Mass Spectral Fragmentations of 2-Phenyl-3*H*-indol-3-one *N*-Oxide (2-Phenylisatogen), 2-Phenyl-4*H*-3,1-benzoxazin-4-one, and 1-Phenylindoline-2,3-dione (*N*-Phenylisatin)

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Summary Mass spectral data provide evidence for an oxaziridine intermediate from the fragmentation patterns of 2-phenylisatogen and 2-phenyl-4*H*-3,1-benzoxazin-4-one.

IN the course of an investigation of the mechanism of the photochemical conversion of 2-phenylisatogen (**1**), into 2-phenyl-3,1-benzoxazin-4-one, (**2**),[1] a comparison between the mass spectral behaviour and photochemical behaviour of compounds (**1**)—(**6**) has been made. There have been numerous descriptions of the parallelism between mass spectroscopy and photochemistry.[2] The photochemical conversion of nitrones into oxaziridines is well documented[3] and it appears that the photoisomerization of (**1**) to (**2**)[1] [and (**5**) to (**6**)][1b] proceeds *via* the oxaziridine intermediate.

It appears that the oxaziridine ion is an important intermediate not only in the mass spectral fragmentation of 2-phenylisatogen, (**1**), but also its sole photoproduct, 2-phenyl-3,1-benzoxazin-4-one, (**2**). The oxaziridine intermediate from (**1**) was not unexpected since similarities in photochemical and mass spectral behaviour exist,[4] but an oxaziridine intermediate from (**2**) was unanticipated.

All of the major ions of (**1**) and (**2**) are listed in Table 1 in addition to the major ions of *N*-phenylisatin, (**3**), and 3-benzoyl-1,2,3-benzotriazin-4-one, (**4**). Compound (**4**) has been photolytically converted into (**2**) by Ege.[5] An attempt in the laboratory to convert (**3**) into (**2**) photolytically was unsuccessful.[6]

Each parent compound shows major ions at *m/e* 195, 167, 90, and 77. Compounds (**1**), (**2**), and (**4**) show major ions at *m/e* 179, 146, and 105. Compound (**1**) has ions at *m/e* 207 ($M - O$) and 206 ($M - OH$). Of the ions from (**1**) listed in Table 1, those at *m/e* 167, 146, and 105 must result from rearrangement in the molecule. It appears that an oxaziridine intermediate is operative in the fragmentation just as that previously reported by Kinstle *et al.*[4] Appearance of an ion at *m/e* 167 in compound (**2**) strongly suggests an intermediate oxaziridine molecule ion in the fragmentation of the benzoxazinone, (**2**).

Initial formation of the oxaziridine intermediate (a) from (**1**) with concurrent rearrangement produces the benzoxazinone molecule ion (b) which can be the direct precursor *via* path (i) of the *m/e* 105 ion (c) and the *m/e* 90 ion (d). Alternative $C \rightarrow N$-phenyl migration and the loss of two carbon monoxide molecules [path (ii)] produce the *m/e* 167 ion, (e), and the *m/e* 77 ion, (f). A third rearrangement process [path (iii)], comparable to the observed photochemical rearrangement of (**1**) → (**2**), results in the formation of the *m/e* 146 ion, (g). Each of the formulations suggested for these ions is supported by the mass spectral data in Table 1.

