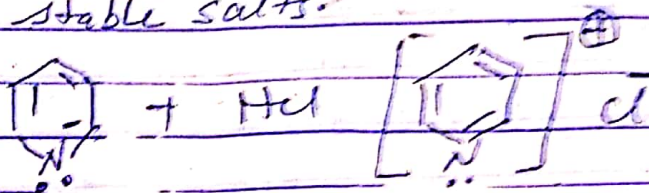


B.Sc. III, P-VII

Chemical properties of pyridine

1. Basic character - Pyridine acts as Lewis base. It reacts with acid to form stable salts.

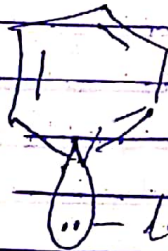


The lone pair of electrons on nitrogen of Pyridine is not involved in the delocalisation of electrons because it is just perpendicular to the plane of molecular plane. This lone pair is free ~~to~~ for formation of N-H bond. This leads to its basic character.

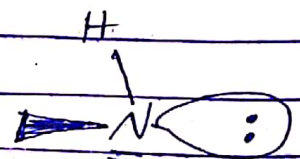
Pyridine is more basic than Pyrrole or aniline because the lone pair of electrons in aniline and pyrrole are involved in the delocalization while lone pair of Pyridine is free.

Pyridine is less basic than trimethyl amine because nitrogen in Pyridine is sp^2 hybridized having more s orbital and lower in size while the nitrogen in trimethyl amine is sp^3 hybridized having less s orbital present than sp^2 and higher in size.

Due to lower size of N hybrid orbital in Pyridine, the lone pair of electrons is more close to the nitrogen atom nucleus than nitrogen of trimethyl amine. This account for the less basic character of Pyridine than trimethyl amine.



lone pair of sp^2 hybrid orbital of Pyridine.



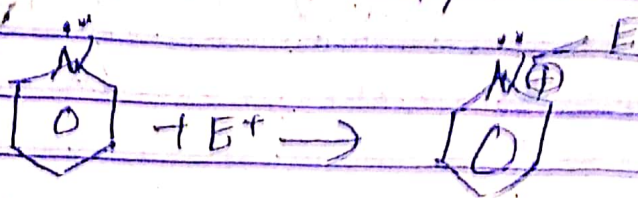
lone pair of sp^3 hybrid orbital of trimethyl amine.

(2) Electrophilic substitution : —

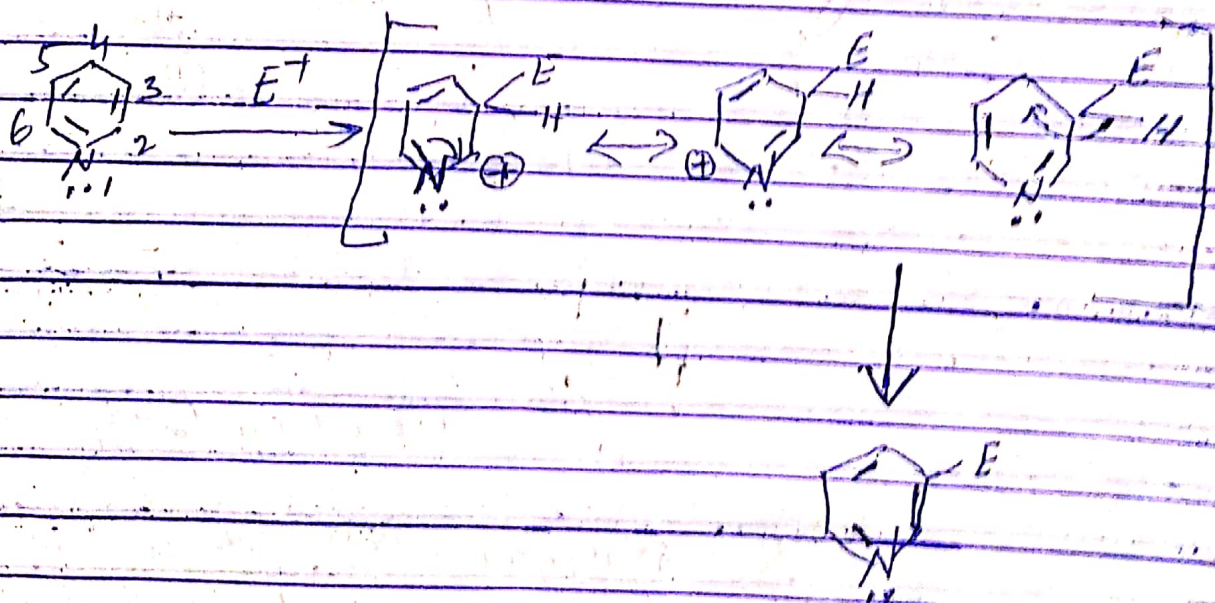
Electrophilic substitution of pyridine is less reactive than benzene ~~towards~~ this is due to following reason.

