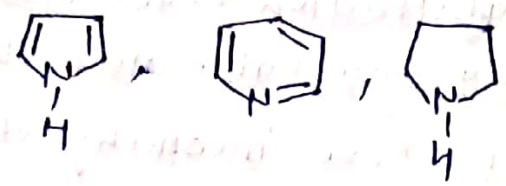
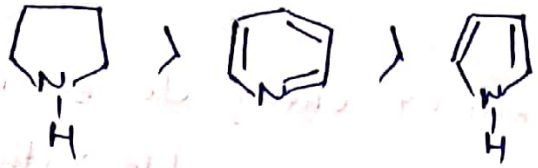
Q. Basic strength among the following compounds.





* Electrophilic substitution Reaction of Pyridine

According to the resonance structure of Pyridine. The electronegativity of the π- system are more localised on N- atom as compaired to the carbon atom in the ring due to electronegativity difference between N and C

Therefore it shows some reluctance or some resistance towards electrophilic substitution Reaction.

* Orientation of Electrophilic substitution.

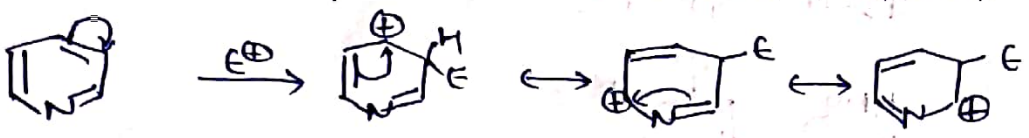
Position

2 = 6

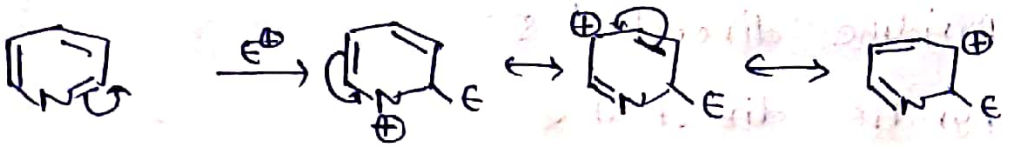
3 = 5

4 = → unique

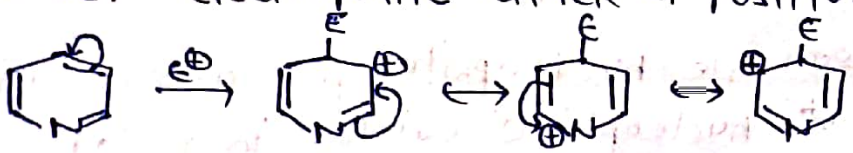
Case I: Electrophilic attacks at 3- position.



Case II: Electrophilic attack at 2- position



case III: Electrophilic attack at position - 4



Conclusion;

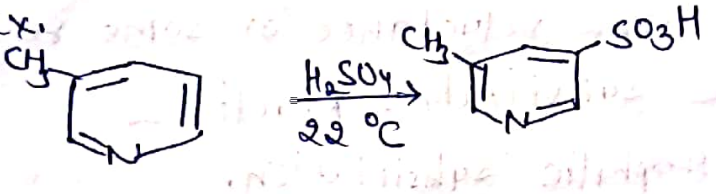
- Pyridine undergo electrophilic substitution reaction at the 3-position ✓ which is energetically favourable and three position is already block then next incoming electrophile will attack at position-5.

Whenever 2 and 4 positions are having change to be attack by electrophile the 2-position is more preferable rather than four.

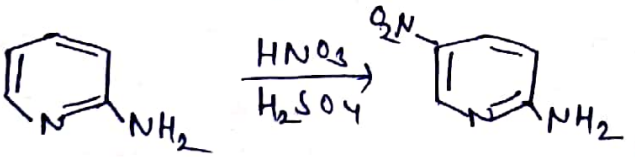
- Alkyl group activate the pyridine ring towards the electrophilic substitution reaction.
- Amino group also activate the ring and direct in coming electrophile to ortho and para position.

for ex.

