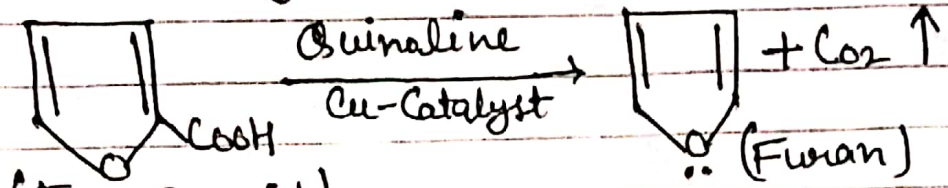
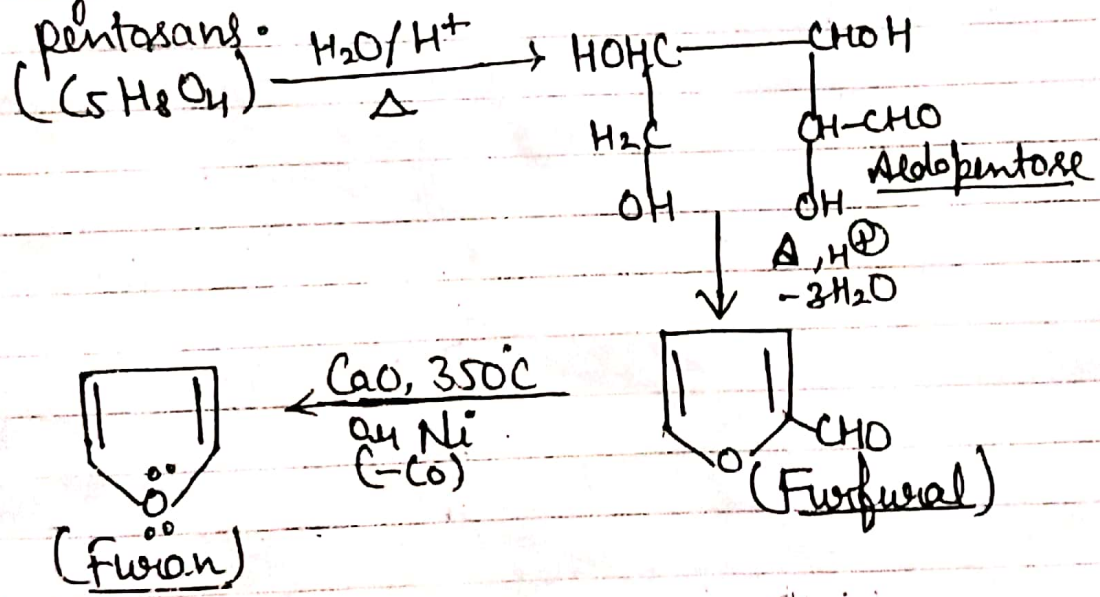
Unit-3 Heterocyclic Compound
Lecture Notes:- 1 to 3.

- **Method of Preparation of Furan:-**

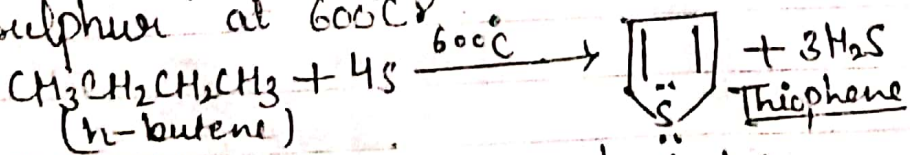
① **By Decarboxylation of Furoic acid:-**



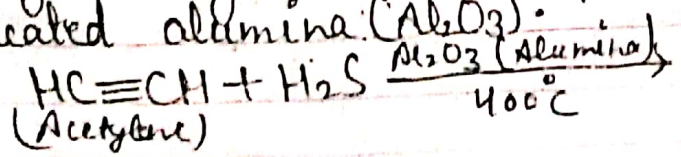
② **Commercial Method:-** It is prepared from agriculture waste (Rice bran, oat hulls) containing pentosans.



- **Method of Preparation of thiophene:-** Commercially thiophene can be prepared by interaction of n-butane which Sulphur at 600°C.



(ii) By passing a mixture of Acetylene and H_2S over heated alumina (Al_2O_3).



