6 Membered Heterocyclic Compounds

α-pyran

γ-pyran

Pyridine (azine)

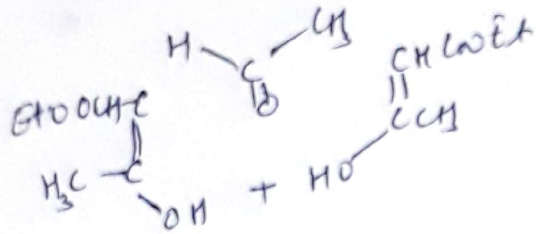
discovered by Anderson in bone oil in 1849.

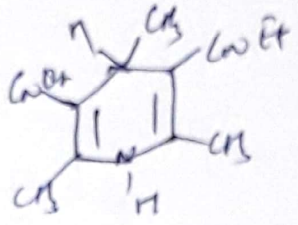
→

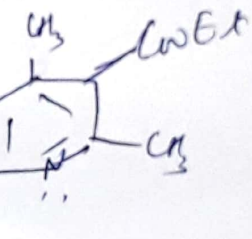
Methods :-

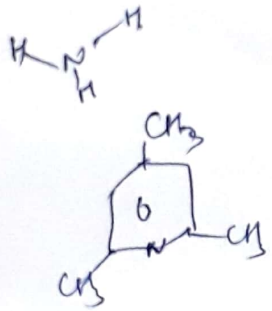
Hantzsch Synthesis :-

a)









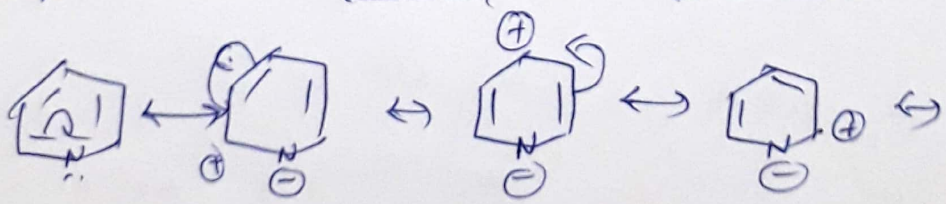
(1) Hydrolysis
(2) $-CO_2$

Structure :-

Since N atom attracts the π e⁻ cloud, so e⁻ density on carbon atom ↓ses on every carbon (< 1) & on N atom, more than 1.

$\mu = 2.23$ D.

→ as compared to 2-4 4-position, decrease in e⁻ density, less on 3 position ∴ ephilic sub. on 3 position & 2, 4- nucleophilic sub.



e⁻ density less on 2 & 4 position.

hygroscopic colourless liquid. (B.P = 115°C).

act as 3° base. pK_b = 8.8 while pyrrole pK_b = 13.6.

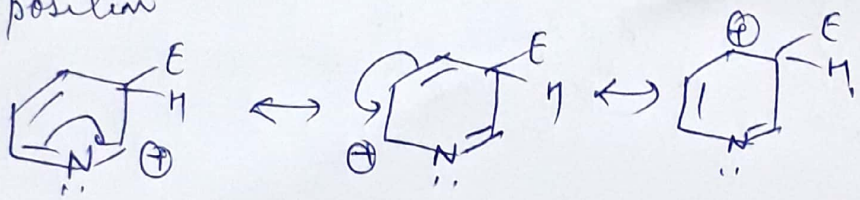
Electrophilic Sub. Rxs :-

As compared to C_6H_6, Pyridine has less e^- density,
∴ less reactive towards e^- Sub rxs & more towards Nu Sub rxs.
Thus e^- rxs in extreme cond. only.

