# Heterocyclic Compds.

**Introduction** - * Homocyclic Compds. - All atoms are same in cyclic struct. of cyclic compds.

** Heterocyclic Compds. - One or more atoms are different from C in cyclic struct. of cyclic compds.

*** Exception - Epoxides (eg. γ- & δ- lactones) having heterocyclic struct are not to be included in heterocyclic compd. series.

Reasons - (i) Ring of these compds. can be broken easily
(ii) These compds. don't have any aromatic characters.

**** Definition - Compds. containing stable ring struct., having aromatic characters & at least one hetero atom in their ring are called as heterocyclic compds.

**Nomenclature - Rules** (1) Prefix of monocyclic compd. shows the nature of hetero atom.

Mono heterocyclic system

Table 1

| eg. Hetero atom | O | S | N | Si | P |
|---|---|---|---|---|---|
| Prefix | oxa | thia | aza | sila | phospha* |



| eg. Hetero atom | Se | Te | As | Sb | Bi | Ge | Sn | B |
|---|---|---|---|---|---|---|---|---|
| Prefix | Selena | Tellura | Arsa* | Stiba* | Bisma | Germa | Stanna | Bora |

Note - * When immediatelly followed by "-in" or "-ine" (6 membered ring),

{"phospha-", "arsa-", "stiba-"} should be replaced by {"phosphor-", "arsen-", "antimon-"}

** The saturated six-membered ring corresponding to phosphorin is named as phosphorinane. (instead of phosphezane)

*** In prefix 'a' can be elided where necessary.

(2) When two or more of the same hetero-atoms are present, the prefixes di-, tri- etc. are used.
eg. two O atoms → dioxa
three N atoms → triaza

(3) When more than one different heteroatoms are present, priority is given to that atom which is of higher gp. in P.T.
eg. O > N > Si
gp. VI V IV

When different heteroatoms are of the same gp., priority is ③ given to that atom which is of low at. no.

Thus O > S > N > P > Si

gp VI V IV

eg. N & S present then prefix ⟶ thiaza-

N & O " " " ⟶ oxaza-

(4) The size of a monocyclic ring from 3 to 10 is indicated by a stem :→ 3, ir (tri) ; 4, et (tetra); 5, ol ; 6, in ; 7, ep (hepta); 8, oc (octa); 9, on (nona) ; 10, ec (deca). [See table2]

(5)(A) The state of hydrogenation is indicated in the suffix as shown in table.

(B) The state of hydrogenation can be indicated by the prefixes dihydro- (hydrogenation of 1 = bond), tetrahydro- (hydrogenation of 2 = bonds) etc.

(C) Complete saturated ring can be represented by prefix perhydro-.

(D) The state of hydrogenation can be indicated by prefixing symbol 'H' (before parent unsaturated compd.) preceded by a number indicating the position of saturation.

④

| No. of members in the ring | Ring containing N (Table 2, Suffix) | | Ring containing no N | |
|---|---|---|---|---|
| | Unsaturation | Saturation | Unsaturation | Saturation |
| 3 | - irine | - iridine | - iren | - iran |
| 4 | - ete | - etidine | - et | - etan |
| 5 | - ole | - olidine | - ole | - olan |
| 6 | - ine | - inidine (b) | - in | - ane |
| 7 | - epine | (b) | - epine | - epan |
| 8 | - ocine | (b) | - ocin | - ocan |
| 9 | - onine | (b) | - onin | - onan |
| 10 | - ecine | (b) | - ecin | - ecan |

Where (b) expressed by prefixing 'perhydro' to the name of the corresponding unsaturated compd. [Ref. I.L. Finar Vol. II]

(6) In a monocyclic compd. containing only one heteroatom, numbring starts at this atom.

(7) The ring is numbered to give substituents or other hetero-atoms the lowest number possible.

(8) If the hetero-atoms are different, then numbring starts at the atom cited first according to the rule (3) & proceeds round

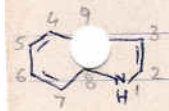
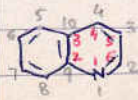
the ring in order of precedence.

