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THE PHOTOLYSIS OF 2-PHENYL SUBSTITUTED QUINOLINE N-OXIDES. A TENTATIVE ASSIGNMENT OF 4,5-BENZ-1,3-OXAZEPINE STRUCTURES TO SOME OF THE PRODUCTS.[x]

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We have irradiated four 2-phenyl substituted quinoline N-oxides (Ia-d) in different solvents.[xx]

When the irradiations were carried out in benzene solution, the 2-phenylquinoline N-oxides isomerized, in excellent yields (ca. 90 %), to a series of compounds[xxx] (IIIa-d). The chemical and spectroscopical properties of IIIa-d are similar to those of the irradiation products, from a series of

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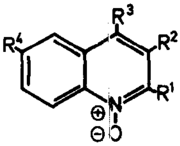
[x] This paper is no. VII in the series "Photochemical Studies".

[xx] Immersion lamp, Hanovia Q-700, Pyrex filter.

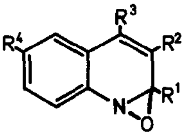
[xxx] All compounds described in this paper showed satisfactory elemental analyses.

quinoline N-oxides, described by Kaneko *et al*. (1-3), and it is seen from the NMR, UV, and IR spectra, as well as the m.p. determination (Table 1-2) that IIIa is identical with the irradiation product obtained from Ia by Kaneko *et al*. (1).

However, on the basis of the chemical properties of IIIa-d we infer that these compounds have the 4,5-benz-1,3-oxazepine structures shown below (III), rather than the oxaziridine structures (II), suggested by Kaneko *et al*. for IIIa and related compounds (1-3).



I



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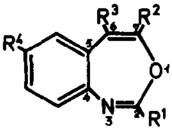
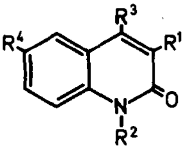


III



IV

a. $R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$.

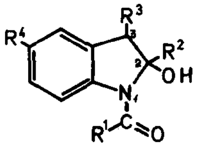
b. $R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = R^4 = H$.

c. $R^1 = C_6H_5$, $R^2 = H$, $R^3 = CH_3$, $R^4 = H$.

d. $R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$.

e. $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$.

f. $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, $R^4 = H$.



V

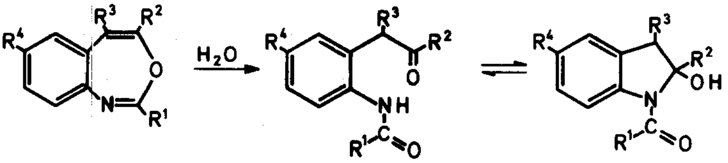
The assignment is based on the following experiments: A. If the irradiations of Ia, Ic, and Id were carried out in 96 % ethanolic solution, Ia yielded 3-phenylcarbostyril (IVa) (8 %), *N*-benzoyl-2-hydroxy-2,3-dihydroindole (Va) (*ca*. 10 %), and IIIa (61 %); Ic yielded 3-phenyl-4-methylcarbostyril (IVc) (12 %), *N*-benzoyl-2-hydroxy-3-methyl-2,3-dihydroindole (Vc) (14 %), and an unidentified crystalline substance (VIa) (26 %); and Id yielded 3-phenyl-6-methylcarbostyril (IVd) (9 %), and IIId (56 %). In another experiment it was found that Ia, by irradiation in 50 % aqueous ethanol, formed a complicated mixture from which only IVa was isolated (10 %). (From the irradiation of Ia in benzene, *ca*. 0.5 % IVa was isolated).

Finally it was found that IVa was formed neither photochemically nor thermally from IIIa, and that Va and Vc result from the solvolysis of IIIa and IIIc respectively:

By irradiating IIIa,c in 50 % aqueous ethanolic solutions, no IVa,c could be isolated, and the solvolysis of IIIa in 50 % aqueous ethanolic solution at room temperature yielded Va (65 %), but no IVa could be detected, and solvolysis of IIIc under similar conditions yielded Vc (*ca*. 50 %), again without detectable amounts of the carbostyril IVc.

These results imply that compounds IIIa,c and IVa,c are formed, during the photolysis, by way of primarily generated unstable intermediates, which may be the oxaziridines IIa,c.

The formation of Va,c in the solvolysis of IIIa,c is consistent with the suggested benzoxazepine structures for the latter compounds, which can also be regarded as imido esters of enoles.[x] The isolation of a series of compounds related to Va and c in the photolysis of quinoline *N*-oxides (5a-c) indicates a similar reaction sceme in the formation of these compounds.



III V' V

B. It has been found that oxaziridines in general are strongly oxidizing (6-7), and liberate iodine from potassium iodide, and even hydrochloric acid can be oxidized to chlorine by these compounds (6). However, IIIa-d do not liberate iodine from potassium iodide *cf*. (1); on the contrary, they consume iodine. A preliminary experiment showed that IIIa consumed 1 mole of iodine per mole by treatment with I_3^- in neutral aqueous ethanolic solution, and it was found that IIIa reduced copper-(II) chloride under quite mild conditions. This seems also to favour the perception that compounds IIIa-d are not oxaziridines, but benzoxazepines, since loss of two electrons from III would give rise to an ion consistent with the Hückel $4n+2$-rule.

