

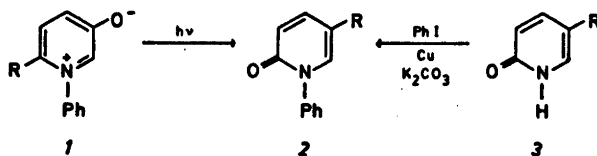
**N-Quaternary Compounds.****Part XLVIII.<sup>1</sup>****Photochemical Rearrangement of Pyridinium-3-olates to 2-Pyridones**

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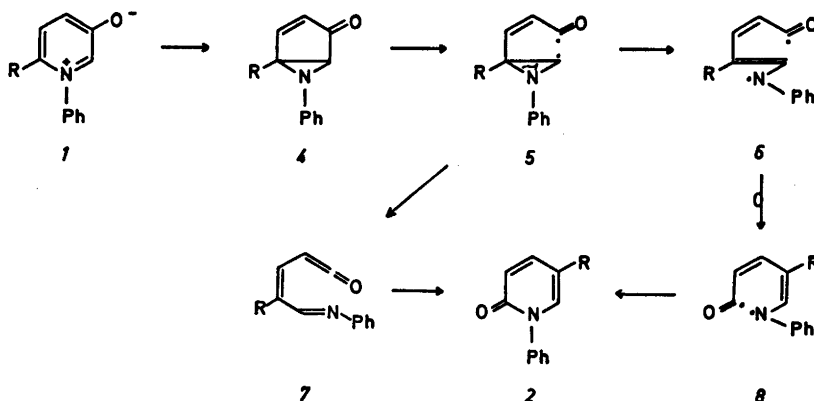
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Irradiation of *N*-phenylpyridinium-3-olate at 350 nm has recently been reported to yield a mixture of products. Three of the products have been identified as dimers whereas a fourth product was identified as the bicyclic valence bond isomer 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (4; Scheme 2).<sup>2</sup> Our attempts to carry out a similar photolysis of *N*-phenylpyridinium-3-olates in ethyl acetate solution using a medium pressure Hanovia Hg-lamp have instead yielded the corresponding 2-pyridones 2 as the major product of the reaction.

The identity of the pyridones 2<sup>3,4</sup> was verified by comparison with authentic 2-pyridones 2 which were prepared by phenylation of the parent 2-pyridone 3 with iodobenzene in the presence of copper and potassium carbonate (Scheme 1).<sup>5</sup>



Scheme 1. a, R = H; b, R = Me.



Scheme 2. a, R = H; b, R = Me.

This extensive rearrangement reaction which amounts to a net exchange of the 2- and the 5-substituents can be rationalised by assuming intermediate formation of 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-ones 4 through a photochemically allowed disrotatory ring closure as reported<sup>2</sup> for the formation of 4a. The latter has a chromophore, however, which makes it photochemically labile resulting in homolytic bond cleavages as postulated in the rearrangement (Scheme 2); the intermediate for cyclisation can be formulated as a ketene 7 or as a biradical 8. The reaction mechanism implies that the 2- and 5-substituents migrate attached to their original carbon atoms; no labelling experiment in support of this assumption has been carried out.

We have previously reported what principally appears to be the same type of photochemical rearrangement; thus irradiation of 2,3-epoxyindanone similarly yielded isocoumarin as the major product.<sup>6</sup> Very recently it has also been shown that 2,5-dimethylcyclopentadienone epoxide is an intermediate in the photochemical conversion of 3,5-dimethyl-4-pyrone to 3,6-dimethyl-2-pyrone.<sup>6</sup> The postulated reaction path would also appear to be in agreement with formation of pyridones on photolysis of thiazolo- and dihydrothiazolo[3,2-*a*]pyridinium-8-olates.<sup>7</sup>

Table 1. Ionisation potentials  $\pm 0.05$  eV.

Compound	IP (eV)
1a (R=H)	7.48
1b (R=Me)	7.27
2a (R=H)	8.26
2b (R=Me)	8.01

The isomer pairs 1 and 2 have been subjected to comparative mass spectrometry studies as part of our program for structure analysis of isomers in the gas phase in the mass spectrometer by measurements of ionisation potentials (IP).<sup>8</sup> The fragmentation modes of each pair of isomers are similar (Experimental). [M] is the base peak and [M-CO] is a major fragment; [M-CHO] is a major fragment in the methyl derivatives. The major difference in fragmentation between the betaines 1 and the pyridones 2 are found in the intensities of [M-H]; 2-3% for 1 and 60-80% for 2. The values of the IP's constitute another differentiation between the isomer pairs. Thus the IP's for the betaines are ca. 0.7 eV lower than the values for the pyridones 2 in agreement with previous findings in analogous series.<sup>8</sup> The methyl substituent lowers the IP by ca. 0.2 eV in both series in accordance with primary ionisation in the pyridine ring system in both isomer pairs.<sup>9</sup>

**Experimental.** The IP values were obtained by the semilog-plot interpretation of the ionisation efficiency curves (AEI MS-902 mass spectrometer) as previously described.<sup>10</sup> The values are the average of three determinations, the deviation being  $\pm 0.05$  eV.

