Mass Spectra of Some 3-Amino-1,2,4-triazines *N*-Oxides

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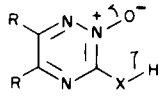
We have recently (1) described the syntheses of various 1,2,4-triazine 1- and 2-oxides. This study showed that 3-unsubstituted and 3-methoxy-1,2,4-triazines are oxidized at *N*-1, while 3-amino-1,2,4-triazines afford the *N*-2 oxides as major products.

As a result of these conclusions, the interpretation of the mass spectra of some erroneously assigned 1,2,4-triazine *N*-oxides now need to be reinterpreted. Thus, the *N*-oxides of 5,6-diphenyl-3-amino-, and 3-methoxy-1,2,4-triazines, which were described as the 2-oxides, are in fact, the 1-oxides, and visa versa (2).

The proposed fragmentation of the presumed 1-oxides was predicated upon the following process:



X = -NH, -OCH_2-

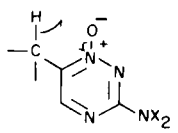
A

This was used to account for the fragmentation involving the loss of a m/e 17 moiety.

In order to account for the loss of 17 mass units in these 2-oxides, it became necessary to prepare and examine the various -ND_2 derivatives.

We now wish to briefly report the results of these mass spectral studies.

The 5,6-dimethyl, as well as the 5,6-diphenyl 3-ND_2-1,2,4-triazine 1-oxides, fragment by loss of 17 mass units, as do the corresponding NH_2 derivatives. Thus, the proposed McLafferty rearrangement does *not* involve the amino functional group and one can conclude that the proton arises from the substituent in the 6-position by the following process:



X = H,D

B

On the other hand, an examination of the mass spectrum of 5,6-dimethyl- and 5,6-diphenyl-3-ND_2-1,2,4-triazine 2-oxide affords a fragment ion resulting from the loss of 18 mass units in accordance with process A.

Thus, the discrepancy of the mass spectral interpretations of the 1,2,4-triazines *N*-oxides are now cleared up and it is now obvious that the loss of 17 mass units from these *N*-oxides cannot be used as a diagnostic test for establishing the site of *N*-oxidation in these compounds.

The remaining mass spectral features follow the patterns described by Sasaki, Minamoto, Nishikama and Shima (2).

REFERENCES

(1) W. W. Paudler and T. K. Chen, *J. Org. Chem.*, 36, March (1970).

(2) T. Sasaki, K. Minamoto, M. Nishikama and T. Shima, *Tetrahedron*, 25, 1021 (1969).