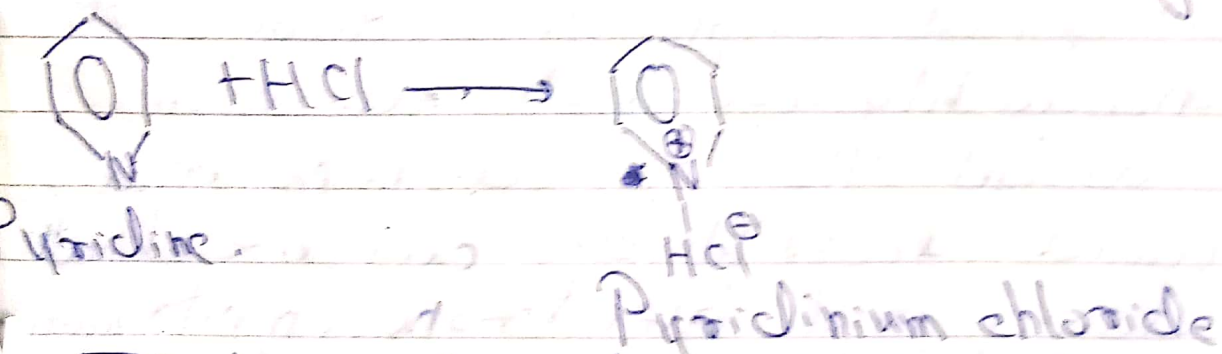


Properties (Chemical).

(1) Basic character:- Pyridine behaves as a base & reacts with acids to form fairly stable salts.



The basic character of pyridine is due to the nitrogen lone pair being in sp^2 hybrid orbital & not involved in the formation of the π system.

decreases as the molecular orbital π is readily available for the formation of a new π -N-H bond with proton.

(ii) Pyridine is a stronger base than pyrrole or imidazole in which the basicity is reduced by delocalisation of the nitrogen lone pair.

(iii) Pyridine is a weaker base than dimethyl amine. This is probably due to the difference in the nature of hybrid orbitals containing the nitrogen lone pair in these molecules. In pyridine, it is an sp^2 orbital whereas in dimethyl amine, it is an sp^3 hybrid orbital. Since sp^2 orbitals are smaller than sp^3 orbitals, this means that the lone pair of electrons on nitrogen in pyridine is more closely associated with the nitrogen nucleus and thereby less available for the formation of bond with proton and consequently the basicity is reduced.

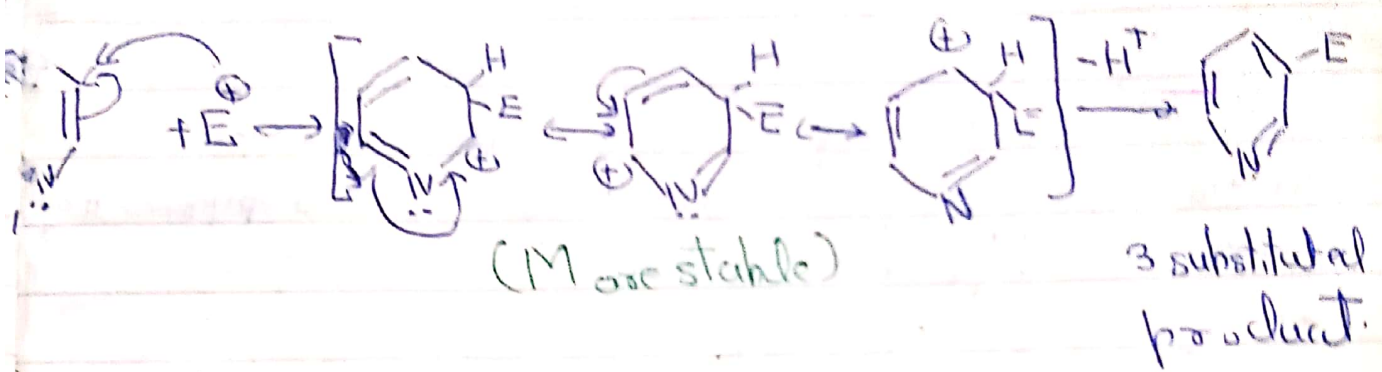
Q. Electrophilic substitution: Pyridine is less reactive than benzene towards electrophilic substitution. This is due to

