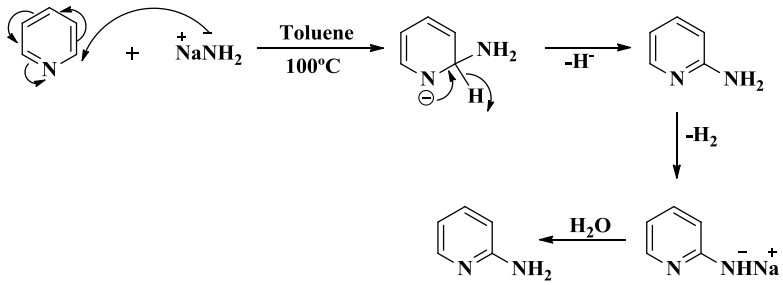
Subject: Chemistry
Semester IV
Paper No.: CHB-401
Topic: Pyridine
Lecture Notes: Dr. Diksha Katiyar

This is in continuation of my lecture on pyridine:

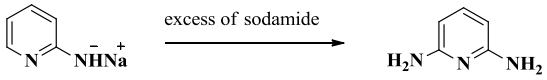
Nucleophilic substitution reactions of pyridine

Amination (Tschitschibabin reaction or **Chichibabin reaction**): Pyridine when treated with sodamide in toluene froms 2-aminopyridine.

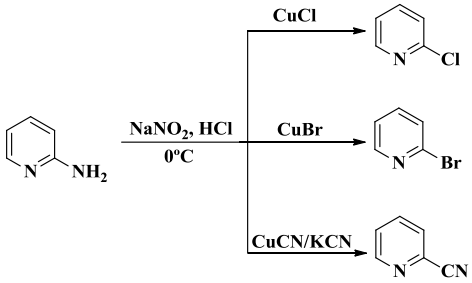


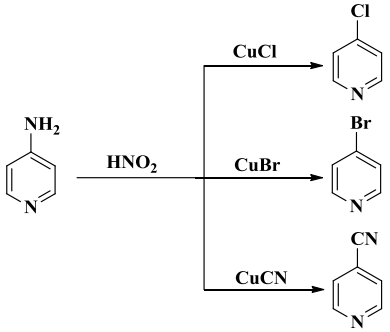
In the first step of reaction, nucleophile attacks at C-2 or C-4 position. In the second step a hydride ion is eliminated which reacts with amino pyridine to evolve hydrogen.

In the excess of sodamide 2,6-diamino pyridine is obtained.

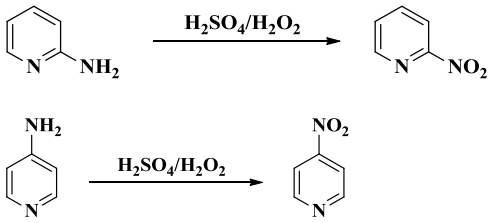


2 and 4 halopyridines are prepared by indirect methods from 2 and 4-amino pyridines.



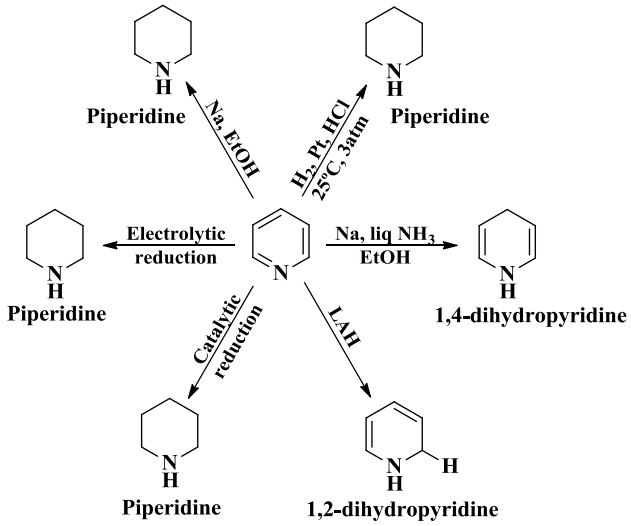


Pyridine is indirectly nitrated by oxidizing 2 or 4 amino pyridine with H_2O_2 and H_2SO_4.

