

## The Photochemistry of Some *N*-(2-Methyl-4,6-diphenyl-1-pyridinio)-anilides

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*N*-(2-Methyl-4,6-diphenyl-1-pyridinio)anilides undergo ready photochemical dissociation into 2-methyl-4,6-diphenylpyridine and the corresponding nitrenes. The subsequent transformations of the nitrene do not allow unambiguous establishment of its electronic configuration.

THE thermal rearrangement of *N*-(2-methyl-1-pyridinio)-anilides (I) to give the corresponding 2-(*o*-aminobenzyl)-pyridines (II) has been known for many years.<sup>1</sup> A recent report<sup>2</sup> indicating that this sigmatropic rearrangement proceeded with facility on photolysis led us to undertake a more detailed examination. Since this study was initiated a number of papers concerning the photolysis of pyridinio *N*-ylides have appeared, showing that they may undergo rearrangement to derivatives of 1*H*-1,2-diazepines<sup>3-6</sup> or 2-aminopyridines,<sup>8</sup> or alternatively dissociate to the corresponding pyridine and a nitrene.<sup>5,7</sup> Of particular relevance is the report<sup>7</sup> that photolysis of *N*-(2,4,6-triphenyl-1-pyridinio)anilide yields 2,4,6-triphenylpyridine, aniline, and, in the

presence of diethylamine, a minor amount of 2-diethylamino-3*H*-azepine. Photolysis of the thermally labile *N*-(2-methyl-4,6-diphenyl-1-pyridinio)anilide in dichloromethane or diethylamine gave 2-methyl-4,6-diphenylpyridine (III) and aniline. Use of benzene as solvent for the photolysis resulted in the additional formation of 4,6-diphenylpyridine-2-carbaldehyde (IV). It was tentatively concluded on the basis of the formation of the azepine and the failure to observe triplet phenylnitrene as a product of photolysis of the ylide by e.s.r. measurements that the phenylnitrene was generated in an excited singlet state. This paper summarises those parts of our independent study which supplement this report.

<sup>1</sup> W. Schneider and K. Weiss, *Ber.*, 1928, **61**, 159.

<sup>2</sup> K. Dimroth, G. Arnoldy, S. von Eicken, and G. Schiffler, *Annalen*, 1967, **604**, 221.

<sup>3</sup> J. Streith and J. M. Cassall, *Angew. Chem. Internat. Edn.*, 1968, **7**, 129; *Tetrahedron Letters*, 1968, 4541; *Bull. Soc. chim. France*, 1969, 2175.

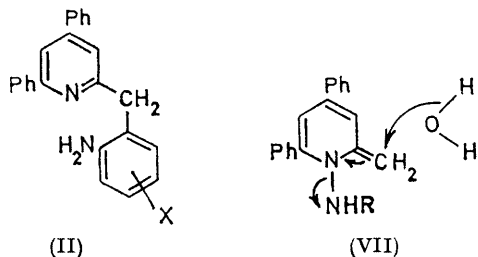
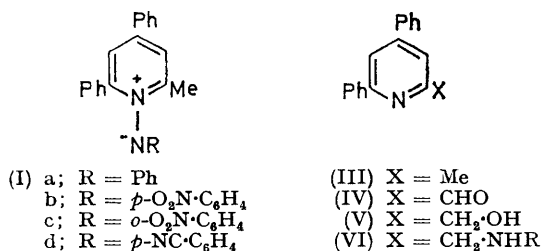
<sup>4</sup> T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, 1970, **35**, 426.

<sup>5</sup> V. Snieckus, *Chem. Comm.*, 1969, 831.

<sup>6</sup> A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, 1970, **35**, 433.

<sup>7</sup> V. Snieckus and G. Kan, *Chem. Comm.*, 1970, 172.

In our own experiments photolysis of *N*-(2-methyl-4,6-diphenyl-1-pyridinio)-*p*-nitroanilide (Ib) in benzene solution gave 4,4'-dinitroazobenzene, *p*-nitroaniline,



2-methyl-4,6-diphenylpyridine (III), and 4,6-diphenylpyridine-2-carbaldehyde (IV). The last compound was identified by its spectral properties and reduction by sodium borohydride to the alcohol (V). Photolysis of the ylide in cyclohexene gave only the pyridine (III) and *p*-nitroaniline. Supporting evidence for a nitrene intermediate in these reactions was provided by irradiation of a benzene solution of *N*-(2-methyl-4,6-diphenyl-1-pyridinio)-*o*-nitroanilide (Ic), when the products were the pyridine (III), the pyridine aldehyde (IV), *p*-nitroaniline, and benzofurazan oxide, which is presumably formed from the intermediary *o*-nitrophenylnitrene.

