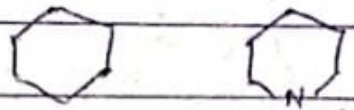
HETEROCYCLIC COMPOUNDS

Atoms other than carbon - Hetero atom.



Homo cyclic — Hetero cyclic

N, O, S - Replace carbon.

5-Membered Ring

Pyrol — furan — thiol.

PYROL

→ Many naturally occuring comp contain pyrol eg Chlorophyll & Haemoglobin, alkaloids

→

Coal tar, bone oil contain pyrol.

Mixture → Distillation → Pyrol

↓

Separate different fraction of coal tar & bone oils to get desire product ie pyrol.

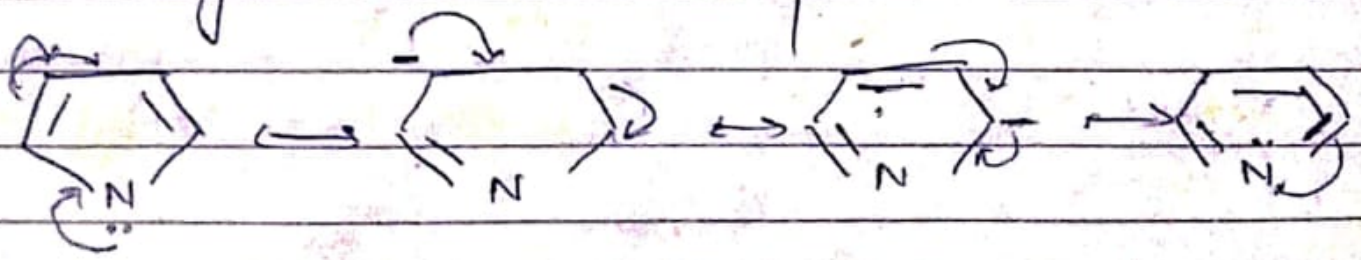
Pyrol can be isolated from bone oil by first washing it with dil H_2SO_4 to remove basic ~~acidic~~ substances then with dil. NHOH to remove acidic substance and then subjected to fractional distillation

Pyrol can be obtained from 100–150°C

After that we treat it with KOH & get potassium salt of Pyrol.

Nature of Pyrol

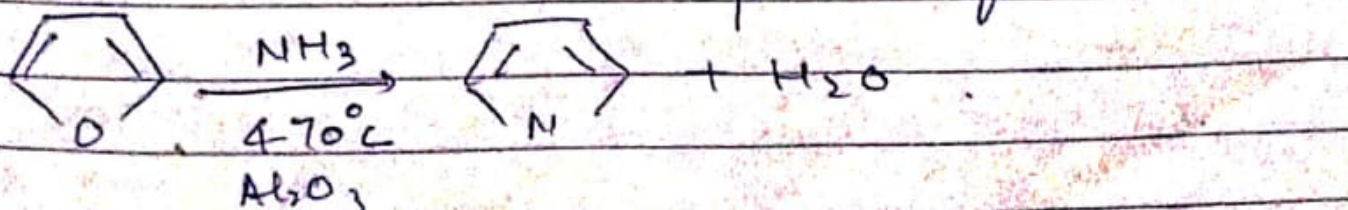
- Pyrol – aromatic compound. $(4n+2)$



Synthesis

1- Lab Method

2- Commercial Method → By rxn of furan with NH_3 in presence of Al_2O_3 at 470°C



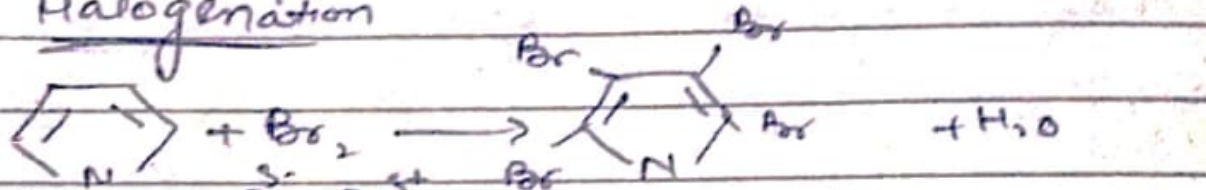
Physical Properties

- Colourless liquids having B.P 131°C
- Slightly soluble in H_2O & soluble in org. comp
- Rapidly turn brown when exposed to air.