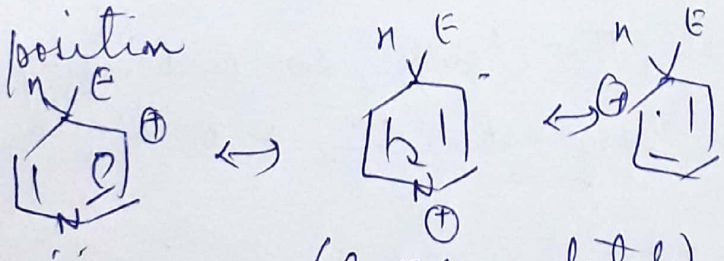
2nd position

(highly unstable)
6 e^- on N

3 position



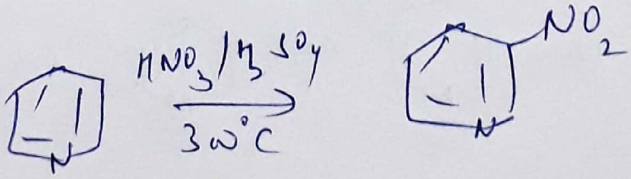
4 position



(highly unstable)

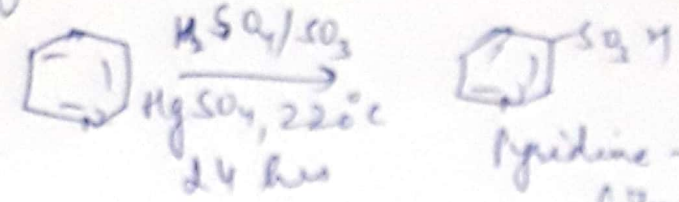
∴ e^- philic Sub. only on 3rd position, in extreme Cond^n ∴ in pyridine, deactivation due to ring nitrogen.

Nitration :-



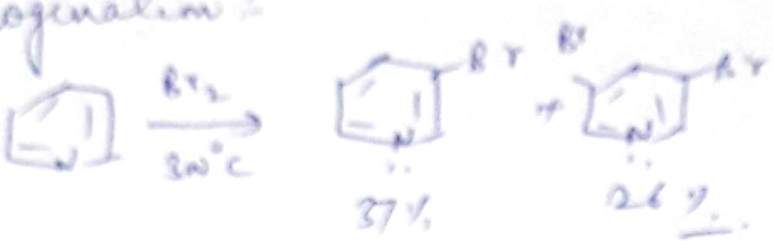
(15% yield)

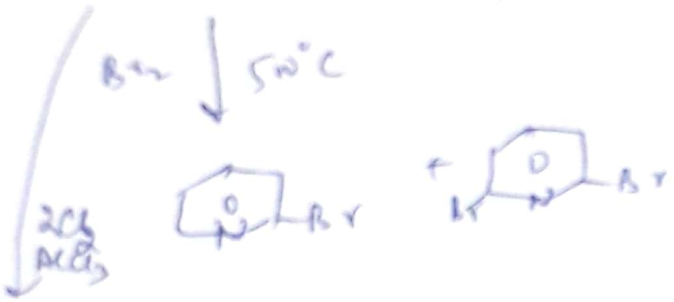
Sulfonation



Pyridine-3-sulfonic acid
(70%)

Halogenation :-

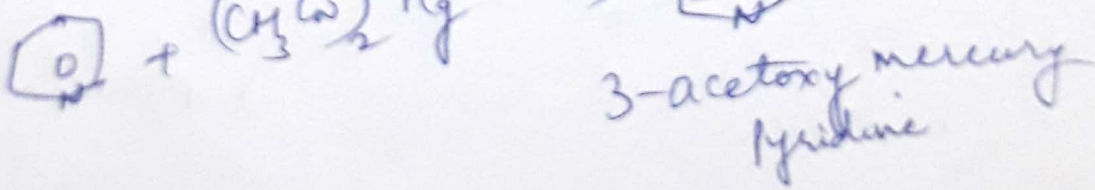




3-chloro pyridine

Friedel Craft Rxt do not take place in pyridine b'coz $AlCl_3$ & other Lewis acid catalyst form coordinate bond c paired e⁻ of N.
Thus pyridine does not give F.C alkylation & acylation rxn.

