Photochemistry of Pyridine *N*-Oxides.[1] Chemical Properties of Single and Triplet Excited States

By FRANÇOIS BELLAMY, LUIS GUILLERMO RUIZ BARRAGAN, and JACQUES STREITH*

(*Laboratoire de Photochimie Organique associé au C.N.R.S., Institut des Sciences Exactes et Appliquées du C.U.H.R., Rue des Frères Lumière, 68-Mulhouse, France*)

Summary Sensitization of the pyridine *N*-oxide triplet state increases the extent of oxygen transfer reactions, whereas quenching with a copper salt in aqueous solution increases the extent of photorearrangement.

ULTRA-VIOLET irradiation of pyridine *N*-oxides leads to the formation of photoisomers and to photolytic oxygen abstraction,[1] these processes being competitive. It has been shown that pyridine *N*-oxide rearranges photochemically in poor yield to 2-formylpyrrole;[2] when benzene is the solvent, oxygen transfer is also observed to give phenol and pyridine.[3] Buchardt has shown that photolytic oxygen abstraction is the only process when benzophenone is used as a sensitizer, photoisomerization being totally suppressed.[3]

We have found that 2-cyanopyridine *N*-oxide undergoes photoinduced oxygen transfer, cyanopyridine being formed in 47% yield.[2] Triplet sensitization of a 2×10^{-2}M-solution of 2-cyanopyridine *N*-oxide in methylene chloride increases the photolytic process (Table 1).

TABLE 1. *Yield of 2-cyanopyridine in the presence or absence of sensitizers*

Lamp	Sensitizer	Concentration of sensitizer	Yield (%)	Filter
Philips HPK 125	None		47·3	Pyrex
Philips HPK 125	Xanthone E_T 74 kcal mol^{-1}	4×10^{-2}M	57·6	Pyrex
		8×10^{-2}M	63·0	Pyrex
		$1{\cdot}6 \times 10^{-1}$M	71·0	Pyrex
Hanau NK 6/20	Tetrabutylammonium phenyltetrazolide† E_T 79 kcal mol^{-1}	3×10^{-2}M	71·7	Quartz
Philips HPK 125	Oxygen bubbled through the solution		33·0	Pyrex

Experiments were conducted in a merry-go-round u.v. multitube reactor under nitrogen. Irradiation was continued until all starting material was consumed. Formation of 2-cyanopyridine was monitored by g.l.c., using 2,4-dimethylphenol as internal standard.‡ When oxygen is bubbled through the solution, the yield of 2-cyanopyridine drops to 33%. These results suggest a triplet-state intermediate during the photolytic cleavage.

In view of the preceding results it seemed reasonable to postulate a singlet excited state to explain the formation of the photoisomers. Quenching of the triplet state of pyridine *N*-oxide should therefore lead to an increased yield of 2-formylpyrrole. A transition metal complex was thought to quench the triplet state but in fact formation of 2-formylpyrrole was increased tenfold when a copper nitrate complex[4] in H_2O was irradiated (Table 2). The formation of 2-formylpyrrole was monitored by measuring the optical density of the pyrrole u.v. absorption band [λ_{max} 292 nm (ϵ 16·000)].

In practice, a solution of pyridine *N*-oxide and the copper salt can be irradiated without prior synthesis of the complex. The shortest reaction time and best yield of 2-formylpyrrole was obtained with a 2×10^{-1}M-solution of $Cu(ClO_4)_2$. On a preparative scale, 320 mg of 2-formylpyrrole are formed from 1 g of pyridine *N*-oxide.

When pyridine *N*-oxide complexes of Zn^{2+}, Fe^{3+}, Ni^{2+}, and Co^{2+} salts were irradiated under the same experimental conditions, no increase in 2-formylpyrrole formation could be detected. The effect of Cu^{II} salts cannot therefore be rationalized on grounds of a simple triplet quenching process by transition metal ions.

The mechanism of the effect of copper salts on pyridine *N*-oxide photochemistry is being investigated.

Financial support by the Instituto Nacional de la Investigación Científica (Mexico) and by the Délégation Générale à la Recherche Scientifique et Technique (France) is gratefully acknowledged.

TABLE 2. *Irradiation of pyridine* N-*oxide in* H_2O *in the presence of copper salts* (*Vycor filter*)

Lamp	Reactant	Yield (%)	Duration (h)
Philips HPK 125	Pyridine *N*-oxide 2×10^{-2}M	2	100
Philips HPK 125	$[PyO]_2Cu[NO_3]_2$ 10^{-2}M	32	100
Philips HPK 125	Pyridine *N*-oxide 2×10^{-2}M $+Cu[ClO_4]_2$ 2×10^{-1}M	40	6

(*Received, December 29th,* 1970; *Com.* 2220.)

---

† We thank Professor Scheiner for a gift of this compound. P. Scheiner, *Tetrahedron Letters*, 1969, 4863.

‡ 10% Carbowax 20 M column on Chromosorb W 60/80.

C. Leibovici and J. Streith, in the press; J. Streith and P. Martz, *Tetrahedron Letters*, 1969, 4899.

[2] J. Streith and C. Sigwalt, *Bull. Soc. chim. France*, 1970, 1157.

[3] (a) J. Streith, B. Danner and C. Sigwalt, *Chem. Comm.*, 1967, 979; (b) A. Altkaitis and M. Calvin, *ibid.*, 1968, 292; (c) P. L. Kumler and O. Buchardt, *ibid.*, 1968, 1321; (d) M. Yamada and H. Arai, *Chem. and Pharm. Bull.* (*Japan*), 1968, 16, 767; *Tetrahedron Letters*, 1969, 2747; 1970, 2213.

[4] J. V. Quagliano and F. Fujita, *J. Amer. Chem. Soc.*, 1961, 83, 3770; R. L. Carlin, *ibid.*, p. 3773.