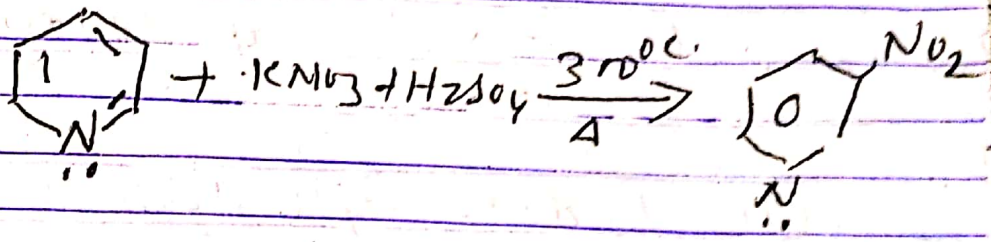
Chemical properties of Pyridine -

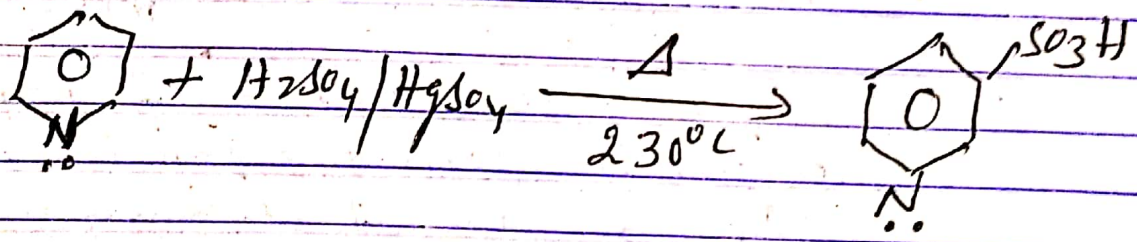
In earlier e-notes, I have discussed the basic character and electrophilic substitution in general. Now I am going to discuss some examples of electrophilic substitution and other chemical properties.

(i) Nitration -



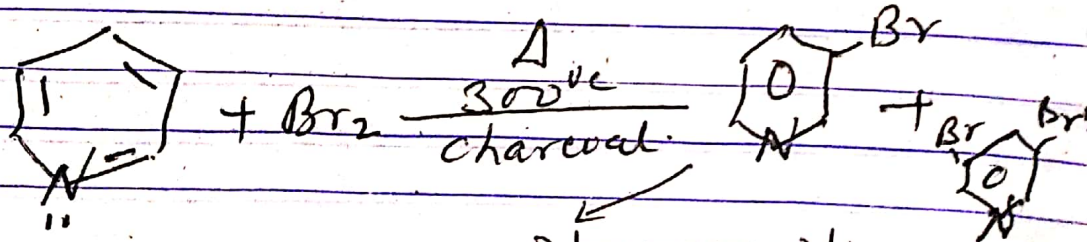
3-nitropyridine.

(ii) Sulphonation



Pyridin-3-sulphonic acid.

(iii) Bromination :-

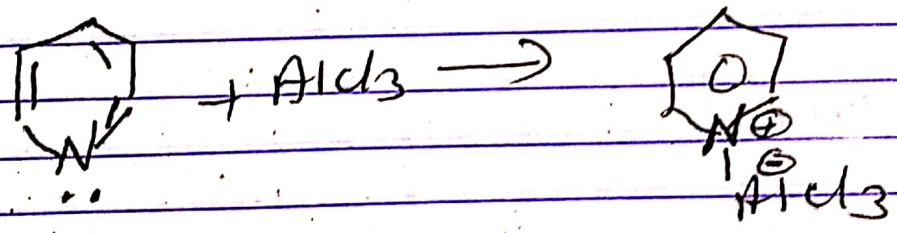


3-bromopyridine, 3,5-Dibromo pyridine.

At higher temperature 500°C, a mixture of 2-bromopyridine and an unexpected 2,6 dibromopyridine is also obtained.

At higher temperature reaction occurs probably by free radical mechanism due to which this type of unexpected result is found.

(ii) Friedal-crafts Acylation and Alkylation :—



In this the lone pair of pyridine nitrogen atom co-ordinate with $AlCl_3$ forming a adduct having Nitrogen atom positively charged and $AlCl_3$ negatively charged.

