ORGANIC MASS SPECTROMETRY, VOL. 26, 247–249 (1991)

Elimination of Carbon Monoxide by Electron Impact on Quinoline *N*-oxide, Carbostyril and 8-Hydroxyquinoline[†]

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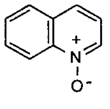
Under electron impact, the molecular ions of quinoline *N*-oxide, carbostyril and 8-hydroxyquinoline lose carbon monoxide giving a fragment ion C_8H_7N (*m/z* 117), which was shown by collision-activated dissociation in each case to have the structure of the molecular ion of indole. Its formation from 8-hydroxyquinoline requires an unusual rearrangement. Isoquinoline *N*-oxide loses HCN rather than CO and gives a fragment which has the structure of the molecular ion of benzofuran. When the first three compounds were subjected to flash vacuum pyrolysis, quinoline *N*-oxide at 500–700 °C gave carbostyril and indole was detected by gas chromatography/mass spectrometry. At 900 °C carbostyril and 8-hydroxyquinoline both gave indole in small amounts, detected by gas chromatography/mass spectrometry.

INTRODUCTION

The molecular ion of quinoline *N*-oxide (**1**) loses carbon monoxide giving a fragment ion C_8H_7N at *m/z* 117. This observation was reported almost simultaneously by Butchardt *et al.*[1] and by Coutts.[2] They postulated that the quinoline oxide molecular ion first rearranged to carbostyril (**2**) and that the ion at *m/z* 117 has the structure of indole (**3**). At about the same time, the rearrangement was observed by Biffin *et al.*,[3] who were reluctant to assign the indole structure to the ion at *m/z* 117, because at that time the structure of the oxygen analogue was in dispute, i.e. the fragment ion formed from the molecular ion of coumarin by loss of carbon monoxide, which was postulated to have the structure of benzofuran (**4**).[4]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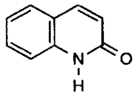
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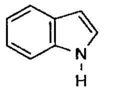
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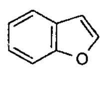
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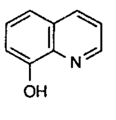
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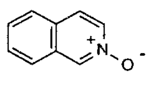
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Using a method developed by Pike and McLafferty,[5] in which the relative abundances of metastable peaks of two different decompositions of the same ion are compared, the last-mentioned group concluded: 'this result is compatible with the hypothesis that quinoline oxide rearranges to carbostyril, which then loses CO giving the indole molecular ion.' They also concluded that the fragment ion formed from 8-hydroxyquinoline had a different but undefined structure.

At a later date, the problem of the structure of the fragment ion formed from coumarin by loss of carbon monoxide was solved by means of collision-activated dissociation (CAD) experiments and was shown to have the structure of benzofuran (**4**).[6,7] We now report the result of a CA mass-analysed ion kinetic energy (MIKE) spectroscopic investigation of the fragment ion formed by loss of carbon monoxide from the molecular ions of quinoline *N*-oxide (**1**), carbostyril (**2**) and from 8-hydroxyquinoline (**5**). We also investigated the fragmentation of isoquinoline *N*-oxide (**6**), which loses HCN rather than CO from the molecular ion and gives benzofuran (**4**). Our flash vacuum pyrolysis studies of compounds which lose simple molecules on electron impact[8] have been extended to **1**, **2** and **5**.

RESULTS AND DISCUSSION

The CA/MIKE spectrum of the fragment ion of *m/z* 118 (C_8H_6O) formed from isoquinoline *N*-oxide is identical with that formed from an authentic specimen of benzofuran (Figs 1 and 2).

The CA/MIKE spectrum of the fragment ions of *m/z* 117 (C_8H_7N) formed from quinoline *N*-oxide (**1**), from carbostyril (**2**) and from 8-hydroxyquinoline (**5**) are not only identical with one another but also with the molecular ion of indole (**3**) (Figs 3–6). In some cases the abundances varied with the pressure in the collision cell. This

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0030–493X/91/040247–03 $05.00
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Received 31 August 1990
Revised manuscript received 16 November 1990
Accepted 20 November 1990

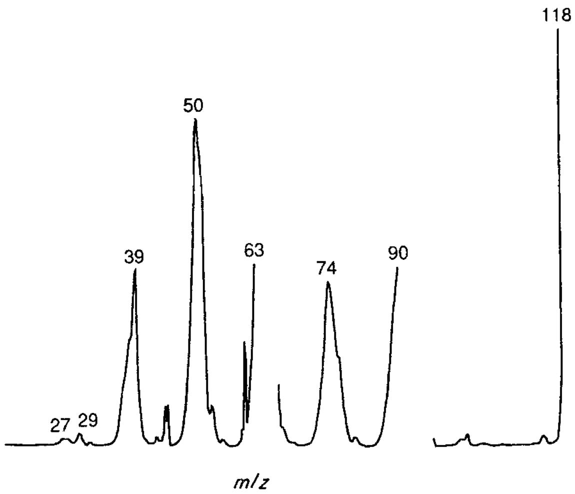


Figure 1. CA/MIKE spectrum of the molecular ion of benzofuran (**4**).

