ABSTRACTS OF LECTURES

Reactivity of Pyridines and Pyridiniums

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General survey of reactivity of pyridine derivatives.
Cycloaddition of pyridinium betaines.
N-vinylpyridinium cations.
Pyridinium ylids and pyridine stabilized carbanions.
Displacement reactions on pyridinium cations.
Elimination reactions dihydropyridines.
Intramolecular rearrangement of pyridinium cations.

Manufacture and Use of Pyridine and Its Derivatives

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During the last quarter-century, synthetic pyridine and picolines have allowed the exploitation of pyridine derivative chemistry on a grand scale. Compounds with applications in medicinal, agricultural, and industrial chemical areas have been developed by functional group manipulation of the readily available derivatives. Continued growth is expected in the future as sophisticated techniques are used to manufacture more complex derivatives.

Synthesis and Selected Applications of Polymers Containing Pyridine Moieties

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The lecture will include the following: A general introduction to the application of functional polymers in organic chemistry, preparation of crosslinked polyvinylpyridines (gel resins, macroporous resins), preparation of crosslinked polymers containing pyridine moieties by chemical modification, selected applications of pyridine containing polymers in organic chemistry, and also a brief discussion of other applications of pyridine containing polymers.

Regioselective Cyanation of Pyridine-1-Oxides

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Pyridine-1-oxides are converted in essentially quantitative yield to the corresponding 2-pyridinecarbonitrile by treatment with equivalent amounts of trimethylsilanecarbonitrile and dimethylcarbamyl chloride in 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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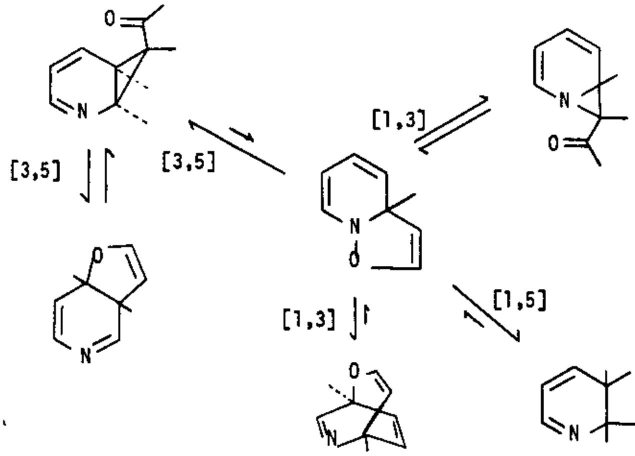
This lecture will summarize many of the rearrangements involving pyridine derivatives uncovered over the years in the author's laboratories. In particular, transformations starting with pyridine 1-oxides will be emphasized but reactions of N-imino derivatives and N-sulfides will also be mentioned.

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.