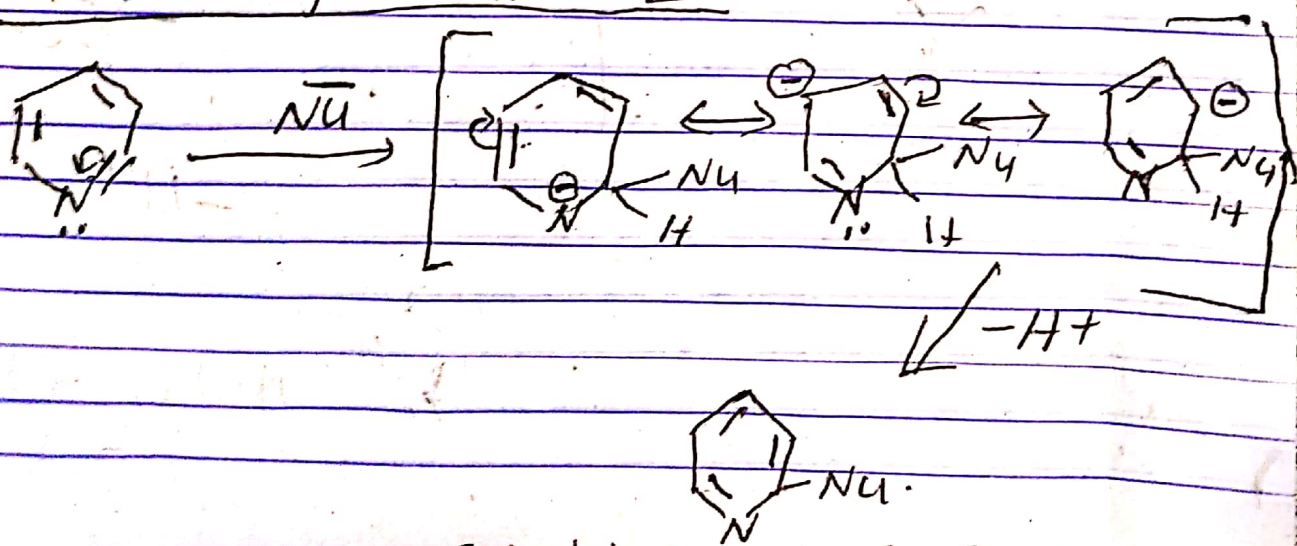
Nucleophilic substitution:— Pyridine

also under goes nucleophilic substitution because due to higher negativity of nitrogen. ring has some electron-deficiency nature. That is why nucleophili attack to the aromatic ring unlike benzene and pyrrole.

nucleophilic substitution occurs mostly at c-2 and c-4 position can be attacked if C-2 is blocked.

