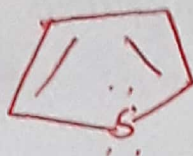


Thiophene C_4H_4S

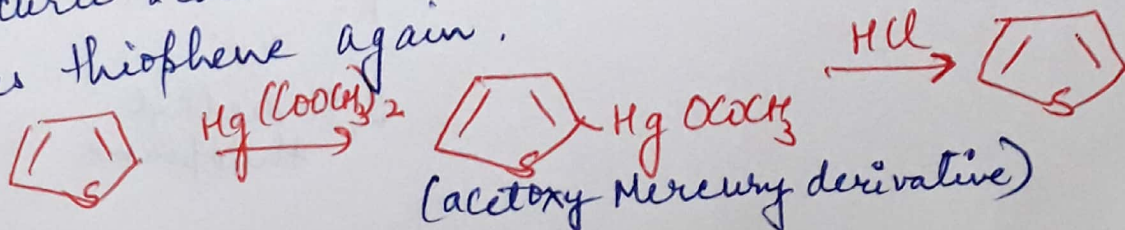


→ Firstly, Victor Meyer (1882) observed trace of thiophene in crude benzene, obtained from fractional distillation of coal tar (0.5 to 0.6%).
→ also occur in shale oil.

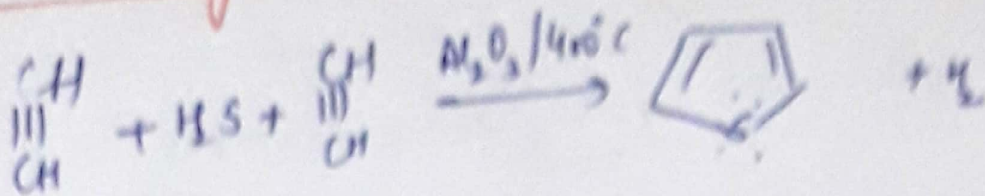
Preparation:

→ Due to closeness of B.P. of Benzene ($80^\circ C$) & thiophene ($84^\circ C$), it is not possible to isolate it from crude benzene by fractional distillation.
→ Thiophene can far more easily be sulfonated and mercurated than benzene.
Therefore, crude benzene containing thiophene is repeatedly shaken with ^{cold} conc. H_2SO_4 which produces water soluble thiophene sulfonic acid.
Thiophene is then recovered from the solution by the action of super heated steam. Here, Benzene do not sulfonate.

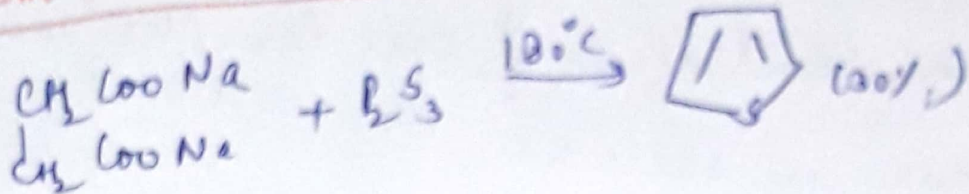
→ Other method of separation is to boil the mix. with aq. mercuric acetate. Here, only thiophene is mercurated to produce insoluble thiophene-2-mercuric acetate which on heating with conc. HCl gives thiophene again.



