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PHOTOLYSIS OF 4-PHENYLQUINAZOLINE 3-OXIDES TO BENZ[f]-1,3,5-OXADIAZEPINES[*1,*2]

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The recent identification of the main products in the photolysis of quinoline, isoquinoline, and quinoxaline N-oxides carrying a phenyl or cyano group in their α-position as benz[d]-1,3-oxazepines,[1a,b] benz[f]-1,3-oxazepines,[2,*3] and benz[d]-1,3,6-oxadiazepines,[1a] respectively, has led us to investigate the photochemical behaviour of quinazoline and 2-methylquinazoline 3-oxides having a phenyl group in 4-position (Ia and Ib).

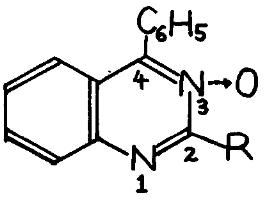
In a typical run, 1.00 g of 2-methyl-4-phenylquinazoline 3-oxide[4,5] (Ib) in 300 ml of benzene was irradiated by 200W Hanovia high-pressure mercury immersion lamp with a Pyrex filter until the disappearance of the starting N-oxide (6 hr). Evaporation of the reaction mixture in vacuo and chromatography of the residue over silica gel afforded 460 mg of 2-phenyl-4-methylbenz[f]-1,3,5-oxadiazepine (IIb) together with a small amount (ca. 5%) of 2-methyl-4-phenylquinazoline. Similarly, compound (IIa) was obtained from Ia[4,5] as a main product. Elemental analyses and molecular weight determinations (mass spectroscopy) of IIa and IIb established the same elemental composition as that of the starting N-oxide.

The correctness of our assignment on these photo-products as having a novel benz[f]-1,3,5-oxadiazepine system (II) is based on the following chemical and spectroscopical observations:

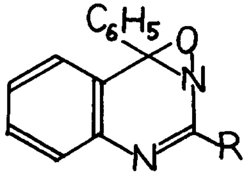
[*1] This paper is No. X in the series entitled "Studies on the N-Oxides of π-Deficient N-Heteroaromatics". For the preceding paper IX, cf. Ref. (1b).

[*2] This and the related works were presented at the 24th Annual Meeting of the Japan Pharmaceutical Society, Kyoto, April, 1967. Abstracts of papers,p.407.

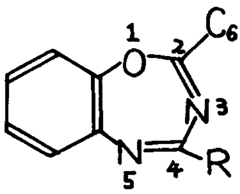
[*3] During the preparation of this manuscript, a paper by Buchardt et al. appeared[3] in which the unambiguous identification of the main products in the photolysis of a series of 1-substituted isoquinoline 2-oxides as benz[f]-1,3-oxazepines was given. However, the same conclusion was obtained by us independently,[*2] and the results have been published already in Ref. (2).



I



III



II

a: R = H
b: R = CH_3

TABLE 1

Compound	m.p.	IR_{max}^{KBr} cm^{-1}	$UV_{max}^{CH_2Cl_2}$ mμ	log ε
IIa	59-61° (hexane)[a]	1635[b]	251, 260, 335[c]	4.18, 4.16, 3.70
IIb	83-85° (hexane)[a]	1640[b]	251, 335[c]	4.27, 3.58

