

Properties -

Physical Properties -

Colourless liquid

B.P  $84^{\circ}\text{C}$

Has odor similar to benzene.

Is not soluble in  $\text{H}_2\text{O}$  but soluble in organic solvent.

Chemical properties:-

Thiophene does not show basic nature.

More stable to acid than pyrrole and furan.

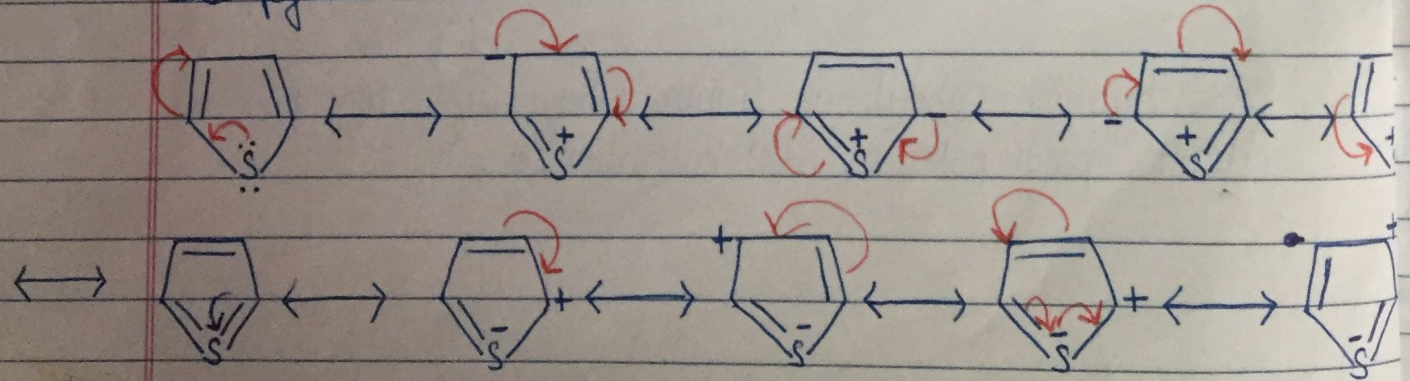
\* Thiophene is more aromatic compared to furan and pyrrole.

1) Sulfur is less electro-ve than N and O.

2) Due to less electronegativity  $e^-$  on sulfur easily take part in delocalization. In this process 3d orbitals are also utilized in S the 3d orbitals are available which are not present in nitrogen and oxygen.]

3) The number of contributing structures in thiophene are much more compared to furan and pyrrole.

4. Due to this, thiophene is more aromatic compared to furan and pyrrole.



utilization of 3d orbital in delocalization

Aromaticity of thiophene may also be explained from its high resonance energy.

Resonance energy

36.0 Kcal mol<sup>-1</sup>

36.0 " "

29.0 " "

16.0 " "

Comp.

Thiophene

Benzene

Pyrrrole

Furan

Order of aromaticity of 5-membered comps.

Thiophene > Pyrrrole > Oxygen.

\* Furan is least aromatic, explain

O is more electro-ve than N & S.

So in furan, the high electro-ivity of O ↓ the delocalization of  $\pi e^-$  (lone pair of in pure p orbital)

↓ resonance stabilization (energy)

↓ the aromatic nature

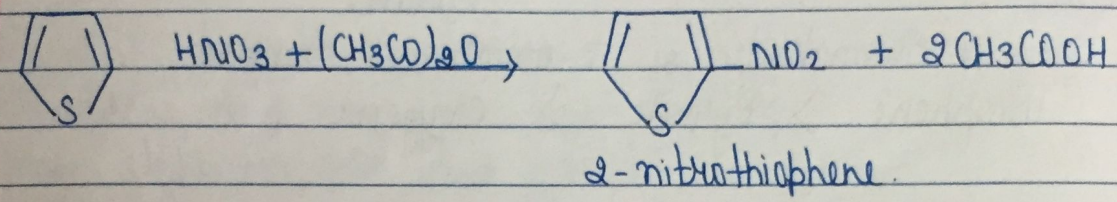
So, Furan is least aromatic than, pyrrrole & thiophene.

