Photochemistry of Pyridine *N*-Oxides. Trapping of the Main Primary Product with Base

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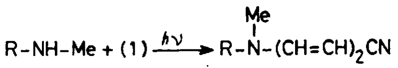
Summary Irradiation of pyridine *N*-oxide and some of its derivatives leads to very unstable unsaturated isocyanides, which have been trapped in matrices at cryogenic temperatures and with base at room temperature.

The photochemistry of pyridine *N*-oxide (**1**) has been the subject of several investigations.[1] Pyridine, 1-formylpyrrole and its acetals, 2-formylpyrrole, 2-pyridone, and oxidation products of the solvents have been observed as products, but the total yields of these were small, apparently owing to polymer formation. The polymer was assumed to be a polyacrylonitrile on the basis of an i.r. band at 2200 cm^{-1}. This was further substantiated by the observation of the light-induced formation of addition products between *NN'*-dimethyltryptamine (**2**) or *N*-methylaniline (**3**), and pyridine *N*-oxide (**1**)[2] (Scheme 1), possibly *via* 4-cyanobut-3-enal (**4**).[2]



$$R\text{-}NH\text{-}Me + (1) \xrightarrow{h\nu} R\text{-}\overset{\overset{\large Me}{|}}{N}\text{-}(CH{=}CH)_2CN$$

(**2**,**3**)

$NC\text{-}CH{=}CH\text{-}CH_2\text{-}CHO$

(**4**)

Scheme 1

We have irradiated pyridine *N*-oxide and some of its simple derivatives under various conditions with the following results. (i) Irradiation of pyridine *N*-oxide at 254 nm, in solvents such as MeOH, ether–pentane–alcohol, or acetonitrile (*ca.* 10^{-4} M) in all cases led to rapid disappearance of the substrate as observed by u.v. spectroscopy without the appearance of any characteristic new absorptions. (ii) In each case attempts to concentrate these solutions led to the formation of a dark polymer with a characteristic i.r. absorption at 2200 cm^{-1}. In acetonitrile traces of 2-formylpyrrole (**2**) were observed, but in no case could any pyridine be detected under these conditions. (iii) By irradiating at 10 K in an argon matrix and analysing by i.r. spectroscopy, we observed a series of new absorptions. The most interesting of these was at 2156 cm^{-1}, which was assigned to an isocyanide function; absorptions at 1705 and 1740 cm^{-1} were assigned to an aldehyde function.

Based on this, structure (**5a**) and/or (**5b**) was tentatively proposed for the observed species (Scheme 2), and an experiment to trap the isocyanide with base was undertaken, the u.v. spectra of which are shown in the Figure.

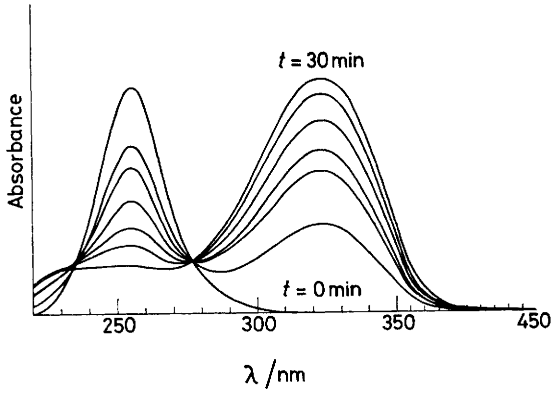
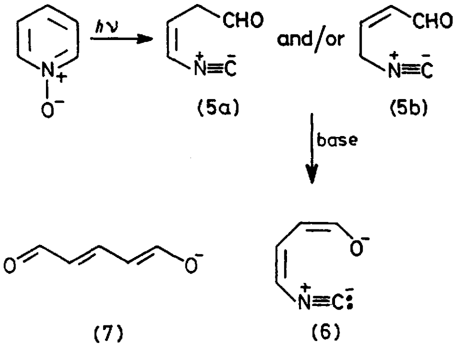


Figure. Photolysis (at 254 nm) of (**1**) (10^{-2} M) in 5×10^{-2} M aq. NaOH. The u.v. spectra were recorded every 5 min.

The presence of the isocyanide function under aqueous basic conditions was substantiated by i.r. spectroscopy, which revealed an absorption at 2145 cm^{-1}, *cf.* ref. 3. The absorption maximum in the u.v. spectrum at 323 nm corresponds well with the proposed structures; *e.g.* the related anion (**7**) shows absorption at 362 nm.[4] Upon catalytic reduction (Raney nickel) at 3 atm of a methanolic solution of (**6**) the absorption at 323 nm disappeared, and upon work-up followed by g.l.c.–mass spectrometry, a species corresponding to *N*-methylpyrrolidine could be observed [*m/e* 85 (55%), 84 (100), 57 (38), 56 (45), 44 (35), and 42 (35)]. This is also in agreement with the proposed structures.

A preliminary examination of the scope of the reaction was achieved by irradiating a series of alkyl- and aryl-substituted pyridine *N*-oxides in the presence of NaOH, and in each case where these possessed an unsubstituted 2-position light-induced formation of a sodium salt could be observed. However, in order to avoid polymerization of the transient under preparative conditions, the base concentration should be $> 10^{-1}$ M. The observation of the i.r. absorption at 2200 cm^{-1} in the polymer, and the formation of the cyanobutadienyl derivatives (Scheme 1) are due most probably to very fast isomerization of isocyanide to the corresponding cyanide.

By flash photolysis it was observed that the base reacted with an intermediate photoproduct, and the kinetics imply two parallel base catalysed reactions, one of which is general base catalysed and the other specific base catalysed.



Scheme 2

We conclude that, besides the previously observed photoproducts from pyridine *N*-oxide, a species is formed in high chemical yield, which can be trapped in the form of a salt with strong base; we tentatively propose the structure (**5a**) and/or (**5b**) for this new product. The reaction appears to take place for a series of pyridine *N*-oxides without substituents in the 2-position.

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