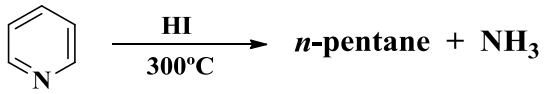


Reduction products of pyridine

Depending upon the reducing agent used, pyridine gives the following products:-

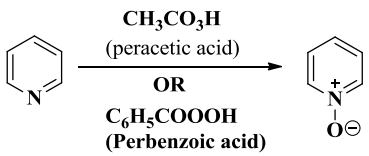


Ring opening reaction

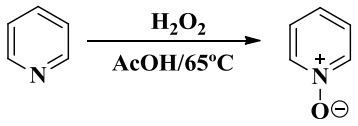


Pyridine-N-oxide

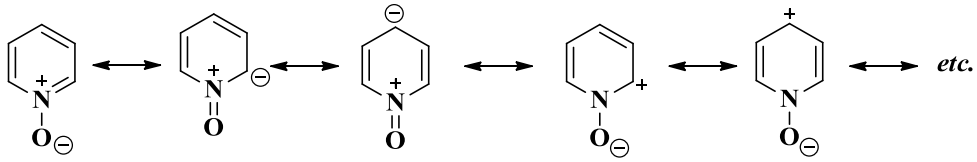
Pyridine is **oxidized** by peracids to pyridine-N-oxide.



Sometimes hydrogen peroxide in acetic acid can also be used.

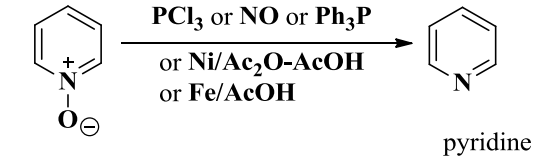


Pyridine-N-oxide is more reactive towards electrophilic aromatic substitution (EAS) reaction than pyridine because the O atom can donate electrons into the ring by resonance.



Resonating structures show that in pyridine-N-oxide **high** and **low** charge densities are produced at positions 2 and 4. Thus pyridine-N-oxide is more reactive towards both electrophilic and nucleophilic reagents than pyridine itself. Thus pyridine-N-oxide provides a synthetically useful way to introduce an electrophile at position C-4 and C-2 of pyridine.

Many methods are available for removal of oxygen from N-oxide i.e. deoxygenation of N-oxide.

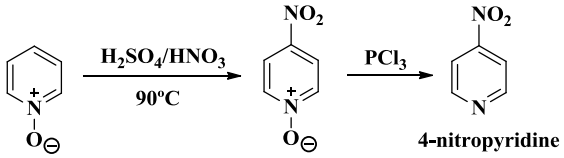


pyriidne-N-oxide

pyridine

For example, 4-nitro pyridine can be prepared using pyridine-N-oxide as follows

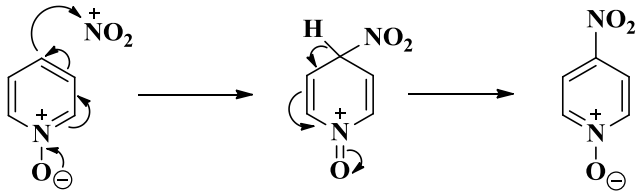
First, pyridine-N-oxide is nitrated by reaction with sulphuric acid and fuming nitric acid to give 4-nitro derivative which on deoxygenation gives 4-nitropyridine.



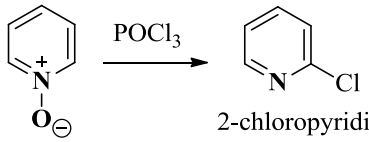
4-nitro pyridine-N-oxide

4-nitropyridine

Mechanism:



Reaction of pyridine-N-oxide with phosphorous oxychloride



2-chloropyridine

x