Electrophilic Substitution  $R^n$  :-

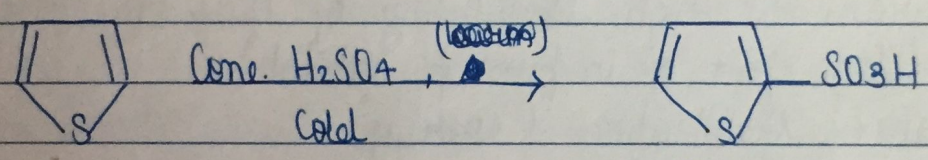
Like pyrazole & furan, Thiophene also undergoes SE  $R^n$  at position C-2.

If C $_{\alpha}$  position ( $\alpha$  &  $\alpha'$ ) are occupied then substitution take place at C-3 position.

a) Nitration :-



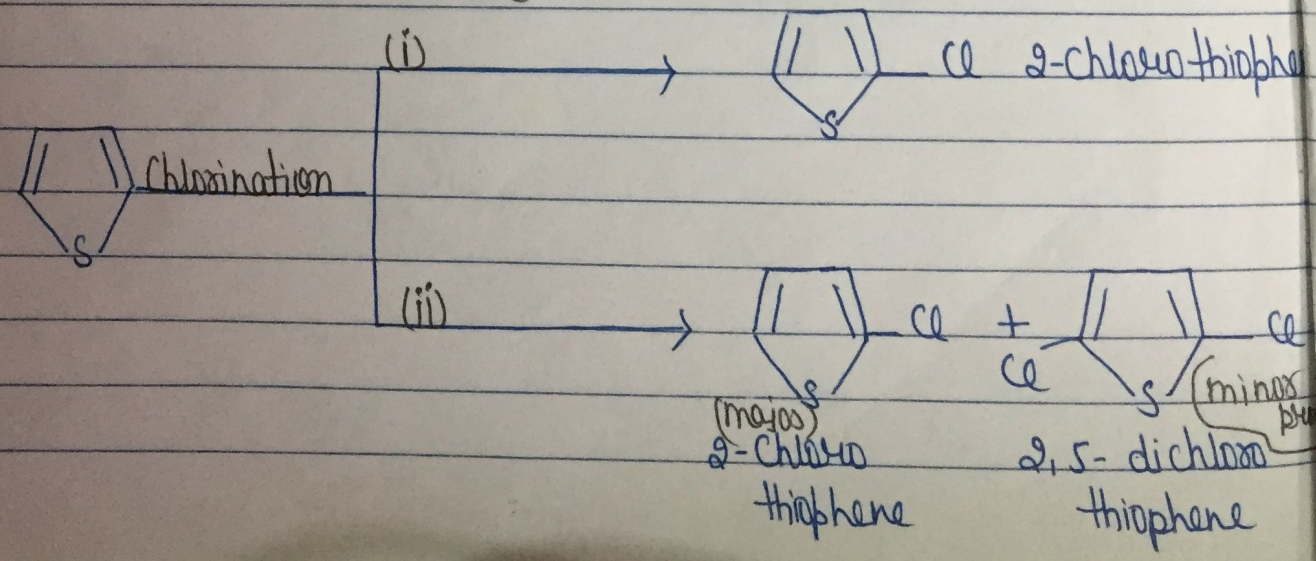
b) Sulfonation :-



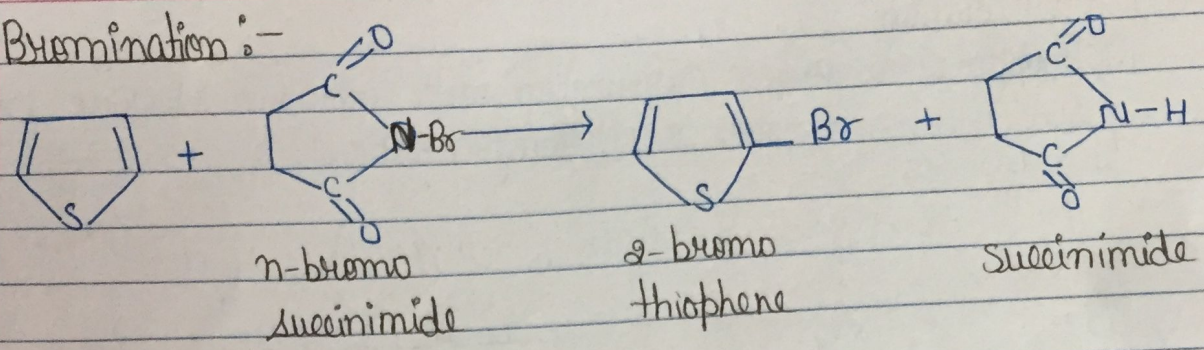
(c) Halogenation :-

(thionyl chloride) [mild conditions are used]