Examples -

| Formula | Trivial Name | IUPAC Name | Formula | Trivial Name | IUPAC Name |
|---|---|---|---|---|---|
|  | Pyrrole | Azole |  | Pyridine | Azine |
|  | Furane | Oxole |  | Pyridazine | 1,2-diazine |
|  | Thiophene | Thiole |  | Pyrimidine | 1,3-diazine |
|  | Imidazole | 1,3-diazole |  | Pyrazine | 1,4-diazine |
|  | Thiazole | 1,3-thiazole |  | – | 1,2,4-triazine |
|  | Oxazole | 1,3-oxazole |  | – | 2H,6H-1,5,2-dithiazine |

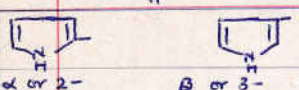
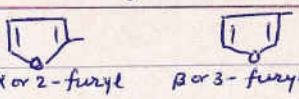
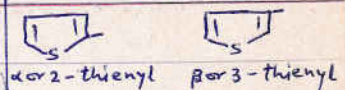
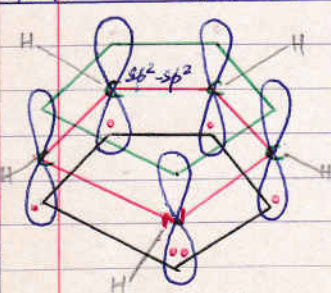
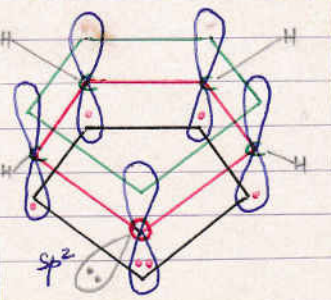
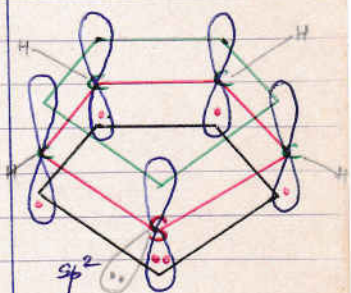
Fused heterocyclic system ⇒ Name is given by assuming the compd., as derivative of heterocyclic system.

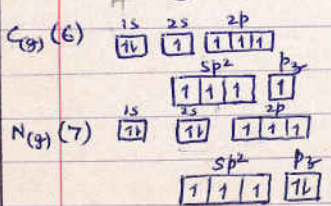
Examples -

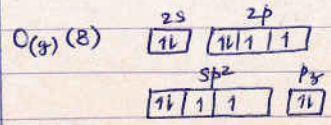
| Formula | Trivial Name | IUPAC Name | Formula | Trivial Name | IUPAC Name |
|---|---|---|---|---|---|
|  | Indole | Benzazole or Benzopyrrole |  | Quinoline | 1-Benzazine or 2,3-Benzopyridine or α,β-Benzopyridine |

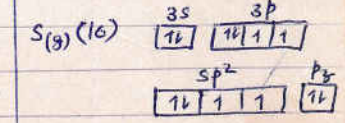
## Simple five-membered heterocyclic Compds.



| Name | Pyrrole | Furan | Thiophene |
|---|---|---|---|
| Structural Formula |  |  |  |
| Radicals |  α or 2-Pyrryl; β or 3-Pyrryl |  α or 2-furyl; β or 3-furyl |  α or 2-thienyl; β or 3-thienyl |
| Molecular Orbital Structure |   |   |   |



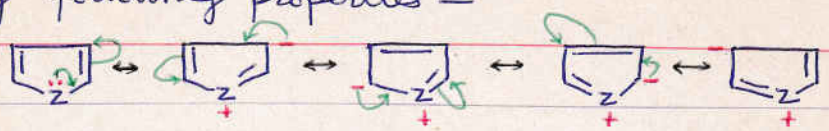



## Aromatic characters of Pyrrole, Furane & Thiophene



Aromatic characters of these compds. can be expl-ained by following properties —

1. **Resonance** -



(Z = O, S, NH)

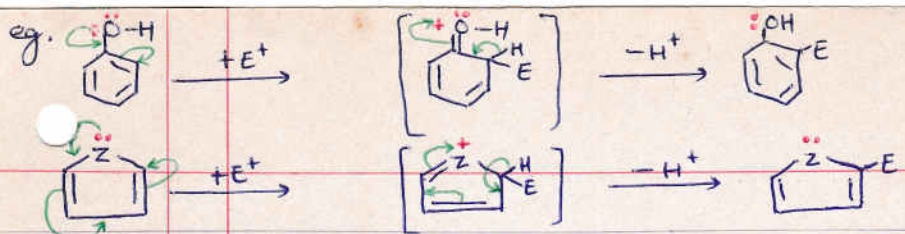
2. **Resonance Energy** - Sufficient but less than $C_6H_6$.

| $C_6H_6$ | > thiophene | > Pyrrole | > Furane |
|---|---|---|---|
| 144.4 K.J./mole | 117 | 87.8 | 71.1 |

3. Delocalisation of e⁻s found in the ring.
4. Give electrophilic substitution rxⁿˢ easily.
5. Give addition rxⁿˢ difficultly.
6. Follows Huckel's (4n+2) rule
7. Less stable & more reactive than $C_6H_6$.