(i) the nitrogen atom in pyridine because of its electronegativity lowers the electron density around the ring carbons and with the usual electrophile can coordinate with the lone pair of electrons on nitrogen. resonance stabilised pyridium salts.

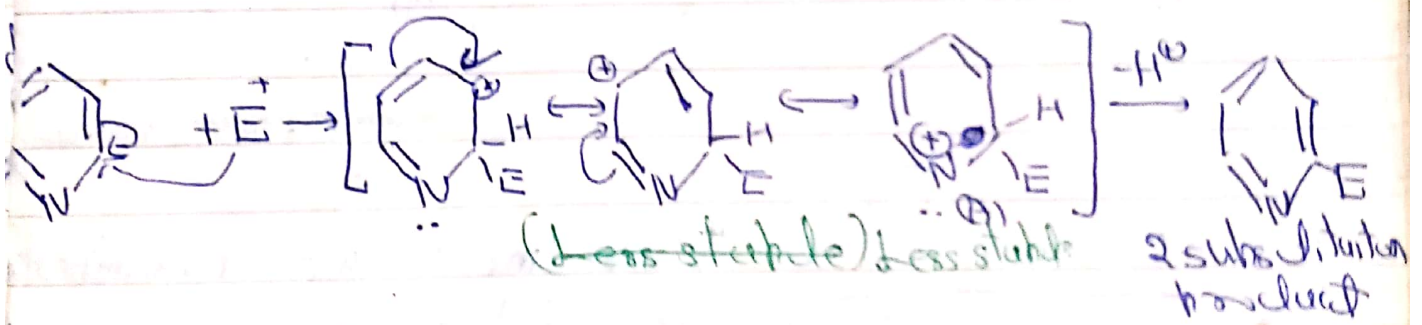
However, pyridine does undergo electrophilic substitution reactions when

vigorous reaction conditions are used. Substitution occurs almost exclusively at C3 (β position). This can be understood if we examine the intermediate cation.

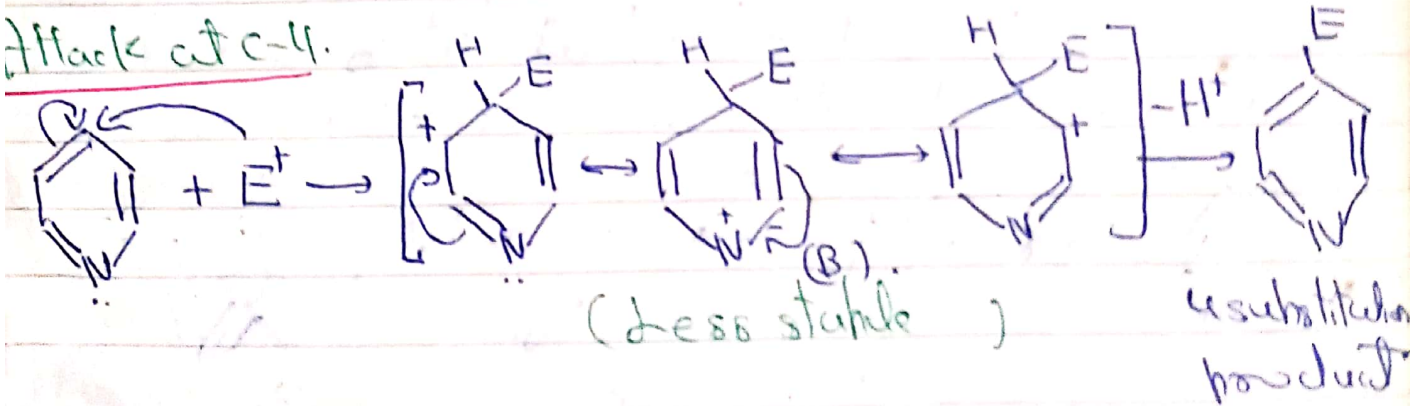
Attack at 3.



