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September 14, 1967

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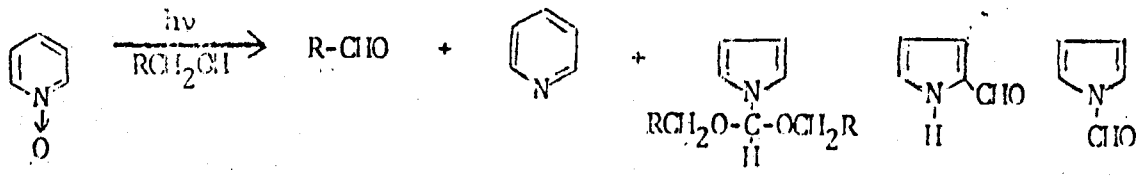
Sir:

We wish to report our results on the photolysis of pyridine N-oxide in alcoholic solution. Both methanol and ethanol solutions of pyridine N-oxide were irradiated.[1] The reaction mixture was analyzed by gas-liquid chromatography (GLC) using a 2.5% FFAP on Chrom G column and a Porapak Q column. In order to collect the products, the volume of the photolysis solution was reduced *in vacuo* and the resulting mixture was separated by preparative GLC.

The following is the result of a typical run (photolysis of 1 g/100 ml RCH_2OH, 10 mmole).



	I	II	III	IV	V
Pyrex filter	0.26 mmole	0.68 mmole	0.27 mmole	0.13 mmole	trace
All quartz	0.42 mmole	0.69 mmole	0.36 mmole	0.50 mmole	trace

With the pyrex filter, 50% of the starting material was recovered after 6 hrs of photolysis. Using the all-quartz system, 10% of the starting material was recovered after 10 min of photolysis.

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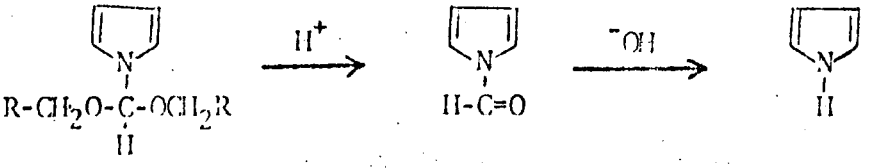
[1] A quartz Hanovia immersion apparatus was used with a Hanovia high pressure 450 watt mercury lamp. Immediately after photolysis, the solution turned very dark reddish brown upon standing, and a brown polymer precipitated.

The structure of I,II,IV,V was proved by comparison of the GLC retention times, the IR spectra, the UV spectra, the NMR spectra, and the mass spectra to those of authentic samples (I and II were available commercially; IV and V were synthesized).

The structure of III is believed to be as shown from the following evidence: the IR 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 of an acetal function. The NMR spectrum of III(R=H) shows a sharp singlet at 3.2δ (6H) and broad singlets at 5.7δ (1H), 6.05δ (2H), 6.75δ (2H). The NMR spectrum of III(R-CH_3) shows a triplet at 1.2δ (6H), a quartet at 3.5δ (4H), and broad singlets at 5.9δ (1H), 6.08δ (2H), 6.8δ (2H).

The UV spectrum in EtOH of both R=H and R=CH_3 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 reacidification, there is no further shift in the λ_{max}. N-Formyl pyrrole (synthesized as a standard for proof of V) shows a λ_{max} in EtOH at 235 mμ, ε 11,200, in the UV. Upon addition of two 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 GLC. The following reactions are consistent with the results.[2]



[2]It was found that III slowly hydrolyzed to N-formyl pyrrole upon standing in an ethanol solution.

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_5H_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[3] in Japan, and Buchardt[4] in Sweden. Streith and Sigwall[5] have reported the photolysis of pyridine N-oxide (the only product reported was pyrrole aldehyde, IV).