- **Chemical Reactions:-** The ring system of pyrole,

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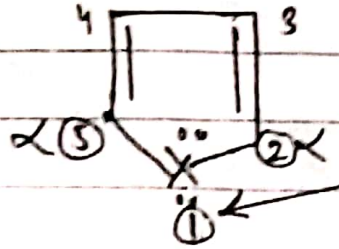
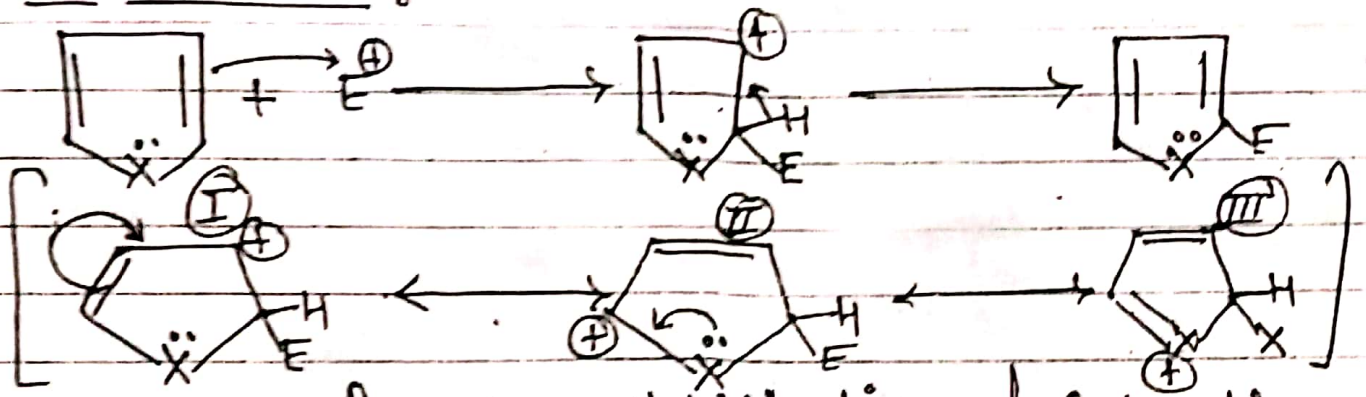
furan & Thiophene are similar to one another & also with benzene. The reactions of diene is observed but aromatic character dominates.

*→ Electrophilic Substitutions reactions:- These reactions occur at IInd and Vth position or α- position.



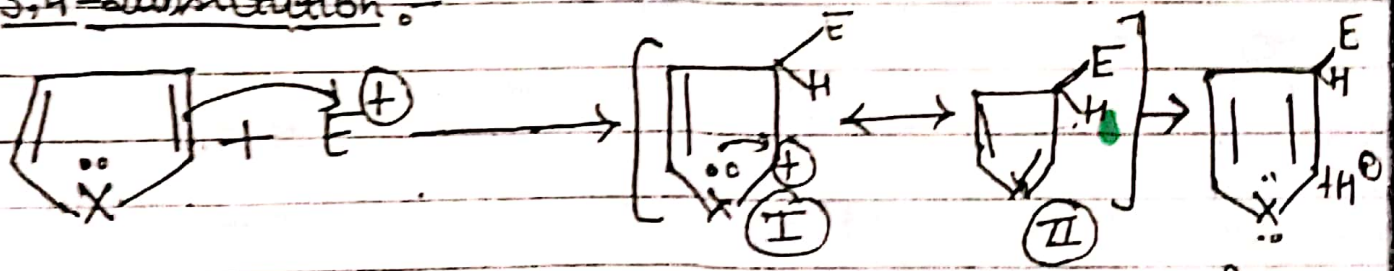
(Carbocation is more stable).

2,5-Substitution:-



Resonance stabilization of Carbocation.

3,4-Substitution:-



The Intermediate Carbocation resulting from the attached of ⊕ Electrophile at IInd and 5th position is more resonance Stabilized as Compared to Substitution at 3 or 4th position.