- (1) Due to presence of more electronegativity of nitrogen the electron density ~~around~~ around the ring at carbon atom is reduced.

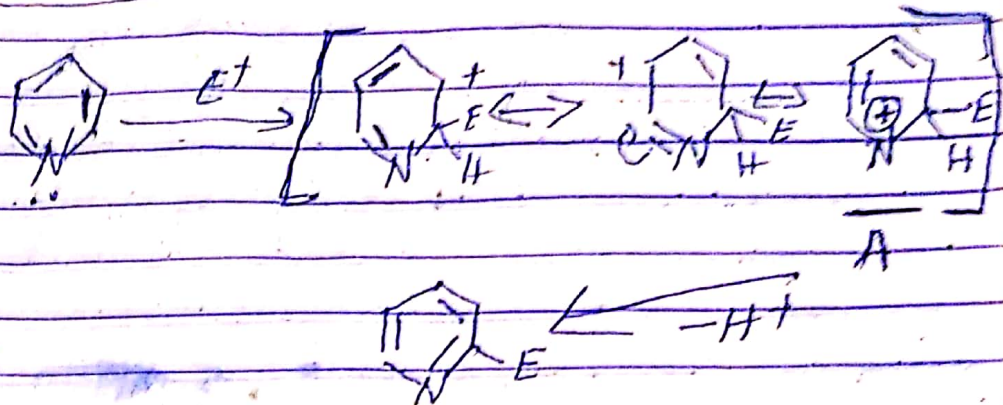
(ii) The usual electrophiles can co-ordinate with the lone pair of electrons on nitrogen to form resonance pyridinium salts.



Electrophilic substitution in pyridine occurs at position-3 predominantly because it has three resonance structures having carbocation while electrophilic substitution on position 2 or 4 has only two resonance structures having carbocation.



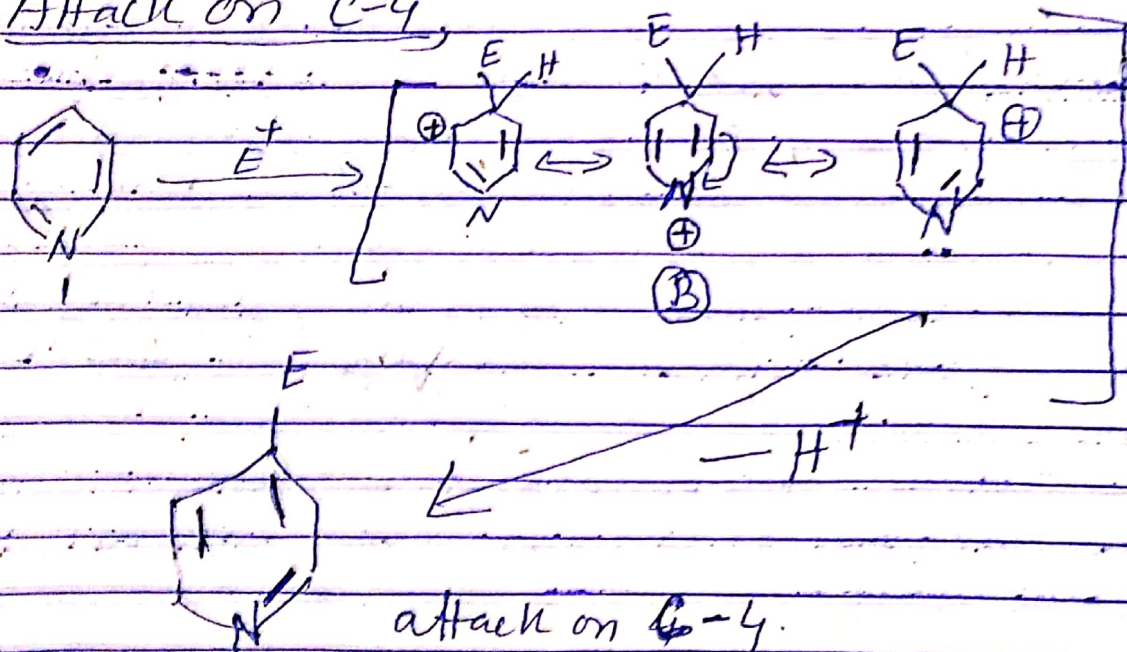
Attack at C-2



Substitution on C-2:

Two carbocation resonating structure (A) is nitrocatation.

Attack on C-4



attack on C-4.

(B) resonance structure is nitrocatation while other two are carbocation resonating structure. When position at C-3 is blocked the substitution occurs at C-5

— X —