**Reason of more reactivity** - In these compds. heteroatom behaves like phenolic —OH or aromatic —$\ddot{N}H_2$ gp. & show +M effect. (Donation of e⁻s to ring)





**Order of reactivity** -

$C_6H_6$ < thiophene < Furane < Pyrrole

**Note** - Furane is less reactive than pyrrole. (Although resonance energy of Furane 71.1 K.J./mole < Pyrrole 87.8 K.J./mole)

**Reason** - Power to detain +ve charge is less in O than N.

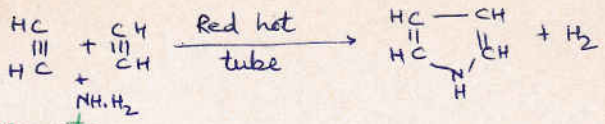
" These compds. are known as Superaromatic compds. because they have ① aromatic characters & ② more reactivity than $C_6H_6$."

## PYRROLE

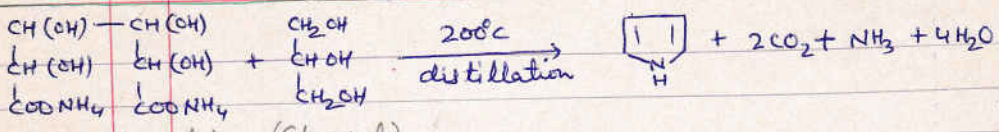
**Preparation** - 1. From Bone Oil -

Bone Oil → (wash with dil base - Acidic impurities) → (wash with acid - Basic impu.) → (Fractional distillation) → Fraction at 100-150°C → (KOH) → Solid Potassiopyrrole salt → (Steam distillation) → Pure Pyrrole

## 2. From Acetylene -

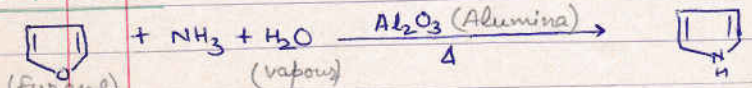


## 3. From Ammonium Mucate -

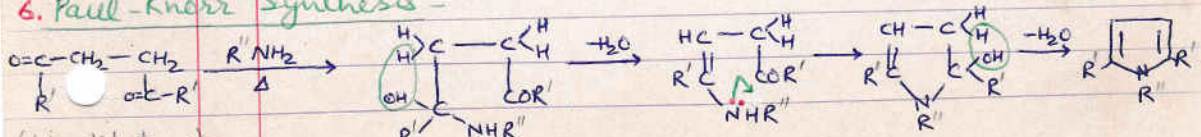



## 4. From Succinimide -


## 5. From Furane -

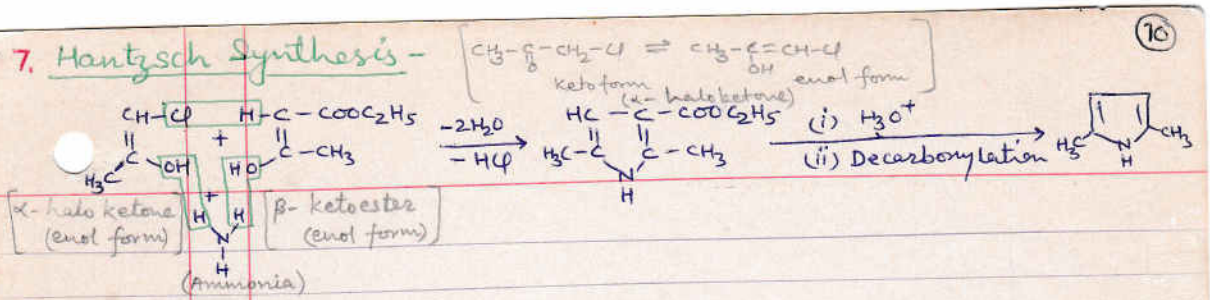



## 6. Paul-Knorr Synthesis -






## 7. Hantzsch Synthesis -

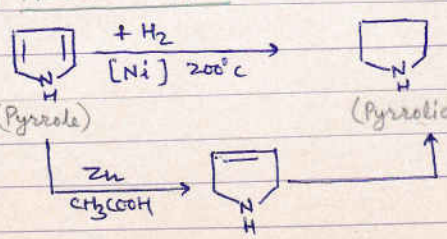



## Properties -

**PHYSICAL -**

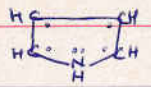
- * Colourless liquid ; B.P. 130°c
- * * Sparingly soluble in $H_2O$ ; soluble in $C_2H_5OH$ & ether
- * * * In air it turns to black
- * * * * Lighter than water