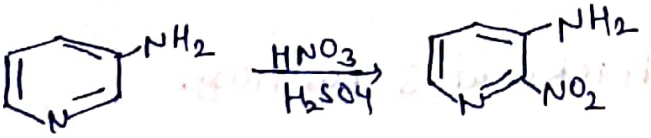
a)



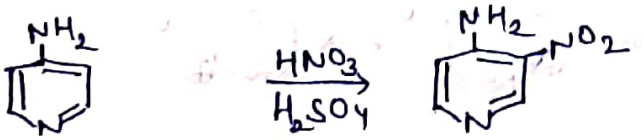
b)



c)



d)

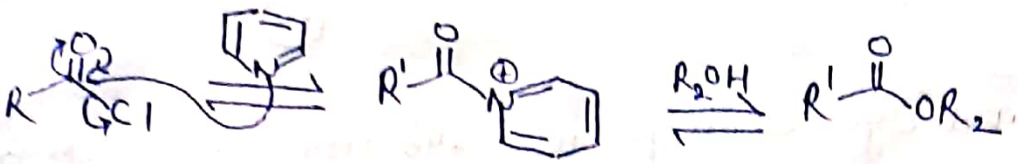


so, 2-Amino Pyridine direct at 5

3-amino Pyridine direct at 2

4-amino Pyridine direct at 3

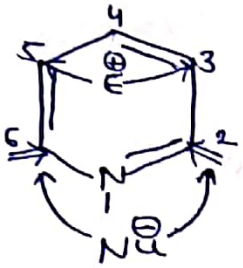
Pyridine is a resonable nucleophile for carbonyl group and is often used as nucleophilic catalyst in acylation



Acyl Pyridinium ion
reactive intermediate

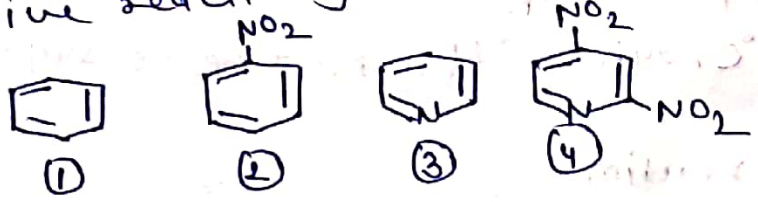
Disadvantages in using pyridine as a solvent.
Pyridine is toxic and has a foul smell. so, there are disadvantages in using pyridine as a solvent but it is and remains a popular solvent inspite of the problem.

Reaction of Pyridine



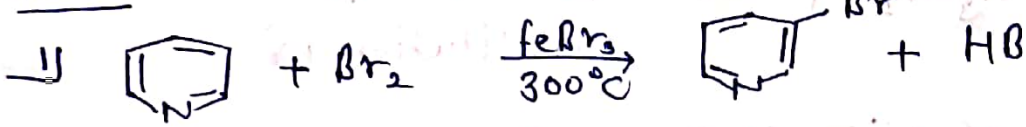
Nucleophilic substitution Reaction is called chichibabin reaction.

Relative reactivity towards electrophilic aromatic substitution



① > ② > ③ > ④

Arse²



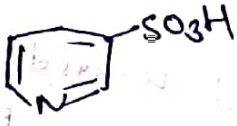
so Pyridine undergo electrophilic substitution reaction only under vigrous conditions and the yields of these reactions are often quite low. If the nitrogen becomes Protonated under the reaction conditions, the reactivity is further decreased because a positively charged nitrogen is more electron withdrawing than a neutral nitrogen

a)  $\xrightarrow[HNO_3 + \text{fuming } H_2SO_4]{\text{fuming}}$ No reaction

b)  $\xrightarrow[H_2SO_5,\ Fe]{KNO_3 + HNO_3}$ 

300 °C

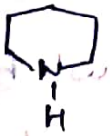
22%, 3-nitropyridine

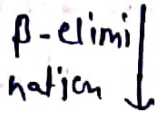
c)  $\xrightarrow[H_2SO_4]{20\%\ SO_3H}$ 

230 °C, 24h 71%. Pyridine-3-sulfonic acid

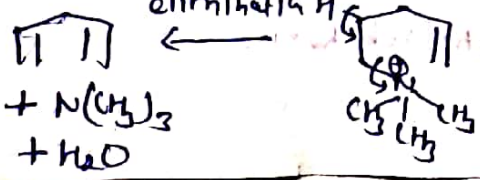
d) Friedel-Craft reaction;

 + CH_3-CH_2-Cl $\xrightarrow{AlCl_3}$ NO electrophilic aromatic substitution Rx^n.

Q.  $\xrightarrow{H_2/Pt}$  $\xrightarrow[(excess)]{CH_3-I}$  $\xrightarrow{Ag_2O}$ 



β-elimination



+ $N(CH_3)_3$

+ H_2O