Skeletal Rearrangement on Electron Impact[1]

By J. H. Bowie

(*Department of Organic Chemistry, University of Adelaide, South Australia*)

R. G. Cooks

(*University Chemical Laboratory, Lensfield Rd., Cambridge*)

S.-O. Lawesson, P. Jakobsen, and G. Schroll

(*Department of Organic Chemistry, Aarhus University, Aarhus C., Denmark*)
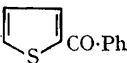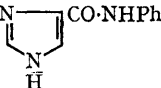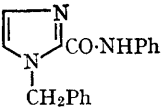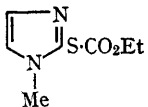
The loss of CO and CO_2 with associated skeletal rearrangement has been shown to occur when certain organic compounds containing carbonyl groups are subjected to electron impact.[2] This is an important feature of mass spectrometry and must be carefully documented because of its obvious relevance to the "element mapping" technique.[3]

Further examples of skeletal rearrangements involving the loss of CO or CO_2 are listed in the Table. The compositions of all rearrangement ions have been established by exact mass measurements and in six cases the decompositions are definitely confirmed by appropriate metastable ions (indicated by the presence of an asterisk). In the case of (VII), [18]O labelling establishes that the CO lost comes from the ketone moiety, in agreement with similar loss of the ketone group in both methyl and ethyl acetoacetate.[4] It is possible that similar eliminations occur in compounds (IV—VI). The possibility of thermal rearrangement in the case of (XII) has been excluded by obtaining the spectrum by the direct inlet procedure at 60°.

Many of the rearrangement ions mentioned fragment further upon electron impact, and full details of all spectra will be published later.

TABLE

Compound	Rearranged ion	Relative abundance (% of base peak)	Migrating group
(I) $MeCO_2 \cdot CH_2 \cdot CH = CH_2$	$\begin{cases} M - CO \\ M - CHO \end{cases}$	2 2	Me
(II) $MeCO_2 \cdot CH_2 \cdot C \equiv CH$	$M - CO$	4	Me
(III) $PhCO_2 \cdot CH_2 \cdot CH = CH_2$	$M - CO_2H$	6	
(IV) $MeCO \cdot CH_2 \cdot CO_2Pr^n$	$M - CO$	2	Me
(V) $MeCO \cdot CH_2 \cdot CO_2Pr^i$	$M - CO$	3	Me
(VI) $MeCO \cdot CH_2 \cdot CO_2 \cdot CH_2 \cdot CH = CH_2$	$M - CO$	2	Me
(VII) $MeCO \cdot CH_2 \cdot CO_2Ph$	$M - CO$ (*)	7	Me
(VIII) $MeCO \cdot NH \cdot COMe$	$M - CO$ (*)	24	Me
(IX) thiophene ring–$CO \cdot Ph$	$M - CO$ (*)	8	Ph
(X) imidazole (NH) ring–$CO \cdot NHPh$	$M - CO$ (*)	2	PhNH
(XI) pyrazole (CH_2Ph on N) ring–$CO \cdot NHPh$	$\begin{array}{l} M - CO \ (*) \\ M - C_4H_3N_2O \ (*) \end{array}$	5 37	PhNH
(XII) pyrazole (Me on N) ring–$S \cdot CO_2Et$	$M - CO_2$	4	Et

[1] Previous paper in this series: I. R. C. Bick, J. H. Bowie, and G. K. Douglas, *J. Org. Chem.*, submitted for publication.

[2] J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Comm.*, 1965, 403; J. H. Bowie, R. Grigg, S.-O. Lawesson, P. Madsen, G. Schroll, and D. H. Williams, *J. Amer. Chem. Soc.*, 1966, **88**, 1699; J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll, and S.-O. Lawesson, *Tetrahedron*, submitted for publication; M. Fischer and C. Djerassi, *Chem. Ber.*, 1966, **99**, 750; W. H. McFadden, K. L. Stevens, S. Meyerson, A. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, 1965, **69**, 1742; P. Natalis and J. L. Franklin, *ibid.*, p. 2935; P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, in the press.

[3] K. Biemann, *Pure Appl. Chem.*, 1964, **9**, 95; K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1964, 1725.

[4] J. H. Bowie, S.-O. Lawesson, G. Schroll, and D. H. Williams, *J. Amer. Chem. Soc.*, 1965, **87**, 5742.