The order of reactivity:-

Pyrole > Furan > Thiophene > Benzene

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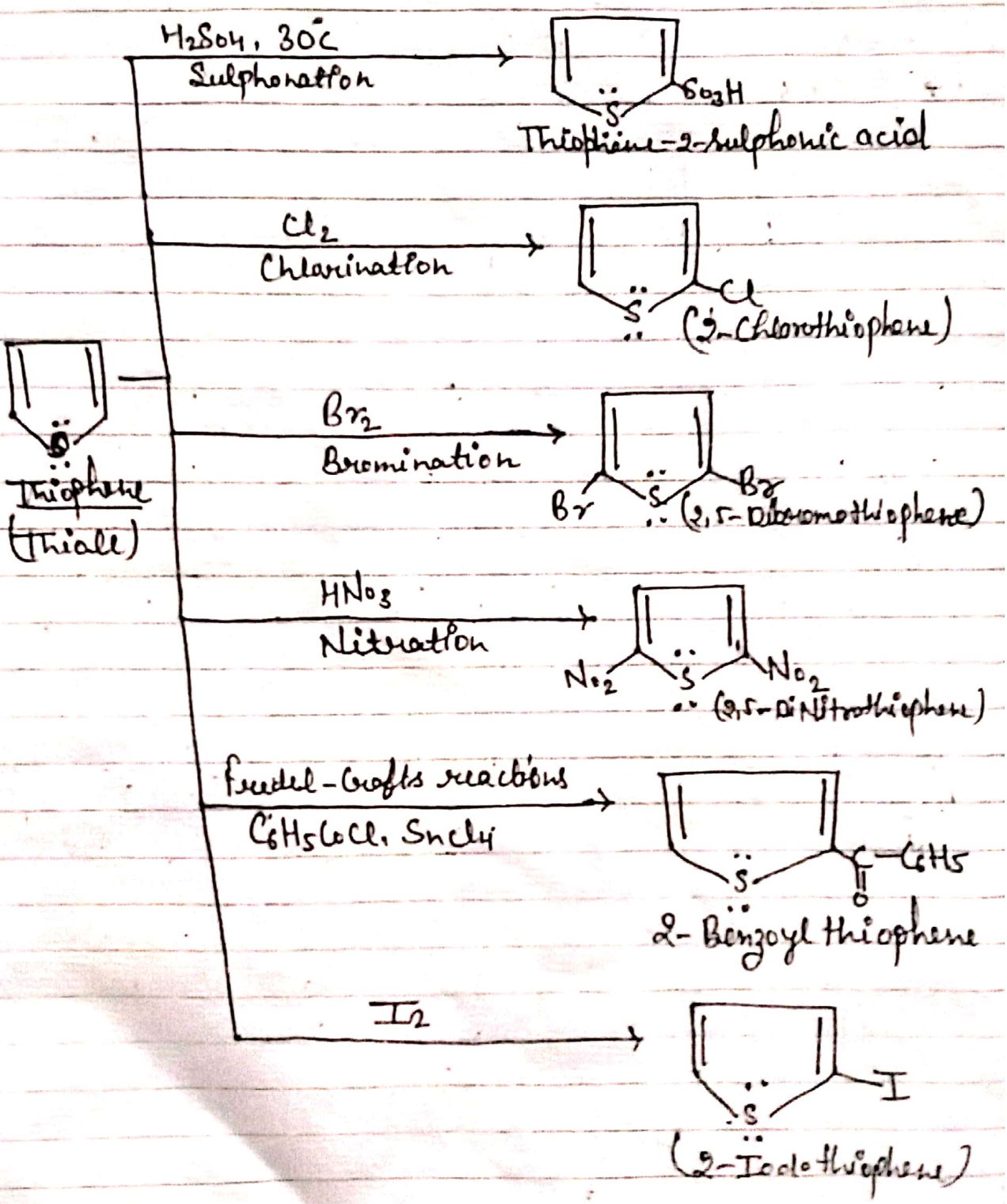
Lecture Note:- 2, 3

(ESR)