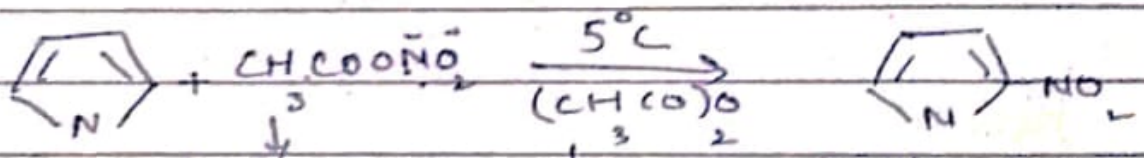
Chemical Properties

- It has heterocyclic ring system with sec amine group which is more reactive than benzene
- Give electrophilic substitution rxn.

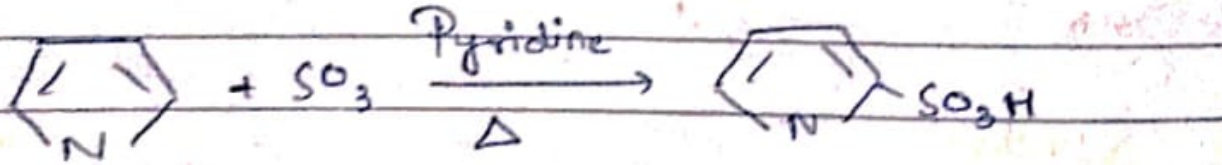
eg Halogenation



Nitration



Sulphonation

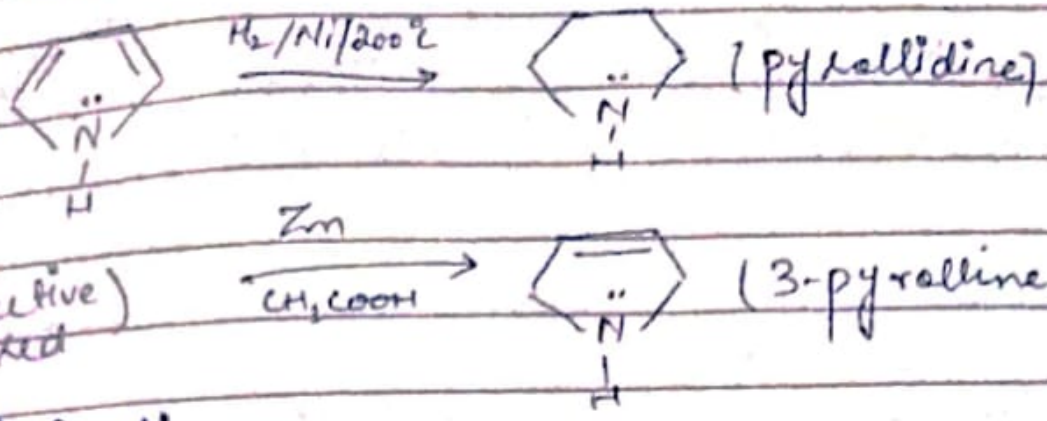


2-pyrol sulphonic acid

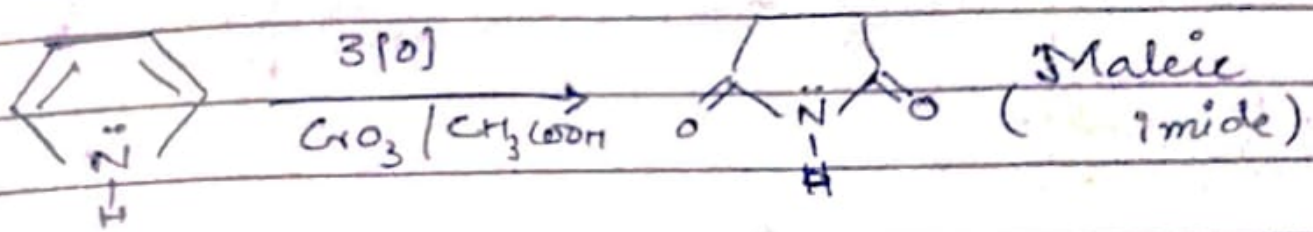
Uses

- It is commercial solvent.
- Used in formation of nylon.
- Imp reagent of pharmaceutical industry.

Reduction



Oxidation



FURAN

Oxygen containing 5-membering. 

Furan is produced on industrial scale from acid hydrolysis of pentosane. Pentosane is C5 polysaccharide $(C_5H_8O_4)_n$.