*N-Phenylpyridinium-3-olates* 1 were prepared from aniline and furfural or 5-methylfurfural as reported for 1a;<sup>9,11</sup> the acid reaction mixture was left in the cold (for 1b, 3 w.) before the product was isolated as HCl-salt and the betaine obtained after chromatography on DEAE-Sephadex and freeze-drying.

*N-Phenylpyridinium-3-olate* 1a:<sup>9,11</sup> UV (0.1 M NaOH/EtOH, log  $\epsilon$ ): 341 (3.55), 243 (4.03), 222 (4.10) nm. MS[70 eV,  $m/e$  (% rel.int.)]: 171 (100, M), 170 (2, [M-H]), 143 (50, [M-CO]), 142 (4, [M-HCO]), 116 (18), 115 (38), 77 (28).

*N-Phenyl-6-methylpyridinium-3-olate* 1b: m.p. 182-183 °C (decomp.) Anal. C<sub>12</sub>H<sub>11</sub>NO: C, H, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.15 (Me), 7.1-7.7 (Pyr., Ph). UV (0.1 M NaOH/EtOH, log  $\epsilon$ ): 343 (3.65), 260 (3.90), 223 (4.24) nm. MS[70 eV,  $m/e$  (% rel.int.)]: 185 (100, M), 184 (3, [M-H]), 157 (35, [M-CO]), 156 (83, [M-HCO]), 116 (3), 115 (4), 77 (46).

**Photolysis of N-phenylpyridinium-3-olates** 1. The betaine (500 mg) was dissolved in refluxing ethyl acetate (1000 ml) and the solution irradiated using a medium pressure Hanovia Hg-lamp with pyrex filter; the progress of the

reaction was monitored by TLC (silica gel, Benzene-EtOAc 1:1). Optimum yields of the pyridones 2 were obtained by irradiation of 1a for 10 h and 1b for 24 h. TLC showed the product to consist of at least five components,<sup>2</sup> the major component being the *N*-phenylpyridone 2. The latter was isolated after preparative TLC on 1 mm thick silica gel layers using the above developer.

*N-Phenyl-2-pyridone* 2a. 10% yield, m.p. 128-131 °C (Benzene-light petroleum) Anal. C<sub>11</sub>H<sub>9</sub>NO: C, H, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.2-7.5 (Pyr., Ph). UV (EtOH, log  $\epsilon$ ): 310 (3.60), 231 (3.44), 221 (3.46) nm. IR (KBr): 1660 cm<sup>-1</sup> (CO). MS [70 eV,  $m/e$  (% rel.int.)]: 171 (100, M), 170 (77, [M-H]), 143 (49, [M-CO]), 142 (5, [M-HCO]), 116 (14), 115 (25), 77 (44).

*N-Phenyl-5-methyl-2-pyridone* 2b. 33% yield, m.p. 103-105 °C (Benzene-light petroleum). Anal. C<sub>12</sub>H<sub>11</sub>NO: C, H, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.1 (Me), 6.6-7.5 (Pyr., Ph). UV (EtOH, log  $\epsilon$ ): 316 (3.64), 227 (3.68) nm. IR (KBr): 1670 cm<sup>-1</sup> (CO). MS [70 eV,  $m/e$  (% rel.int.)]: 185 (100, M), 184 (61, [M-H]), 157 (33, [M-CO]), 156 (74, [M-HCO]), 116 (23), 115 (18), 77 (41).

*N-Phenyl-2-pyridones* 2 by *N*-phenylation. The parent 2-pyridone 3 was condensed with iodobenzene in the presence of potassium carbonate and finely divided, freshly prepared Cu.<sup>3</sup> The properties of the authentic specimen, *N*-phenyl-2-pyridone<sup>4</sup> and *N*-phenyl-5-methyl-2-pyridone,<sup>5</sup> were as described for the products from photolysis.

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