- Reactions of Thiophine:-

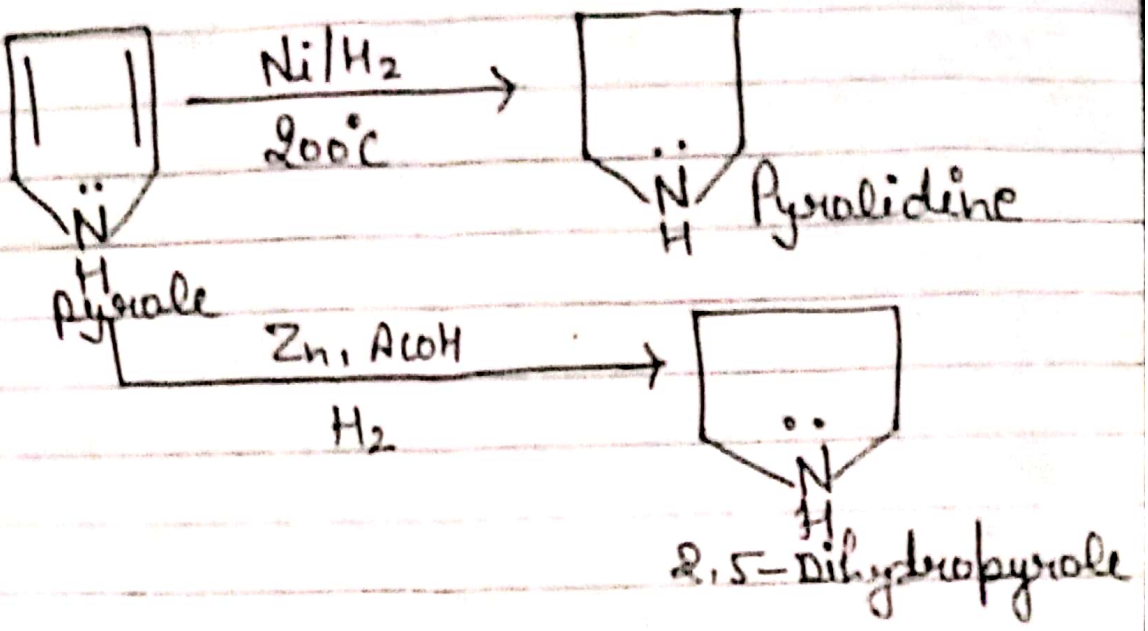


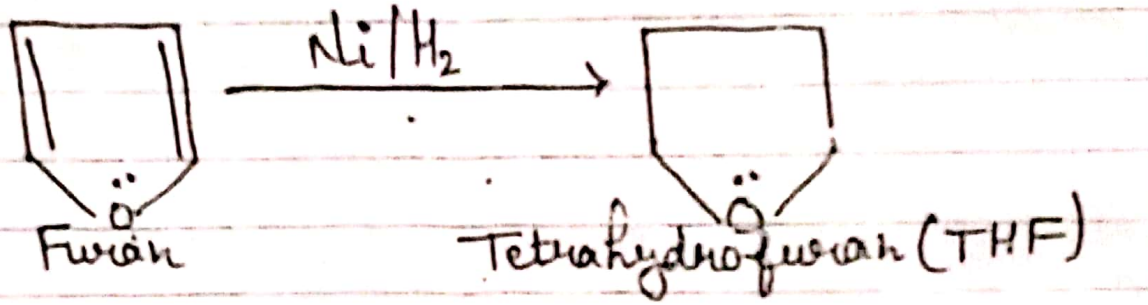
- Addition Reactions:-

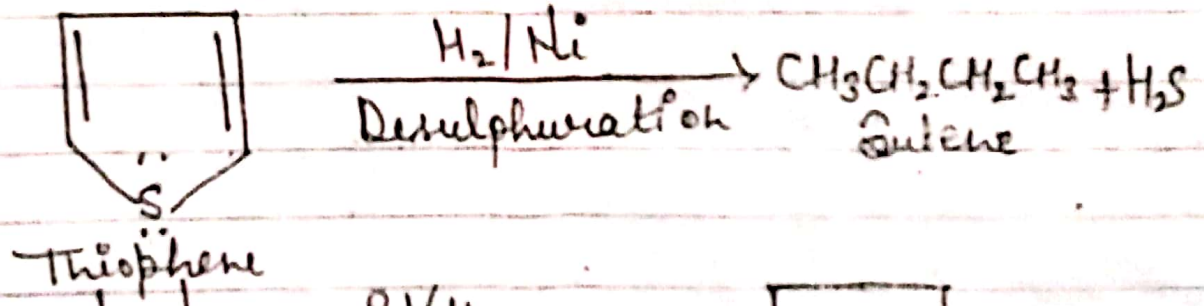
(1). (Hydrogenation) (Addition of Hydrogen):- By selecting proper catalyst these compounds can be

hydrogenated to corresponding saturated Compounds.

