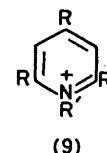


# Reactions of Pyridinium Salts and Pyridinium Betaines with Hydrogen Peroxide: Novel Ring Transformations to Pyrroles, $\beta$ -Hydroxylation, and Ring-opening

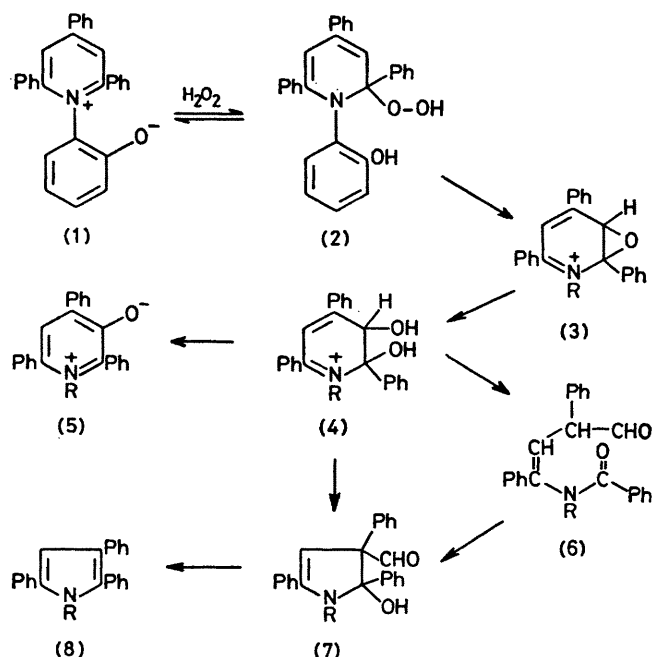
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**Summary** *N*-(2-Oxidophenyl and 2-oxido-1-naphthyl)-2,4,6-triarylpyridiniums are oxidised by hydrogen peroxide to mixtures of tetra-arylpyrroles and 3-oxido-pyridinium betaines whereas 2,4,6-triarylpyridinium salts and alkaline hydrogen peroxide give  $\beta$ -amino- and  $\beta$ -aroylamino-chalcones.



1-(2-OXIDOPHENYL)-2,4,6-TRIPHENYLPYRIDINIUM (1) is converted by hydrogen peroxide in ethanol into a mixture of 1-*o*-hydroxyphenyl-2,3,5-triphenylpyrrole (8; R = *o*-HO-C<sub>6</sub>H<sub>4</sub>) (41%), m.p. 166 °C, and 1-*o*-hydroxyphenyl-2,4,6-triphenylpyridinium-3-olate (5; R = *o*-HO-C<sub>6</sub>H<sub>4</sub>) (26%), m.p. 294 °C. This reaction appears to be general for 1-*o*-oxidoaryl-2,4,6-triaryl betaines: analogous products



SCHEME. Mechanistic route for production of pyrroles and pyridinium-3-olates.

were obtained utilising the 2-oxidophenyl, and the 2-oxido-1-naphthyl *N*-substituted 2,4,6-triphenyl- and 2,4,6-tri-*p*-tolyl-pyridiniums (9a-c). 1-(4-Oxidophenyl)-2,4,6-triphenylpyridinium (9d) gives 1-*p*-hydroxyphenyl-2,4,6-triphenylpyridinium-3-olate (5; R = *p*-HO-C<sub>6</sub>H<sub>4</sub>) (14%), m.p. 330 °C (decomp.), but no pyrrole was isolated in this case.

R	R'
a; <i>p</i> -Tolyl	2-Oxidophenyl
b; Ph	2-Oxidonaphthyl
c; <i>p</i> -Tolyl	2-Oxidonaphthyl
d; Ph	4-Oxidophenyl
e; Ph	Ph
f; Ph	Me
g; Ph	PhCH <sub>2</sub>
h; Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>
i; Ph	<i>o</i> -Tolyl
j; Ph	<i>m</i> -OHC <sub>6</sub> H <sub>4</sub>
k; <i>p</i> -Tolyl	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>