**CHEMICAL -** 1. Addition Rxns -



## 2. Amphoteric Nature –

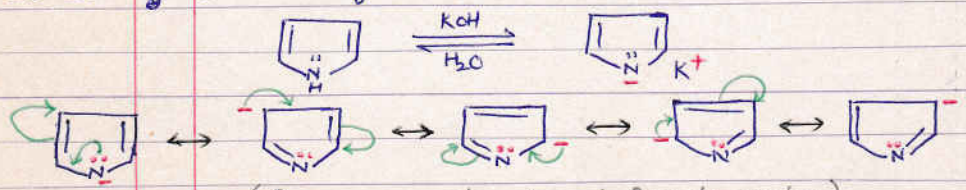
* Pyrrole acts as a base due to lp of N (11) e⁻s. But it acts as a weak base because lp is used in forming aromatic sextet, so it is not such free as ⊖ in (S) amines.



Pyrrole $pK_b = 13.6$ (Weak base)

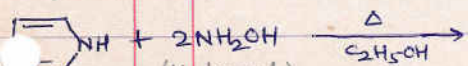
Ammonia $pK_b = 4.8$ (strong base)

** Pyrrole acts as a weak acid also because in Pyrrole N feels e⁻ deficiency due to use of lp in forming aromatic sextet. So it looses $H^+$ easily & pyrrole anion stabilised by resonance after loosing $H^+$.




(Resonance structs. of Pyrrole anion)

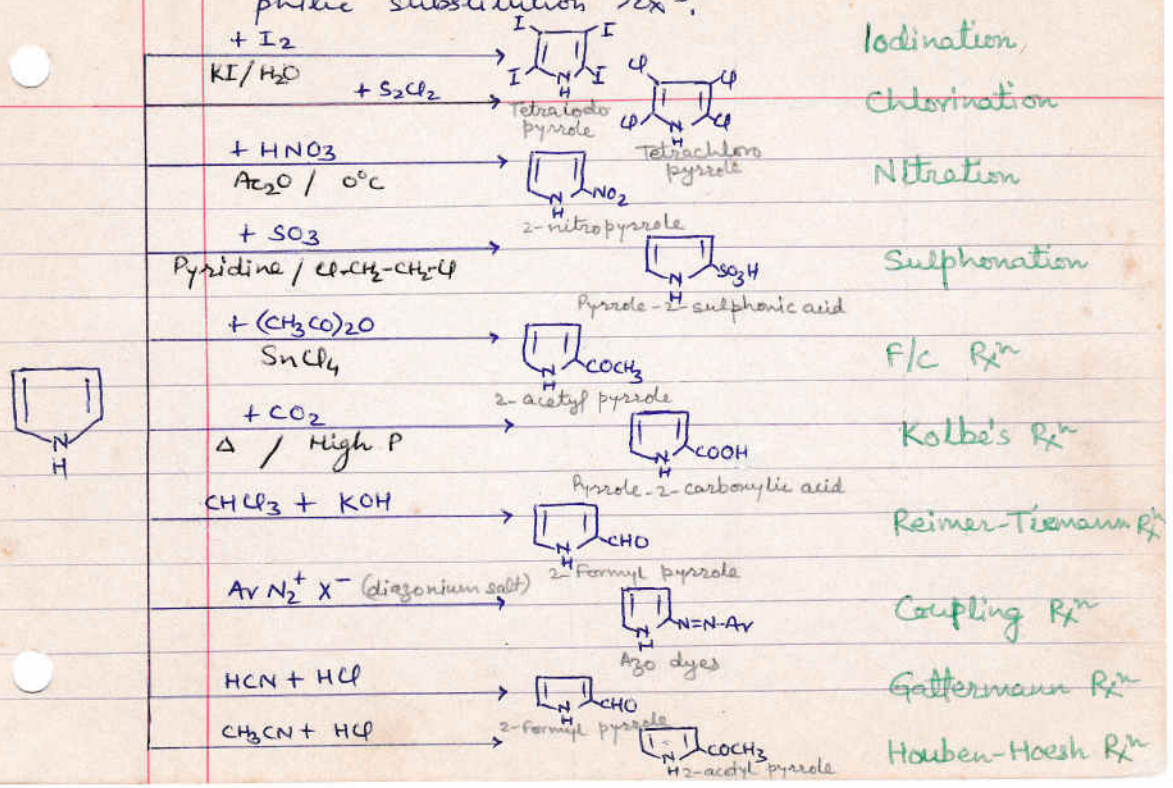
## 3. Ring Opening –



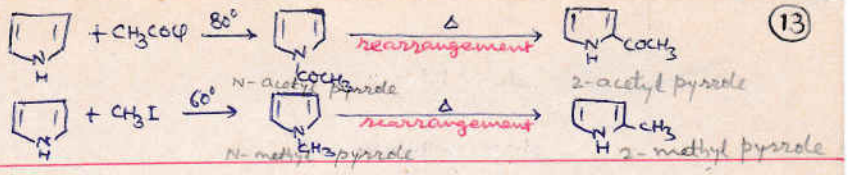

(Hydroxyl amine)