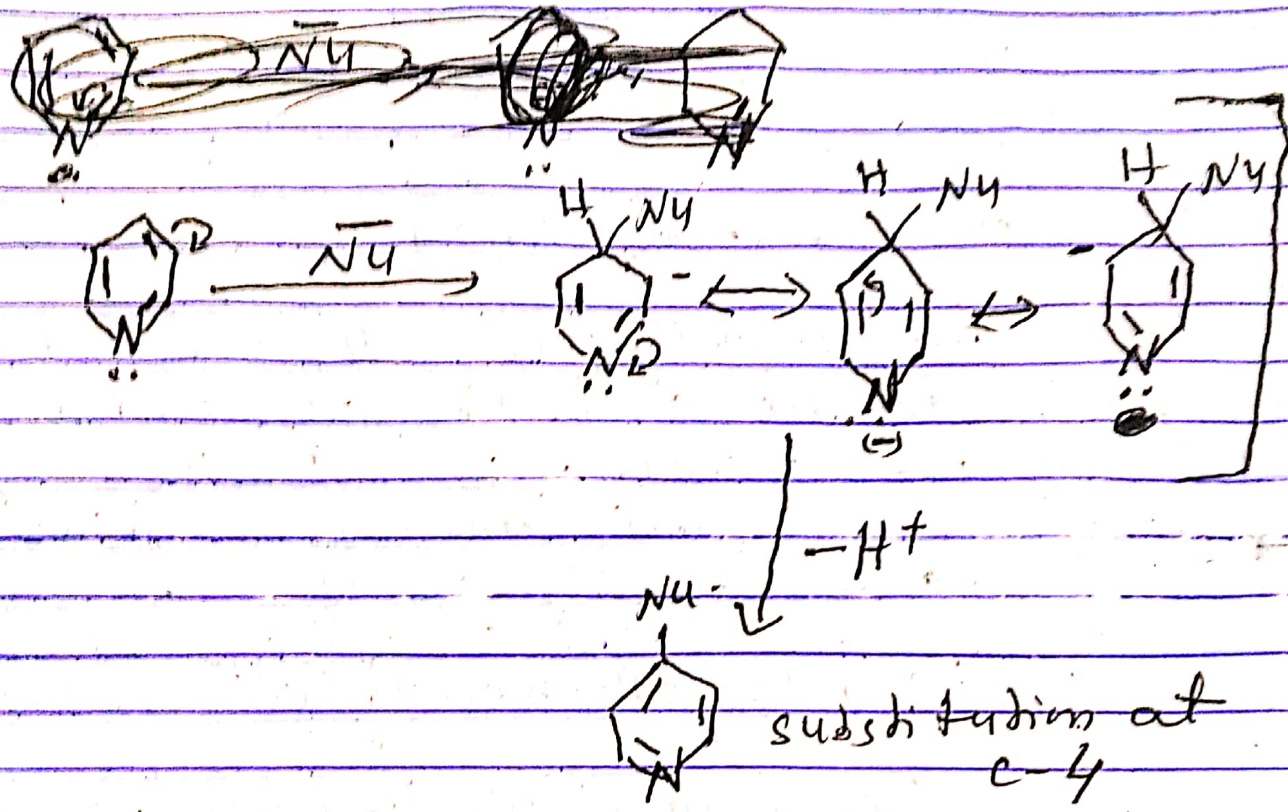
The general mechanism is given below. ~~process the attacked copies for further attack.~~