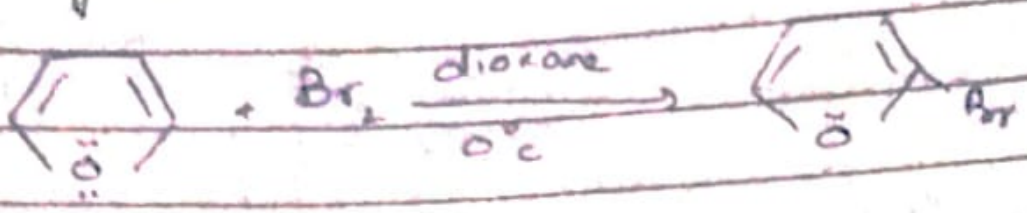
Physical Properties

- Colourless liquid
- has B.P 31.4°C having odour like chloroform
- Insoluble in ether but soluble in most org. solvents
-

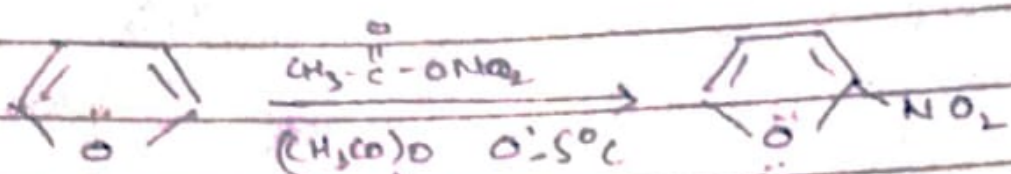
Chemical Properties

- Like pyrrol, furan undergo electrophilic sub rxn preferably at position 2.

Halogenation

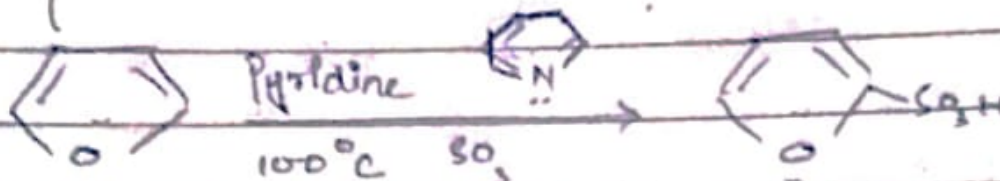


Nitration



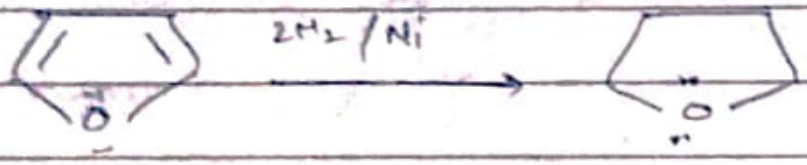
2-nitro furan

Sulphonation



2-furan sulphonic acid

Reduction Rxn



Tetra hydrofuran (THF)

USES

- Used for acetylation rxn in friedal craft alkylation
- Used in pharmaceutical industry for preparation of many medicines / drugs

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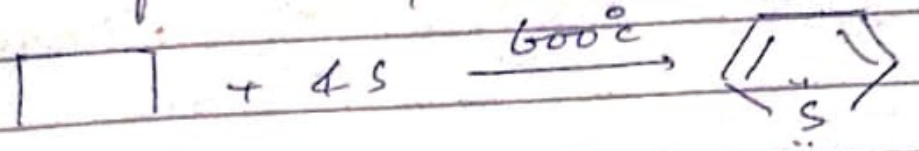
Date: __/__/20__

THIOPHENE

Sulphur containing 5-memb heterocyclic comp.
Can be prepared on industrial scale by Rxn of butane / alkane at high temp.



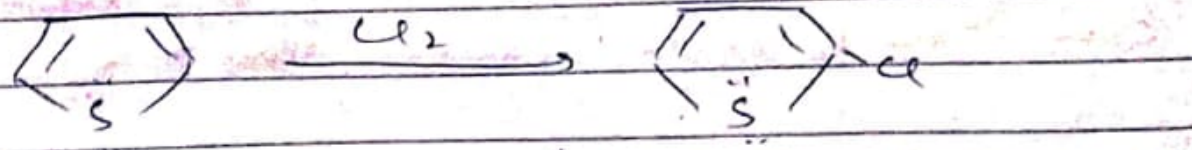
Physical Properties

- Colourless liquid has B.P 84°C
- Odour like Benzene
- Insoluble in H_2O but soluble in org. solvents
- Flammable & toxic.

Chemical Properties

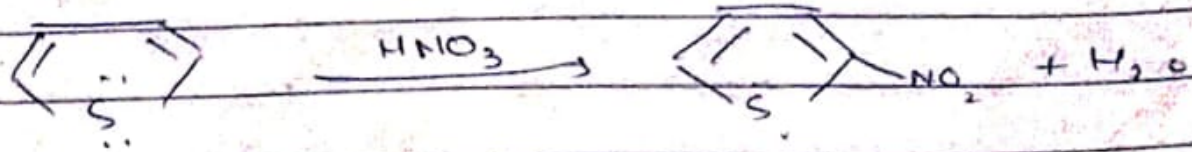
Undergo electrophilic sub Rxn.

