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ORGANIC MASS SPECTROMETRY VIII *. M-16 AND M-17 IONS FROM AROMATIC N-OXIDES UPON ELECTRON IMPACT.

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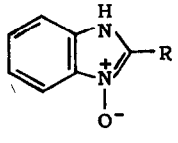
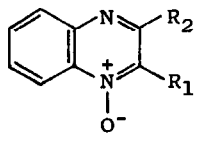
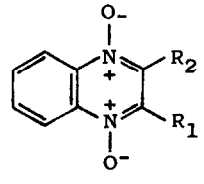
A first study of the fragmentation of aromatic N-oxides upon electron impact was made by Bryce and Maxwell in 1965 (1) and they reported that the presence of M-16 peaks was diagnostic for these N-oxides. However, Grigg and Odell (2) observed the decrease of the M-16 peak and the appearance of an M-17 peak in the mass spectra of 2-alkyl substituted pyridine N-oxides, and argued that the M-16 peak was not always characteristic for this type of compound. In continuation of our studies on the mass spectrometry of nitrogen-containing aromatic compounds, the mass spectra of benzimidazole-(A) and quinoxaline-(B and C) N-oxides have been examined for the presence of M-16 or M-17 peaks.



(A)



(B)



(C)

* Part VII: A.Tatematsu, T.Goto and S.Matsuura, J.Chem.Soc.Japan(Pure Chem.Sect.), 87, 1226 (1966).

i) Benzimidazole N-oxides (A).

The base peak in the mass spectra of most 2-alkyl substituted benzimidazole N-oxides as well as benzimidazole N-oxide itself is the M-16 peak, which arises from elimination of an oxide oxygen atom from the molecular ion.

On the other hand, the spectrum of 2-methylbenzimidazole N-oxide 2 gives an M-17 peak (m/e 131) with a relative intensity of 62 % (Fig.1). In the spectrum of the corresponding 2-methylbenzimidazole (Fig.2), the relative intensity of m/e 131 (M-1) peak is also about 60 %.

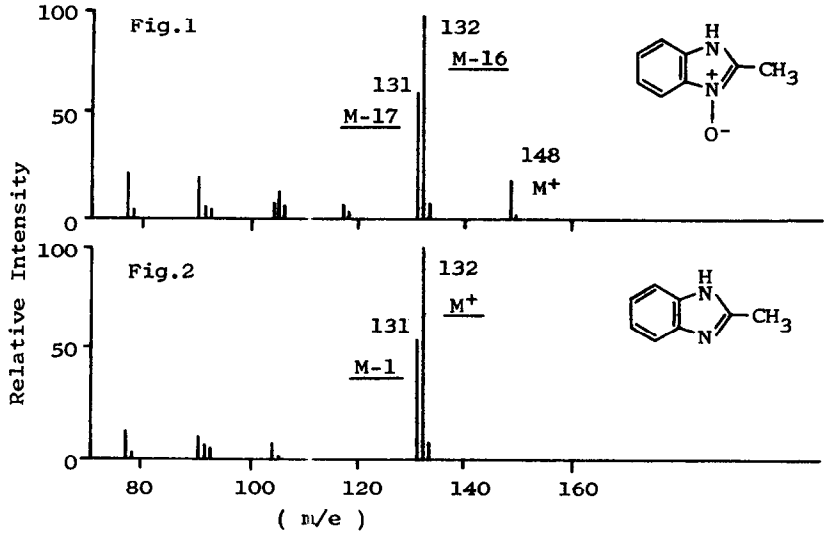


Fig.1 Mass spectrum of 2-methylbenzimidazole N-oxide.
Fig.2 Mass spectrum of 2-methylbenzimidazole.

Intensities of M-17 peaks of other N-oxides 2-4, (Table I), are very much similar to those of M-1 peaks of the corresponding benzimidazoles. Therefore, it seems that the M-17 peak of the 2-alkyl benzimidazole N-oxides (A) would not arise through a one-step fragmentation process, but is equivalent to the M-16-1 ion peak. Although the interaction between the oxygen atom and the alkyl side-chain, the so-called ortho-effect, is possible, the elimination of an OH radical is not a significant process. This is presumably ascribable to the strain in a five-membered ring which has these participating groups.

From these results, we suggest that the primary fragmentation pathway of the benzimidazole N-oxides is elimination of an oxygen atom from the molecular ion to give a relatively strong M-16 peak followed by the expulsion of a hydrogen atom.

Table I Comparison of Relative Intensities of Benzimidazole Derivatives.

