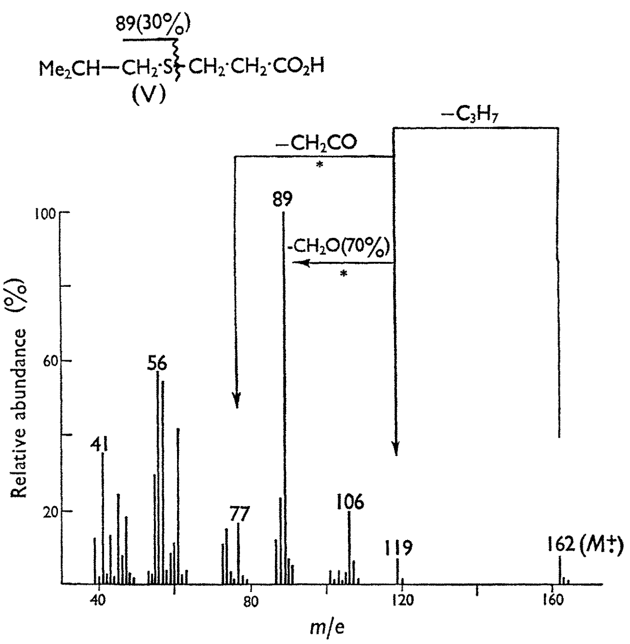
SKELETAL-REARRANGEMENT fragments are found in the spectra of many sulphur compounds.[2] Migration of groups to carbonium-ion centres[3] occurs when β-thioxo-esters are subjected to electron impact.[4] We report the occurrence of specific rearrangements which involve migrations to both carbonium-ion centres and to charged sulphur.

The spectra of the β-alkylthiopropionic acid derivatives (I)—(VII) show rearrangement ions produced by the processes $M - R^{1\cdot} - CH_2{\cdot}CO$ ($a \rightarrow c$) and $M - R^{1\cdot} - CH_2O$ ($a \rightarrow e$). The abundances of these ions (Table) increase with the size of the alkyl side chain. These rearrangement processes are illustrated in the spectrum (Figure) of (V). The compositions of all ions have been established by exact mass measurement. Appropriate metastable peaks substantiate process $d \rightarrow e$ but not process $a \rightarrow b$ or $b \rightarrow c$.

In contrast, neither of these rearrangement processes are observed in the spectra of the esters (VIII)—(XII). A different rearrangement, $M - R^1CH_2{\cdot} - CH_2{\cdot}O$ ($f \rightarrow i$), can be seen in these spectra, with process $h \rightarrow i$ (but generally not $f \rightarrow g$) substantiated by metastable peaks. The abundance of i depends upon both the ease of cleavage of the C–S bond ($f \rightarrow g$) and the extent to which the ion g retains the charge.

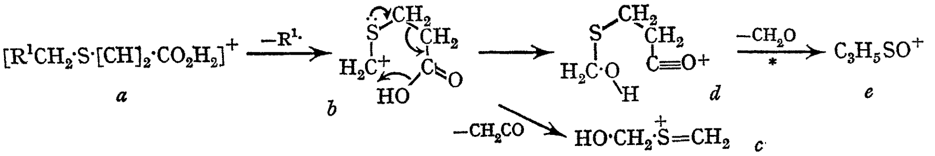
The bond-forming and elimination reactions outlined above are supported by deuterium-labelling studies for (II) and (X).

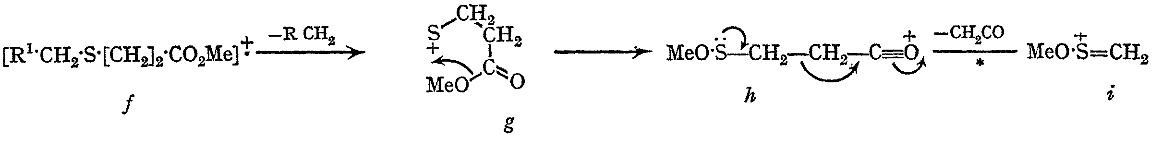


FIGURE

Relative abundances of rearrangement ions in the spectra of (I)—(XI)

$R^1CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2R^2$			$M - R^{1\cdot}$ ($a \rightarrow b$)	$(M - R^{1\cdot}) - CH_2CO$ ($b \rightarrow c$)	$(M - R^{1\cdot}) - CH_2O$ ($d \rightarrow e$)	$M - R^1CH_2{\cdot}$ ($f \rightarrow h$)	$(M - R^1CH_2{\cdot}) - CH_2CO$ ($h \rightarrow i$)
	R^1	R^2					
(I)	H	H				4	
(II)	Me	H	2	4	3	2	
(III)	Et	H	3	5	14	3	
(IV)	Pr^n	H	14	13	60	4	
(V)	Pr^i	H	8	16	70	2	
(VI)	$CH_2{=}CH$	H	1	3	12	30	
(VII)	Ph	H				1	
(VIII)	Me	Me	1			19	12
(IX)	Pr^n	Me	21			50	13
(X)	$CH_2{=}CH$	Me				61	23
(XI)	$CH_2{=}CH$	Et				44	12
(XII)	Ph	Me				9	3





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[1] Previous paper in this series, C. Nolde, J. Ø. Madsen, S.-O. Lawesson, and J. H. Bowie, *Arkiv Kemi*, submitted for publication.

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[4] J. O. Madsen, S.-O. Lawesson, J. H. Bowie, and R. G. Cooks, *Chem. Comm.*, 1968, 697.