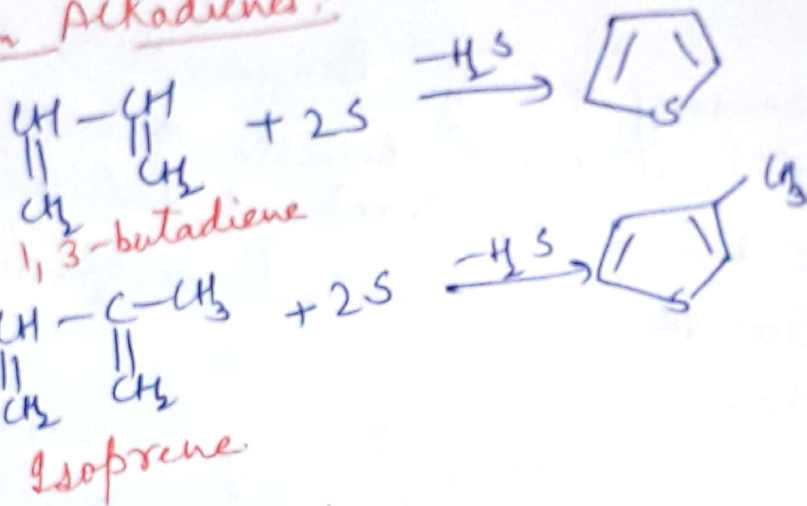
From Acetylene :-



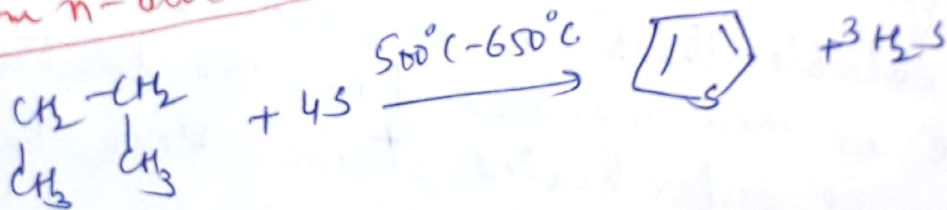
From Sodium Succinate



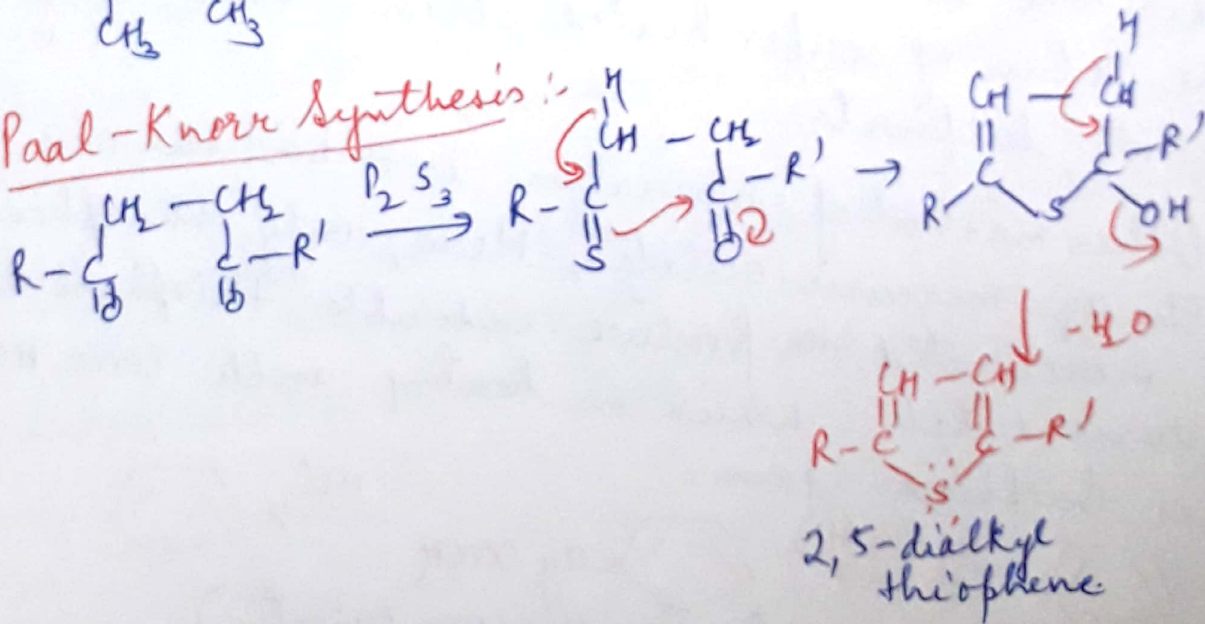
From Alkadienes :-



From n-butane :-



Paal-Knorr Synthesis :-



Structure :-

(3)