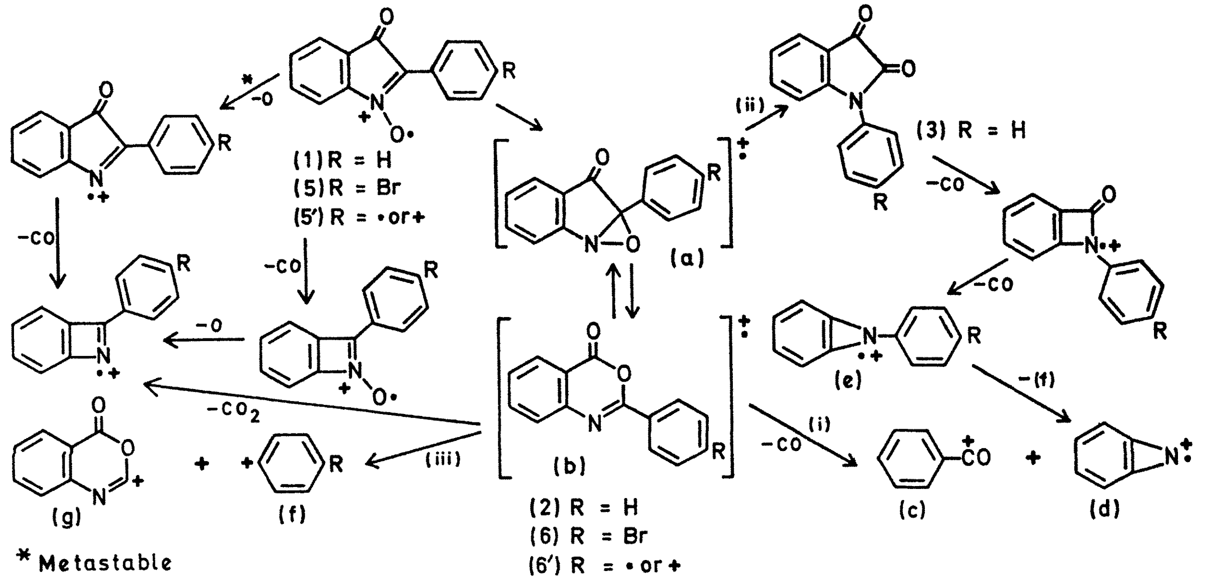
TABLE 1

m/e in (**1**) (**2**) and (**3**)	(**1**) Relative intensity	(**2**) Relative intensity	(**3**) Relative intensity	*m/e* in (**4**)	(**4**) Relative intensity
251	—	—	—	M^+	0·6%
223 M^+	100·0%	100·0%	39·6%	$M - N_2$	13·9
207 $M - O$	14·3	—	—	—	—
206 $M - OH$	59·2	—	—	—	—
195 $M - CO$	10·1	4·3	100·0	$M - (N_2 + CO)$	3·5
179 $M - CO_2$	9·0	43·9	—	$M - (N_2 + CO_2)$	3·2
167 $M - 2CO$	17·5	1·7	28·5	$M - (N_2 + 2CO)$	1·2
146 $M - C_6H_5$	2·7	18·3	—	$M - (N_2 + C_6H_5)$	2·4
105	13·7	64·3	—	—	100·0
90	3·0	12·2	2·7	—	4·7
77	24·2	52·6	24·8	—	36·8

TABLE 2

m/e in (**5**) and (**6**)	(**5**) Relative intensity	(**6**) Relative intensity
303 $M^+(^{81}Br)$	98·9%	94·6%
301 $M^+(^{79}Br)$	100·0	100·0
287 $M - O$	10·9	—
285 $M - O$	11·4	—
286 $M - OH$	54·5	—
284 $M - OH$	54·5	—
275 $M - CO$	1·8	2·0
273 $M - CO$	1·9	2·1
259 $M - CO_2$	3·2	25·0
257 $M - CO_2$	3·4	25·9
247 $M - 2CO$	2·5	—
245 $M - 2CO$	2·6	—
185	13·5	41·1
183	16·9	42·9
157	13·2	22·3
155	14·3	23·6
222 $M - Br$	4·5	13·9
206 $M - (Br + O)$	2·7	—
205 $M - (Br + OH)$	4·8	—
194 $M - (Br + CO)$	5·3	3·2
178 $M - (Br + CO_2)$	8·6	10·5
166 $M - (Br + 2CO)$	22·5	4·1
146 $M - C_6H_4Br$	5·7	25·5
104	6·4	5·5
90	10·2	13·9
76	50·0	26·3

It may have been expected that there would be some observed $N \rightarrow C$-phenyl migration from (**3**) in mass spectral



fragmentation, but the similarity of the mass spectral fragmentation of (**3**) with compounds (**1**), (**2**), and (**4**) with the conspicuous absence of *m/e* ions at 179, 146, and 105 indicates that there is no mass spectral *N* → *C*-phenyl migration in compound (**3**).

In order to show unambiguously that the *m/e* 105 ion is obtained from the 2-phenyl group of (**1**), mass spectral fragmentations of compounds (**5**) and (**6**) are shown to have major ions at *m/e* 185 and 183. All of the major ions of (**5**) and (**6**) are listed in Table 2. Incipient loss of Br from (**5**) and (**6**) to give (**5′**) and (**6′**) gives rise to analogous fragmentation patterns as those of (**5**) and (**6**).

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[1] (a) D. R. Eckroth and R. H. Squire, *Chem. Comm.*, 1969, 312; (b) D. R. Eckroth and R. H. Squire, Paper (ORGN 13), presented at the 158th National Meeting of the American Chemical Society, New York, September 1969.

[2] See, for example, M. M. Bursey, *Tetrahedron Letters*, 1968, 981; P. Kinston and B. M. Trost, *ibid.*, 1969, 1075; and H. Nakata, H. Sakurai, H. Yoshizumi, and A. Tatematsu, *Org. Mass Spectrometry*, 1968, **1**, 199.

[3] Splitter and M. Calvin, *J. Org. Chem.*, 1965, **30**, 3427; A. Alkaitis and M. Calvin, *Chem. Comm.*, 1968, 292.

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[5] G. Ege, *Angew. Chem.*, 1965, **77**, 723.

[6] D. R. Eckroth, unpublished observations.