

THE PHOTOLYSIS OF 1-PHENYL AND 1-CYANO SUBSTITUTED  
ISOQUINOLINE N-OXIDES TO BENZ[f]-1,3-OXAZEPINES\*

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The recent unambiguous identification of the main products in the photolysis of a series of 2-phenyl- and 2-cyanoquinoline N-oxides as benz[d]-1,3-oxazepines (1) cf. (2), has led us to investigate the photochemical behaviour of some 1-phenyl- and 1-cyanoisoquinoline N-oxides (Ia-d).

Photolysis\*\* of Ia-d in acetone resulted in the formation of a series of compounds (IIIa-d) (Table 1), which are isomers of the starting materials.\*\*\*

In a typical run, 1.00 g of 1-phenyl-3-methylisoquinoline N-oxide (Ib) in 200 ml of acetone was irradiated until approximately 90% of the starting material was consumed. Evaporation in vacuo of the reaction mixture and preparative layer chromatography of the remaining oil yielded 485 mg of 2-phenyl-4-methylbenz[f]-1,3-oxazepine (IIIb). In a similar way IIIa could be obtained in ca. 50% yield. Compounds IIIc and IIId were isolated from the irradiated acetone solutions of Ic and Id respectively by evaporation of the solvent in vacuo (temp. <20°) and extraction of the remaining oils with pentane.

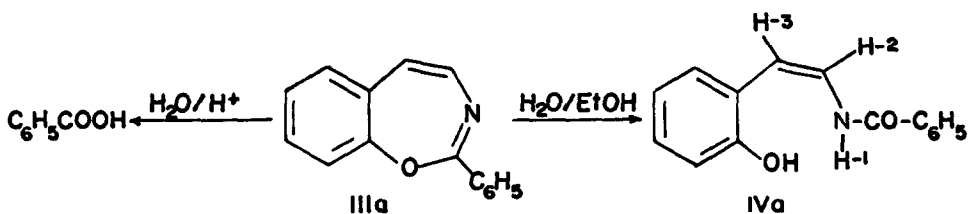
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\*\* External light source: Hanovia Q-700 medium pressure mercury lamp, filter cutoff: 90% at 320 mμ.

\*\*\* All new compounds described in this paper showed satisfactory elemental analyses.



from oxaziridines like II (cf. Ref. 7). The solvolysis of IIIa in boiling 50% aqueous ethanol gives in good yield a compound whose elemental analysis and spectroscopic properties indicate that it has the structure IVa. Solvolysis of IIIb in a similar way yields *o*-hydroxyphenylacetone (cf. Ref. 8). The acid hydrolysis of IIIa yields benzoic acid and an impure oil, the NMR spectrum of which shows no aldehydic proton signal. Finally it should be noted that Kaneko *et al.* (8) have isolated *o*-hydroxyphenylacetone in quantitative yield by the solvolysis of IIIc; however it should be noted that we have been unable to reproduce this experiment so far. The solvolysis and hydrolysis experiments are consistent with the benz[f]-1,3-oxazepine structure III).



c. From the UV spectra of IIIa-d and Ia-d (Table 1), it is seen that the conjugation in III is increased relative to that in I. Furthermore, it should be noted that the presumed benz[f]-1,3-oxazepines (III) absorb at slightly longer wavelengths than the benz[d]-1,3-oxazepines (1,2), indicating the presence of two conjugated double bonds between the phenyl groups in III.

The IR spectra of IIIa-d (Table 1) contain a characteristic band near  $1640\text{ cm}^{-1}$  which is superimposed on a weaker band. These bands are tentatively assigned to the vibration in the seven membered ring (cf. Refs. 1 and 2).

