The Photochemistry of Pyridine *N*-Oxide

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IN view of the recently reported[1] formation of phenol upon irradiation of pyridine *N*-oxide in benzene solution, it seems appropriate to report our results on the photolysis of pyridine *N*-oxide in alcoholic solution, since a different course (*via* the primary formation of an oxaziridine) seems involved. Both methanol and ethanol solutions of pyridine *N*-oxide were irradiated.[†] The reaction mixture was analysed by g.l.c. using a 2·5% FFAP on Chrom G column and a Porapak Q column.[‡]

The result of a typical run (photolysis of 1g./100 ml. RCH_2OH, 10 mmoles) is shown in sequence 1. With the Pyrex filter, 50% of the starting material was recovered after 6 hr. of photolysis. Using the all-quartz system, 10% of the starting material was recovered after 10 min. of photolysis.

The structures of (I), (II), (IV), and (V) were proved by comparison of the g.l.c. retention times, their i.r., u.v., n.m.r., and mass spectra with those of authentic samples [(I) and (II) were available commercially; (IV) and (V) were synthesized].

The structure of (III), as yet obtained only by this method, is indicated by the following evidence: the i.r. spectrum shows no N–H stretch at 3400 cm.$^{-1}$ and no carbonyl stretch; there is a strong absorption pattern at 1000 to 1550 cm.$^{-1}$ indicative

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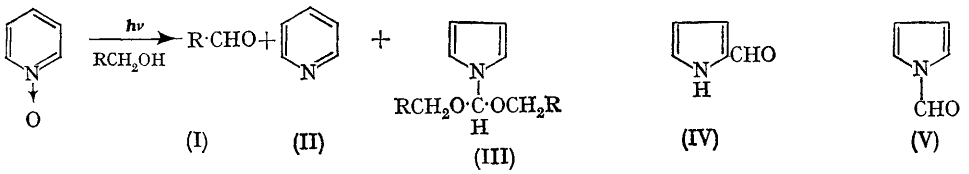
[†] A quartz Hanovia immersion apparatus was used with a Hanovia high pressure 450 watt mercury lamp. Nitrogen was bubbled through the solution throughout the irradiation. After the lamp was turned off, the solution gradually darkened, and an unidentified brown polymer precipitated.

[‡] Obtained from Varian-Aerograph, Walnut Creek, California.

(1)



	(I)	(II)	(III)	(IV)	(V)
Pyrex filter	0·26	0·68	0·27	0·13 (mmole)	trace
All quartz	0·42	0·69	0·36	0·50 (mmole)	trace

of an acetal function; the n.m.r. spectrum of (III; R = H) s, (sh), τ 6·8 (6H); and s (br), at τ 4·3 (1H), 3·95 (2H), 3·25 (2H); n.m.r. of (III; R = Me) t, τ 8·8 (6H); q, τ 6·5 (4H); and s (br), τ 4·1 (1H), 3·92 (2H), 3·2 (2H).

The u.v. spectrum in EtOH of both R = H and R = Me shows a λ_{max} at 220 mμ, ϵ 5,600. Upon addition of one drop of 0·1 N-HCl the λ_{max} shifted to 235 mμ with an increase in ϵ. Upon addition of 3 drops of 0·1 N-NaOH the λ_{max} shifted to 210 mμ. Upon re-acidification, there is no further shift in the λ_{max} value. *N*-Formylpyrrole [synthesized as a standard for proof of (V)] shows a λ_{max} in EtOH at 235 mμ, ϵ 11,200 in the u.v. Upon addition of 2 drops of 0·1 N-NaOH, there is a shift of the λ_{max} to 210 mμ. A parallel experiment was performed on a more concentrated solution of (III) and the reaction with acid and base was followed by g.l.c. The reactions shown in sequence (2) are consistent with the results.§

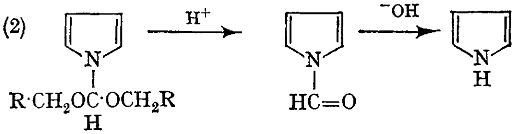
A high-resolution mass spectrum was taken of (III; R = H). The base peak was *m/e* 75, $C_3H_7O_2$. The other major peaks were: parent peak (18% of base peak) at 141, $C_7H_{11}NO_2$; $M-30$, C_6H_8NO (32% base); $M-46$, C_5H_5NO (30% base); $M-74$, C_4H_5N (40% base).

The photolysis of substituted quinoline *N*-oxides has been reported by Kaneko[2] in Japan, and Buchardt[3] in Sweden. Streith and Sigwalt[4] have reported the photolysis of pyridine *N*-oxide [the only product reported was pyrrolealdehyde (IV)].

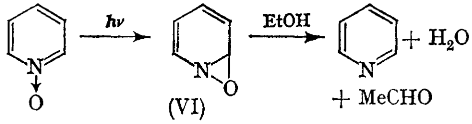
It is generally postulated that the first step in the photochemical reaction of the aromatic *N*-oxide is the formation of a non-isolable, unstable oxaziridine, of the type (VI), with subsequent rearrangement.[2–4]¶ The postulate arises from the observation of Calvin and Splitter[5] that isolable alkyl- and phenyl-substituted oxaziridines, formed photochemically from the nitrones, rearrange thermally to amides, which would correspond to pyridone in the cyclic case.

The finding of the previously unreported oxidation product of the solvent (acetaldehyde from ethanol) is direct evidence for the more powerful oxidant, an oxaziridine (VI), as an intermediate. It is known[6] that an oxaziridine will oxidize iodide to iodine. Since in the oxidation of iodide by an oxaziridine, the parent imine is formed as a product,[6] the presence of the deoxygenated heteroatomic compound may also be explained by reaction (3).

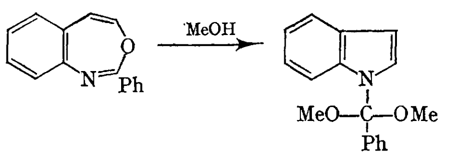
(2)



(3)



(4)



If the solvent is susceptible to oxidation by some photochemical intermediate, it may be possible to oxidize a carbon–carbon double bond and obtain an oxygen transfer (perhaps to give an epoxide) instead of a hydrogen abstraction as in the case of ethanol. The trace of *N*-formylpyrrole (V) found in the photolysis mixture may arise from hydrolysis of (III).

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§ It was found that (III) slowly hydrolyzed to *N*-formylpyrrole upon standing in ethanol solution.

¶ Although the pyridone-type derivatives were reported as products of photolysis of quinoline *N*-oxides, no pyridone could be detected in the pyridine *N*-oxide photolysis.

A corresponding compound** has formed from 2-phenylquinoline *N*-oxide[4c] through the stable intermediate[4,5c] 2-phenyl-3,1-benzoxazepine which, in turn, is suggested as a rearrangement product of the initially formed oxaziridine [see reaction (4)].[4c] Buchardt[5c] reports that oxazepines will not oxidize iodide, but will reduce iodine to iodide. While our evidence for the primary formation of the good oxidant, oxaziridine (VI), from pyridine *N*-oxide is substantial, we have no independent indication, as yet, of the participation of an oxazepine in the formation of (III).

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** Only an n.m.r. spectrum was used to assign the structure.

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