a solvent for recrystallization
b strong intensity band
c shoulder peak

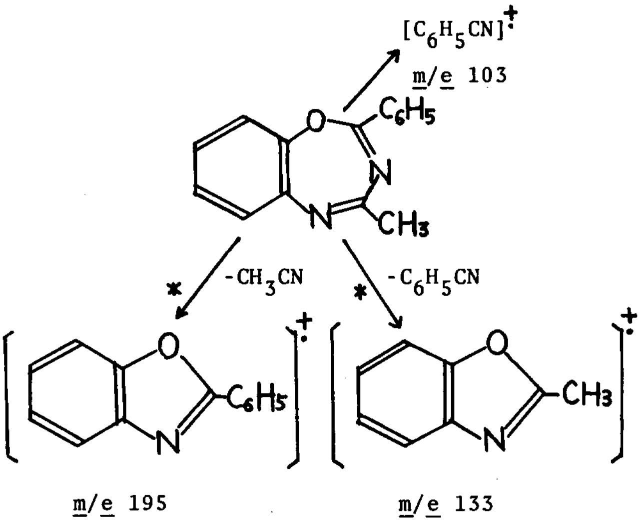
i) The solvolysis of IIa in boiling aq. methanol gives 2-phenylbenzoxazole (IV) m.p. 102°, benzoxazole (Va), m.p. 30°, and o-formamidophenol (VIa), m.p. 129°. Solvolysis of IIb in a similar way yields IV, 2-methylbenzoxazole (Vb), and o-acetamidophenol (VIb), m.p. 209°. The structures of these products were assured by direct comparison with the authentic samples (by mixed melting point determination, IR, UV, and gas-phase chromatography) prepared separately.[6)] Though the yields of these products varied with a slight change in the reaction condition (such as the ratio of water to methanol), 2-phenylbenzoxazole (IV) is the common main product (40-60%) of these reactions. The acid hydrolysis of IIa and IIb with 5% aq. H_2SO_4 gives o-aminophenol[6b)] (VII), m.p. 172-174°, as a common main product.

ii) The UV spectra of IIa and IIb exhibit the longest absorption maxima at around 330-340 mμ and the positions and intensities of these maxima are in good accord with those of 2-phenylbenz[f]-oxazepines reported by Buchardt *et al.*[3)] The IR spectra of IIa and IIb contain a strong band near 1640 cm^{-1} which may be asscribed to the presence of two C=N functions.

iii) The mass spectra of these photo-products are consistent with the assigned structures. For example, the 70 ev spectra of IIb and Ib show the relative intensities listed in Table 2. The decomposition scheme shown can account for the major ionic products (m/e 195 and 133) for the former compound (IIb). The spectrum of IIa also contains peaks of 20 and 100% relative abundance at m/e 195 and 119 due to the loss of HCN and C_6H_5CN radicals respectively.

TABLE 2

Mass	IIb	Ib
236(M^+)	4	34
235		43
220		53
219		100
207		8
195	6	
178		9
163		9
151		7
143		13
139		6
133	100	
117		7
103	19	
102		16



a The mass spectra were determined with a Hitachi RMU-6E double-focussing spectrometer with an all-glass heated inlet system.

b An asterisk indicates the processes supported by the presence of a metastable ion.

It is noteworthy that though in the mass spectra of 2-cyanoquinoline 1-oxide$^{7)}$ and 1-cyanoisoquinoline 2-oxide[*4] the respective formation of the corresponding benz[d]- and benz[f]-oxazepine ions were established, no indication of the formation of the corresponding benz[f]-1,3,5-oxazepine ions was noted in the spectra of Ia and Ib, since their mass spectra do not contain the corresponding M-C_6H_5CN ions. The lack of a parallelism between electron impact and photolysis in these N-oxides (Ia and Ib) may at least partly be due to the ortho-participation of the phenyl group.

[*4] The mass spectra of 1-cyanoisoquinoline 2-oxides and their photo-products were discussed in the 24th Annual Meeting of the Pharmaceutical Society of Japan at Kyoto, April 8, 1967. S. Sakai, C. Kaneko, et al., Abstracts of papers, p. 379.

Finally, it should be worthy to note the results of the photolysis of quinazoline 3-oxide.[8] In the photolysis under an identical condition as above, this N-oxide (Ic) gives 4-quinazolone[8] (VIII), m.p. 215-216° (40%), quinazoline (5%), and a so far unidentified oily product. If ethanol is used as the irradiation solvent, the yield of VIII increases to 80%, while that of quinazoline remains the same. These observations and the trapping experiment of the unstable 1,2-epoxyquinolines by amines in the photolysis of 2-cyanoquinoline 1-oxides reported in the subsequent communication[9] clearly indicate that the photolysis of aromatic amine N-oxides invariably proceeds via the corresponding oxaziridine compounds (such as III) as the intermediates and the fate of this unstable intermediates to a variety of final products (II, VIII etc.) is dependent both on the kind of substituent and the solvent used.

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