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STUDY MATERIAL

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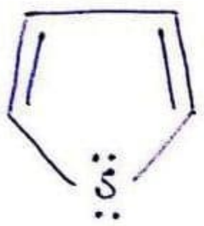
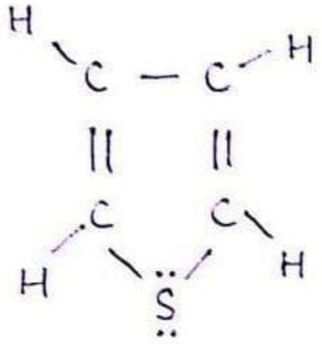
THIOPHENE

- It is five membered heterocyclic compound containing sulphur (S) as a heteroatom.



OR



- Discovered by Victor meyer in 1882.

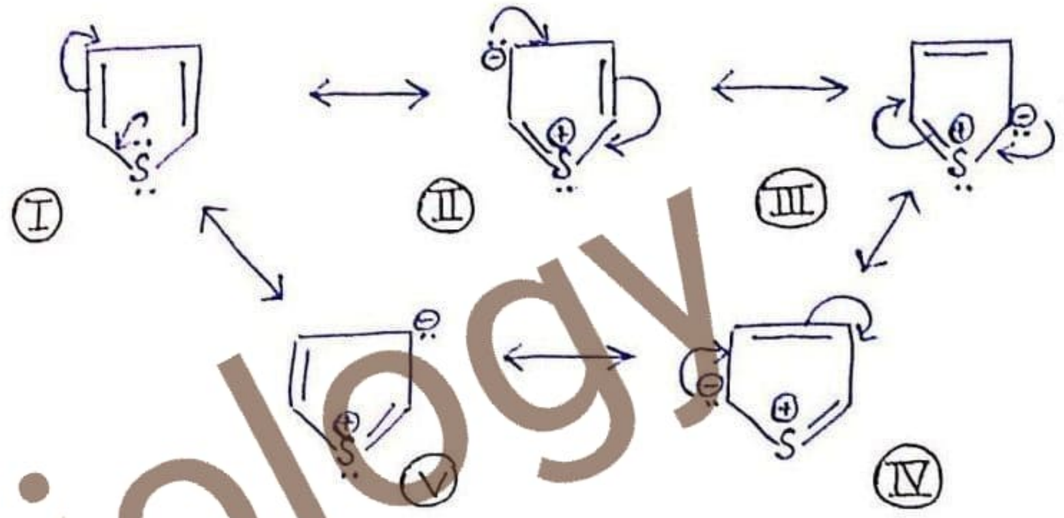
Chemical formula → C_4H_4H

Molecular wt. → 84

Hybridization → (4 Carbon + 1 Sulphur)
Sp^2

- Thiophene is an aromatic in nature.

* Resonance

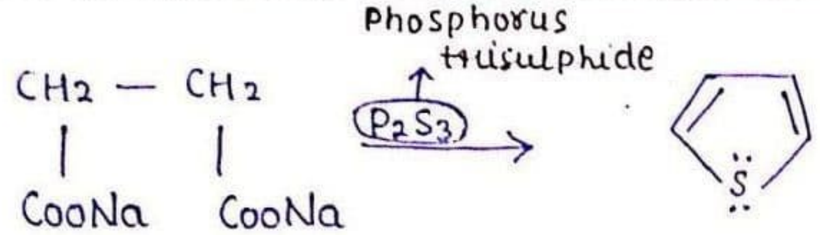


* Physical Property :-

- It is a colourless liquid.
- It is insoluble in water, but miscible with most organic solvent.
- It have an odour very similar that of benzene.
- Boiling Point is 84°C.