It has been suggested that formation of the pyridine-carbaldehyde proceeds *via* C-H insertion of the aryl-nitrene, forming compound (VI), followed by hydrogen abstraction and hydrolysis of the resulting Schiff base. However it seemed surprising that in the photolysis of (Ic) appreciable amounts of the aldehyde (IV) should be formed in preference to intramolecular cyclisation of *o*-nitrophenylnitrene. This raised the question as to whether the benzofurazan oxide was in photochemical equilibrium with *o*-nitrophenylnitrene, as the analogous anthranils undergo photochemical rearrangement *via* *o*-acylphenylnitrenes.<sup>8</sup> However, no reaction could be detected on irradiation of a benzene solution of benzofurazan oxide and 2-methyl-4,6-diphenylpyridine.

An alternative mechanism \* entails attack of water on the ylide tautomer (VII), leading to the alcohol (V), and subsequent hydrogen abstraction by the nitrene. Careful t.l.c. examination of the photolysis products of the ylide (Ic) revealed the presence of traces of the pyridine alcohol (V), which might alternatively have resulted from photoreduction of the pyridine aldehyde (IV).

\* We thank a referee for this suggestion.

<sup>8</sup> M. Ogata, H. Kano, and H. Matsumoto, *Chem. Comm.*, 1968, 397.

Repetition of the photolysis of the ylide (Ic) in the presence of the pyridine alcohol (V) resulted in a mixture of reaction products similar to that obtained before and an almost quantitative recovery of the alcohol (V). These results however do not exclude a more attractive variation of this mechanism, in which addition of arylamine to (VII) produces the intermediate (VI). This route would provide an explanation for the reported failure<sup>7</sup> to observe the formation of the aldehyde (IV) when phenyl azide was photolysed in the presence of the pyridine (III).

The formation of 4,4'-dinitroazobenzene in the photolysis of (Ib) suggests the formation of a triplet nitrene, in apparent contrast to other evidence. Although it is known that a nitro-substituent facilitates intersystem crossing, additional evidence on the electronic configuration appeared desirable. The extensive light absorption of these ylides throughout the visible and u.v. regions<sup>2</sup> makes the application of sensitisation techniques difficult. The demonstration<sup>9</sup> that singlet and triplet *p*-cyanophenylnitrene, from photolysis of *p*-cyanophenyl azide, can be distinguished by their behaviour towards dimethylamine led us to prepare and photolyse the *p*-cyanophenyl ylide (Id). The products were the pyridine (III), a trace of the pyridine aldehyde (IV), and *p*-cyanoaniline. No azo-compound was detected, in keeping with the supposed singlet nature of the *p*-cyanophenylnitrene. However when the photolysis was repeated in the presence of dimethylamine the same products were obtained. No *N'*-*p*-cyanophenyl-*NN*-dimethylhydrazine, which is the expected product from the electrophilic singlet *p*-cyanophenylnitrene,<sup>9</sup> was detected. In summary, our evidence is not consistent with the evidence adduced elsewhere<sup>7</sup> that these ylide photolysis reactions proceed *via* an excited singlet aryl-nitrene.

#### EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls with a Unicam SP 200 spectrophotometer. Unless otherwise stated, the identities of known compounds were established by comparison (mixed m.p.s and i.r. spectra) with authentic samples. Mass spectra were determined by the P.C.M.U., Harwell.

*Ylides*.—These were prepared from 2-methyl-4,6-diphenylpyrylium perchlorate and the appropriate arylhydrazine.<sup>2</sup> The following *N*-(2-methyl-4,6-diphenyl-1-pyridinio)anilides have not been reported previously: *o*-nitro-, m.p. 147–148° (Found: N, 10.9.  $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_2$  requires N, 11.0%); *p*-cyano-, m.p. 157–158° (Found: N, 11.6.  $\text{C}_{25}\text{H}_{19}\text{N}_3$  requires N, 11.6%).

*Photolysis of N*-(2-Methyl-4,6-diphenyl-1-pyridinio)-*p*-nitroanilide.—A solution of the ylide (2.9 g) in benzene (400 ml) under nitrogen was exposed to direct sunlight until the characteristic colour had been discharged (*ca.* 2 weeks). The solution was chromatographed on silica gel. Elution with benzene gave a red solid which was crystallised from acetone and identified as 4,4'-dinitroazobenzene (0.38 g,

<sup>9</sup> R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, 1969, **91**, 5680.

