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THE FORMATION OF 2a,7a-DIHYDROBENZOFURO[2,3-b]AZETE DERIVATIVES IN THE PHOTOLYSIS OF ISOQUINOLINE N-OXIDES

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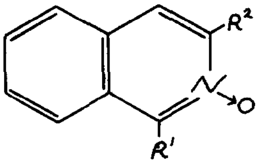
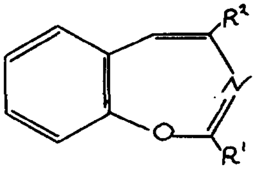
The formation of 1,3-oxazepine derivatives in the photolysis of aromatic amine oxides has recently been described in a number of papers (1). This paper reports the photochemical rearrangement of isoquinoline N-oxides (I) to 2a,7a-dihydrobenzofuro[2,3-b]azete derivatives (III) via benz[f-1,3]oxazepine intermediates (II).



I



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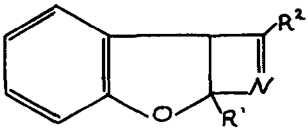
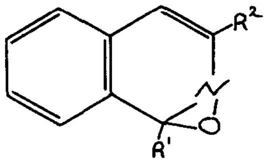
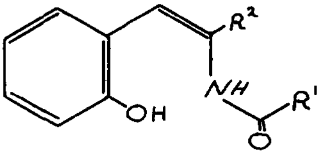


III



V



IV

	R^1	R^2
a	CN	CH_3
b	CH_3	H

In a typical run, a solution of 300 mg of 1-cyano-3-methylisoquinoline N-oxide (Ia) was irradiated[x] until all the starting material was consumed. Evaporation of the solvent *in vacuo* yielded an oil which was treated with a mixture of pentane-

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[x] External light source: Philips type KL7070, medium pressure mercury lamp

ether. On cooling 205 mg of a white crystalline compound did precipitate.

On the basis of the spectroscopic data and the chemical properties studied until now of (IIIa) it is concluded that this compound has the 7a-cyano-2-methyl-2a,7a-dihydrobenzofuro[2,3-b]azete structure (IIIa):

A. The elemental analysis shows that the compound is isomeric with the starting material.[x]

TABLE 1

Compound	M.p.	IR^{KBr}(cm^{-1})	UV$^{Ether}_{Max}$(mμ, logε)			
Ia (1c)			339	3,78		
IIa (1c)	86-87°	1645	343	3,44		
IIIa	70-71°	3060 3000 1600 810 760	289	3,46	282	3,43
IIIb			290	3,52	281	3,55
IVb	175-76°	3250 1625	299sh	3,72	265	4,21
1,2-naphthalene oxide (2)		(Dioxane)	304	3,20	268	3,94

B. The tabulated IR absorption bands of IIIa indicate the presence of a benzene ring, with 4 adjacent H. Neither IIa nor IIIa show any absorption in the 2200 cm^{-1} region. If a CN group is still present in the molecule this indicates an O-C-CN-arrangement (3).

C. From the UV spectrum it is seen that the conjugation in IIIa is decreased relative to that in Ia and IIa. It should be noted that the UV spectrum of IIIa is different from that of 1,2-naphthalene oxide (2).

D. The NMR spectrum (60 Mc/s in CDCl$_3$ with TMS as internal reference) of IIIa supports the assigned structure: The aromatic protons show resonance at 2,5-3,2τ, multiplet, 4H. Aliphatic methine proton at 5,02τ, broad singlet, 1H. Methyl protons at 7,8τ, doublet, J = 1,0 cps, 3H.

E. Compound IIIa does not liberate iodine from potassium iodide. This shows that the compound is not so strongly oxidizing as would be expected of the isomeric

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[x] All new compounds described in this paper show satisfactory elemental analysis

oxaziridine Va (4).

F. In analogy with similar results in cycloheptatriene photochemistry (5) it is possible to convert IIIa to IIa by thermolysis in boiling toluene (5 min., 50 % yield).

Finally it should be noted, that IIIa can be obtained in 80 % yield on photolysis of IIa under conditions quite similar to these described above.

Photolysis of Ib in benzene solution at 18° in an argon atmosphere resulted in a colourless solution. During evaporation of the solvent *in vacuo* at 20°C the solution turned yellow and a brown oil remained. This oil was separated by preparative layer chromatography to give 78 % of a compound for which the elemental analysis and spectroscopic properties indicate that it has the structure IVb.

IR and UV: Table 1. NMR: Aromatic protons at 3,0τ, multiplet, 4H. NH proton at 1,66τ, singlet, 1H. OH proton at 0,68τ, singlet, 1H. Methyl protons at 8,01τ, singlet, 3H. Aliphatic methine protons at respectively 2,50τ, 1H and 4,38τ, doublet J = 10 cps, 1H.

It has previously been shown (1c) that type IV compounds arise from the corresponding oxazepines II by a hydrolytic process. Examination of a benzene solution of Ib immediately after irradiation by UV and thin layer chromatography showed that no compound was present with neither UV spectrum nor R_F value similar to those of IIa, just as IVb could not be detected in this solution. From Table 1 it is seen that the UV absorption of the primary photoproduct from Ib (IIIb in Table 1) is very similar to that of IIIa and we thus assign the structure IIIb to this product.

On the basis of these observations it is concluded that the photolysis of 1-substituted isoquinoline N-oxides results in two consecutive photochemical reactions: The first reaction leads to a benz[f-1,3]oxazepine structure (III) and the second reaction transforms III to 2a,7a-dihydrobenzofuro[2,3-b]azete derivatives. The second process can be reversed thermally. Several other isoquinoline N-oxides have been subjected to photochemical transformations. These results will be described in a future paper.

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