- **Synthesis (Method of Preparation)**

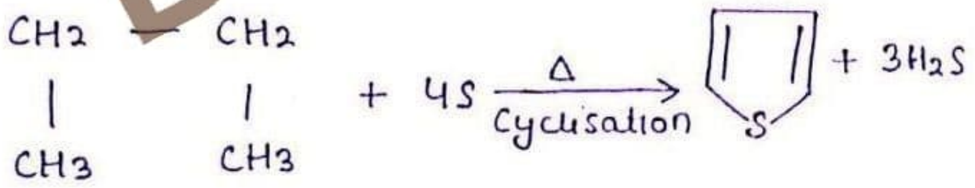
① **From Sodium Succinate (in laboratory) :-**



[Sodium Succinate] [Thiophene]

In this reaction, thiophene is synthesized by heating sodium succinate with phosphorus thiosulphide.

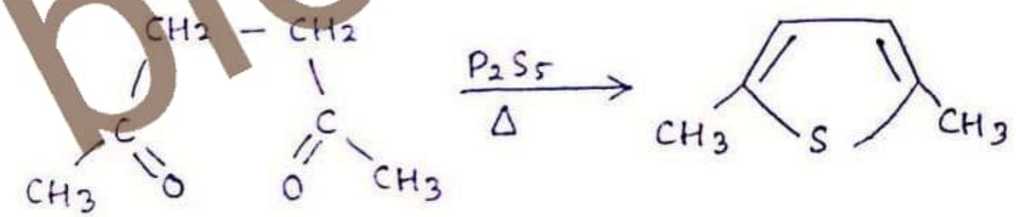
② **From n-butane**



[n-butane] [Thiophene]

In this reaction, n-butane is heated with sulphur at 400°c and undergoes cyclization and formed thiophene.

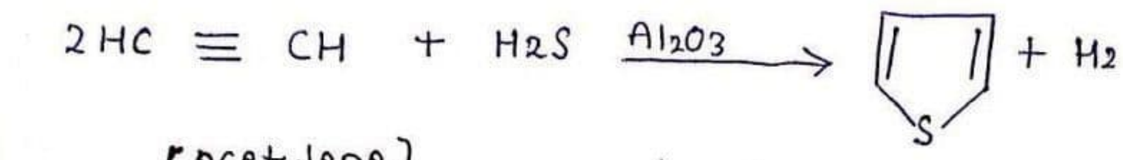
③ **Paal Knorr Synthesis :-**



[Hexa-2,5-dione] [2,5-dimethyl thiophene]

In this reaction, Acetonylacetone heated with phosphorus pentasulphide and formed derivatives of pyrrole [2,5-dimethyl thiophene].

(iv) From acetylene :-



[Acetylene] [Thiophene]

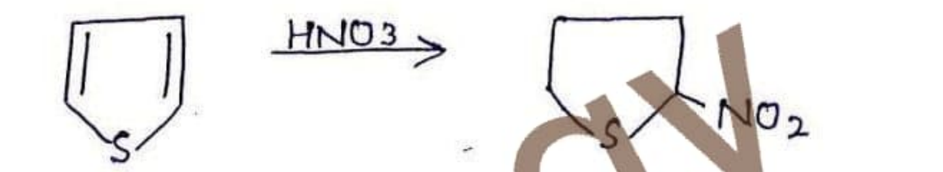
- In this reaction, mixture of acetylene and hydrogen sulphide is passed through a tube containing alumina at 673 K.

* Chemical Reaction :- It also shows aromatic character but it is less ~~than~~ reactive than pyrrole and furan.

(1) Electrophilic Substitution reaction :-

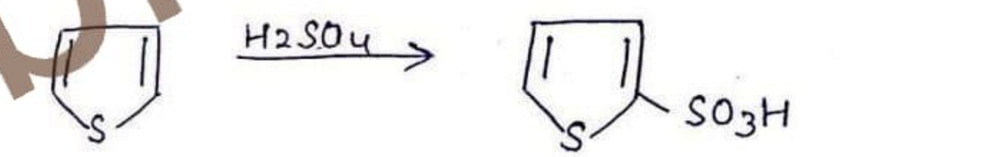
Thiophene can easily give this reactions (occurs at α or 2- position)

