

dichloromethane solution. 2- and 4-Substituted pyridine-1-oxides as well as pyridine-1-oxide itself give only one product, the related 2-pyridine-carbonitrile.

The behavior of 3-substituted pyridine-1-oxides is more interesting. The methoxy and n-butyl derivatives give 3-substituted 2-pyridinecarbonitrile exclusively. The methyl, chloro, bromo, and acetyl ethylene glycol ketal derivatives give predominantly the 3-substituted-2-pyridinecarbonitrile contaminated with variable amounts of 5-substituted-2-pyridinecarbonitrile, the amounts of 2,5-isomer increasing in order listed. The acetyl, carbomethoxy, and cyano derivatives give approximately equal amounts of 2,3- and 2,5-disubstituted products.

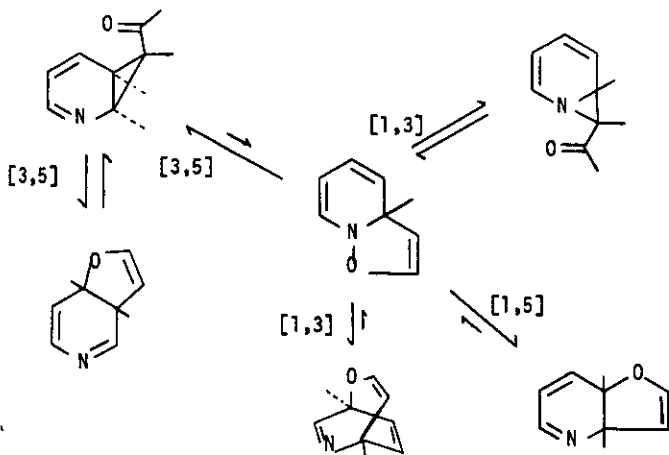
These results as well as our current understanding of mechanistic details of the reaction will be discussed.

### Rearrangements in the Pyridine Series

R. A. Abramovitch,  
Department of Chemistry  
Clemson University,  
Clemson, SC 29631

This lecture will summarize many of the rearrangements involving pyridine derivatives uncovered over the years in the author's laboratories. In particular, transformations starting with pyridine 1-oxides will be emphasized but reactions of N-imino derivatives and N-sulfides will also be mentioned.

Those rearrangements that lead to ring substitution products are summarized in the scheme below:



Which product(s) is formed depends on the nature of the substituent in the pyridine ring and examples of each will be given.

Rearrangements leading to substitutions into a side chain will also be described. Lastly, rearrangements leading to ring transformations will be presented. Possible applications of these rearrangements will be described.