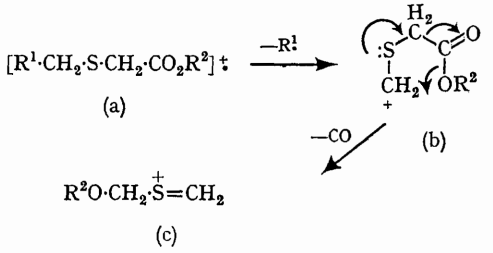
Skeletal-rearrangement Fragments in the Mass Spectra of Substituted Thioglycollic Acids and Esters[1]

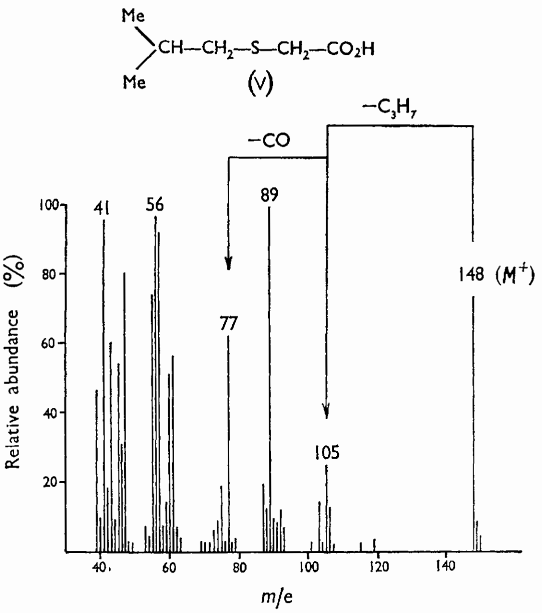
By J. Ø. MADSEN and S.-O. LAWESSON*
(*Department of Organic Chemistry, Aarhus University,* 8000 *Aarhus C, Denmark*)
J. H. BOWIE*
(*Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia,* 5001)
and R. G. COOKS
(*University Chemical Laboratory, Lensfield Road, Cambridge*)

THE presence of skeletal-rearrangement fragments in the mass spectra of organic compounds is currently exciting much interest.[2] Rearrangement ions are found in the spectra of a variety of sulphur compounds.[3] We report the occurrence of a novel rearrangement, which probably involves migration to a carbonium-ion centre.

The spectra of the thioglycollic acid derivatives (I—XII) contain ions of the general formula, $R^2C_2H_4SO^+$. The abundances of these species are recorded in the Table and they range from 3% (for VIII) to 63% (for V). The compositions of all ions have been established by high-resolution measurements. The rearrangement process is generally more pronounced in the spectra of the acids ($R^2 = H$) than the esters ($R^2 = Me$), and occurs when the thioglycollic acid (or ester) is of type $R^1CH_2{\cdot}SCH_2{\cdot}CO_2R^2$.



The majority of spectra contain $M - R^{1\cdot}$ ions as well as the rearrangement ions $[(M - R^{2\cdot}) - CO]$. Although the $M - R^{1\cdot}$ process is not substantiated



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

Compound $R^1CH_2{\cdot}SCH_2{\cdot}CO_2R^2$			$M - R^{1\cdot}$ ($^+CH_2SCH_2CO_2R^2$)		$(M - R^{1\cdot}) - CO$ ($R^2OCH_2{}^+S{=}CH_2$)		
	R^1	R^2	*m/e*	(%)	*m/e*	(%)	Metastable ion
(I)	Me	H	105	2	77	13	
(II)	CD_3	H	,,	3	,,	9	
(III)	Et	H	,,	6	,,	34	
(IV)	Pr^n	H	,,	10	,,	38	
(V)	Pr^i	H	,,	25	,,	63	
(VI)	$CH_2{=}CH$	H	,,	0	,,	4	
(VII)	Ph	H	,,	0	,,	0	
(VIII)	Me	Me	119	0	91	3	
(IX)	Et	Me	,,	3	,,	6	69·4
(X)	Pr^n	Me	,,	5	,,	7	69·4
(XI)	Pr^i	Me	,,	13	,,	18	69·5
(XII)	Ph	Me	,,	0	,,	0	

by metastable ions, loss of carbon monoxide from $M - R^{1\cdot}$ is definitely established by appropriate metastable ions, in three cases (IX—XI). In these cases the probable mechanism is (a) → (c). Other examples of migration to carbonium ion centres have been reported.[2,4] Even though there are no M — CO ions in many of the spectra [that of (I) contains a 1% M — CO ion], a mechanism involving migration of R^2O to sulphur followed by β-cleavage (to sulphur) cannot be precluded for those spectra where metastable peaks do not substantiate the process (b) → (c).

(*Received, April* 16*th*, 1968; *Com.* 458.)

---

[1] Previous paper in this series: J. H. Bowie, G. E. Lewis, B. Søgaard Larsen, S.-O. Lawesson, and G. Schroll, *Austral. J. Chem.*, in the press.

[2] P. Brown and C. Djerassi, *Angew. Chem.*, 1967, **79**, 481.

[3] F. Duus, P. Madsen, S.-O. Lawesson, J. H. Bowie, and R. G. Cooks, *Arkiv Kemi*, 1968, **28**, 423 (and references therein).

[4] R. G. Cooks and D. H. Williams, *Chem. Comm.*, 1967, **51**.