Q.21. How is pyridine obtained on a large scale and what are its uses ?

Ans. : It is obtained on large scale from light oil fraction which is isolated from the distillation of coaltar. The light oil is treated with dil. H_2SO_4. The acid layer containing pyridine and other bases is treated with NaOH and the liquid so obtained is carefully fractionated to get pure pyridine.

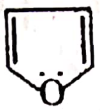
Uses of pyridine :

1. As a mild base in acylation, dehydrohalogenation etc.
2. As a solvent.
3. As a denaturant for ethanol.
4. As a starting material in the manufacture of many sulpha drugs.
5. As a catalyst in some reactions e.g. Knoevenagel reaction.

Q.22. Thiophene is more aromatic than furan—Why ?

Ans. : Both thiophene and furan have five membered ring and obey Huckel's rule—

Thiophene



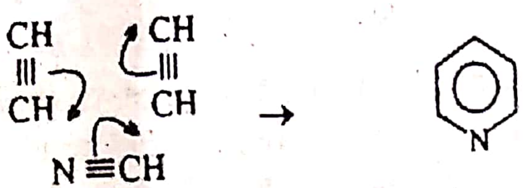
Furan

But the +M effect of sulphur is weaker than that of oxygen because the overlap of 2*p*-orbital of carbon and 3*p*-orbital of S is less than 2*p*-orbitals of C & O-atoms. Hence thiophene is more aromatic than furan.

Q.23. Discuss the methods of synthesis of pyridine.

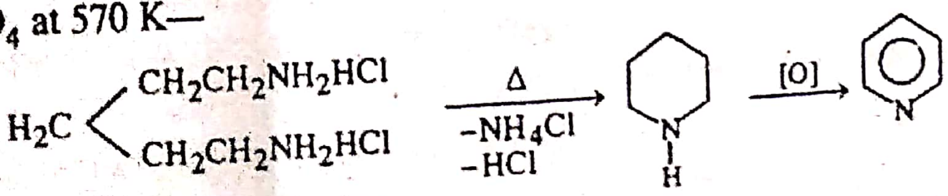
Ans. : Synthesis of Pyride :

1. It is prepared by passing a mixture of acetylene and HCN through a red hot tube



(Pyridine)

2. It can be synthesized by heating pentamethylene diamine hydrochloride when piperidine is obtained and oxidising the latter with conc. H_2SO_4 at 570 K—



Penta methylene diamine hydrochloride

Piperidine

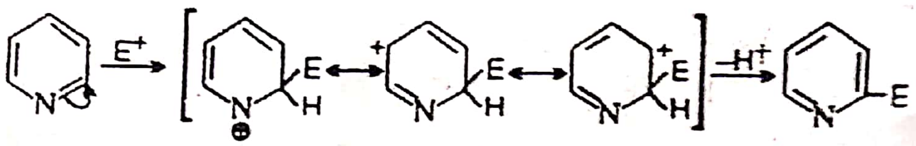
Pyridine

Q.24. Pyridine undergoes electrophilic substitution mainly at position-3 (or β –). Why ?

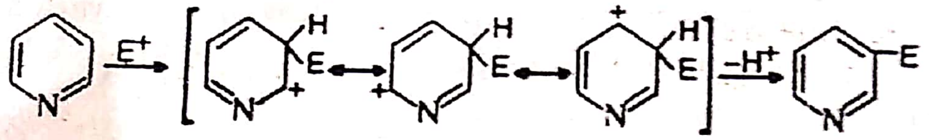
Or, Electrophilic attack of 3-position of pyridine is more favourable than its 2 & 4-positions—Why ?

Ans. : We know that electrophilic substitution in pyridine occurs through a carbocation intermediate followed by deprotonation. The electrophilic substitution at position-3 in pyridine gives the most stable carbocation due to resonance while in other cases say 2 or 4, one of the resonating structures is unfavourable due to the presence of positive charge more concentrated on the more electronegative N-atom. Therefore the electrophilic substitution at position-3 is preferred to the others.

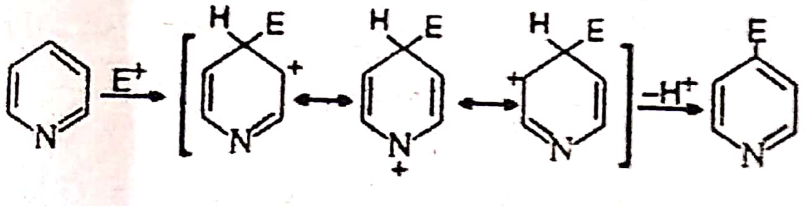
(i) Electrophilic attack at position-2 :



(ii) Electrophilic attack at position-3 :



(iii) Electrophilic attack at position-4 :



Further in each case, the positive charge is relatively less well accommodated than in the electrophilic reactions of benzene due to the fact that the N-atom is more electronegative than C-atom. Thus all the positions 2, 3 and 4 are deactivated. 2 and 4 positions are particularly more strongly deactivated due to the high energy of resonating structures with doubly positively charged N-atom. Therefore pyridine is highly deactivated towards electrophilic substitution reactions.

Q.25. The nucleophilic attack in pyridine occurs preferentially at position-2. Give reasons.

Ans. : If we examine the resonance stabilisation of the intermediate that would arise in the event of attack of nucleophilic at position-2 and 4, we find that