Rationalisation of a Variety of Electron-Impact Induced Rearrangements in Ions

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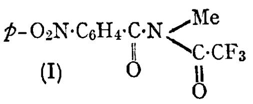
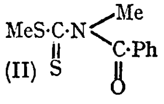
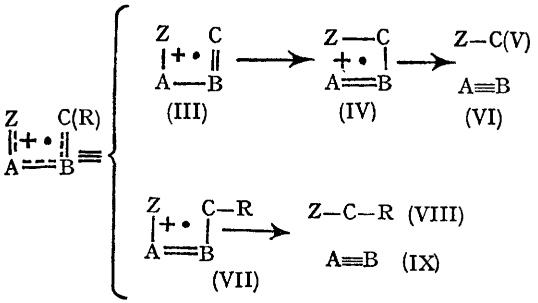
THE manual, and ultimately automated, interpretation of mass spectra would be simplified by classification of skeletal rearrangement processes. Here, we describe one such class of reactions in conjugated π-systems.

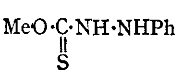

(I)

$p\text{-}O_2N\cdot C_6H_4\cdot\underset{\underset{O}{\|}}{C}\cdot N{<}^{Me}_{\underset{\underset{O}{\|}}{C}\cdot CF_3}$


(II)

$MeS\cdot\underset{\underset{S}{\|}}{C}\cdot N{<}^{Me}_{\underset{\underset{O}{\|}}{C}\cdot Ph}$




(X)

$MeO\cdot\underset{\underset{S}{\|}}{C}\cdot NH\cdot NHPh$

Electron-impact induced aryl migration from nitrogen to oxygen in amides has been described by us,[1] and we have now observed a corresponding aroyl migration in the imide (I) to give an ion at *m/e* 110 ($C_3H_3F_3N$). Similarly, the loss of carbon dioxide from cyclic imides [2a,3] may be regarded as occurring after aroyl migration, again from nitrogen to oxygen. A corresponding aryl migration can be seen in *N*-phenylphthalimide, which gives a weak ion at *m/e* 130 (C_8H_4NO). In *N*-anilinophthalimide, a migration of an anilino-group must occur in the formation of an ion at *m/e* 130 (C_8H_4NO). Aroyl migration from nitrogen to sulphur has been observed[4] in the thiocarbamate (II), and migration of a thioaroyl group from nitrogen to sulphur, followed by ejection of CS_2, in *N*-methylthiophthalimide has been reported.[5]

As a formal generalisation of these and other results, one may consider that rearrangement occurs in the basic π-system (III; A,B,C providing p_π orbitals), in which Z represents any grouping also having a p_π orbital, *e.g.* methylene,[6] aryl, aroyl,[2a,3,4] thioaroyl,[5] anilino, sulphonyl,[6] and tropylium[6] groups. Apart from hydrogen, which constitutes a special case,† no migration of a group not possessing a p_π oribtal has been observed. In the

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† Rearrangements through cyclic transition states, involving hydrogen transfer, are relatively common. (K. Biemann in "Mass Spectrometry, Organic Chemical Applications", McGraw Hill, New York, 1962, p. 77; F. W. McLafferty in "Mass Spectrometry of Organic Ions", Academic Press, New York, 1963, p. 331).

products [(V), (VI)] of fragmentation of the rearranged ion (IV), ZC is normally ejected as a neutral moiety with AB bearing the positive charge. Ejection of an aryloxy-radical from aromatic azoxy-compounds[7] may also fit this classification.

Phenyl migration in the closely similar π-system (VII) to give the charged fragment (VIII) and the neutral fragment (IX) can be seen in the mass spectra of benzophenone oxime,[2b] *O*-methylacetophenone oxime,[6] and 1,1-dicyano-2-phenylethylene.[8] In system (III), where A is also bonded to hydrogen, migration both of H and Z to C can be observed, as for example in the thiocarbamate (X) which ejects C_2H_3NO[4] and *N*-trifluoroacetylaniline, which yields an ion corresponding to phenol; this rearrangement has been considered to proceed *via* the tautomer (VII; $R = H$).[4]

Evidence for the participation of an electronically excited four-centre transition state, at least in some cases, has been presented elsewhere,[1,3,9] and supplements the five- and six-centre excited-state reactions already described by us.[10]

The extent to which skeletal rearrangement processes can be observed in the systems [(III), (VII)] is partly governed by the ease of competing simple cleavage reactions so that in some cases no rearrangement is found.[6,11] However, where the basic four-centre π-system [(III), (VII)] exists in a molecule, rearrangement of the molecular ion should be sought.

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[3] T. W. Bentley and R. A. W. Johnstone, *J. Chem. Soc.* (*C*), in the press.

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[6] Unpublished results from this laboratory.

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[10] R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc.* (*C*), in the press.

[11] C. Nolde, S.-O. Lawesson, J. H. Bowie, and R. G. Cooks, *Tetrahedron*, 1968, **24**, 1051.