Halogenation

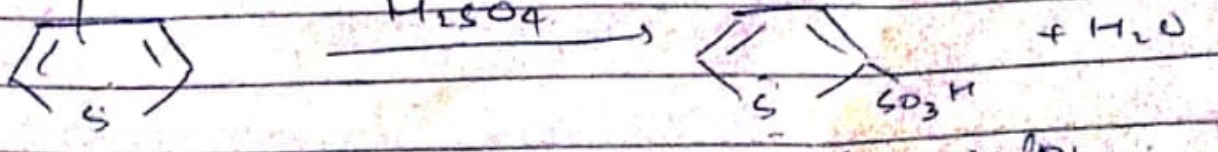


(2-Chloro thiophene)

Nitration

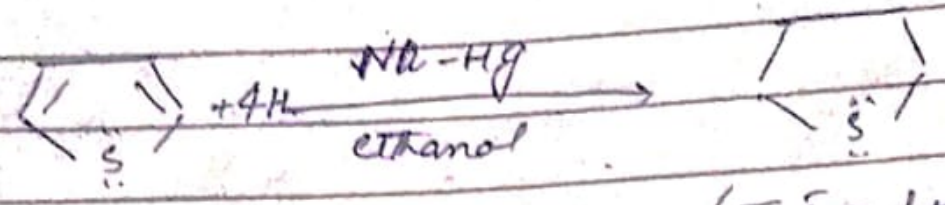


Sulphonation



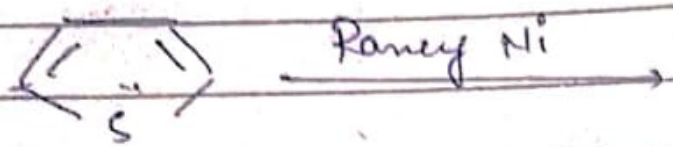
2-thiophene sulphonic acid

Reduction



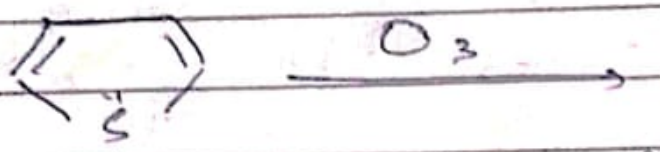
(Tetrahydro thiophene)

Catalytic Reduction



(n-butane)

Oxidation

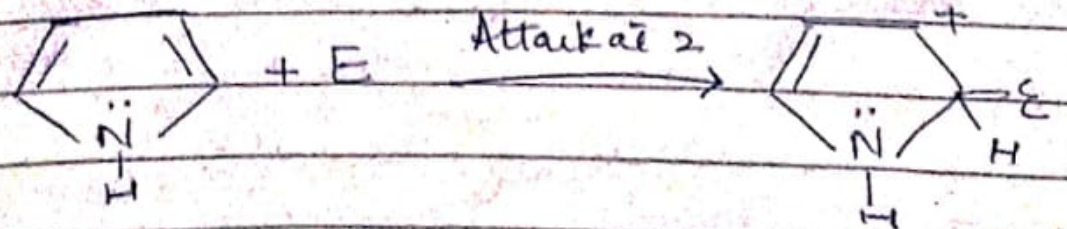


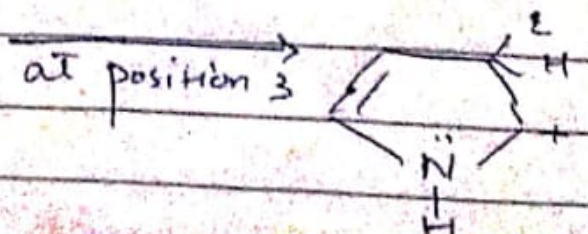
(Oxino-mercapto benzaldehyde)

Comparison of reactivity

→ Thiophene is less reactive than Pyrol & furan. But 300 x more reactive than benzene.

→ Which one is more aromatic?