TABLE 2  
NMR spectra<sup>a</sup>

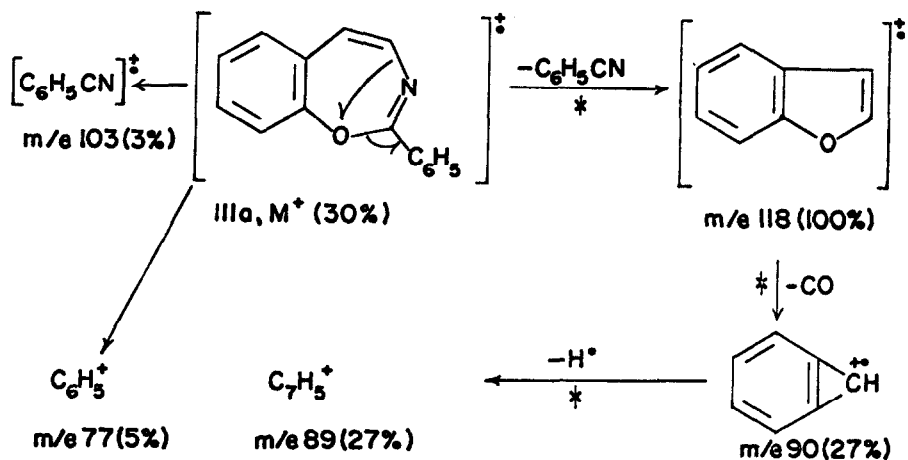
Compound	H-4	H-5	CH <sub>3</sub>
IIIa	3.08, d, $\underline{J}=7.5$	3.58, d, $\underline{J}=7.5$	
IIIb		3.71, q, $\underline{J}=1$	7.83, d, $\underline{J}=1$
IIIc	3.25, d, $\underline{J}=8$	3.40, d, $\underline{J}=8$	
IIId		3.57, q, $\underline{J}=1$	7.88, d, $\underline{J}=1$
IVa <sup>b</sup>	-0.83, s, 1H; -0.53, d, $\underline{J}=10$ , 1H;	2.0-3.3, m, 10H;	4.25, d, $\underline{J}=10$ , 1H

<sup>a</sup>60 Mc/s in CDCl<sub>3</sub> with TMS as internal reference. Chemical shifts are in  $\tau$ -units, coupling constants in cps; s = singlet, d = doublet, q = quartet, m = multiplet.  
<sup>b</sup>Like <sup>a</sup>, with DMSO-d<sub>6</sub> as solvent.

The NMR spectra of IIIa-d (Table 2) are similar to the spectra of the benz[d]-1,3-oxazepines (1,2), and support the assignment.

The UV and IR data of IVa (Table 1) are consistent with the structure assigned. In the NMR spectrum of IVa (Table 2) the signal at  $-0.83\tau$  ( $-\text{OH}$ ) disappeared by addition of water. The doublets at  $-0.53\tau$  and  $4.25\tau$  could be decoupled by double irradiation at  $+211$  cps and  $-67$  cps respectively. This gives good support to the assigned structure, indicating that the doublet at  $-0.53\tau$  is due to H-1, the doublet at  $4.25\tau$  due to H-3, whereas the signal from H-2 is part of the multiplet.

D. The mass spectra of compounds IIIa-d are consistent with their assigned structures and were measured with an Atlas CH-4 mass spectrometer using the direct inlet procedure. The electron energy was 70 ev unless stated otherwise. Scheme I depicts a mechanistic rationalization for the principal peaks in the spectrum of IIIa. At low electron energy (19 ev) only the molecular ion and the peak at  $m/e$  118 were visible.



<sup>a</sup>Figures in parenthesis denote relative abundance; an asterisk indicates processes supported by the presence of a metastable ion.

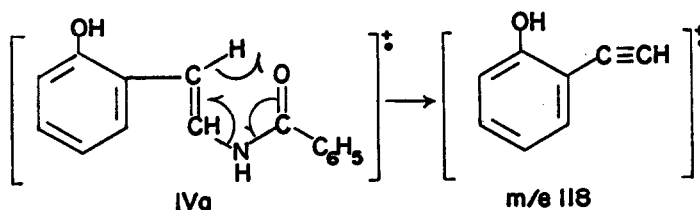
It is noteworthy that the two benz[f]-1,3-oxazepines (IIIc-d) which lack a C-2 phenyl substituent exhibit ions of low abundance (10 and 4% relative abundance) due to the loss of carbon monoxide from the molecular ion.

Both IIIb and IIIc eliminate the equivalent of acetonitrile (yielding peaks of 9 and 47% relative abundance) from their molecular ions. In the case of IIIc (no C-2 phenyl group) this ion ( $m/e$  143) then expels carbon monoxide (metastable ion) to yield a fragment of mass 115.

Loss of X-CN (formula III) from the molecular ions of IIIb and IIIc yield an ion of mass

132 of 94 and 86% relative abundance respectively. The base peak (100% relative abundance) in both instances is generated by the further loss of a hydrogen atom (metastable ion recognized). The ion at mass 132 would formally correspond to the molecular ion of 3-methyl-benzofuran which is known (9) to readily lose a hydrogen atom. Further loss of carbon monoxide would yield the ions of mass 103 in each instance.

The mass spectrum of compound IVa ( $M^+$  239) contains peaks of 2 and 3% relative abundance at  $m/e$  222 and 134 due to the loss of OH and  $C_6H_5CO$  radicals respectively, while the occurrence of a peak at  $m/e$  118 (21% relative abundance) can be rationalized in the following manner.



The most intense peak in the spectrum of IVa occurs at  $m/e$  105 and corresponds to the benzoyl radical ion. The mass spectral fragmentation of IVa is thus consistent with its assigned structure.

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