Attack at C-2.

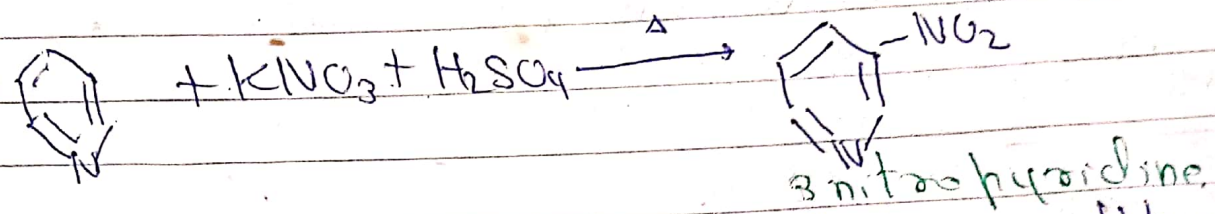


Attack at C-4.

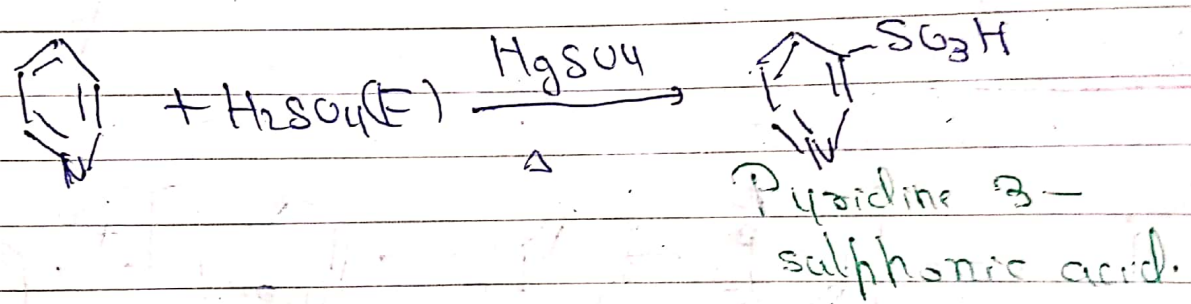


Thus intermediate arising from attack at C-2 and C-4 have two resonance form each and consequently the product with a substituent at C-3 predominates. If C-3

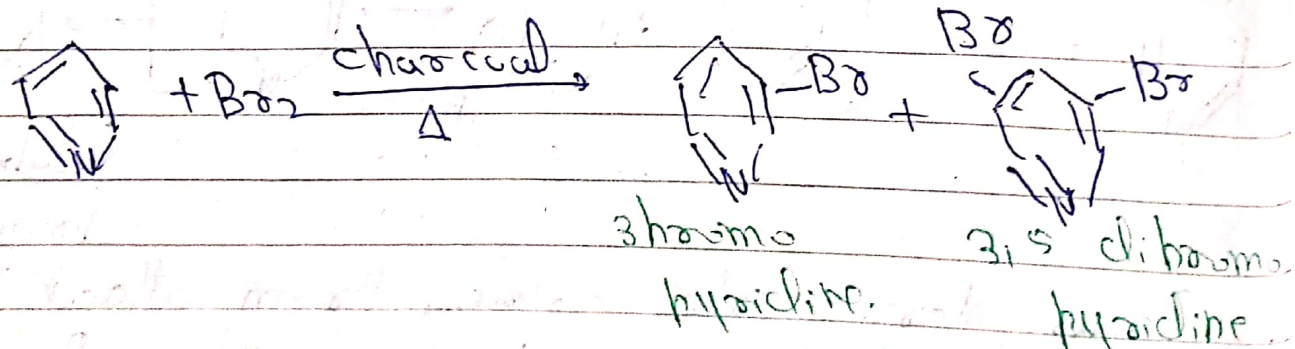
(a) Nitration - Pyridine undergoes nitration with potassium nitrate in the presence of sulphuric acid at 300°C to yield 3 nitropyridine.



