

Identification of the *N*-Oxide Group by Mass Spectrometry

By T. A. BRYCE and J. R. MAXWELL

(Department of Chemistry, The University, Glasgow, W.2)

It is difficult to detect the presence of an *N*-oxide function in a molecule by means of infrared spectroscopy, the N–O stretching frequency occurring in the 'fingerprint' region between 1300

and 1200 cm^{-1} for aromatic *N*-oxides. Mass spectrometry, however, easily resolves the problem, even if a nitro-group is present in the molecule.

The mass spectra of a series of new quinoline

N-oxides¹ of general formula (I) have been determined. Abundant parent ions, 70–100% of the base peak intensity, were observed. In all the spectra there was an abundant (P – 16)⁺ ion corresponding to the loss of a single oxygen atom from the molecular ion. The abundance of this ion is ranged from 15–40%.

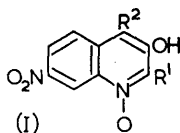
To establish a comparison the mass spectra of several quinolines of general formula (II) were measured. This group showed (P – 16)⁺ ion abundances of 0–0.4%, the very small (P – 16)⁺ ion arising from fission within the nitro-group.

In order to test the generality of this method for the detection of *N*-oxides the mass spectra of a number of other compounds were determined. In these, abundant parent ions were again observed. The (P – 16)⁺ ion was the base peak in the spectra of phenazine di-*N*-oxide and 2,6-dichlorophenazine di-*N*-oxide. The spectra of these two compounds also showed abundant (P – 32)⁺ ions, 75% and 63% respectively, corresponding to the loss of two oxygen atoms. Large (P – 16)⁺ ions were also observed in the spectra of azoxybenzene (38%) and 4-nitropyridine *N*-oxide (68%). In addition, the

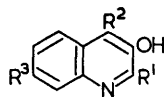
spectra of a 1-hydroxy-2-oxisoquinoline (III) and a 1-hydroxy-4-oxoquinoline (IV) (each of which can tautomerise to the corresponding *N*-oxide) were recorded. Compound (III) showed a (P – 16)⁺ ion of 44%. Although the (P – 17)⁺ ion was the base peak in the spectrum of compound (IV) the (P – 16)⁺ ion amounted to 42%.

Loss of a single oxygen atom from a molecular ion has been observed for nitro-compounds,² anthraquinones,³ and epoxides.⁴ The largest losses reported are 6% for *p*-nitrophenol² and 8% for 1,5-dihydroxyanthraquinone.³ All other losses reported are less than 3%.

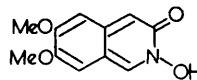
The mass spectra were determined with an A.E.I. M.S. 9 double focussing mass spectrometer. The spectra of azoxybenzene and 4-nitropyridine *N*-oxide were measured using a heated inlet system maintained at 250°. The other spectra were determined using a direct inlet system since it was found that the *N*-oxides decomposed in the heated inlet system and only the spectra of the corresponding amines were recorded. All ion abundances quoted have been corrected for naturally occurring carbon-13 where appropriate.



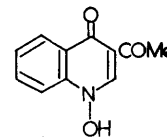
(I)



(II)



(III)



(IV)

- a. R¹ = R² = H.
 b. R¹ = Ph, R² = H.
 c. R¹ = Ph, R² = CO₂Et.
 d. R¹ = R² = CO₂Et.

- a. R¹ = R² = H, R³ = NO₂
 b. R¹ = Ph, R² = H, R³ = NO₂
 c. R¹ = R² = CO₂Et, R³ = MeCONH.
 d. R¹ = Ph, R² = CO₂Et, R³ = MeCONH.

(Received, April 29th, 1965.)

¹ J. P. Cairns, J. D. Loudon, J. R. Maxwell, and A. S. Wylie, to be published.

² J. H. Beynon, R. A. Saunders and A. E. Williams, *Ind. chim. belge.*, 1964, **29**, 311.

³ J. H. Beynon, and A. E. Williams, *Appl. Spectroscopy*, 1960, **14**, 156.

⁴ A. McCormick, unpublished results.