Example:-







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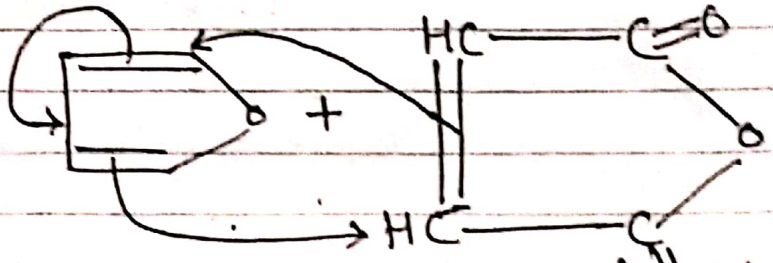
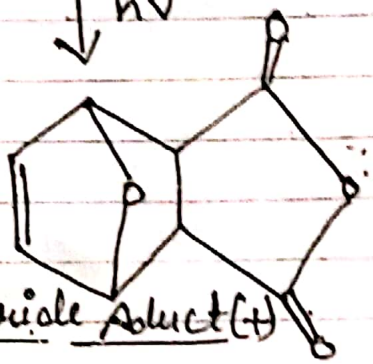
② Diels-Alder Reactions:- Furan is least aromatic as compared to thiophene and Pyrrole. It behaves as Conjugated diene. to give Diels Alder Reaction.

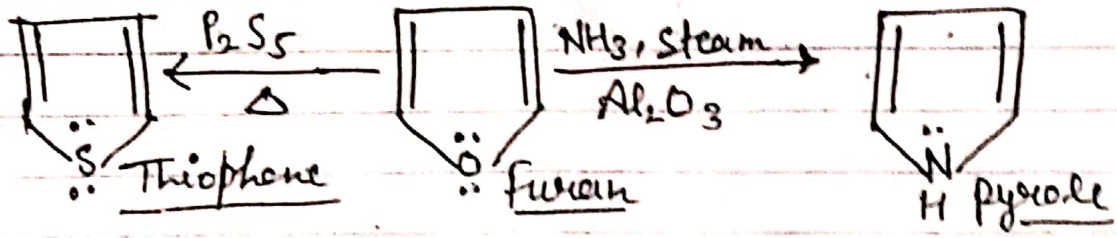
Furan



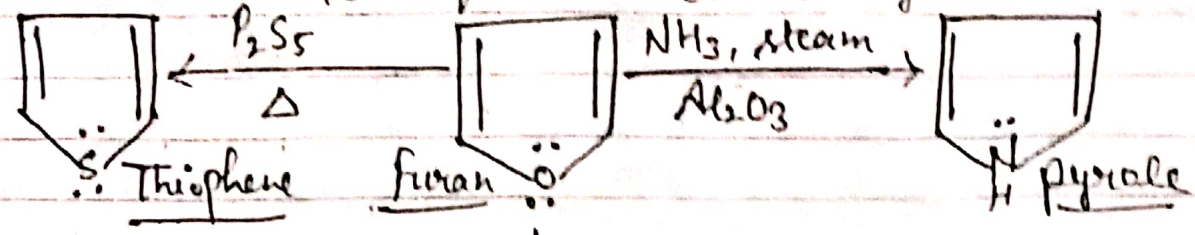
Maleic anhydride

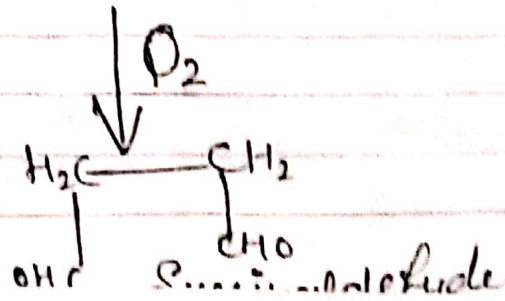


Maleic Anhydride Adduct(+)



• Oxidation:- Furan can undergo oxidation in air to form Succinaldehyde.





Succinaldehyde

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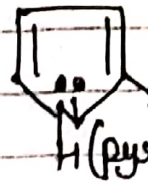
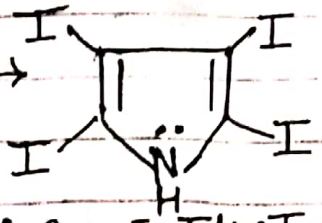
- ESR Reactions of Pyrole :-

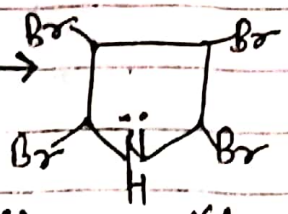
Pyrole

Nitration; 10°C
$(CH_3CO)_2O$, HNO_3 → NO_2 (2-Nitropyrole)

SO_3, Pyridine, 100°C
Sulphonation →  SO_3H
(pyrole-2-sulphonic acid)

(Halogination)