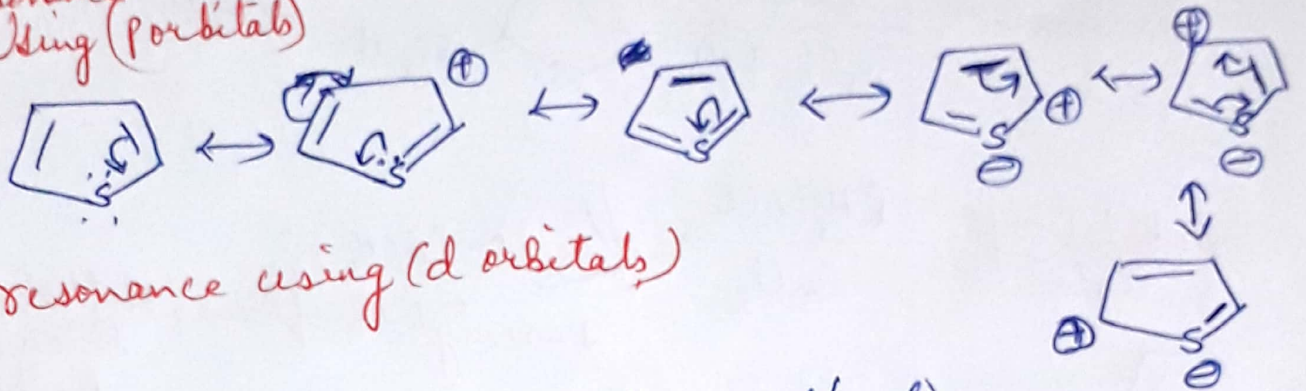
It is similar to pyrrole & furan.

→ more resonating structure than pyrrole & furan

δ^- negativity of S is less than N & O and uses their 3d vacant orbitals.



Resonance Using (p orbitals)



Resonance using (d orbitals)

$$R.E. = 117 - 130 \text{ kJ/mol } (29 \text{ kcal/mol})$$

→ Orbital diagram similar to pyrrole.

Physical Properties :-

→ Colourless liquid (B.P. 84°C).

→ benzene like odour.

→ insoluble in H_2O but miscible with most organic solvents.

→ Chemically resembles with benzene, but less stable than benzene.

→ More stable than pyrrole & furan.

Electrophilic Substitution Rxs:-

(9)

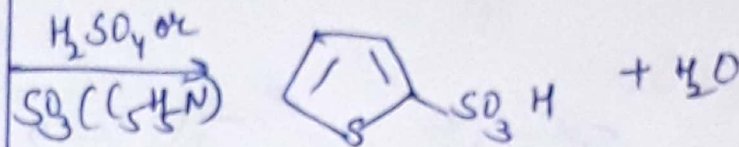
→ on 2nd & 5th position, similar to pyrrole & furan.

Due to reactivity of thiophene like phenol, electrophilic sub rx took place in mild conditions.

Nitration



Sulfonation

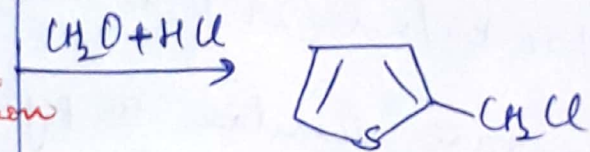


Friedel Craft acylation



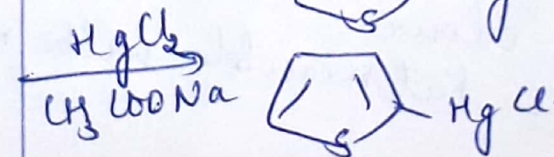
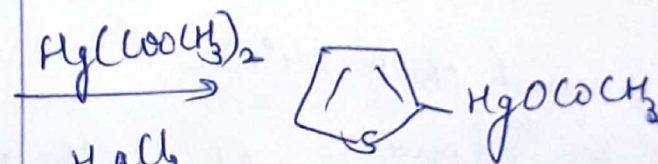
2-acetyl thiophene / Methyl thiocarbonyl ketone