C. Further evidence was found in the reduction of IIIa with lithium aluminium hydride in ether, to yield *N*-benzylindole (70 %),

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[x] During the preparation of the present paper, a paper by Kaneko *et al.* appeared (4), in which they suggested the formation of benzoxazepines like III, as *unstable intermediates*, in some of the reactions of the presumed stable oxaziridines (II).

whereas oxaziridines according to (6), under similar conditions are reduced to the parent imines. This, by analogy, for the presently described experiment, led us to expect the formation of 2-phenylquinoline if IIIa contained the oxaziridine structure.
D. Finally it should be noted that IIIa was unchanged after boiling for ten days in benzene solution in the presence of water, just as IIIa could be sublimed at atmospheric pressure without destruction, whereas Emmons (6) found that oxaziridines with a phenyl group in the 2- or the 3- position were highly unstable, and Shinzawa et al. (8) succeded to prepare solutions of 2,3-diphenyloxaziridine, but reported that this compound was so labile that it could not be isolated from the solutions.

The spectroscopical data do not permit unequivocal identification of IIIa-d as 4,5-benz-1,3-oxazepines. They are, however, in good agreement with this assignment.

The infrared spectra of IIIa-d (Table 1) show two characteristic lines at ca. 1670 cm^{-1} and ca. 1640 cm^{-1}, which we assign to the absorption from the seven membered ring. It should be noted that oxaziridines show no absorption in the 1600 cm^{-1} region (9).

The UV spectra of IIIa-d (Table 1) show absorption at a somewhat higher wavelength than found in the spectrum of cis-stilbene. A similar pattern is found in the UV spectra of other seven membered heterocyclic compounds (10).

The NMR spectra (Table 2) show a pattern which do not permit to distinguish between structures II and III.

TABLE 1.

Melting Points. IR Absorptions[a] (in KBr). Long Wavelength UV Absorptions (in 96 % ETOH).

Compound	M.p.	IR cm^{-1}	cm^{-1}	UV mμ	log ε
IIIa	65-66°	1670	1635	317	3.75
IIIb	72-73°	1675	1645	312	3.76
IIIc	57-58°	1660	1640	309	3.81
IIId	38-39°	1670	1635	327	3.76

a. Medium intensity

The carbostyrils IVa, IVc, and IVd were identified by elemental analysis, IR, UV, and NMR spectroscopy.

Compounds Va and Vc show the expected IR and UV absorptions, and in the NMR spectra of Va and Vc (Table 2) the aliphatic ring protons show signals very similar to the signals found in the NMR spectra of the corresponding N-acetyl compounds (5a-b). From Table 3 it is seen that Vc, like Vf exists as a mixture of the trans- and cis- form in solution (5c).

N-Benzylindole was identified by elemental analysis and by IR, UV, and NMR spectroscopy. The experimental details of this work will be described in a future paper.

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TABLE 2.

NMR Spectra.[a]

Compound	Solvent	Chemical shifts and coupling constants			
		H-6	H-7		CH_3
IIIa^b	$CDCl_3$	4.08,d,J=5.8	3.71,d,J=5.8		
IIIb^b	"	4.08,q,J$\sim$1			7.95,d,J$\sim$1
IIIc^b	"		3.70,q,J=1.5		8.05,d,J=1.5
IIId^b	"	4.10,d,J=6	3.75,d,J=6		7.72,s
		H-2	H-3		CH_3
			A	B	
Va^b	$DMSOd_6$	4.34,d,J=6.5	6.60,dd,^{c} J_1=6.5,J_2=17	7.20,d,J=17	
Ve^d	"	4.16,d,J=7	6.62,dd J_1=7,J_2=17	7.15,d,J=17	
Vc^b cis	"	4.48,d,J=6.6	6.5,m		8.72,d^e,J=7.5
Vc^b trans	"	4.80,s	6.92,d,J=7		8.88,d^e,J=7.5
Vf^d cis	"	4.18,d,J=7	6.55,qui J_1=7,J_2=7		8.54,d,J=7
Vf^d trans	"	4.53,s	6.79,q,J=7		8.69,d,J=7

a. Chemical shifts are in τ-units, coupling constants in cps; s = singlet, d = doublet, dd = doublet of doublets, q = quartet, qui = quintet, m = multiplet.

b. 60 Mc/sec with TMS as internal reference.

c. Partly obscured by the signal from H_2O, present in the solvent.

d. 100 Mc/sec with TMS as external reference.

e. The doublet from the cis-form was merged with the doublet from the trans-form to a triplet. When $CDCl_3$ was used as solvent, the signals appeared as two doublets.

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