Further Studies on the Photochemical Reactions of 6-Substituted Phenanthridine 5-Oxides

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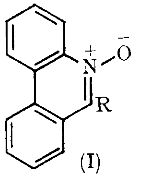
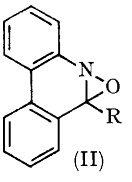
IN view of recent communications dealing with photolyses of aromatic amine oxides,[1] it seems appropriate to report our recent observations on some photochemical reactions of 6-substituted phenanthridine 5-oxides.

In our previous Communication,[2] it was reported that 6-substituted phenanthridine 5-oxides rearrange in high yield to the corresponding 5-substituted phenanthridin-6(5*H*)-ones when irradiated in ethanol solution. It has been found that the course of the photochemical reaction of 6-arylphenanthridine 5-oxides is very dependent upon the solvent employed. Thus, while 6-phenylphenanthridine 5-oxide (Ia) rearranged almost quantitatively to 5-phenylphenanthridin-6(5*H*)-one (IIIa) when irradiated in ethanol solution,[2] irradiation† of (Ia) in benzene solution led to the formation of (IIIa) (16·7%), 2-phenyldibenz[*d,f*][1,3]oxazepine [(VIa), 3·0%], 9-benzoylcarbazole [(Va), 1·0%], 6-phenylphenanthridine [(IVa), 10·8%], and 2-benzamido-2′-hydroxybiphenyl [(VIIa), 34·8%].



(I)



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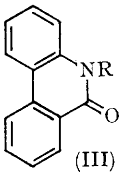

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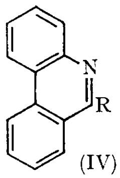

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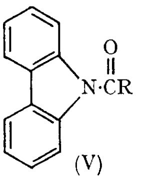

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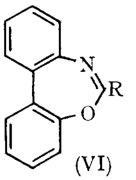
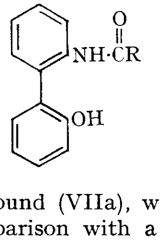


(VI)



(VII)

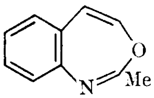
(a) R=Ph
(b) R=CHEtPh
(c) $R{=}CHPh_2$
(d) R=H

Compound (VIIa), whose structure was proved by comparison with a sample synthesized independently, was shown to arise by hydrolysis of (VIa), probably on the Florisil column used to separate the products.

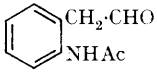
The formation of (VIa) is analogous to the recently reported photochemical rearrangements of quinoline 1-oxides to benz[*d*][1,3]oxazepines,[3,4b] isoquinoline 2-oxides to benz[*f*][1,3]oxazepines,[4a] quinoxaline 1-oxides to benz[*d*][1,3,6]oxadiazepines,[4b,d] and quinazoline 3-oxides to benz[*f*][1,3,5]oxadiazepines.[4c]

Compound (IVa) is formed by simple deoxygenation of (Ia). Photolytic deoxygenation of *N*-oxides has been observed often in the past.[1b,c,4b,5]

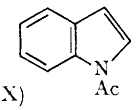
The formation of (Va), however, was unexpected. It is formally analogous to the formation of indole derivatives on irradiation of quinoline 1-oxides. Thus, irradiation of quinaldine 1-oxide gives *o*-acetamidophenylacetaldehyde[5e] (IX) [which arises by hydrolysis of the initially formed benz[*d*][1,3]oxazepine (VIII)], which subsequently cyclizes to 1-acetylindole (X). A similar mechanism cannot be operative, however, in the conversion of (Ia) into (Va); hydrolysis of the dibenz[*d,f*][1,3]oxazepine (VIa) gives (VIIa), but the latter cannot close to form the carbazole (Va). The latter must therefore be formed in a photochemical process either directly from (Ia) or from (IIa).



(VIII)



(IX)



(X)

When 6-(α-phenylpropyl)phenanthridine 5-oxide (Ib), $[\alpha]^{22}_{\mathrm{D}}$ + 7·85°, was irradiated in either ethanol or benzene, the 5-(α-phenylpropyl)phenanthridin-6(5*H*)-one (IIIb) formed was found to be racemic. The total loss of optical activity indicates that the α-phenylpropyl group, in migrating from carbon to nitrogen, must be either a planar species, or a species which can rapidly invert about the α-carbon. Although an anionic intermediate is not ruled out, it would seem more probable that the migrating species is either a carbonium ion or a radical.

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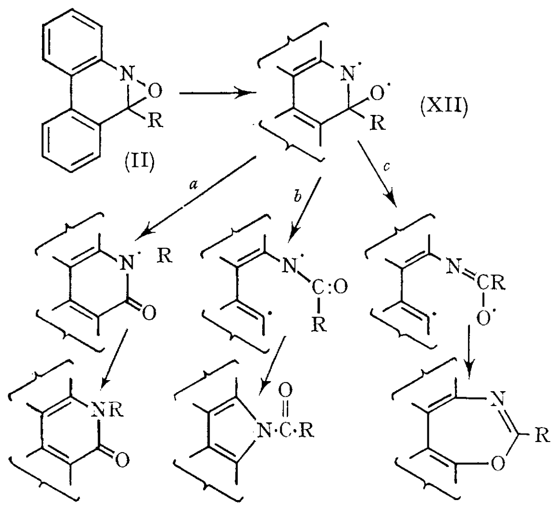
† The source of u.v. radiation was a Rayonet Photochemical Reactor with 3000 Å lamps. The reaction vessel was made of Pyrex.



Irradiation of 6-diphenylmethylphenanthridine 5-oxide (Ic) in benzene gave phenanthridin-6(5*H*)-one [(IIId), 17·2%], and 1,1,2,2-tetraphenylethane [(XI), 15·8%]. We suggest that (XI) is formed by the dimerization of a diphenylmethyl radical, while (IIId) is formed by extraction of a proton from the solvent (slightly wet benzene) by the 5,6-dihydro-6-oxophenanthridin-5-yl radical, which remains after escape of the diphenylmethyl radical from the solvent cage.

On the basis of the above observations, we propose that the photolysis of 6-arylphenanthridine 5-oxides in benzene‡ involves initial formation of the oxaziridine (II), which then undergoes homolysis of the N–O bond to give (XII) (a similar step has been proposed for the oxaziridine → amide rearrangement[6]). The diradical (XII) then rearranges *via* paths *a*—*c* to give the observed products.

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‡ Different results are obtained from photolysis in ethanol solution (ref. 2), indicating that another mechanism may be operative.

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