39%), m.p. 222—224° (lit.,<sup>10</sup> 222—223°). Further elution, with benzene-ethyl acetate (49 : 1), produced a viscous red oil. Molecular distillation at 150° and 0.5 mmHg pressure, followed by crystallisation from light petroleum (b.p. 60—80°) yielded 4,6-diphenylpyridine-2-carbaldehyde (0.11 g, 5%), m.p. 113—114° (lit.,<sup>7</sup> 110—113°),  $\nu_{\max}$  1695  $\text{cm}^{-1}$  (Found:  $M$ , 259.0993. Calc. for  $\text{C}_{18}\text{H}_{15}\text{NO}$ :  $M$ , 259.0997). Reduction with sodium borohydride in ethanol gave 4,6-diphenylpyridine-2-methanol. Benzene-ethyl acetate 93 : 7 eluted another viscous oil which after molecular distillation at 150—170° and 1.6 mmHg pressure gave 2-methyl-4,6-diphenylpyridine (0.87 g, 45%), m.p. 68—69° (lit.,<sup>11</sup> 73°). Finally, benzene-ethyl acetate (9 : 1) eluted *p*-nitroaniline (0.32 g, 29%), m.p. 147° (from water).

**4,6-Diphenylpyridine-2-methanol.**—4,6-Diphenylpyridine-2-carboxylic acid<sup>11</sup> was converted by ethereal diazomethane into its *methyl ester*, m.p. 111—112 [from light petroleum (b.p. 60—80°)] (Found:  $M$ , 289.1092.  $\text{C}_{15}\text{H}_{15}\text{NO}_2$  requires  $M$ , 289.1103). The ester (2.2 g) in dry ether was treated with lithium aluminium hydride (1 g) and kept under reflux for 0.5 h. Excess of hydride was destroyed by dropwise addition of ethyl acetate. Water was then slowly added to coagulate the alumina. The supernatant ether solution was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give 4,6-diphenylpyridine-2-methanol (1.3 g, 65%), m.p. 87—88° (from aqueous ethanol) (Found:  $M$ , 261.1148.  $\text{C}_{18}\text{H}_{15}\text{NO}$  requires  $M$ , 261.1153).

**Photolysis of N-(2-Methyl-4,6-diphenyl-1-pyridinio)-o-nitroanilide.**—The ylide (1 g) in benzene (40 ml) was exposed to direct sunlight until the characteristic colour was discharged; the solution was chromatographed on silica gel. Elution with benzene gave first a greenish solid (80 mg,

22%), which crystallised from aqueous ethanol yielding benzofurazan oxide, m.p. 69°, and secondly orange-red crystals (90 mg, 24%) identified as *o*-nitroaniline, m.p. 70—71° (from water). Further elution, with benzene-ethyl acetate mixtures as in the preceding experiment yielded 4,6-diphenylpyridine-2-carbaldehyde (0.1 g, 14%) and 2-methyl-4,6-diphenylpyridine (0.4 g, 60%).

**Photolysis of p-Cyano-N-(2-methyl-4,6-diphenyl-1-pyridinio)anilide.**—(a) A solution of the ylide (1.1 g) in benzene (240 ml) was rapidly decolourised by exposure to sunlight. Chromatography on silica gel and elution with benzene gave first a mixture (0.15 g) of 2-methyl-4,6-diphenylpyridine and 4,6-diphenylpyridine-2-carbaldehyde, as indicated by t.l.c. and i.r. spectrum, and then 2-methyl-4,6-diphenylpyridine (0.28 g). Elution with benzene-ethyl acetate (19 : 1) gave *p*-cyanoaniline (0.29 g), m.p. 83—84° (from carbon disulphide).

(b) The ylide (1.0 g) and dimethylamine (6.8 g) in benzene (350 ml) were irradiated as before. The solution was evaporated *in vacuo* and chromatographed. The products were 4,6-diphenylpyridine-2-carbaldehyde (trace), 2-methyl-4,6-diphenylpyridine (0.45 g), and *p*-cyanoaniline (0.12 g). Two unidentified fractions (*ca.* 10 mg) were examined by i.r. and n.m.r. spectroscopy but showed none of the features reported<sup>9</sup> for *N'*-*p*-cyanophenyl-*NN*-dimethylhydrazine.

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<sup>10</sup> I. Antener, *Helv. Chim. Acta*, 1938, **21**, 816.

<sup>11</sup> C. Gastaldi, *Gazzetta*, 1922, **52**, 169.