Mechanisms of Mass Spectral Fragmentations of Nitrones

By T. H. KINSTLE* and J. G. STAM

(*Department of Chemistry, Iowa State University, Ames, Iowa* 50010)

AROMATIC and olefinic nitro-compounds have shown some mechanistically novel and important mass spectral fragmentations,[1,2] now nitrones are being studied. All the major ions of the parent compound α,*N*-diphenylnitrone (I), are listed in the Table.[†] Several of these ions, namely m/e 91, 94, 105, 168, and 169 must result from rearrangement[3] in the molecule ion and we report here the results of isotope labelling studies which clarify the mechanisms of formation of these and other ions in the spectra of nitrones.

TABLE

m/e in (I)	Relative intensity	m/e in (II)	m/e in (III)
197 M^+	27·8%	198	198
196 $M-H$	14·8%	197	197
181 $M-O$	3·5%	182	182
180 $M-OH$	4·8%	181	180 (>85%)
169 $M-CO$	3·0%	170	170
168 $M-HCO$	5·1%	169	169
105	13·3%	106	105
94	5·7%	94	95
91	100·0%	91	91
77	37·0%	77	77

We conclude that an oxaziridine ion (a) is an important intermediate in the fragmentation of nitrones. The photochemical conversion of nitrones to oxaziridines is well documented,[4] and since similarities in photochemical and mass spectral behaviour exist,[5] this result was not totally unexpected. We feel that the intermediate (a) leads directly to the m/e 91, 94, and 105 ions in the spectrum of (I).

Migration of the hydrogen atom from carbon to nitrogen with concurrent ring opening (path i) produces the ion (b) which can be the direct precursor of the m/e 105 ion (c).[6] Alternative $\mathrm{N}\rightarrow\mathrm{C}$ oxygen migration and loss of benzaldehyde (path ii) produces the m/e 91 ion (d) in one of several possible structural formations. A third, more complex rearrangement process results in the formation of the m/e 94 ion (e). The formulations suggested for each of these ions are supported by high resolution mass spectral data and more significantly by the appropriate mass shifts (see the Table) in the spectra of the carbon-13 (II) and deuterium-labelled (III) compounds and the spectra of several α-phenyl substituted and *N*-phenyl substituted derivatives of (I).

A priori one might have expected alternative aryl migration in (a) to produce the *N*-formyl ion (f) which could serve as the precursor of the $M-CHO$ ion at m/e 168 and possibly the $M-CO$ ion at m/e 169. Alternatively, carbon monoxide might be lost from ion (b).[7] That neither of these possibilities are operative, even to a minor extent, is obvious from the spectrum of (II). Since *all* of the carbon-13 label is retained in the metastable loss of CO, an oxaziridine intermediate is unimportant in their formation. The source of carbon in the carbon monoxide is undoubtedly one of the

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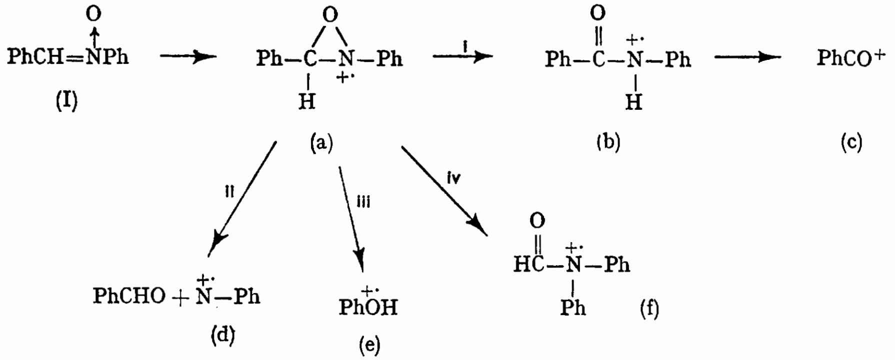
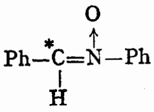
[†] The fragmentations illustrated for α-phenyl-*N*-phenylnitrone, except for m/e 94, were found to be general for fifteen aryl nitrones investigated. Several aryl-alkyl nitrones investigated gave somewhat different mass spectral behaviour which was more sensitive to specific structural features.

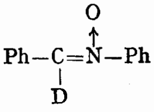


ortho-carbons in the α-phenyl ring from an intermediate ion such as (g). This reaction of nitrones is similar to that of the nitro-group in nitrostyrenes[2] and nitro-aromatics[1] and the azoxy-functional grouping.[8] A metastable loss of a hydrogen atom leads to the $M-$CHO ion in the spectrum of (I).



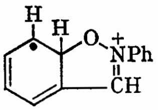
$\mathrm{Ph}-\underset{\mathrm{H}}{\overset{*}{\mathrm{C}}}=\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{N}}-\mathrm{Ph}$

(II)



$\mathrm{Ph}-\underset{\mathrm{D}}{\mathrm{C}}=\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{N}}-\mathrm{Ph}$

(III)



(g)

Aryl migrations, however, do occur in the spectra of αα-diaryl nitrones. This aryl migration is sensitive to substituents on the aryl nucleus and a quantitative treatment of this migratory aptitude is now underway.

Finally, the sources of the hydrogen atoms in the $M-$H and $M-$OH ions are shown to be the α-aryl ring and (primarily) the α-carbon atom, respectively, on the basis of no loss of hydrogen atom in the spectrum of α-pentafluorophenyl-*N*-phenyl nitrone and greater than 85% loss of OD in the spectrum of (III).

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[3] See P. Brown and C. Djerassi, *Angew. Chem. Internat. Edn.*, 1967, **6**, 477.

[4] J. Splitter and M. Calvin, *J. Org. Chem.*, 1955, **20**, 1086; 1965, **30**, 3427.

[5] See, for example, N. J. Turro, D. S. Weiss, W. F. Hadden, and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1967, **89**, 3370.

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