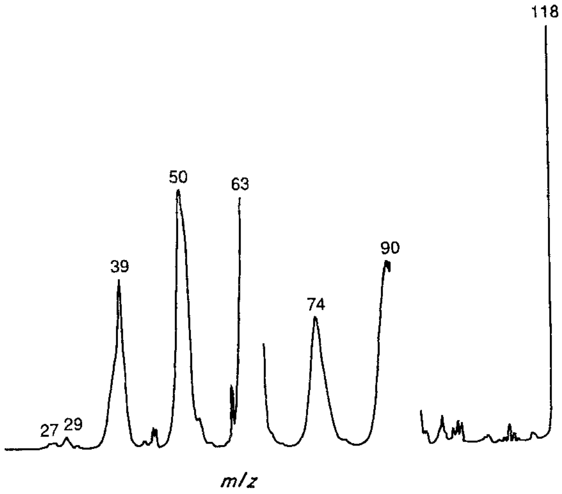


Figure 2. CA/MIKE spectrum of ion of m/z 118 formed by loss of HCN from **6**.

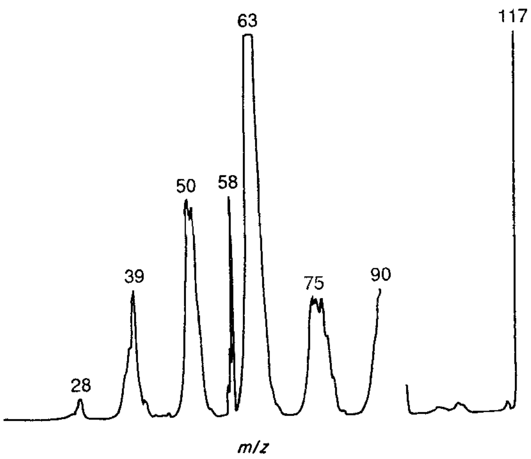


Figure 3. CA/MIKE spectrum of the molecular ion of indole (**3**).

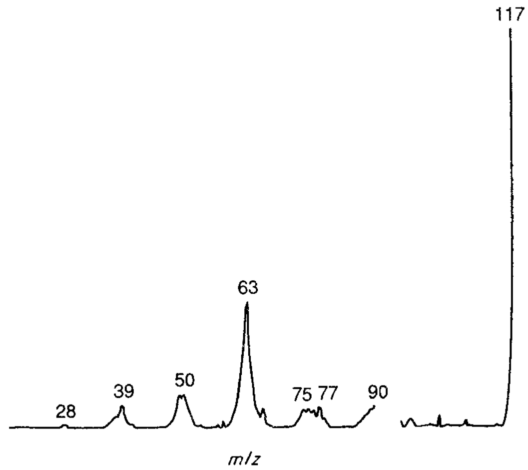


Figure 4. CA/MIKE spectrum of ion of m/z 117 formed by loss of CO from **1**.

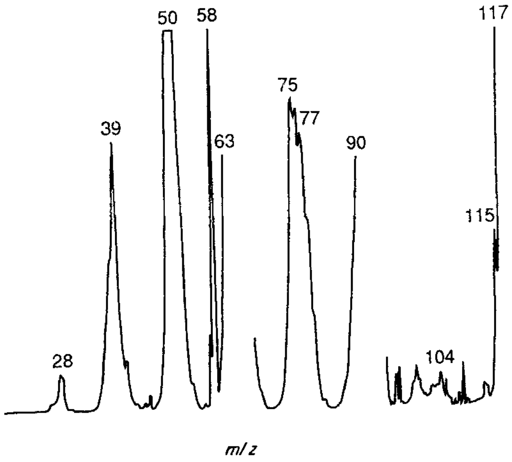


Figure 5. CA/MIKE spectrum of ion of m/z 117 formed by loss of CO from **2**.

