Skeletal Rearrangement of Mercapto-esters upon Electron Impact[1]

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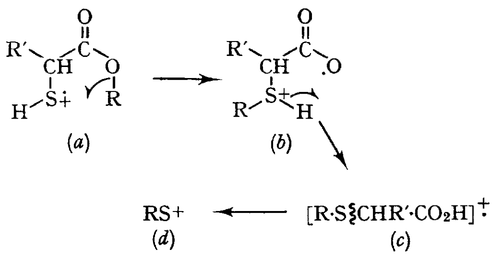
SKELETAL-REARRANGEMENT ions have been observed previously in the mass spectra of a variety of sulphur compounds.[2] We report the general occurrence of RS^+ ions (*d*) in the spectra of a series of mercapto-esters. When the substituent attached to sulphur is hydrogen, the rearranged ions are produced in a one-step process from the molecular ion (Table). The composition of all rearranged ions have been established by exact mass measurements. In general, RS^+ ions are more prominent in those spectra where R is able to stabilise the cation (*e.g.*, allyl and benzyl). It is important to note that when the substituent attached to sulphur is acetyl, no evidence is available to indicate that the rearranged ion is



TABLE

Compound	Rearranged ion (RS+) (*m/e*)	Relative abundance of RS+ (%)	Metastable ion for process *M* → RS+ Calc.	Found
$HS\cdot CH_2\cdot CO_2R$				
R = Et	61	3	31·0	—
= Pr^n	75	12	42·0	42·0
= Pr^i	75	12	42·0	42·0
= Bu^n	89	13	53·5	53·4
= Bu^s	89	17	53·5	53·6
= iso-C_5H_{11}	103	6	65·4	65·4
= Cyclohexyl	115	12	76·8	77·0
= CH_2Ph	123	28	83·2	83·1
$HS\cdot CH_2\cdot CH_2\cdot CO_2\cdot CH_2Ph$ ..	123	16	77·2	77·3
$HS\cdot CHMe\cdot CO_2R$				
R = Pr^i	75	16	38·0	38·0
= allyl	73	66	36·5	36·4
= CH_2Ph	123	46	77·2	—
$\underset{\text{S·CO·Me}}{\underset{\vert}{\text{Me·CH}}}\text{·CO}_2\text{Pr}^i$	75	3	29·6	—
$\underset{\text{S·COMe}}{\underset{\vert}{\text{MeCH}}}\text{·CO}_2\text{·CH}_2\text{Ph}$	123	12	60·9	—

produced in a one-step process. A possible mechanism (for the general case *a*, *a* → *d*) is suggested to explain this rearrangement process. This process limits both the prediction of fragmentation modes and the application of the 'element-mapping' technique[3] for this class of compound.

(*Received, February* 13*th*, 1967; *Com.* 140.)

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[1] Previous paper in this series, J. H. Bowie, R. G. Cooks, and G. E. Lewis, *Chem. Comm.*, 1966, 284

[2] J. H. Bowie, F. C. V. Larsson, G. Schroll, S.-O. Lawesson, and R. G. Cooks, *Tetrahedron*, in the press; J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, 1966, **22**, 3515, and references therein; J. O. Madsen, S.-Ø. Lawesson, A. M. Duffield, and C. Djerassi, *J. Org. Chem.*, in the press; E. Bach, A. Kjær, R. H. Shapiro, and C. Djerassi, *Acta Chem. Scand.*, 1965, **19**, 2438; J. B. Thomson, P. Brown, and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 4049.

[3] K. Biemann, P. Bommer, D. M. Desiderio, and W. J. McMurray in "Advances in Mass Spectrometry," ed. W. L. Mead, The Institute of Petroleum, London, 1966, Vol. 3, pp. 639–653.