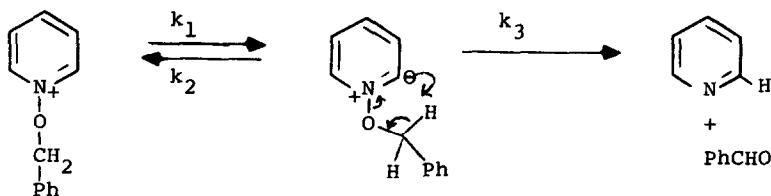
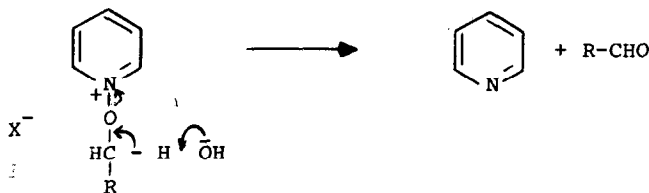


MECHANISM OF THE BASE-CATALYZED CONVERSION OF
N-ALKOXPYRIDINIUM SALTS TO ALDEHYDES

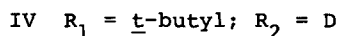
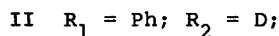
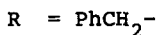
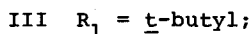
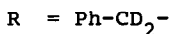
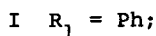
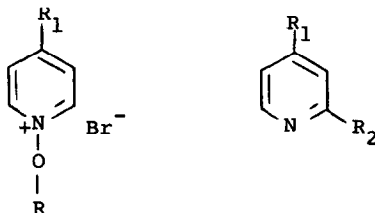
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The reaction of N-alkoxy-pyridinium salts with base to yield the corresponding aldehyde and pyridine is well-known and represents a useful two-step process for the conversion of alkyl halides to aldehydes. The mechanism of this reaction is depicted in the literature¹ as involving abstraction by hydroxide ion of a proton from the carbon atom attached to the oxygen atom leading to elimination of pyridine and formation of the aldehyde (Scheme A)



We wish to report evidence which supports for this type of transformation the pathway outlined in Scheme B.



Treatment of a solution of I in water with aqueous sodium hydroxide solution yields II, containing one deuterium atom in an alpha position according to the integration of its NMR spectrum. Reaction of III with a solution of potassium carbonate in deuterium oxide affords IV, which also contains according to integration of its NMR spectrum one deuterium in an alpha position. This finding implies complete base-catalyzed exchange of the alpha hydrogen atoms of the pyridine nucleus in III prior to irreversible transformation to IV and benzaldehyde (i.e., $k_1, k_2, \gg k_3$). It has been previously reported that pyridine-N-oxides², N-methoxypyridinium³ and N-phenoxy pyridinium⁴ salts undergo base-catalyzed α -proton exchange. The intramolecular decomposition step is reminiscent of that established for the Pfitzner-Moffatt oxidation.⁵

1. Pyridine and Its Derivatives, Vol. 14, Supplement, Part 2; Edited by R. A. Abramovitch; John Wiley & Sons, New York. pp 81.
2. R. A. Abramovitch, G. M. Singer, and A. R. Vinutha; Chem. Comm. 55 (1967).
3. J. A. Zoltewicz and L. S. Helmick; J. Am. Chem. Soc. 92 7547 (1970).
4. R. A. Abramovitch, S. Kato and G. M. Singer; Am. Chem. Soc. 93 3074 (1971).
5. A. H. Fenslau and J. G. Moffatt; J. Am. Chem. Soc. 88 1762 (1966).