(Dioxyme of succinaldehyde)

## 4. Substitution Rxns – Due to aromatic nature it gives electro- (12) philic substitution rxns.



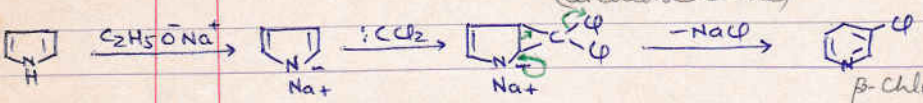
5. Rxns of Amino gp. –



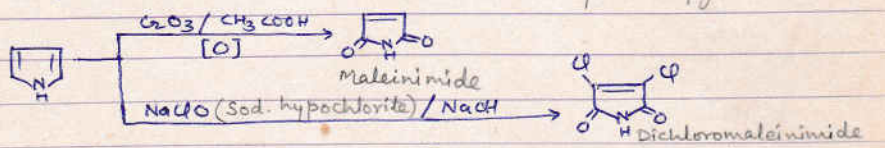

6. Expansion of the ring –

$$CHCl_3 + C_2H_5O^-Na^+ \longrightarrow :CCl_2 + NaCl + C_2H_5OH$$

(dichlorocarbene)




7. Oxidation –



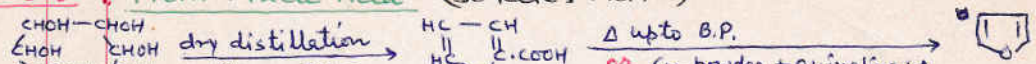

8. Rxn with G.R. – N ⇄ attach, active H के कारण ~~rxn~~ rxn होकर alkane बनती है –


Pyrrole-N-magnesium halide



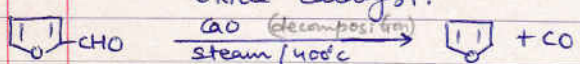
# FURAN

**Preparation** – 1. From Mucic Acid – (Scheele's Method)



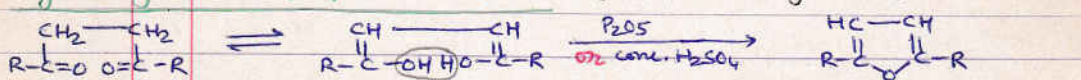

Mucic acid → Furoic acid → Furan

2. From Furfural – decomposition of furfural in steam in presence of oxide catalyst.




Furfural → Furan

3. By dehydration of 1,4-diketones – (Paal-Knorr Synthesis)



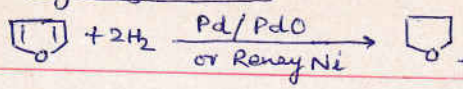

1,4-diketone ⇌ 1,4-dienol → Furan derivative

**Properties** – PHYSICAL –

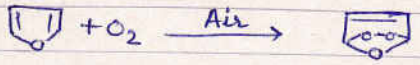
- Colourless liquid, B.P. 32°C
- Insoluble in $H_2O$; Soluble in $C_2H_5OH$ & ether
- Specific smell like $CHCl_3$
- Turns green a pine splint moistened with HCl
- Dipole moment = 0.7 D

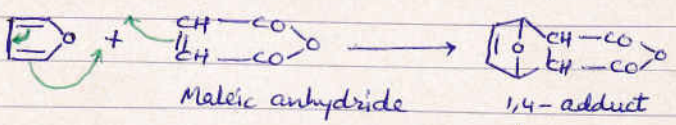
CHEMICAL - 1. Addition $R_x^{ns}$ -

① Hydrogenation -

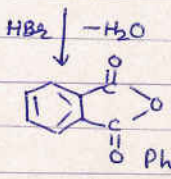



Tetrahydrofurane (THF)
(Imp. Solvent)

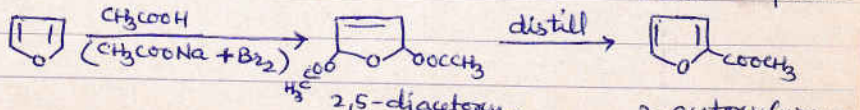
② Oxidation -  Furane-2,5-peroxide

③ Diels-Alder $R_x^n$ - 

Maleic anhydride 1,4-adduct




Phthalic anhydride

④ $R_x^n$ with $CH_3COOH$ - 


2,5-diacetoxy-2,5-dihydrofurane

2-acetoxyfurane

2. Electrophilic Substitution $R_x^n$ - कुछ विशेष परिस्थितियों में ही सम्पन्न होती है, क्योंकि इसमें aromatic characters होने के कारण इसकी reactivity अधिक होती है।



