# The Photochemistry of 2,4,6-Triphenylpyridine *N*-Oxide†

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THE photochemical behaviour of pyridine *N*-oxides[1] has not been as extensively investigated as that of various quinoline *N*-oxides.[2] To gain further information concerning the photochemical behaviour of aromatic amine *N*-oxides in general, we have examined (*cf.* ref. 3) the solution-phase photolysis of 2,4,6-triphenylpyridine *N*-oxide (I).

Photolysis‡ (acetone solution, wavelength >3000 Å) of 2,4,6-triphenylpyridine *N*-oxide (I) and separation of the reaction mixture by preparative layer chromatography yielded three crystalline fractions.

The first fraction (21%) was a mixture of 2,4,6-triphenylpyridine (II) (*ca.* 60%) and a compound tentatively assigned the 1,3-oxazepine structure (III) (*ca.* 40%). Although it has not as

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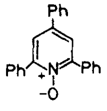
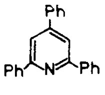
† Part of the series "Photochemical Studies"; for previous papers, see ref. 11.

‡ The light source for all photolyses was the RUL-3500 lamps of a Rayonet reactor, type RPR-208.

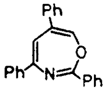
yet been possible, by any of a variety of techniques, to separate this mixture into its components, the structures were assigned on the basis of the spectroscopic properties of the mixture. The presence of the parent pyridine (II) in the mixture was detected by n.m.r.§ ($\tau$ 2·33, sharp s, characteristic of the pyridine ring protons of 2,4,6-triphenylpyridine). The 1,3-oxazepine structure (III) was assigned on the basis of n.m.r. $\tau$ 3·65 (d, $J$ 1·5 c./sec.), i.r. (KBr), 1640 cm.$^{-1}$ and u.v. $\lambda_{max}$ (EtOH) 351 m$\mu$, ($\epsilon \approx 1500$), (broad absorption tailing into the visible region which accounts for the observed yellow colour of the mixture); these spectral features seem to be general for the 1,3-oxazepine ring system.[2]



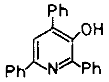
(I)



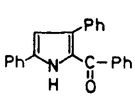
(II)



(III)



(IV)



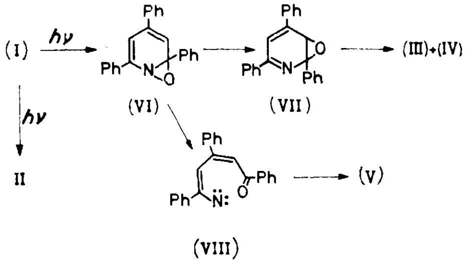
(V)

The second fraction (10%, m.p. 139—141°) was identified as 3-hydroxy-2,4,6-triphenylpyridine (IV)¶ on the basis of chemical tests (positive $FeCl_3$ test), i.r. [($CHCl_3$), OH absorption at 3540 cm.$^{-1}$], u.v. [$\lambda_{max}$ ($CHCl_3$) 322 ($\epsilon$ 9800) and 253 m$\mu$ ($\epsilon$ 26,800)], and n.m.r. [$\tau$ 1·7—2·8 (m, 16H, phenyl protons and pyridine C*H***) and 4·53 (br s, 1H, disappears upon shaking with $D_2O$, OH)].

The third photoproduct (56%, m.p. 163—164°) was identified as 2-benzoyl-3,5-diphenylpyrrole (V)¶ by i.r. [($CCl_4$) 3460 (free NH), 3310 (bonded NH), and 1610 cm.$^{-1}$ (carbonyl)], u.v. [$\lambda_{max}$ (cyclohexane) 345 ($\epsilon$ 17,600) and 272 m$\mu$ ($\epsilon$ 17,100)], and n.m.r. [$\tau$ 0·03 (br s, 1H, disappears on shaking with $D_2O$, NH), 2·3—3·4 (m, 15H, phenyl protons), and 3·53 (d, 1H, $J$ 3 c./sec., collapses to a singlet upon shaking with $D_2O$ or upon decoupling by double irradiation at $\tau$ 0·03, pyrrole CH)].

If the photolysis is performed in methanol as solvent, the same products are observed, but the distribution is different: (II) + (III) (8%), (IV) (38%), (V) (37%). If the irradiation is conducted in ethanol solution with benzophenone present, the only product observable by t.l.c. is the parent pyridine (II).

The above results are consistent with the following mechanism:



We have previously suggested[4] that deoxygenation of aromatic amine *N*-oxides proceeds *via* a different excited state than that leading to other photo-products. The present results, *i.e.* a high yield of deoxygenated product in the presence of benzophenone, suggest that photochemical deoxygenation of 2,4,6-triphenylpyridine *N*-oxide proceeds *via* the excited triplet state. Formation of 1,3-oxazepine ring systems during photolysis of aromatic amine *N*-oxides has been established and the mechanism of their formation *via* oxaziridines and oxirans, analogous to (VI) and (VII), was also discussed.[2,3,5,6] Photochemical formation of 3-hydroxyquinolines and 3-hydroxypyridines from quinoline and pyridine *N*-oxides has already been reported.[1e,7,8] Similar ring-contracted products, *i.e.* 2-acylpyrroles [1d–f] and 2-acylindoles[9] have also been observed during aromatic amine *N*-oxide photolyses, but this is the first time that a high yield of compounds of this type has been realized. We suggest that the 2-acylpyrrole (V) arises *via* initial cleavage of the oxaziridine (VI) to the nitrene (VIII) and subsequent conversion of the nitrene into the 2-acylpyrrole by insertion into the vinyl CH bond. Formation of this nitrene is analogous to the photochemical formation of phenylnitrene from 2,3,3-triphenyloxaziridine observed by Splitter and Calvin.[10] Furthermore, we have recently reported the formation and detection of a transient diazo-compound during the photolysis of 3,6-diphenylpyridazine *N*-oxide,[11] presumably formed by a process formally analogous to that presented here.

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§ 60 Mc./sec., $CDCl_3$ solution, $Me_4Si$ as internal standard.

¶ This compound gave satisfactory analytical data and molecular weight (mass spectrometry).

** The signal due to this proton appeared as a sharp spike at $\tau$ 2·38, and was readily discernible from the rest of the multiplet due to the phenyl protons.

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