Unusual Fragments of Some Substituted β-Lactams Under Electron Impact[1]

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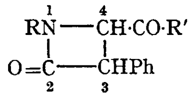
APART from the mechanistic interest inherent in molecular rearrangement, skeletal rearrangement under electron impact is of particular significance in mass spectroscopy (specially in the technique of "element mapping"[2]) for structure determination. We report here several unusual modes of fragmentation—including skeletal rearrangement—observed in the mass spectra of β-lactams of type (I).

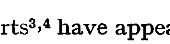


(I)

	R	R′	
a;	Ph	Ph	
b;	p-Me-C_6H_4	Ph	
c;	p-Br-C_6H_4	Ph	
d;	p-MeO-C_6H_4	p-Br-C_6H_4	
e;	Ph	Ph	2-[^{13}C]
f;	Ph	Ph	3,4-[$^2H_2$]
g;	Ph	Ph	[^{15}N]

These β-lactams showed strong peaks at $(M-44)^+$ [6% for (Ia)]* and $(M-45)^+$ [10% for (Ia)].* They also exhibited metastable peaks corresponding to the transition $(M-44)^+ \rightarrow (M-45)^+$. The only reasonable fragment of m/e 44 that could be lost from (I) is CO_2. This was verified by a high-resolution mass spectrum of (Ib). The peak at $(M-28)^+$ produced by the expulsion of CO from the molecular ion was weak [0·5% for (Ia)].*

To determine which carbon was lost in the CO_2 fragment, the labelled β-lactam (Ie) (^{13}C-level *ca.* 56%) was prepared. Its mass spectrum showed the same twin peaks (m/e 283 and 282) that appeared in the spectrum of (Ia). Therefore, the lactam carbonyl carbon (C-2) must form a direct link with the oxygen of the keto-carbonyl and be lost as CO_2 under electron impact. It may be noted that with some distortion of the β-lactam ring, it is possible to bring C-2 within bond-forming distance of the keto-oxygen in the side-chain even though they are separated by several bonds. However, it is also possible that the four-membered ring undergoes scission first and then rearranges to form a heterocycle, such as (II), containing the ·CO·O· moiety. Whatever be the precise mechanism, the fact remains that two functional groups separated by several bonds are undergoing interaction and producing a fragment in a significant amount although no less than four bonds must be broken in that process. It may be noted that the peak at m/e 91 in the spectrum of (Ia) is shifted in part to m/e 93 in the spectrum of (If) indicating the formation of the fragment $[C_7H_7]^+$ to be expected from (II).



(II)

Recently reports[3,4] have appeared about the loss of carbon dioxide under electron impact from phthalimides involving the interaction of two

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* Abundance relative to the base peak.

carbonyls joined to the same nitrogen. The linking of a carbonyl group with a "remote"[5] alkoxy-group in the mass spectrometer has also been observed.[5]

The dideuterated derivative (If) also gives rise to $(M-44)^+$ and $(M-45)^+$ ions. Evidently there is a loss of a proton from one of the aromatic rings. A similar loss of an aromatic proton was observed by us in the mass-spectral fragmentation of some amidines.[1] The effect of nuclear substituents on this ready loss of an aromatic proton in different types of compounds is under study.

The mass spectrum of (I) shows a very minor peak (<0·1%)* at *m/e* 312 $(M-15)$ although there is no possibility of the formation of a methyl group by hydrogen migration. Since this peak appears at *m/e* 313 $(M-16)$ in the spectrum of the dideuterated compound (If) and at *m/e* 312 $(M-16)$ in the spectrum of the ^{15}N-derivative (Ig), the fragment lost from the molecular ion must be N–H. Such a loss is possible only if the *N*-aryl group migrates and is replaced by a proton. Previously, we have reported instances of aryl migration in aromatic amides.[6] The presence of a peak (6%)* at *m/e* 179 of composition $C_{14}H_{11}$ (high-resolution spectrum) in the mass spectrum of (Ib) is further evidence for aryl migration in these β-lactams.

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* Abundance relative to the base peak.

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