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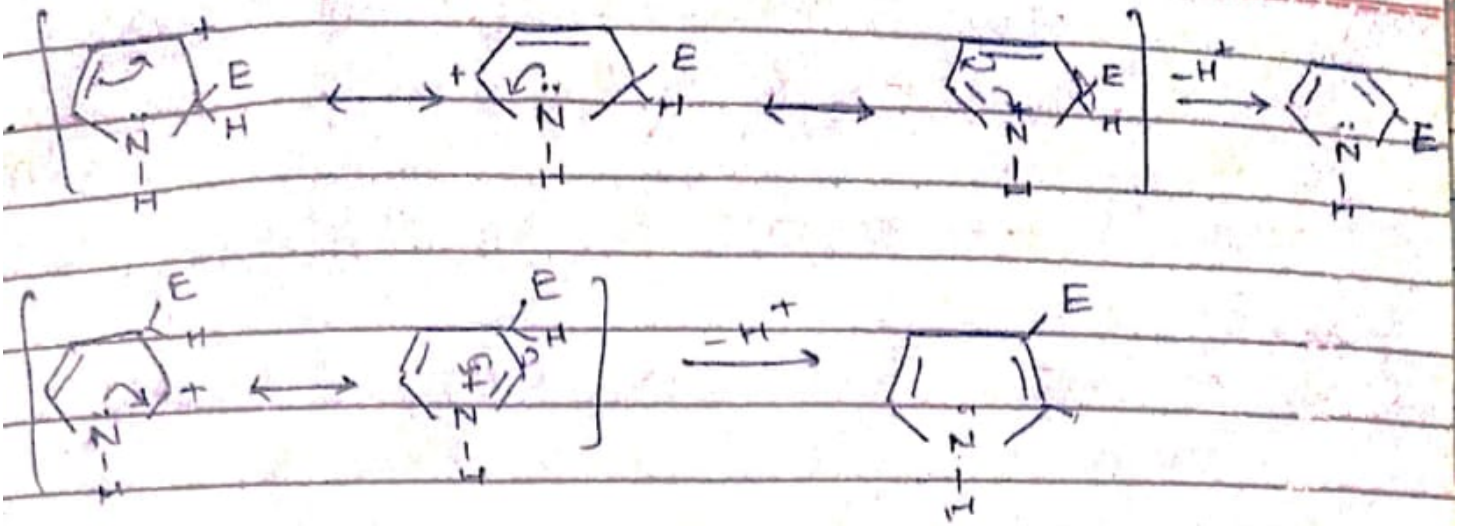


Because carbocation form by attack at position 2 has 3 resonance structure whereas for position 3 there are only 2 resonance structure. Therefore, carbocation form by attack at position 2 is more stable than attack at position 3.

Pyridine

6-memb heterocyclic N. containing comp.

- B.P 115°C.
- Colourless liq. soluble in H_2O & most org. comp
- Imp point about structure of pyridine is tertiary amino group.

Synthesis

$$2\,CH\equiv CH + HCN \xrightarrow{500^\circ C}$$  Cyclization.

- Pyridine is planar hexagonal structure like benzene. Each carbon is sp^2 hybridized,

But heteroatom Nitrogen is sp^2 hybridized but not linked with hydrogen.

Pyridine is aromatic like benzene because it follows Huckel rule.

It also called azo benzene (contain 1 Nitrogen atom)

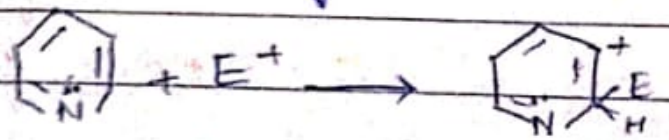
3 - double bonds in ring are pair of delocalization system so it is called aromatic

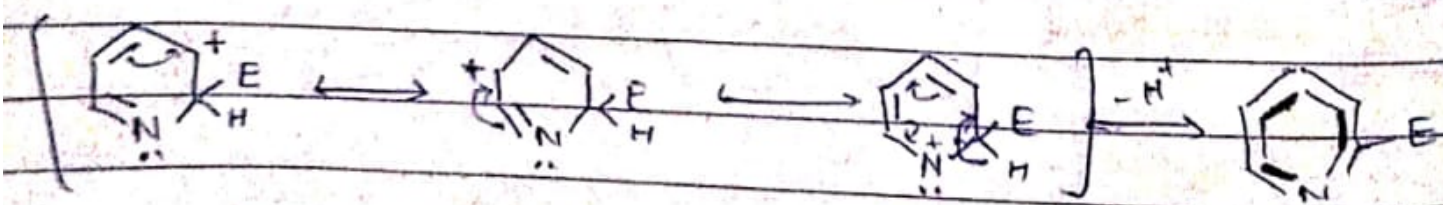
Stable like benzene because of resonance energy.