Mercuration :-



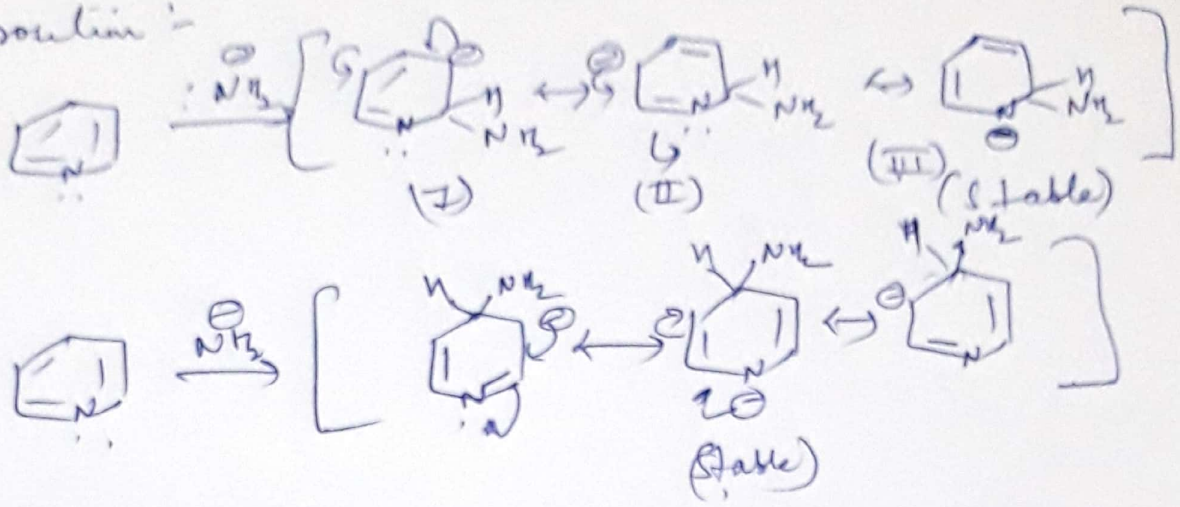
3-acetoxy mercury pyridine

Nucleophilic sub. Rxn :-

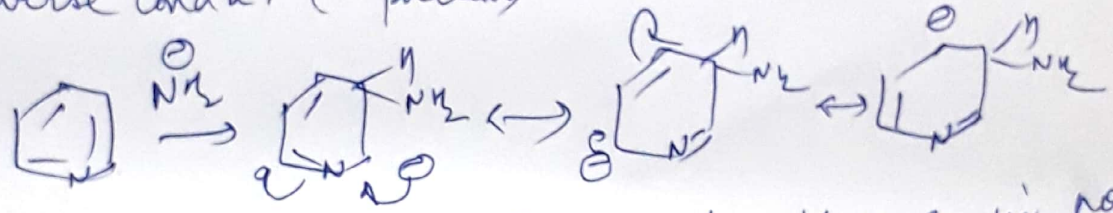
on 2 & 4 position

i) Favourable conditions :-

2 position :-

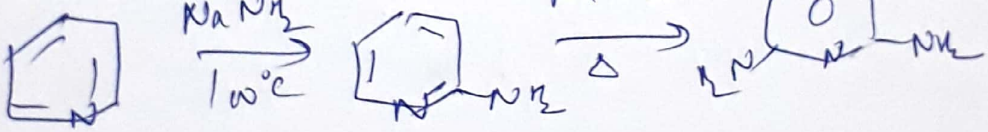


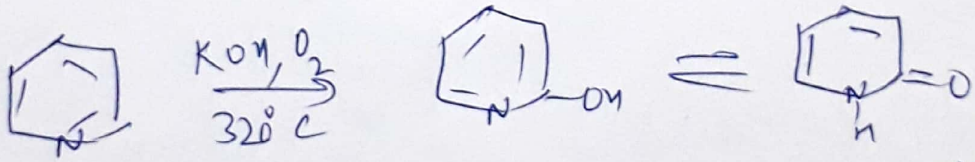
ii) Adverse condn :- (3 position)

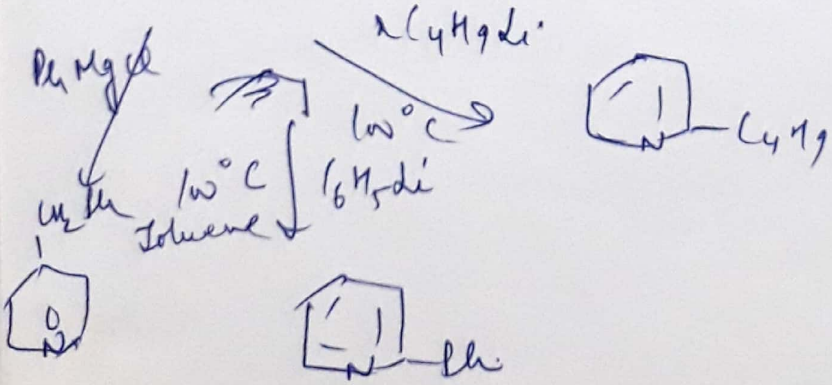


∴ on 3 position, no $Nu^{\ominus}$ sub takes place as in no res. st, $\ominus$ve charge on N.