I_2, NaOH
Iodination → 
(2,3,4,5-TetraIodopyrole)

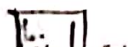
Br_2, CH_3OH
Bromination → 

S_2Cl_2
Chlorination →
(2,3,4,5-Tetrachloropyrole)

Friedal Graft reaction → $COCH_3$
(2-Acetyl pyrole)

CO_2/Δ/Pressure
kolbe Reaction → $COOH$
Pyrole 2-Carboxilic Acid

HCN, HCl
Crattermann koch rxn → CHO
(2-Formyl pyrole)

$CHCl_3$, KOH →  CHO 2-formyl pyrole

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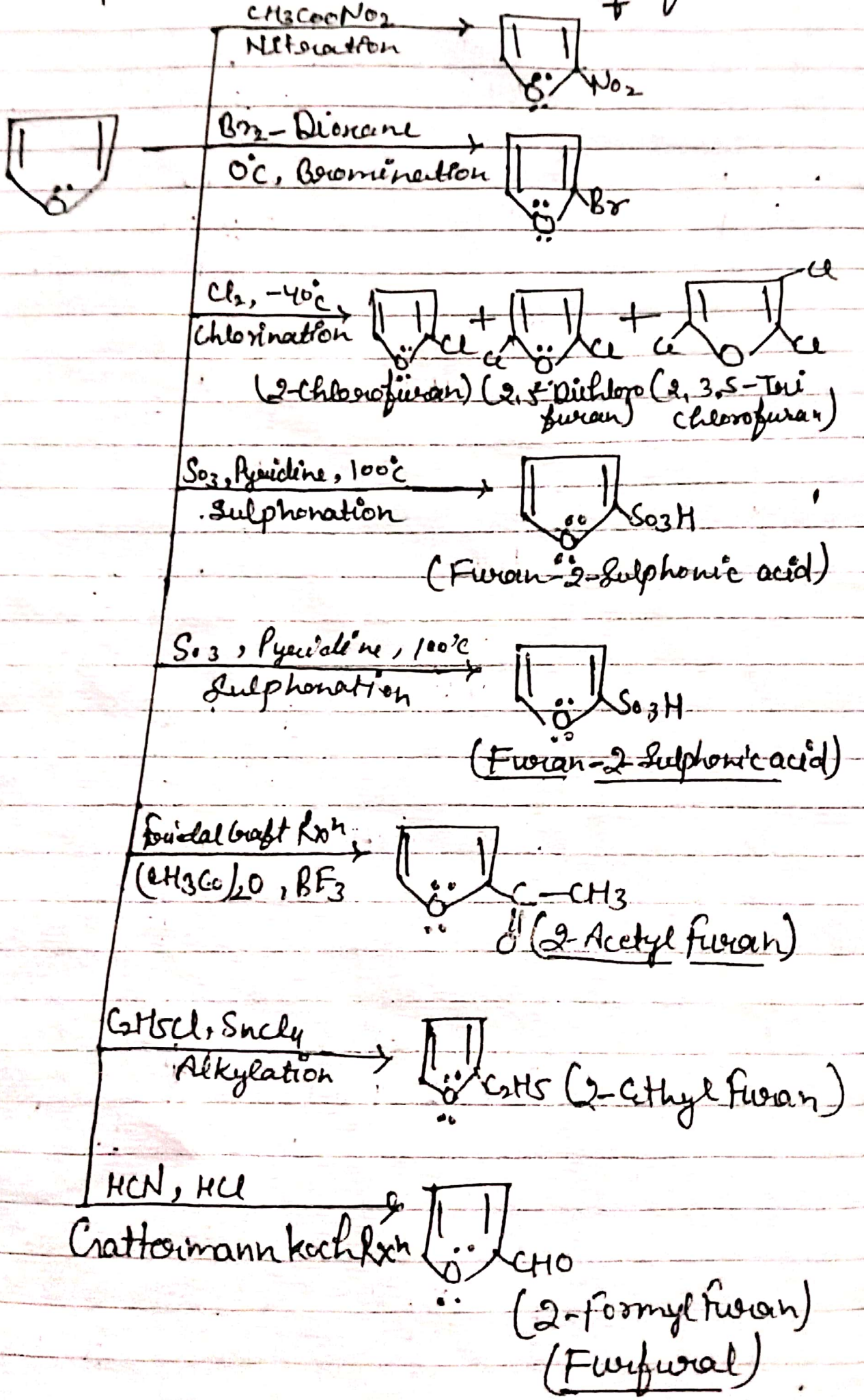
• Electrophilic Substitution reactions of furan:-