		N-oxides (A)		Corresponding Benzimidazoles	
No.	Compds.	M-16	M-17	M^+	M-1
1	R = H	100	5	-	-
2	R = Me	100	62	100	60
3	R = Et	60	100	58	100
4	R = Ø	100	17	100	16
5	R = OMe	100	37	-	-
6	R = OEt	100	7	-	-

ii) Quinoxaline N-oxides (B).

The mass spectra of 2-methyl- and 2-ethyl-quinoxaline N-oxides, 7 and 8, which have six-membered rings, show an M-17 ion with a distinct meta-stable ion peak. The fragmentation process is obviously the one-step elimination of an OH radical and is possibly due to the operation of an ortho-effect as in 2-alkyl pyridine N-oxide (2). This presents a striking contrast to the case of benzimidazole N-oxides discussed above.

The M-17 peak was also observed when the alkyl group is in the 3 position. For the 3-ethyl derivative 13 even a meta-stable ion peak for this process was clearly observed. Futhermore, 3-isopropyl and 3-tert.-butyl derivatives, 15 and 16, gave a meta-stable ion peak for $M\text{-}CH_3 \longrightarrow M\text{-}CH_3\text{-}17$ (see Table II). Therefore, the presence of an alkyl group in the 2 position is not necessarily required for the one-step expulsion of an OH radical if the other neighboring hydrogen atom is available.

Table II The Relative Intensities of M^+ and M-17 Peaks and the Meta-stable Ion Peak observed in the Spectra of Quinoxaline Derivatives (B).

No.	Compds.(B) R_1	R_2	M.W.	Relative Intensity M-17	M^+	Ratio M-17/M^+	Meta-stable(obs.) M-16	M-17
7	Me	H	160	100	78	1.28	-	127.9
8	Et	H	174	100	42	2.38	-	141.7
9	Me	Me	174	100	65	1.54	-	141.7
10	H	H	146	8	100	0.08	115.8	-
11	H	Me	160	12	100	0.12	129.8	-
12	H	OMe	176	14	100	0.14	145.5	-
13	H	Et	174	18	100	0.18	-	141.7
14	H	OEt	190	9	100	0.09	-	157.6
15	H	i-Pr	188	13 (M-15-17)	100 (M-15)	0.13	-	140.7 (M-15-17)
16	H	t-Bu	202	5 (M-15-17)	100 (M-15)	0.05	-	154.8 (M-15-17)
17	CN	Ø	247	-	-	-	216.1	-
18	Et	Ø	250	100	16	6.25	-	217.2
19	n-Bu	Ø	278	31	7	4.43	-	245.1
20	Ø	CN	247	-	-	-	216.1	-
21	Ø	Et	250	80	100	0.80	-	217.2
22	Ø	i-Pr	264	88	100	0.88	-	231.1

As is shown in Table II, this relationship between 2- and 3-alkyl substituted quinoxaline N-oxides is essentially the same as in phenyl analogues of these compounds (17-22).

It is of interest to compare the intensities of molecular ion peaks with those of M-17 peaks for isomeric compounds. We found M-17/M^+ $>$ 1 for 2-substituted quinoxaline N-oxides and M-17/M^+ $<$ 1 for 3-substituted isomers.

iii) Quinoxaline N,N'-dioxides (C).

In the case of quinoxaline N,N'-dioxides, the M-16 peak was larger than the M-17 peak, and the meta-stable ion peak for the process M-16 $\longrightarrow$ M-16-17 was

observed (Table III). This result shows the preferential loss of an oxygen atom from the molecular ion rather than the expulsion of an OH radical through the ortho-effect of alkyl groups.

Table III The Relative Intensities of M-16,M-17 and M-16-17 Peaks and the Meta-stable Ion Peak observed in the Spectra of Quinoxaline N,N'-dioxides (C).

No.	Compds.(C) R_1	R_2	M.W.	Relative Intensity M-16	M-17	M-16-17	Meta-stable(obs.) M-16	M-17	M-16-17
23	H	Et	190	84	44	100	-	-	141.7
24	H	i-Pr	204	46	18	100	-	-	155.6
25	Ø	Et	266	32	20	100	-	-	217.2

Most compounds used in the present work were prepared by previously reported methods (3,4,5,6). The mass spectra were measured by a Hitachi Mass Spectrometer Model RMU-6D, using an all-glass inlet system. Heating temperature of the sample was about 150°C and ion-source temperature was 200°C. The ionizing energy was kept at 70 eV. and the ionizing current at 80 μA.

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