

## Oxidative Demethylation of $\alpha$ - and $\gamma$ -Methyl-N-heterocyclonium Salts: a New Method for Preparation of N-Substituted- $\alpha$ - and - $\gamma$ -oxo-N-heterocycles

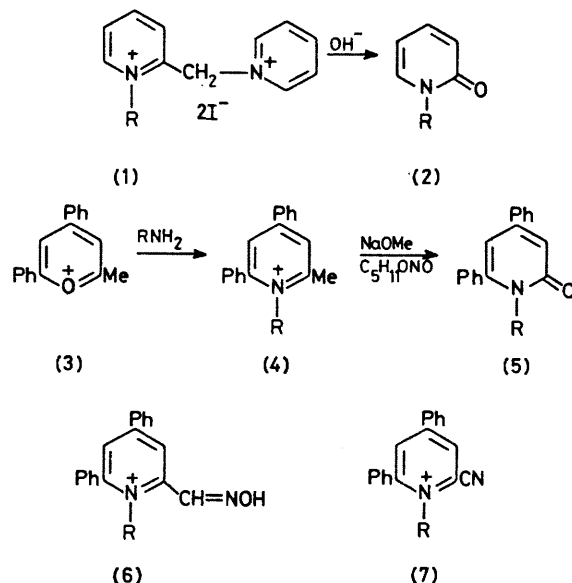
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**Summary** 1-Substituted-2-methyl- and -4-methyl-pyridinium cations are converted by pentyl nitrite and sodium methoxide into 1-substituted-2- and -4-pyridones respectively.

THE classical conversion of N-heterocyclonium salts into  $\alpha$ -oxo-N-heterocycles by ferricyanide oxidation suffers from lack of regioselectivity, and is usually not applicable to the  $\gamma$ -oxo-analogues.<sup>1</sup> Other methods are of limited generality or require starting materials that are not easily accessible.<sup>2</sup> Berson and Cohen<sup>3</sup> have described the conversion of N-substituted picolinium salts into the pyridones (2) via the King reaction intermediates (1); however, the yield is rather low over the two steps required<sup>4</sup> and some reactions fail completely.<sup>5</sup>

We now show that the picolinium salts (4) [conveniently prepared from the pyrylium derivatives (3) in yields averaging 76% over seven examples] react smoothly with pentyl nitrite and sodium methoxide at 5 °C to give the corresponding 1-substituted-2-pyridones (5) in 64% average yield [seven examples: (5), R = n-butyl, n-hexyl, n-octyl, benzyl, *o*-chlorobenzyl, *p*-methylbenzyl, and phenyl]. The reaction course probably involves the oximes (6) (in suitable conditions, such oximes can be isolated as tetrafluoroborate salts‡) and the cyano-derivatives (7). Purification of the 1-substituted-2-pyridones from dark by-products is facilitated by either (i) use of an excess of ethyl nitrite in place of pentyl nitrite or (ii) elution with ethyl acetate from an alumina UG-01 column.



The generality of this reaction has been further explored: 1-benzyl-2-methyl- and 1-benzyl-4-methyl-pyridinium cations give acceptable yields of 1-benzyl-2- and 1-benzyl-4-pyridone, respectively. We believe that this reaction will be of considerable general utility in heterocyclic chemistry.

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† Details will be given in the full paper.

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<sup>3</sup> J. A. Berson and T. Cohen, *J. Amer. Chem. Soc.*, 1956, **78**, 416.

<sup>4</sup> A. R. Battersby and J. C. Turner, *J. Chem. Soc.*, 1960, 717.

<sup>5</sup> J. A. Berson and J. S. Walia, *J. Org. Chem.*, 1959, **24**, 756.