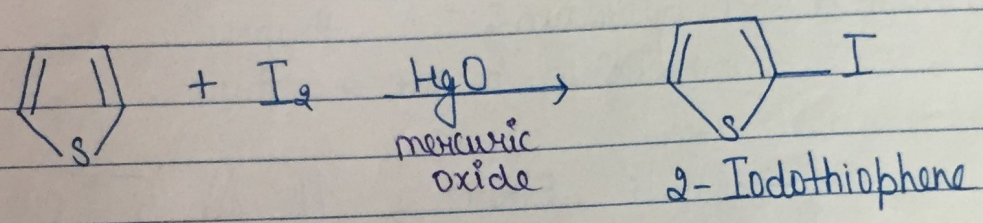
Chlorination - (i) with  $SO_2Cl_2$ , (ii)  $Cl_2$  -30°C (low temp) -30°C



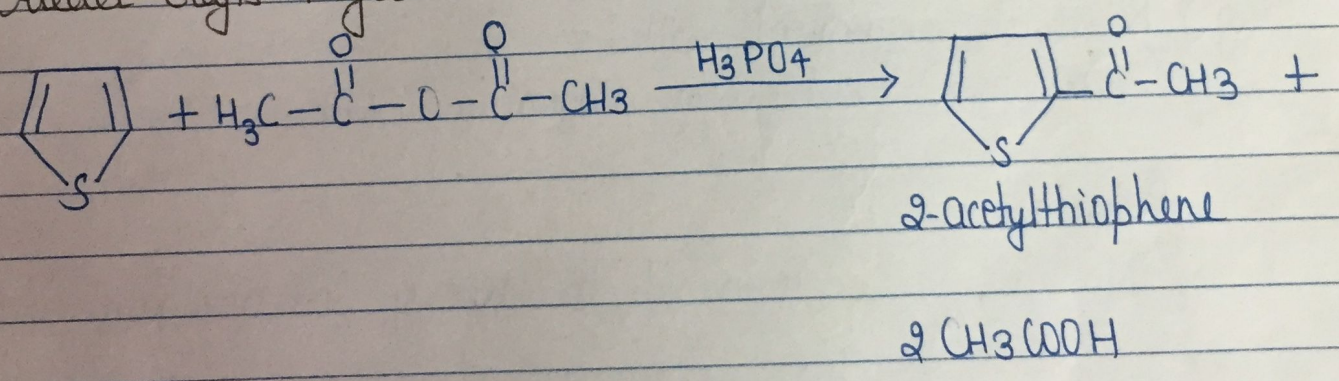
Bromination :-



Iodination :-



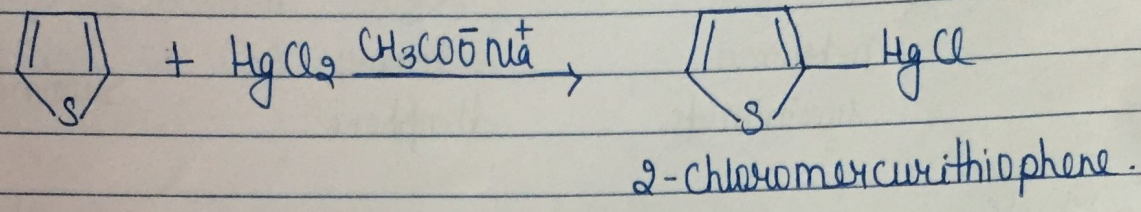
(d) Friedel-Crafts Acylation :-



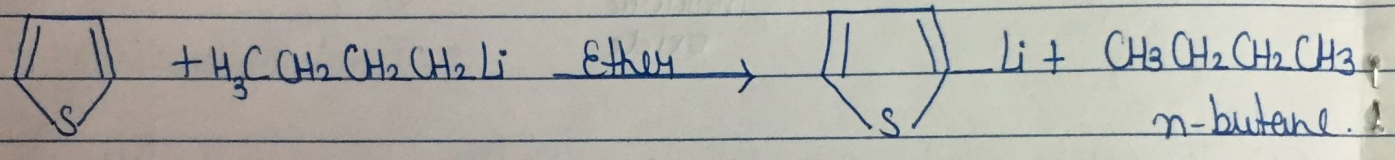
Acylation may be carried out either with acetic anhydride in the presence of phosphoric acid or with acetyl chloride in the presence of SnCl<sub>4</sub> also to produce 2-acetylthiophene.

