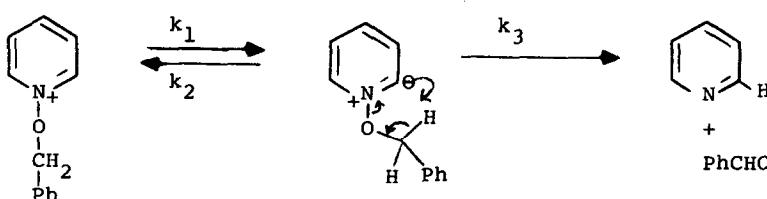
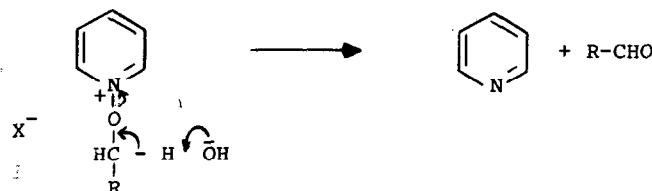


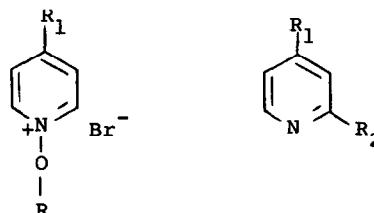
MECHANISM OF THE BASE-CATALYZED CONVERSION OF  
N-ALKOXYPYRIDINIUM SALTS TO ALDEHYDESR. E. Manning\* and F. M. Schaefer  
Sandoz, Inc.Research and Development Section  
East Hanover, New Jersey, 07936, U.S.A.

(Received in USA 29 October 1974; received in UK for publication 10 December 1974)

The reaction of N-alkoxypyridinium 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 literature<sup>1</sup> 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.



I  $R_1 = Ph$ ;

$R = Ph-CD_2-$

III  $R_1 = t\text{-butyl}$ ;

$R = PhCH_2-$

II  $R_1 = Ph; R_2 = D$ ;

IV  $R_1 = t\text{-butyl}; R_2 = D$

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-oxides<sup>2</sup>, N-methoxypyridinium<sup>3</sup> and N-phenoxyypyridinium<sup>4</sup> salts undergo base-catalyzed  $\alpha$ -proton exchange. The intramolecular decomposition step is reminiscent of that established for the Pfitzner-Moffatt oxidation.<sup>5</sup>

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