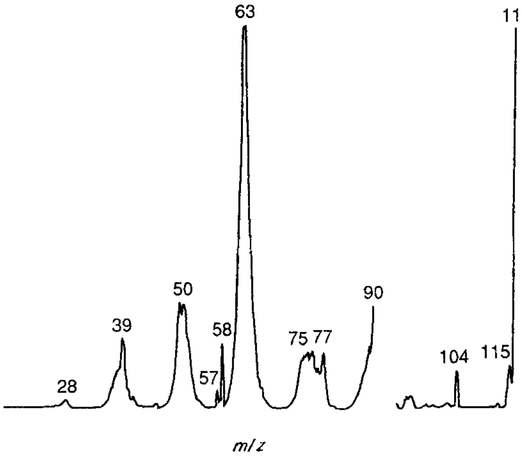
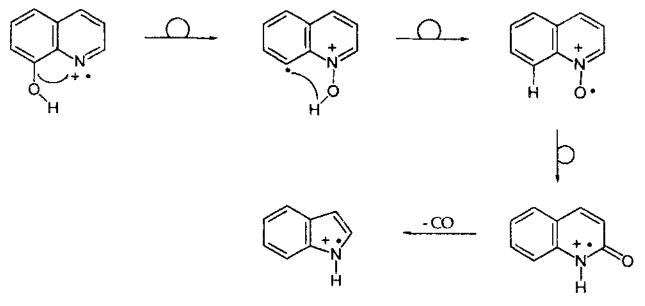


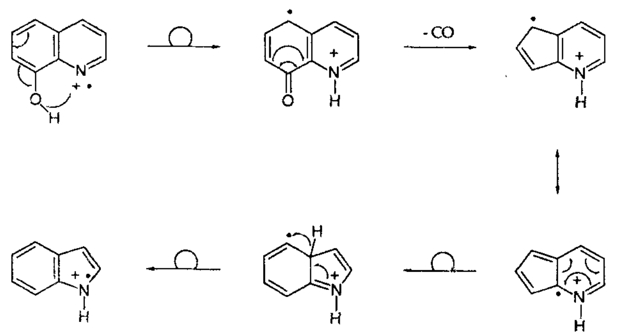
Figure 6. CA/MIKE spectrum of ion of m/z 117 formed by loss of CO from **5**.

result, which was unexpected in the case of 5, can only be explained by a rearrangement in the molecular ion of 8-hydroxyquinoline, and two possible routes are shown in Scheme 1.

In the first, C(2) is lost as carbon monoxide following a migration of the oxygen to nitrogen and then to carbon; in the second C(8) is lost following hydrogen migration and rearrangements in the C_8H_7N fragment ion as shown. To distinguish between these possibilities requires isotopic labelling of the appropriate carbon



Loss of C-2 as CO.



Loss of C-8 as CO.

Scheme 1. Possible rearrangement pathways for the formation of indole molecular ion after loss of carbon monoxide from 8-hydroxyquinoline molecular ion.

atom; at present we are not in a position to attempt to solve this problem. Under flash vacuum pyrolysis conditions, quinoline *N*-oxide (**1**) forms carbostyril (**2**) readily. Indole (**3**) is formed only at higher temperatures and in low yield. This result supports the original hypothesis that **1** rearranges to **2** on electron impact.

EXPERIMENTAL

Mass spectra were determined with a VG Micromass 7070F instrument at the University of Melbourne under the following conditions: ionizing energy, 70 eV; trap current, 180 μA; accelerating voltage 4 kV; source temperature, 200 °C, direct insertion probe; indicated source pressure, 8.0×10^{-4}–8.5×10^{-4} Pa. Collision-activated dissociation experiments were performed on a VG ZAB 2HF instrument at the University of Adelaide with helium as collision gas.

Flash vacuum pyrolysis experiments were performed as described elsewhere[8] using an unpacked quartz tube in an apparatus purchased from Aldrich; the compound was sublimed into the tube when the vacuum was in the range 0.01–0.5 Pa. Gas chromatography/mass spectrometry was performed with a Hewlett-Packard Model 5890 gas chromatograph connected to a Jeol JMS AX505 mass spectrometer.

Quinoline *N*-oxide (**1**) and isoquinoline *N*-oxide (**6**) were prepared by stirring each base separately with 30% hydrogen peroxide at room temperature. Acetic anhydride was added slowly, and when the addition was complete the mixture was heated on a steam-bath for 5 h. After neutralization with aqueous sodium hydroxide, the amine oxide was extracted with chloroform, the extract was again washed with aqueous sodium hydroxide, then with water followed by saturated brine and finally filtered through anhydrous magnesium sulphate. Removal of the chloroform gave the amine oxides. The melting points agreed with literature values and in particular the mass spectra agreed with those published.[1–3]

Carbostyril was isolated from the pyrolysis products of **1** at 500, 600 and 700 °C, by preparative thin-layer chromatography. It was identified by melting point and proton NMR. Pyrolysis at 900 °C of **2** and **5** gave a product which gas chromatography/mass spectrometry showed to contain indole, but in amounts too small for isolation by thin-layer chromatography and characterization.

Acknowledgements

Professor Albert T. Lebedev is thanked for helpful discussions on the suggested mechanisms, and Mr Miroslav Dosen for non-technical assistance.

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