(e) Mercuriation:-

Thiophene undergoes mercuriation with mercuric chloride in aq. sod. acetate to give 2-chloromercurithiophene.



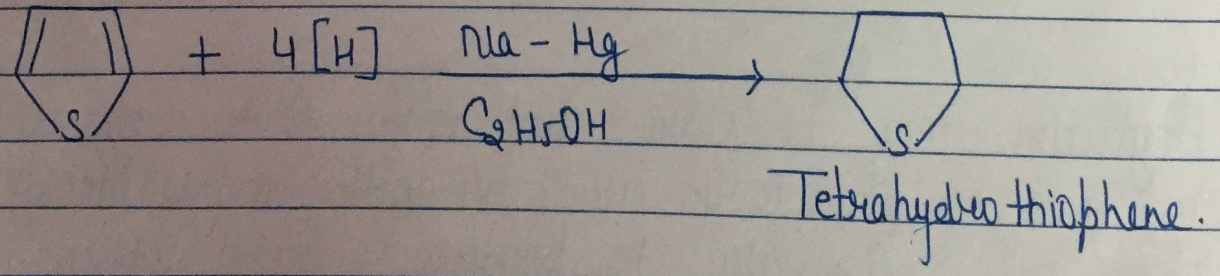
(f) Reaction with n-butyllithium:- thiophene  
It reacts with n-butyllithium to give 2-lithium.



(g) R<sup>n</sup> with diazonium salt:-  
Does not react with diazonium salt,

2. Reduction:-

Thiophene is hydrogenated in the presence of sod. amalgam and C<sub>2</sub>H<sub>5</sub>OH

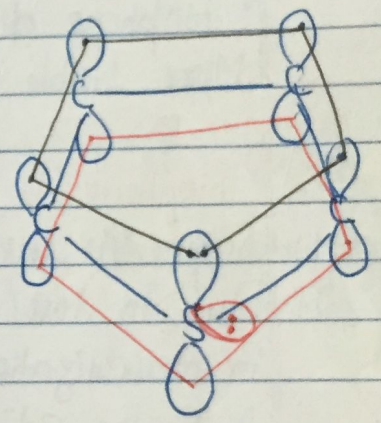
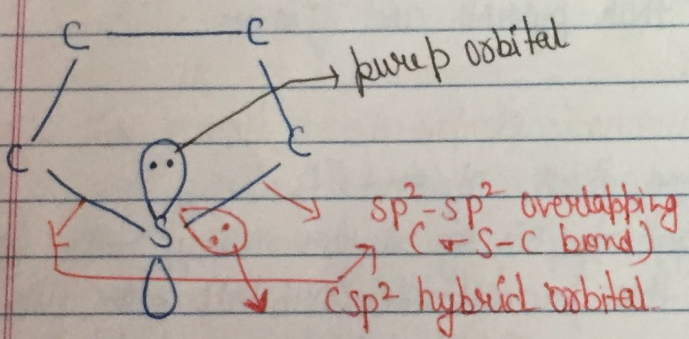


## Thiophene

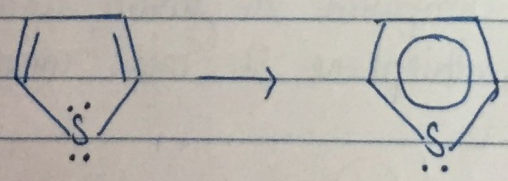
### Structure and Aromaticity :-

In thiophene

- (i) Carbon and Sulfur atoms  $\rightarrow$   $sp^2$  hybridized.
- (ii)  $sp^2$  hybrid orbitals of S are used for -  
To form a S-C bond ( $sp^2-sp^2$  overlap)
- (iii) 3<sup>rd</sup>  $sp^2$  orbital carry a lone pair of  $e^-$ .
- Pure p orbital (not take part in hybridization) carry 2  $e^-$ .



Bonding representation in thiophene.



Thiophene.

$sp^2$  hybrid orbital of sulfur carry ~~not~~ lone pair of  $e^-$  don't participate in delocalization.