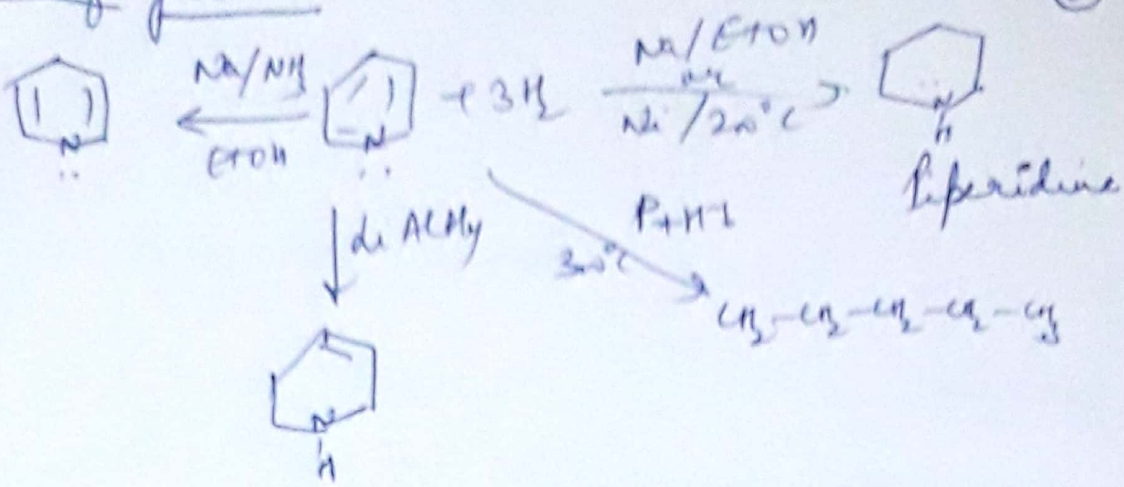
Chichibabin Rxn :-



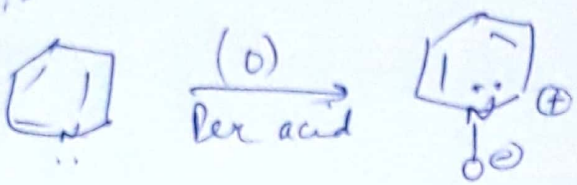


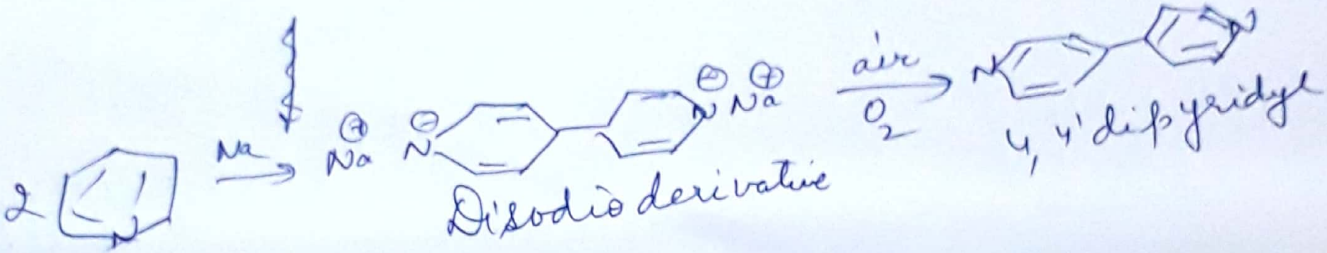


Red^{n} of Pyridine :-



Oxidation :-





Disodio derivative