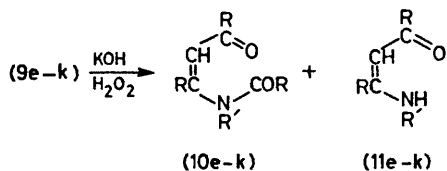
The structures of the pyridinium-3-olates (5) and the pyrroles (8) are supported by their n.m.r., i.r., and u.v. spectral properties and by *X*-ray crystal structure determinations on two representative examples: 1-*o*-hydroxyphenyl-2,3,5-triphenylpyrrole (8; R = *o*-HO-C<sub>6</sub>H<sub>4</sub>) and 1-*p*-hydroxyphenyl-2,4,6-triphenylpyridinium-3-olate (5; R = *p*-HO-C<sub>6</sub>H<sub>4</sub>).

*Crystal data:* (8; R = *o*-HO-C<sub>6</sub>H<sub>4</sub>), C<sub>28</sub>H<sub>21</sub>NO, triclinic, space group *P* $\bar{1}$  *a* = 10.374(1), *b* = 12.195(1), *c* = 9.876(1) Å,  $\alpha$  = 114.19(1),  $\beta$  = 112.45(1),  $\gamma$  = 88.41(1)°, *Z* = 2. The basic structure (*i.e.*, four six-membered rings attached to a five-membered ring) was solved by direct methods (MULTAN). The refinement of the structure was halted at an *R* of 0.146 [isotropic thermal parameters for O, N, and C; 133 variables, 3279 reflections with *I* > 2 $\sigma$ (*I*)] due to a serious disorder problem. (5; R = *p*-HO-C<sub>6</sub>H<sub>4</sub>), C<sub>29</sub>H<sub>21</sub>NO<sub>2</sub>, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 14.231(4), *b* = 14.577(3), *c* = 10.186(2) Å,  $\beta$  = 93.06(2)°, *Z* = 4, *D*<sub>c</sub> = 1.308 g cm<sup>-3</sup>. The structure was solved by direct methods and refined by the full-matrix least-squares with C, N, O anisotropic and H(5) and H(17) isotropic to *R* = 0.048 for 1617 data and 297 variables. Data for both compounds were collected on a Syntex *P*2<sub>1</sub> diffractometer with the crystal cooled to -35 °C (Mo-*K* $\alpha$  radiation,  $\lambda$  = 0.71069 Å).†

Our tentative mechanistic interpretation for the production of pyrroles (8) and pyridinium-3-olates (5) is shown in the Scheme. The pyrroles (8) are not formed by further oxidation of the betaines (5) which are stable under the reaction conditions. In addition to (3), an oxazepine intermediate (resembling intermediates postulated and in

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

part isolated from photochemical transformations of pyridine and other *N*-oxides<sup>1</sup>) may be involved.



In contrast to the above reactions, 2,4,6-triarylpyridinium salts (**9e—k**) generally react with alkaline hydrogen peroxide to give  $\beta$ -aroylaminochalcones (**10e—k**) and/or  $\beta$ -aminochalcones (**11e—k**) as we have shown for seven

examples (**9e—k**; R = Ph and *p*-tolyl; R' = Me, Ph, PhCH<sub>2</sub>, *o*-tolyl, *p*-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, and *m*-HO·C<sub>6</sub>H<sub>4</sub>) in an average total yield of *ca.* 60% of isolated and separated products. 1-Methyl-3-carbamoylpyridinium chloride was previously reported<sup>2</sup> to give a pyrrolidinone hydroperoxide with alkaline hydrogen peroxide.

It is not clear why such different products are obtained from the pyridinium salts and the pyridinium betaines: experiments<sup>3</sup> suggested that pH differences are not responsible, so subtle electronic effects may be implicated.

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<sup>1</sup> P. L. Kumler and O. Buchardt, *Chem. Comm.*, 1968, 1321; A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic N-Oxides,' Academic Press, London, 1971, pp. 320—329.

<sup>2</sup> D. W. Bristol and D. C. Dittmer, *J. Org. Chem.*, 1970, **35**, 2487.

<sup>3</sup> For details see Z. Zakaria, Ph.D. Thesis, University of East Anglia, 1978.