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- Aromatic Character of Pyrole:-
- Molecular Structure of Pyrole :- Pyrole is having C_4H_5N and is generally represented by diene structure. The diene structure of pyrole fails to explain the following —

1. It shows aromaticity as it undergo electrophilic substitution reaction like Nitrogen, Sulphonation, Halogenation and Friedal Craft reaction.
2. It is more aromatic than benzene because it undergoes coupling reaction with diazonium salt.
3. It is neutral and does not show basic character as 2° Amines.
4. Heat of combustion shows its resonance energy = 87.8 kjmol^{-1}. which is less than Benzene = 150 kjmol^{-1}. But more than Diene = 12.5 kjmol^{-1}.
5. Pyrole is a flat molecule.
6. All these facts suggest that pyrole is having aromatic character similar to Benzene.

- Orbital structure :- All Carbon atom and one Nitrogen atom in pyrole are sp^2 Hybridization. The Carbon having three sp^2 Hybrid orbital each containing an unpaired electron and an unhybridized orbital with one electron. These unhybrid orbital

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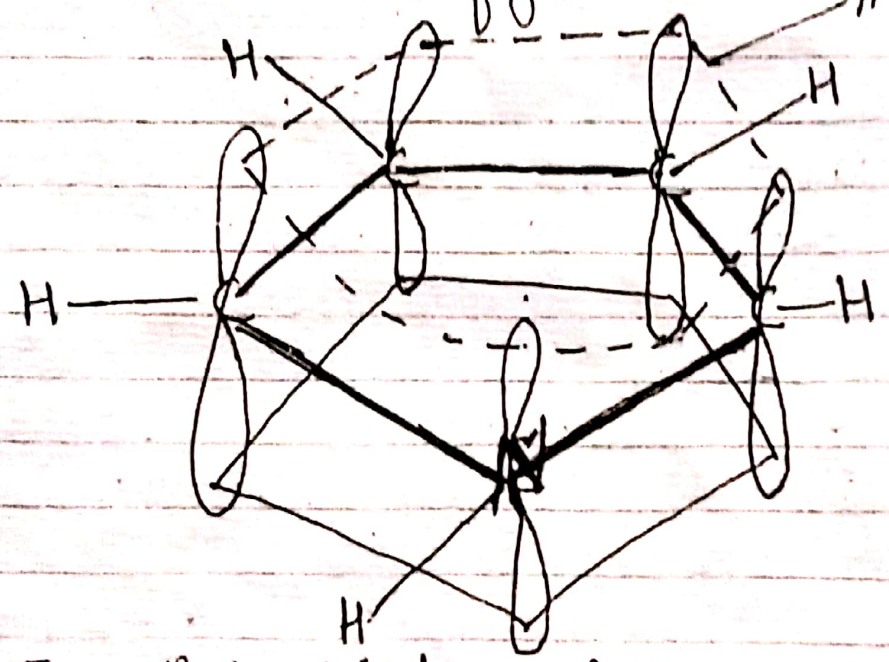
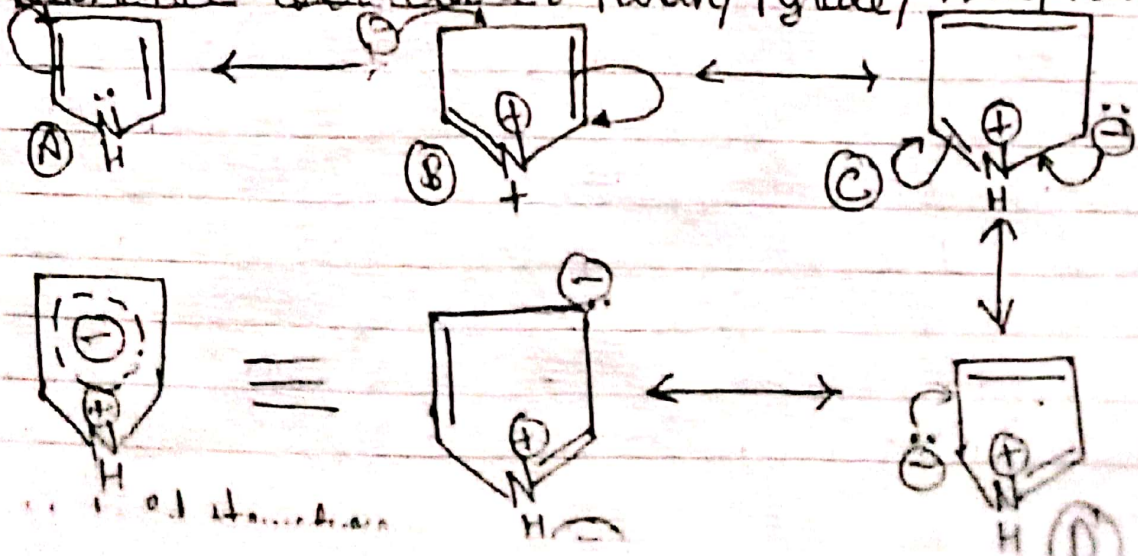
are perpendicular to the plane of hybrid orbital. Nitrogen also has three sp^2 orbital and unhybridized p-orbital perpendicular to the 2 hybrid orbitals. These p-orbital overlap side by side to form a cyclic delocalised π molecular orbital. These Delocalised orbital form two π electron clouds above and below the plane of the ring as shown in the figure.