Attack on position C-2



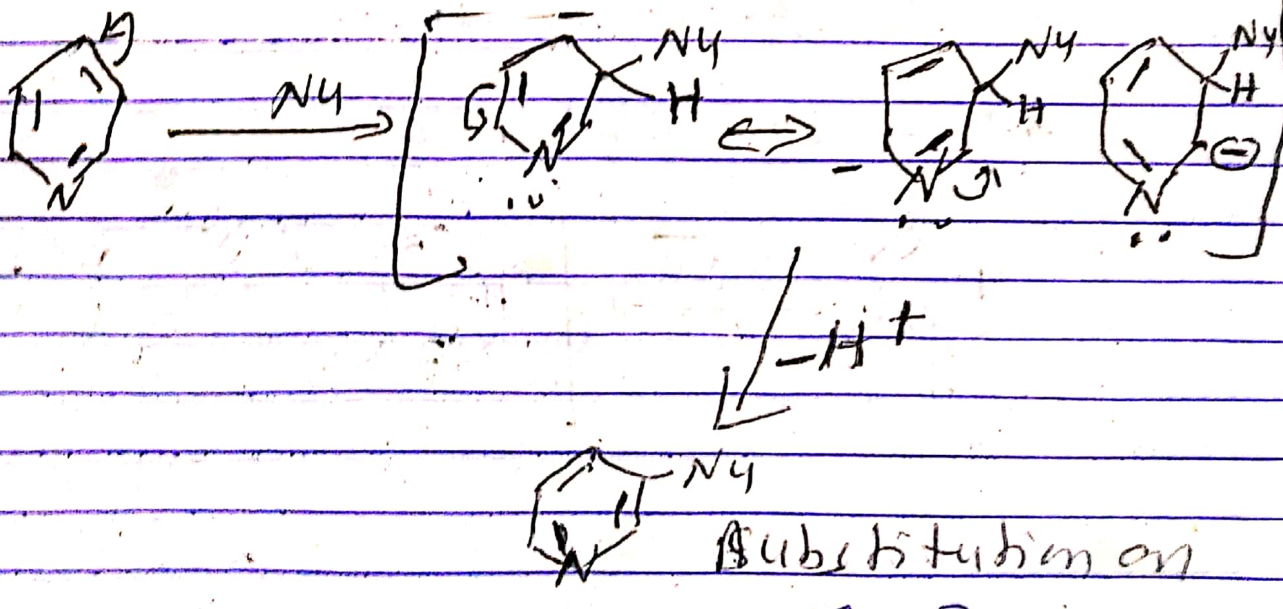
Substitution on C-2

Substitution on C-4



substitution at C-4

Substitution at C-3



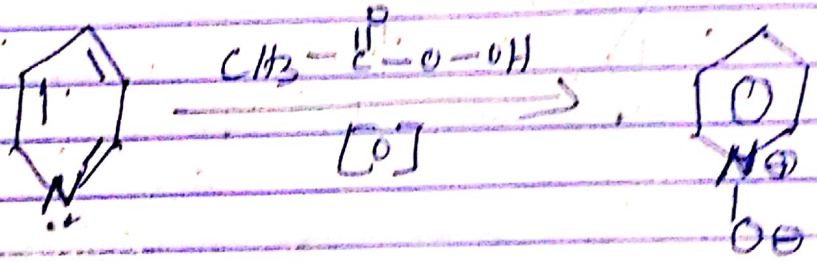
Substitution on C-3

(iii)  + $CH_3(CH_2)_2CH_2Li$ ⟶

$(CH_2)_2-CH_3$

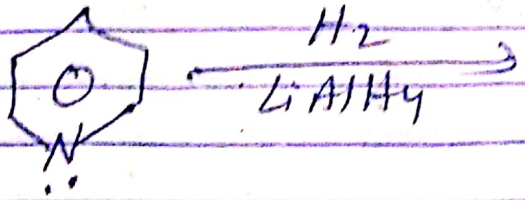
2-n-butyl pyridine.

(iv) **Oxidation:** — It is stable towards oxidising agent like cromic acid or nitric acid but it is oxidised with peroxy acetic acid to pyridine-N-oxide



Pyridine-N-oxide.

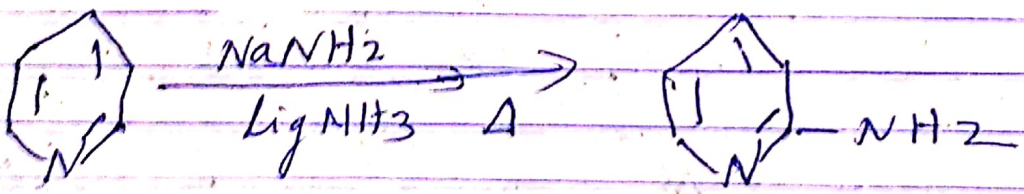
(vi) **Reduction** ⟶



piperidine

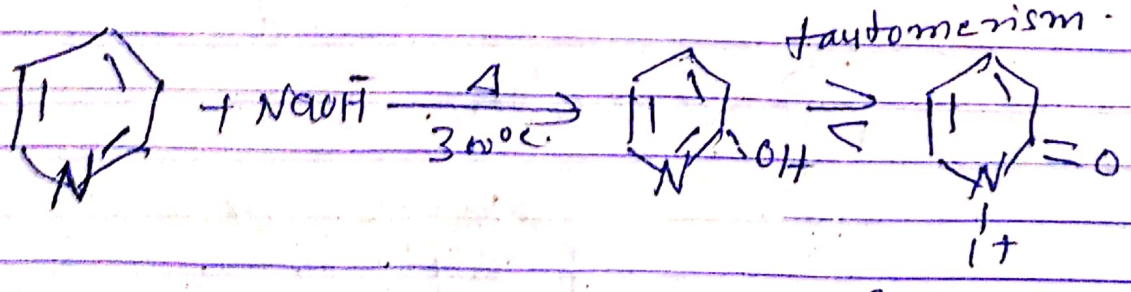
It is seen that resonating structure of c-2 and c-4 attack has two resonating form having negative charge on nitrogen. while attack at c-3 does not have any resonating form on which Nitrogen negatively charged. Therefore resonating structur of c-2 and c-4 is more stable. Nucleophilic substitution does not occurs at position c-3. Some nucleophilic substitution are given below

(i)



2 amino pyridine.

(ii)



2 Pyridone.