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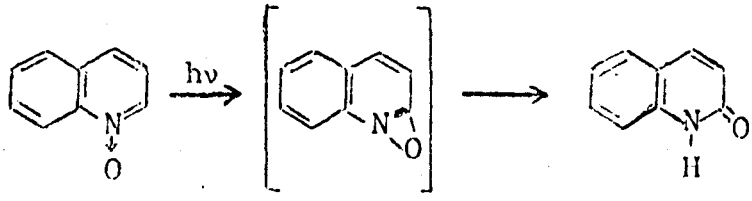
5

It is generally postulated that the first step in the photochemical reaction of the aromatic N-oxide is the formation of the non-isolatable, unstable oxaziridine, with subsequent rearrangement.[3-6]



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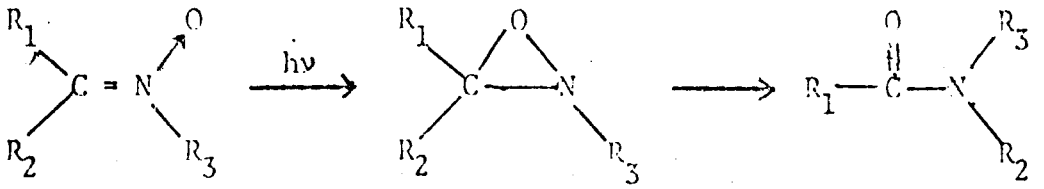
[3]a. M. Ishikawa, S. Yamada, H. Hotta and C. Kaneko, Chem. Pharm. Bull. (Tokyo), 14, 1102 (1966).
b. C. Kaneko, S. Yamada, M. Ishikawa, Tetrahedron Letters, 2145 (1966).
c. C. Kaneko, S. Yamada, I. Yokoe, Tetrahedron Letters, 4701 (1966).
d. C. Kaneko, S. Yamada, I. Yokoe, M. Ishikawa, Tetrahedron Letters, 1873 (1967).

[4]a. O. Buchardt, J. Becher, C. Lohse, Acta Chem. Scand. 19, 1120 (1965).
b. O. Buchardt, C. Lohse, Tetrahedron Letters, 4355 (1966).
c. O. Buchardt, Tetrahedron Letters, 6221 (1966).
d. O. Buchardt, C. Lohse, Acta Chem. Scand. 20, 2467 (1966).
e. O. Buchardt, C. Lohse, A. Duffield, C. Djerassi, Tetrahedron Letters, 2741 (1967).

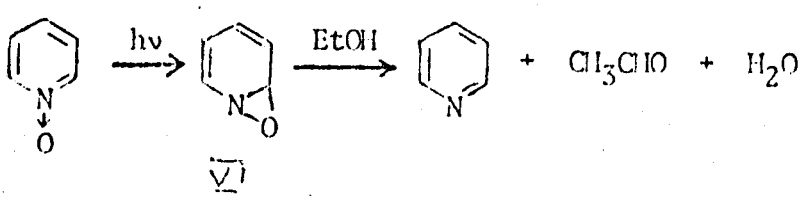
[5]S. Streith, G. C. Sigwalt, Tetrahedron Letters, 1347 (1966).

[6]Although the pyridone derivatives were reported as products of photolysis of quinoline N-oxides, no pyridone could be detected in the pyridine N-oxide photolysis.

This postulate arises from the observation of Calvin and Splitter[7] that isolatable alkyl and phenyl substituted oxaziridines, formed photochemically from the nitrones, rearrange thermally to amides:



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[8] 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,[8] the presence of the deoxygenated heteroatomic compound may also be explained by the following reaction:



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 an epoxide) instead of a hydrogen abstraction as in the case of ethanol.

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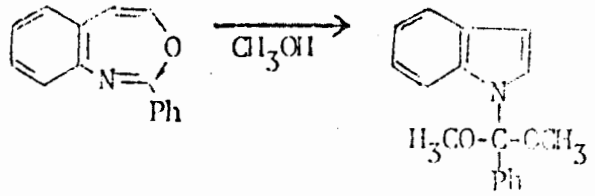
[7] J. S. Splitter and M. Calvin, J. Org. Chem. 30, 3427 (1965).

[8] W. D. Emmons, J. Am. Chem. Soc. 79, 5739 (1957).

The trace of N-formyl pyrrole (V) found in the photolysis mixture may arise from hydrolysis of III.

A corresponding compound[9] has been described as formed from 2-phenylquinoline N-oxide,[3c] through the stable intermediate[3d,4c] 2-phenyl-4,5-benz-1,3-oxazepine which, in turn, is suggested as a



rearrangement product of the initially formed oxaziridine.[3c] Buchardt[4c] reports that oxazepines will not oxidize iodide, but rather will reduce iodine to iodide. While our evidence for the primary formation of the good oxidant, oxaziridine (VI), from pyridine N-oxide is good, we have no independent indication, as yet, of the participation of an oxazepine in the formation of III.

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[9]Only an NMR spectrum was used to assign the structure.

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