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

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

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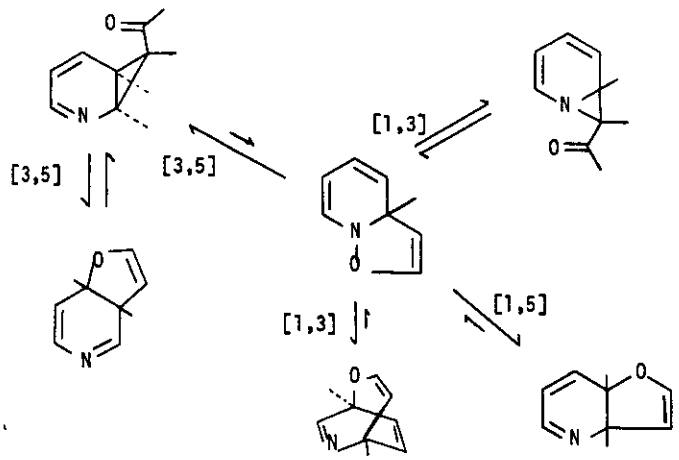
This lecture will summarize many of the rearrangements involving pyridine derivatives uncovered over the years in the author's laboratories. In particular, transformations starting with pyridine 1-oxides will be emphasized but reactions of N-imino derivatives and N-sulfides will also be mentioned.

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.