Rearrangement Ions in the Mass Spectrum of Thionylaniline

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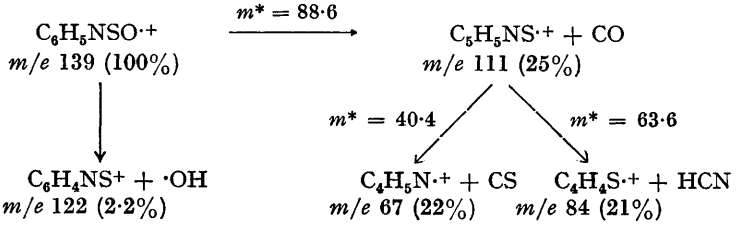
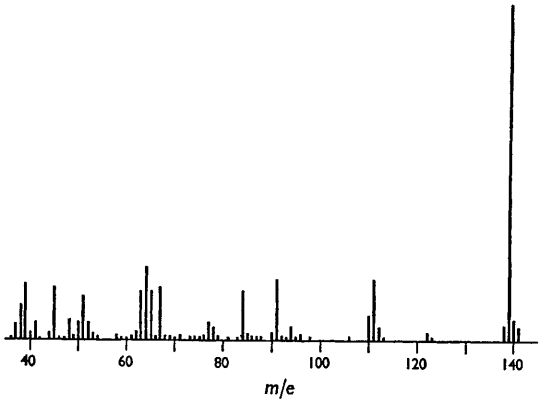
THE mass spectrum of thionylaniline was obtained on an A.E.I. MS9 mass spectrometer and is shown in the Figure. Accurate mass measurement and "metastable peaks" (m^*) indicated that a large number of the fragment ions arose as the result of intramolecular rearrangements. The sequence discussed here is summarised below and a suggested mechanism is shown in the Scheme.



The symbolism of Budzikiewicz *et al.*,[1] and Shannon[2] is used throughout.

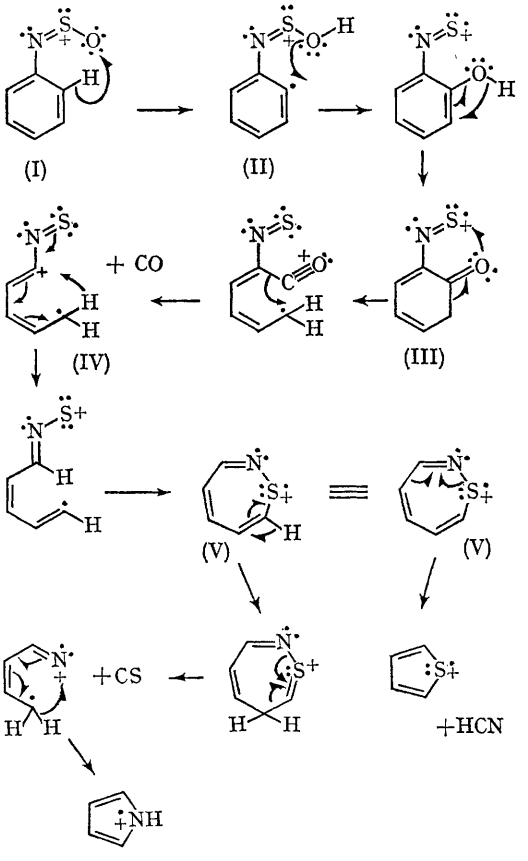


FIGURE

If the structure of the molecular ion is formalised as (I), an *ortho*-hydrogen atom can migrate to the oxygen *via* a six-membered transition state, to form the hydroxyl species (II). The hydroxyl group in (II) can be split off to give the ion at m/e 122 or return to the aromatic ring, when a rearrangement to the keto-form (III) can be visualised; loss of carbon monoxide from such a structure is well known.[3]

An analogous six-membered intermediate and hydroxyl migration has been postulated to explain the loss of carbon monoxide from the molecular ion of 1-nitronaphthalene.[4]

The product ion (IV) can readily eliminate "nitric sulphide" to leave the $C_5H_5^+$ ion at m/e 65 (23%) but can also fragment by loss of either hydrogen cyanide or carbon monosulphide. To explain this observation it is suggested that (IV) can



rearrange to the seven-membered ring (V) from which either loss is straightforward. The most stable structures of the ions of *m/e* 84 and 67 would be those of the molecular ions of thiophen and pyrrole, respectively.

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[1] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, 1964, pp. xi, xii.
[2] J. S. Shannon, *Proc. Roy. Austral. Chem. Inst.*, 1964, **31**, 323.
[3] J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1861.
[4] J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch*, 1966, **21a**, 210.