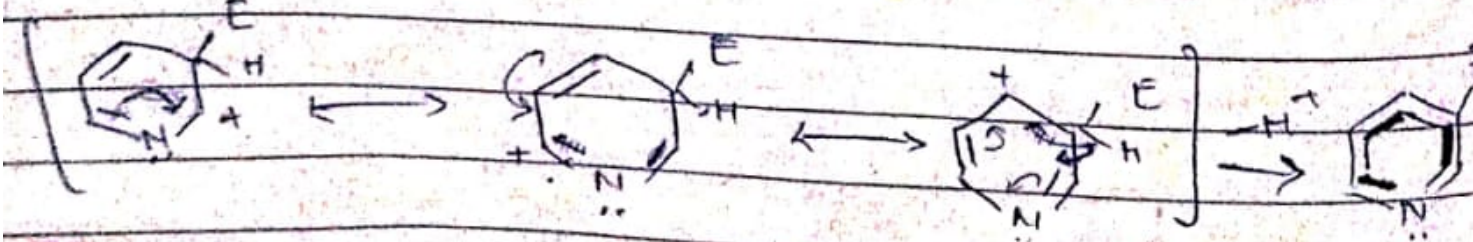
Basic characters

Pyridine is basic even more basic than pyral because lone pair of e^- on nitrogen in pyridine is not pair of aromaticity. So this e^- pair is available for bonding with any proton. But in pyral e^- pair is pair of aromatic but not available for any protons. system

Reactivity







Electrophilic Sub. Rxn

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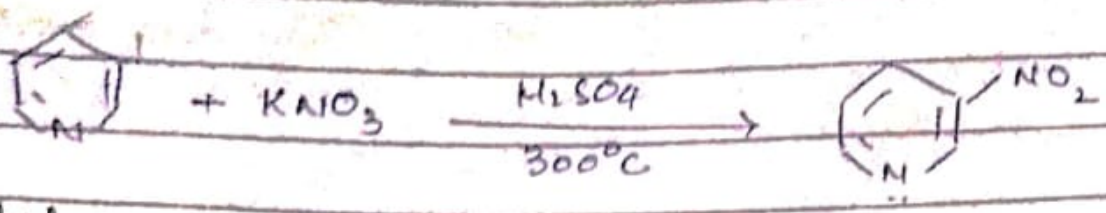
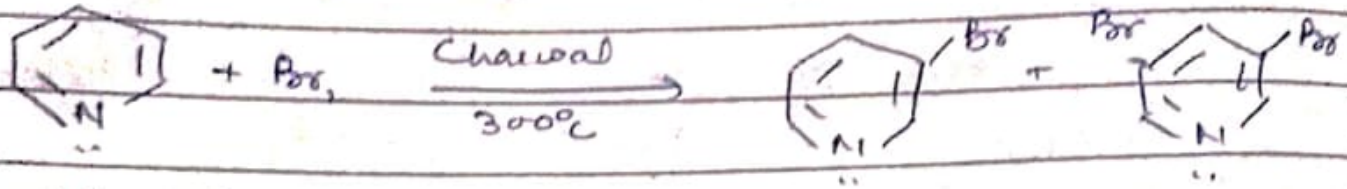
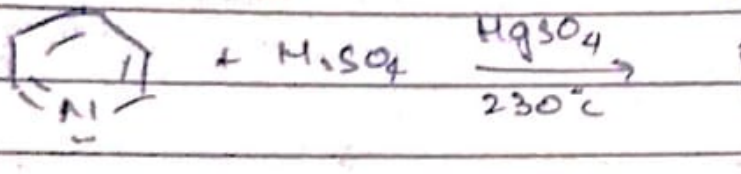
Nitration