The Delocalised π-electron cloud is responsible for aromatic character of pyrrole.

- Resonance Structure :- Furan/Pyrrole/Thiophene



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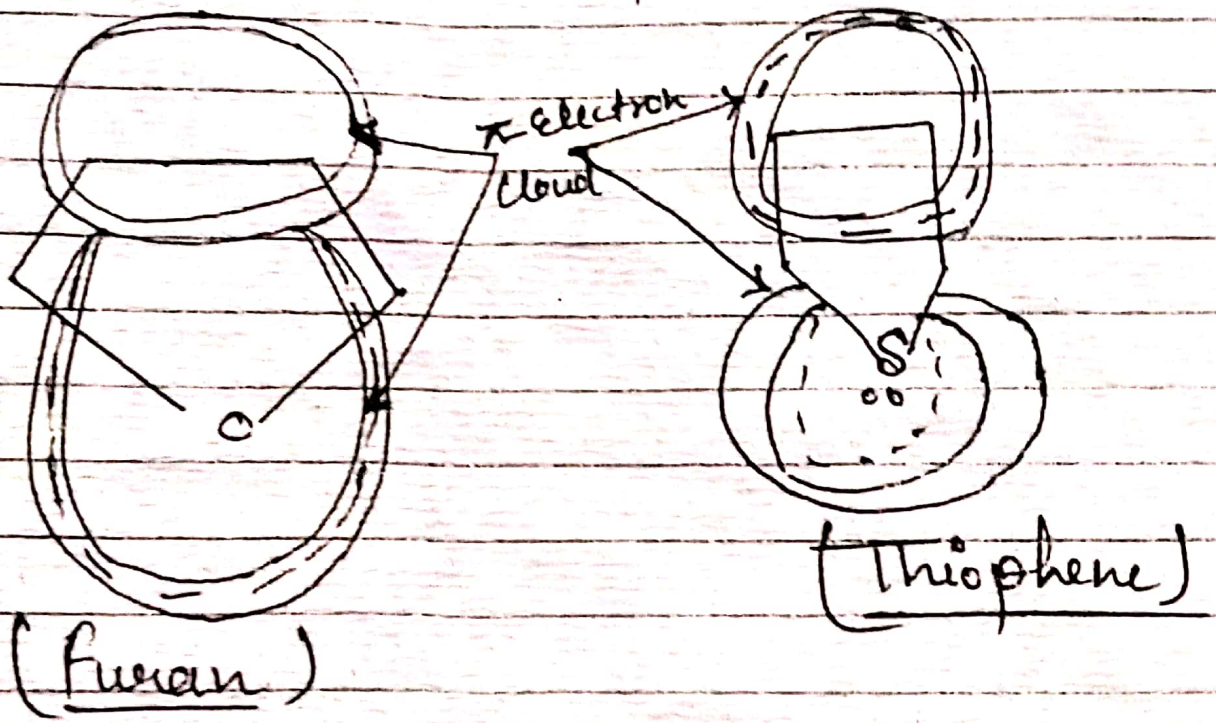
Structure of Furan and Thiophene:- Similar to pyrole furan and Thiophene also have structure with flat pentagonal rings having sp^2 hybrid Carbon & Hetero atoms with cyclic π electron cloud above and below the plane of the ring



(Furan) (Thiophene)

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