Chloromethylation



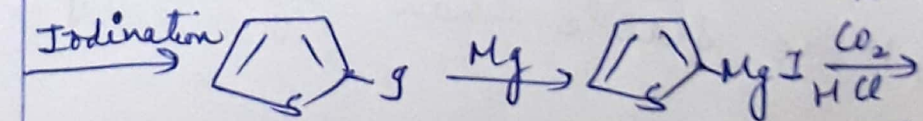
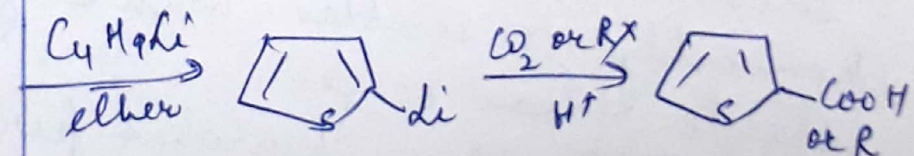
2-Thienyl chloride or 2-chloromethyl thiophene

Mercuriation

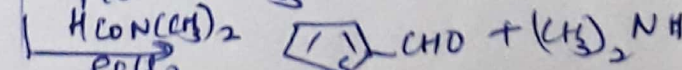
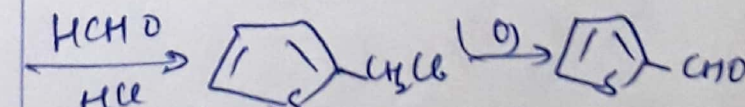