(b) Sulphonation - Pyridine undergoes sulphonation with fuming sulphuric acid in the presence of mercuric sulphate at 230°C to yield 3-sulphonic acid.

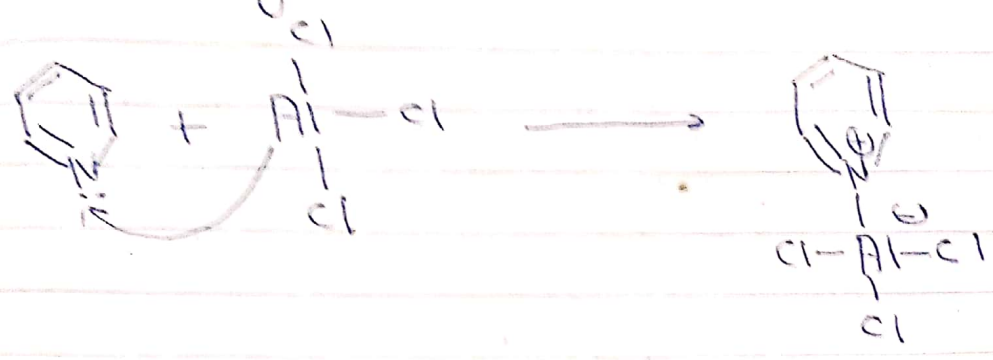


(c) Bromination - Pyridine may be brominated by passing the vapour of pyridine and bromine over charcoal catalyst at 300°C to yield mono and dibromo derivative.



(d) Friedel-Crafts reaction - Pyridine does not undergo Friedel-Crafts reaction because the Lewis acid AlCl₃ which are used as a catalyst co-ordinates with the lone pair of electrons.

on nitrogen.

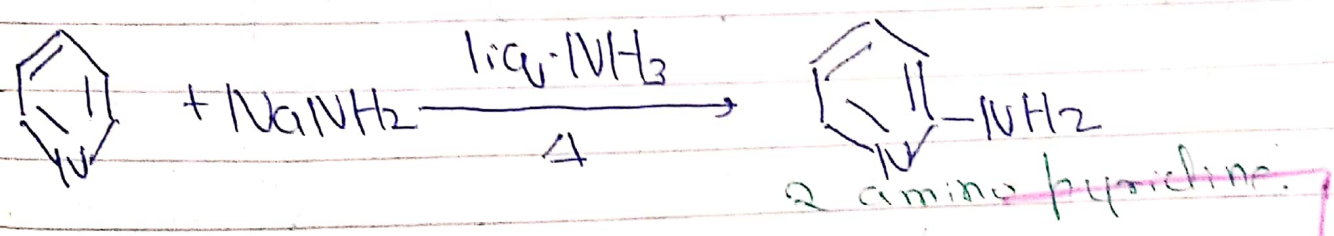


Pyridine 3 aluminium complex.

Nucleophilic substitution - Unlike pyrrole, pyridine undergoes nucleophilic substitution reactions. The preference of attack at C-2 or C-4 or C-3 is rationalised on the basis of stability of intermediate and consequently the product with substituents at C-2 and C-4 predominates.