Halogenation



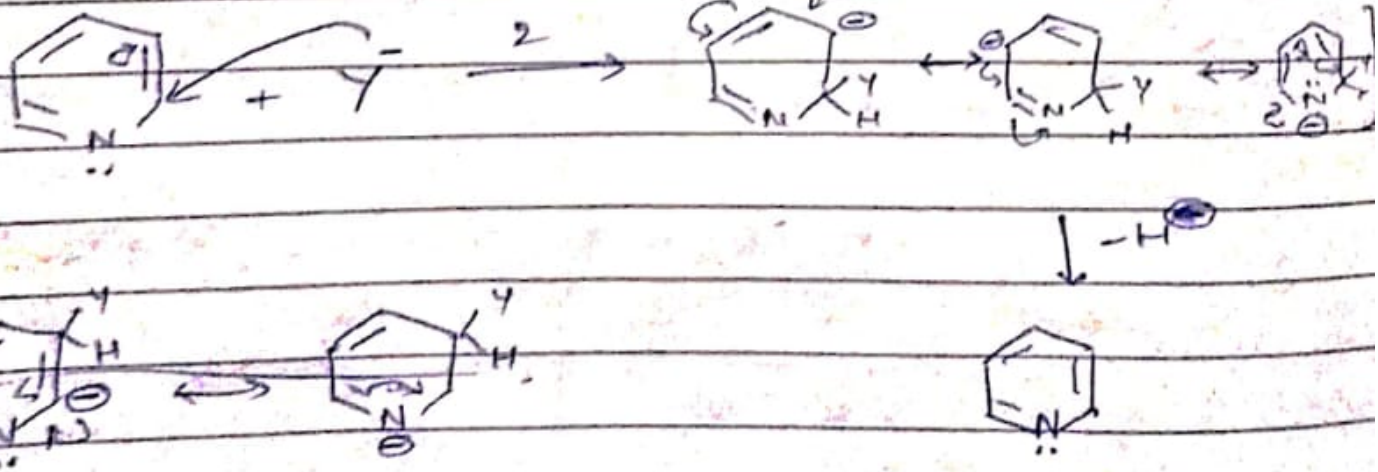
Sulphonation

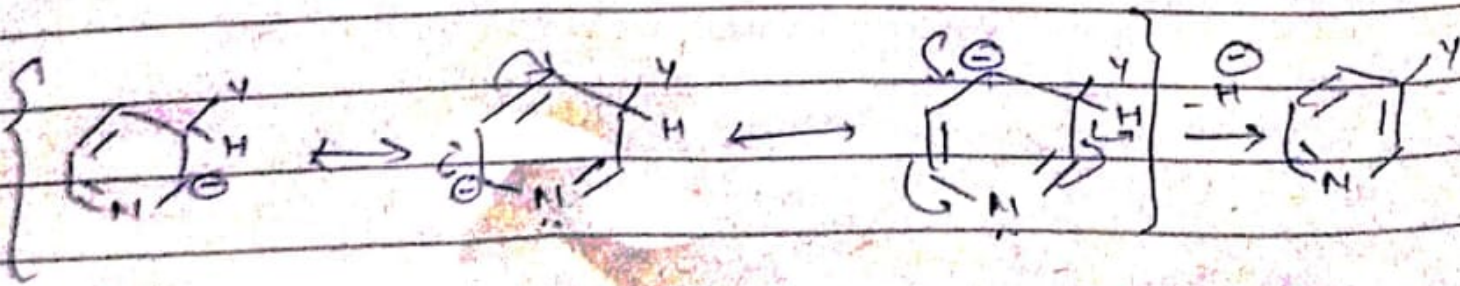


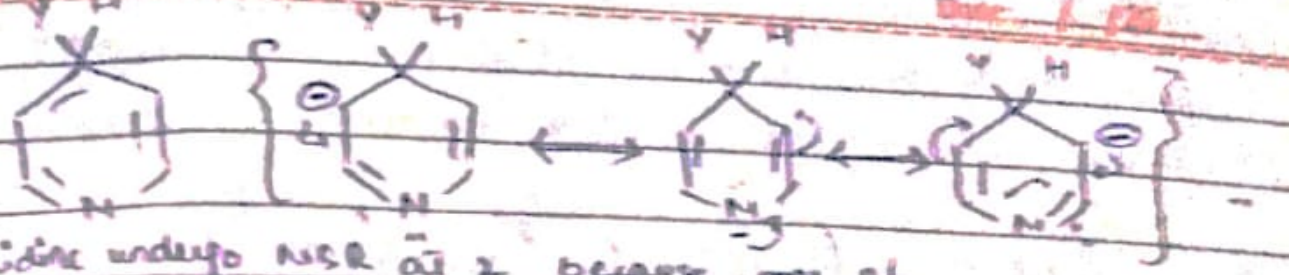
(Pyridine 3-Sulphonic acid)

Nucleophilic Sub Rxn of Pyridine

- It is very reactive to nucleophile.
- 2-substituted product.

