Photochemistry of Pyridine Oxides: Atomic Oxygen Transfer in Solution; a New Synthesis of Phenol

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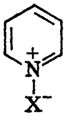
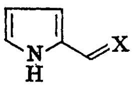
RECENTLY we reported the photochemical cleavage of pyridinium dicyanomethylide (I) in benzene solution; the resulting dicyanocarbene adds to benzene and leads to 7,7-dicyanonorcaradiene.[1] This photolytic reaction is strongly wavelength-dependent and does not occur if a special cut-off filter is used in connection with light of a high-pressure mercury lamp, when only photorearrangement to the pyrrole (III) occurs.

Pyridine *N*-oxides (II) whose photochemical behaviour is being studied,[2,3] exhibit in a formal sense the same electronic configuration as pyridinium ylids, and behave similarly when irradiated with ultraviolet light, *i.e.*, oxygen is released in the gas phase;[4] on the other hand, ultraviolet irradiation of pyridine *N*-oxides in benzene solution leads, *inter alia*, to the parent pyridines; atomic oxygen seems to be generated *at ordinary temperature* and phenol, derived from the solvent, is formed in a moderate yield (15%). The formation of oxepine (V), the more abundant valence tautomer of benzene oxide,[5] could have been expected, but no choice could be made between the addition or insertion reaction of oxygen, since compound (V) is known to rearrange to phenol with very mild bases, *e.g.*, collidine. Such a rearrangement could well have been triggered by the photogenerated pyridine. The photochemical ring contraction of pyridine *N*-oxides (II) into 2-formylpyrroles (IV),[2] a reaction which parallels the pyridinium ylid ring contraction, is a further argument in favour of similar electronic configurations for (I) and (II).

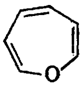
We have now found a third class of photocompounds derived from pyridine *N*-oxides, namely β-hydroxypyridines, the counterpart of which we could not detect in the photochemical mixture derived from the pyridinium ylid. For example, irradiation of 2,6-lutidine *N*-oxides in diethyl ether leads, *inter alia*, to 3-hydroxy-2,6-dimethylpyridine, m.p. 187° (decomp.), the structure of which was confirmed by a synthesis according to Fétizon's procedure;[6] similarly, irradiation of 2-methylpyridine *N*-oxide gave, besides the expected pyrrole derivatives,[2] an equimolar mixture (5% in all) of 3-hydroxy- and 5-hydroxy-2-methylpyridine. This type of reaction parallels the photochemical isomerisation of certain quinoline *N*-oxides into 3-hydroxyquinolines,[7] although the photochemical behaviour of the former compounds is different when ring contraction is involved.



(I) $X = C(CN)_2$
(II) $X = O$



(III) $X = C(CN)_2$
(IV) $X = O$



(V)

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