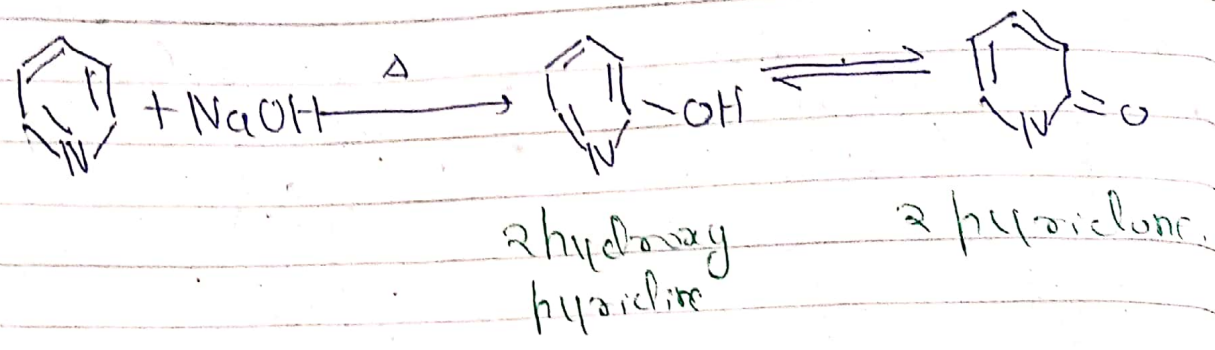
(i) Reaction with sodium amide
(Chichibabin reaction)

Pyridine reacts with sodium amide in liquid ammonia at 100°C to form 2-amino pyridine.

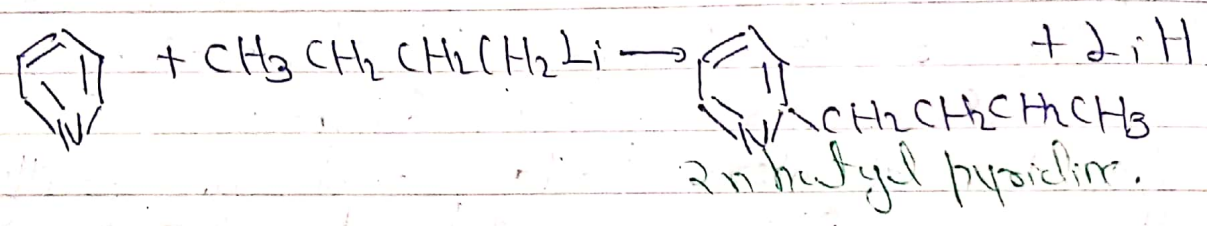


(ii) Reaction with sodium hydrosulfide - Pyridine reacts with sodium hydrosulfide at 300°C to yield a mixture of 2-

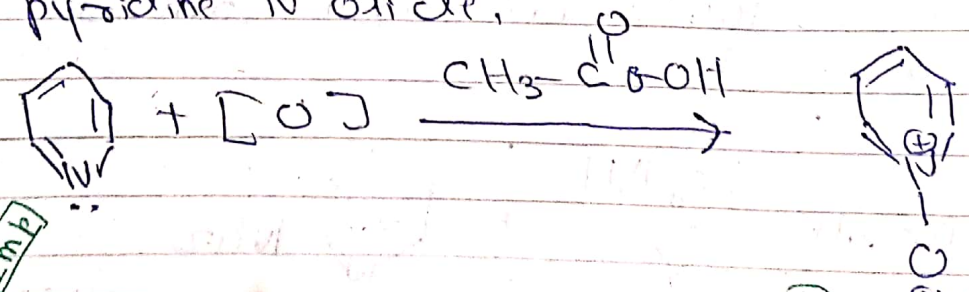
hydroxy pyridine and a pyridone.



(c). Reaction with n-butyl lithium - Pyridine reacts with n-butyl lithium at 100°C to give n-butyl pyridine.



(d). Oxidation - Pyridine is quite stable towards mild oxidising agents, chromic acid and nitric acid. However it may be oxidised by peracetic acid to give pyridine N-oxide.



Reduction - Pyridine undergoes reduction with H₂ or Hydrogen in the presence of Ni to form piperidine.