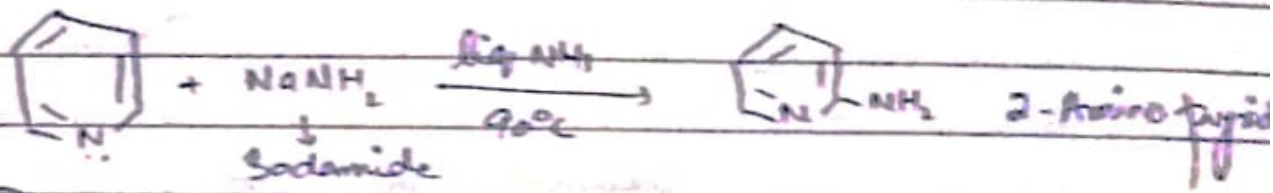




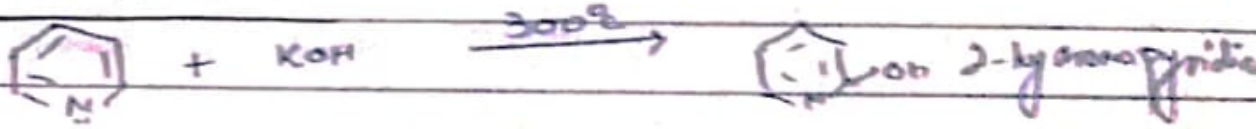


Pyridine undergo NSR at 2 because one of resonance structure carry -ve charge on nitrogen atom but not in case of 3- Also -ve charge on 4

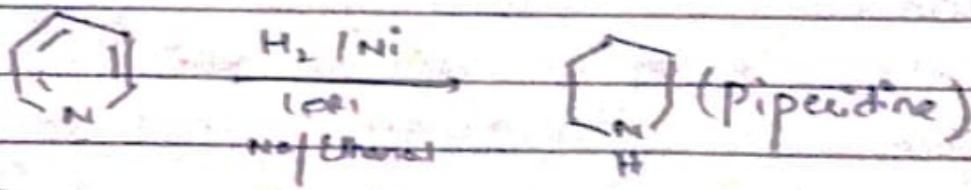
Sodamide (Chichibabin Rxn)



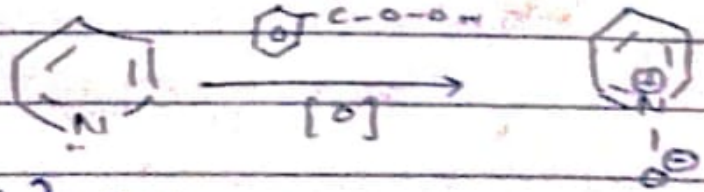
Rxn with KOH



Reduction reaction



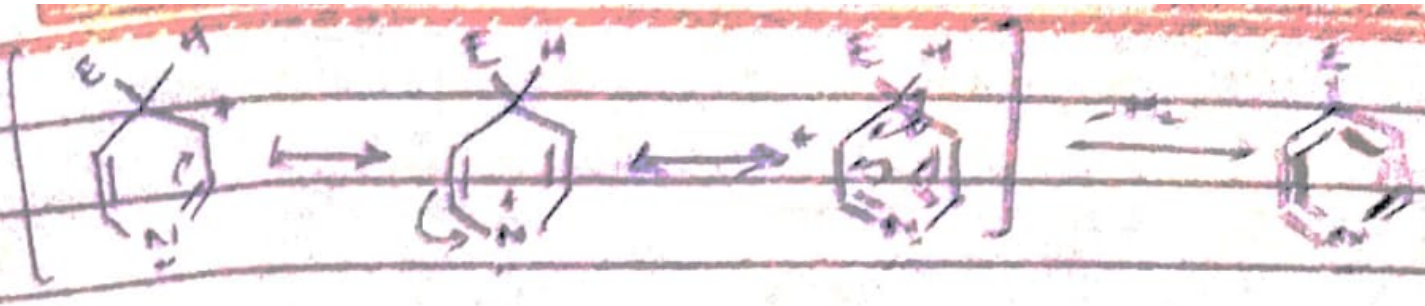
Oxidation



USES

- Used as basic solvent in org. synthesis
- Also used to denature alcohol.
- Used for preparation of diff pharmaceutical reagent.

⇒ Pyridine is less reactive towards Electrophilic Sub. rxn than benzene. eg Pyridine (Nitration) take place in presence of $NaNO_3$ / H_2SO_4 at 300°C



The carbocation form by attack at position 3 is more liable than 2 & 4 because Pyridine have one unstable resonance structures with positive charge on nitrogen in case of 2 & 4 but not 3 so position 3 will undergo electrophilic sub. rxn.

→ Thiophene is less reactive than furan & pyrol but 300 × more reactive than benzene because in pyrol – N , Furan-O , thiophene-S are present. N & O are ↑ E.Neg and more reactive than thiophene. But , in benzene no heteroatom & lone pair present hence is stable than thiophene.

→ Benzene > Pyridine > Pyrol > furan > thiophene.

↓

More E.Neg diff + follow Huckle's rule