① $R_x^n$ with Acetyl Nitrate -


Acetyl nitrate

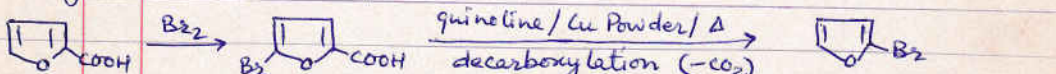
2-nitrofurane

② $R_x^n$ with Pyridine & $SO_3$ -


Sulphur trioxide

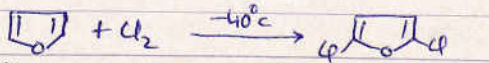
Furane-2-sulphonic acid

③ Halogenation - * Furane की halogens से $R_x^n$ तो हो जाती है किन्तु बने हुए halogen compd. का polymerisation हो जाता है अतः bromination के लिए Furoic acid (-I effect वाले gp. युक्त derivative) का bromination करवाकर उसका decarboxylation करवाते हैं।



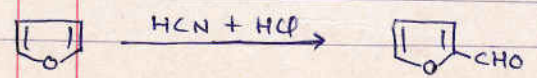

Furoic acid

2-bromofurane

** Chlorination - 

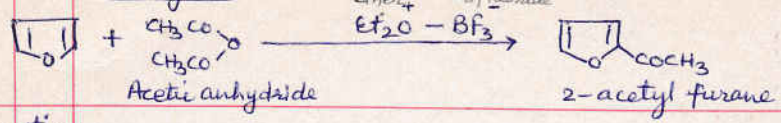

2,5-dichlorofurane

④ Gattermann Koch $R_x^n$ -



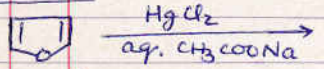

Furfural

⑤ Friedal-Crafts acylation –

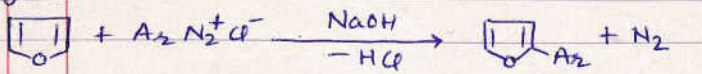



Acetic anhydride — 2-acetyl furane

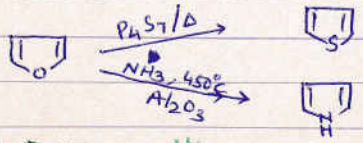
⑥ Mercuration –



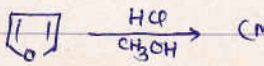

⑦ Gomberg $Rx^n$ –

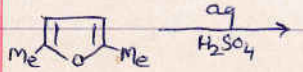



3. Preparation of Pyrrole and Thiophene –




4. Decomposition –



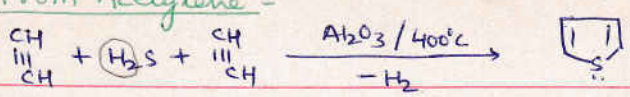




(1,4-dioxo compds.)



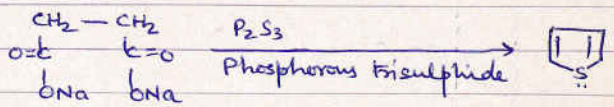
# THIOPHENE

Preparation – 1. From Acetylene –




2. From n-Butane –

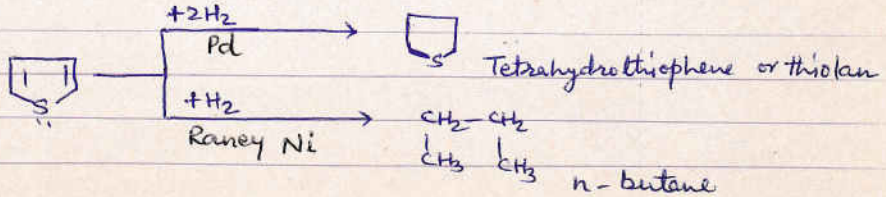

3. From Sodium Succinate –




Properties – PHYSICAL –

* Colourless liquid
* * B.P. = 84°C
* * * Insoluble in $H_2O$; Soluble in org. solvents