- Nitration :-



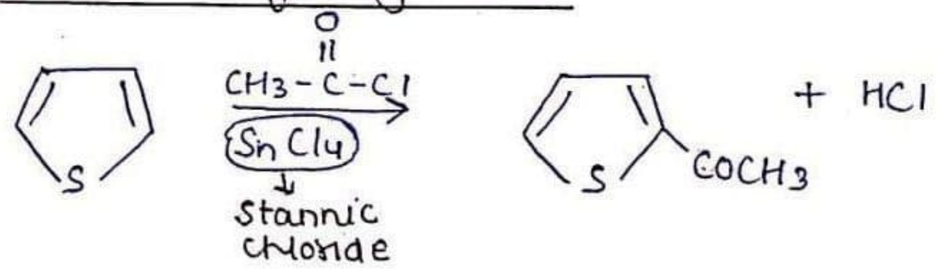
[Thiophene] [2-Nitrothiophene]

- Sulphonation :-



[Thiophene] [2- thiophenesulphonic acid]

- Friedel craft acylation :-



[Thiophene] [2-Acetylthiophene]

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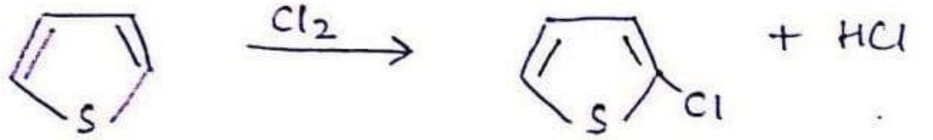
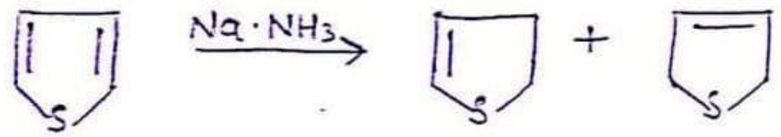
• Chlorination :-



[Thiophene] [2-Chlorothiophene]

② Reduction :-



[Thiophene] [2-Thiolen] [3-Thiolen]

In this reaction, Thiophene reduced with sodium in the presence of liq. Ammonia give a mixture of 2-thiolen and 3-thiolen.

* Medicinal Use of thiophene :-

• Thiophene and its deruvative has many Pharmaceutical importance. (used as mediam

• Used as anticancen agent (chemotherapeutic agents) and diuretic, antiasthmetic agent etc.

• They have sedative, hypnotic, anti convulsant and antixiolytic effect.

• Some drugs →

(i) Raltitrexed → anticancer activity

(ii) Cephalothin, Cefoxitin → antimicrobial agent.

(iii) Tiaminidine → antihypertensive

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• thiophene derivatives are also useful as pesticides.

* <u>Relative aromaticity and reactivity of pyrrole, furan and thiophene</u>

The compound must be aromatic when it follow :-

ⓐ Cyclic

ⓑ Must be in conjugation

ⓒ Planar

ⓓ follow Huckle's rule → $(4n+2)\pi$ electron

• Pyrrole, furan and thiophene, all are aromatic in nature.

* <u>Relative Aromaticity</u> :-

• Pyrrole contain 'N', furan contain 'O', thiophene contain 'S'.

• Electronegativity → O > N > S

• E.N. ↑ → Delocalisation ↓ → Aromatic character ↓

• Acc. to this,

Thiophene > Pyrrole > furan.

• But all are low (less) resonance energy than benzene. So less aromatic than benzene.

• <u>Relative Aromaticity</u> :-

Benzene > Thiophene > Pyrrole > furan

* Relative reactivity :-

are more reactive than benzene.

- More electronegative → more reactive
- acc. to this :-

  Furan > Pyrrole > thiophene

- But in case of furan, oxygen accumodate a positive charge are less reactive than nitrogen. So furan is less reactive than pyrrole. (N is trivalent).
- So order of reactivity

  Pyrrole > Furan > thiophene

- Heterocyclic compounds's resonance energy are much smaller hence they

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