CHEMICAL – 1. Addition $Rx^{ns}$ –

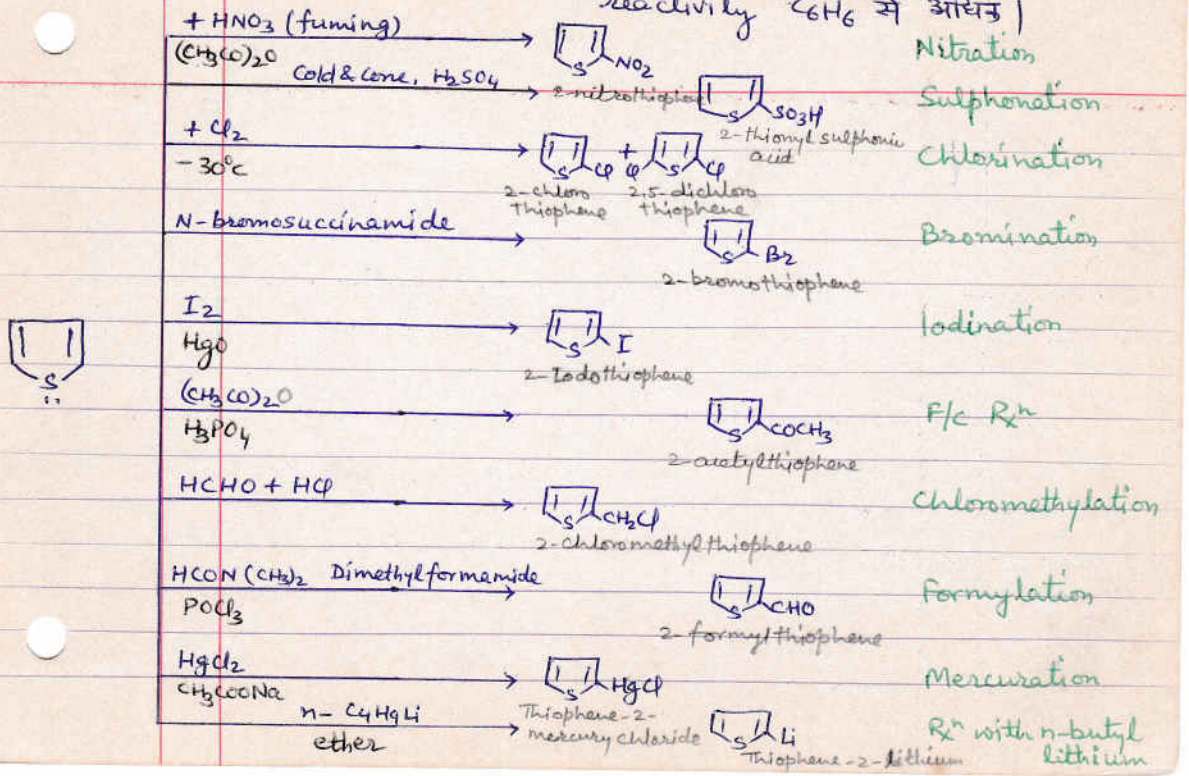



Tetrahydrothiophene or thiolan

n-butane

## 2. Electrophilic Substitution $R^{xn}$ –

Rxns benzene के समान किंतु reactivity $C_6H_6$ से अधिक।



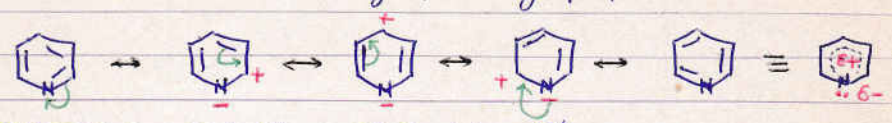



# Simple Six Membered Heterocyclic Compds.

## PYRIDINE (AZINE)

**Structure & Aromaticity** – Aromatic characters of pyridine can be explained by following properties –

1. **Resonance** –



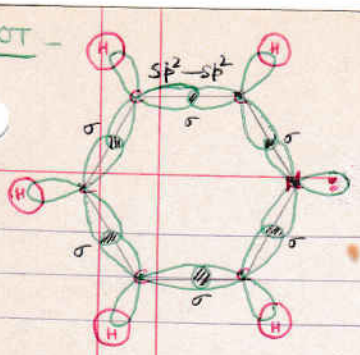
resonance energy = 125.5 KJ $mol^{-1}$

2. Do not give characteristic rxns of unsaturated compds. i.e. addition & oxidation rxns.
3. Gives electrophilic & nucleophilic substitution rxns
   (Characteristic properties of saturated compds.)

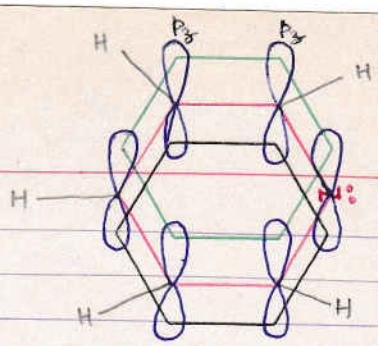
Note – Electrophilic Substitution की तुलना में Nucleophilic Subst. rxns easily सम्पन्न होती हैं क्योंकि resonance के कारण ring पर +ve charge आ जाता है।

4. Delocalisation of π e⁻s found in the ring
5. Follows Huckel's (4n+2) rule (6 e⁻ system)
6. Having coplaner cyclic structure. It can be explained by MOT.

7. MOT –

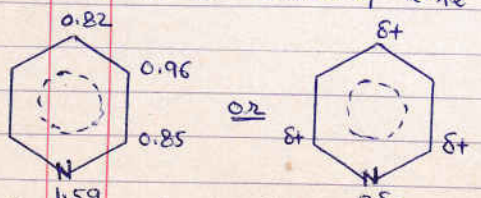



σ - bond system of Pyridine




π - bond System of Pyridine

8. Pyridine में $C_6H_6$ की अपेक्षा π-$e^-$ cloud थोड़ा भिन्न होता है क्योंकि E.N. अधिक होने के कारण N atom $e^-$ cloud को अपनी ओर attract करता है। अत: C atoms पर $e^-$ density इकाई से कम व N पर इकाई से अधिक होती है।

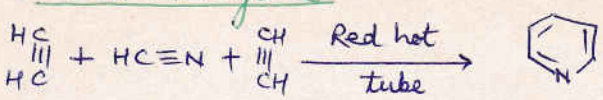



$\mu = 2.3D$

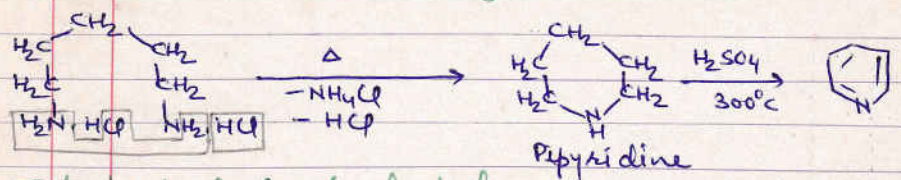
अत: Pyridine का struct  के स्थान पर  लिखना अधिक उपयुक्त होता है।



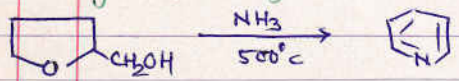
## Preparation – 1. From Acetylene –




## 2. From Pentamethylenediamine hydrochloride –



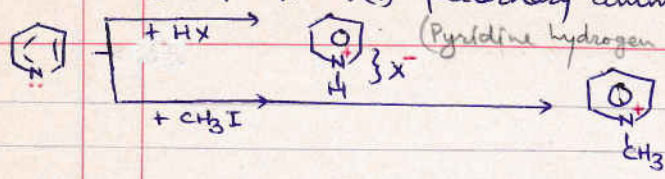

## 3. From Tetrahydrofurfuryl alcohol –




## Properties –

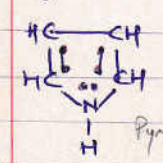
PHYSICAL –
- * Colourless liq.; bp 115°C
- * * अरुचिकर गंध
- * * * जल में विलेय
- * * * * Dipole moment = 2.3D
- * * * * * B.P. more than $C_6H_6$ (due to more vanderwaals force of attraction)
- * * * * * * Good Solvent

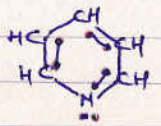
CHEMICAL - 1. Basic Characters - * Py एक strong base है (23)
बनाता है तथा $CH_3I$ से $S_N2$ करके quaternary ammonium salts बनाता है।
अतः mineral acids से reaction करके salt




(Pyridine hydrogen halide) or (Pyridinium halide)
(N-methyl pyridinium iodide)

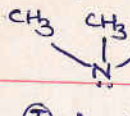
** Basicity of Py > Basicity of Pyrrole
कारण - Pyrrole में N का lp of $e^-$ aromatic sextet में सम्मिलित होने के कारण proton को देने के लिए ~~~~ उपलब्ध नहीं होता जबकि Py में lp of $e^-$ ring से बाहर होने के कारण proton को देने के लिए उपलब्ध होता है।


Pyrrole


Pyridine

*** Basicity of Py < Basicity of ⓣ amine
कारण - ⓣ amines में N $sp^3$ hybrid state में, जबकि Py में N $sp^2$ hybrid state में अतः Py के N में s गुणों की अधिकता (33%) के कारण lp of $e^-$ नाभिक के अधिक नजदीक होगा क्योंकि s orbital की

penetration power अधिक होती है। अतः Py द्वारा proton को $e^-$ pair उतनी (24)
आसानी से नहीं दिया जायेगा जितनी आसानी से ⓣ amine देता है।


ⓣ Amine


Pyridine

2. Reduction -