Thiophene-2-mercury chloride

Rx with alkyl hi →

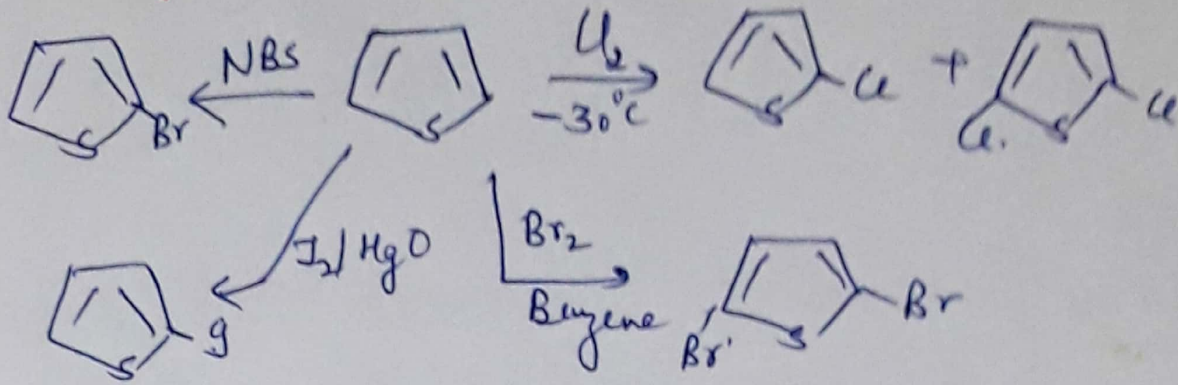


Formylation



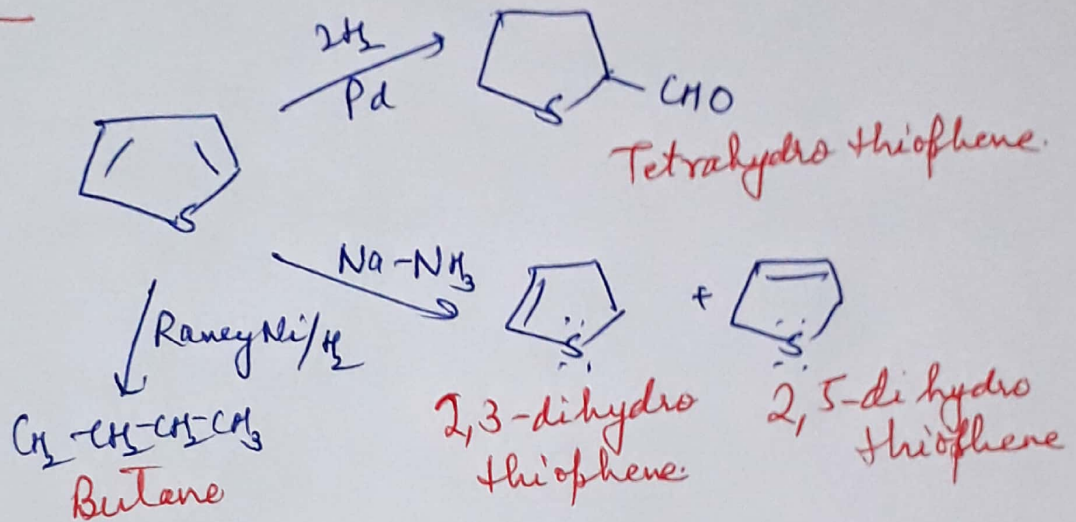
Halogenation !:

(5)

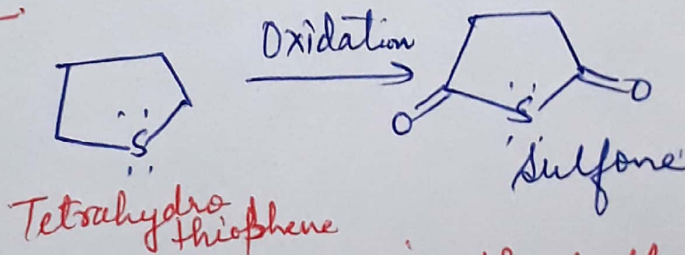


Other Rxs:-

Reduction



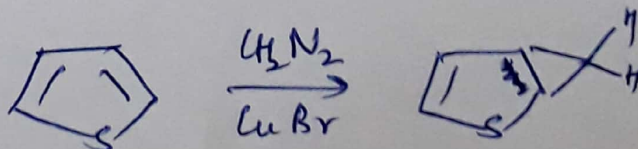
Oxidation

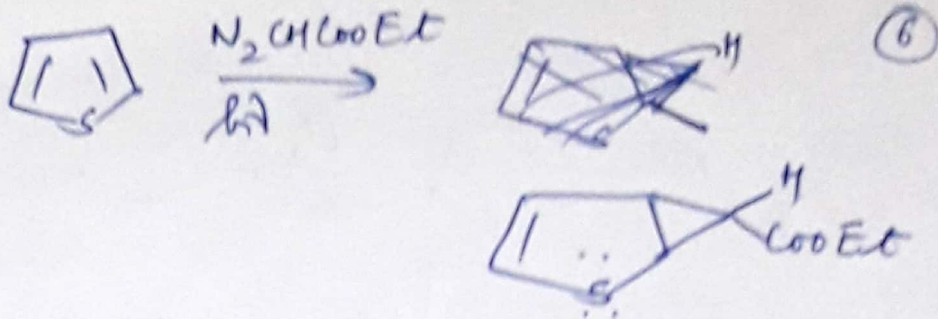


* Thiophene do not oxidize in the sulfoxide or sulfone but its tetrahydro derivative easily oxidize.

* Thiophene \rightarrow NO Rx with diel Alder Rx

With CH_2N_2 !:





Test of thiophene :- on rx with iodoine & H_2SO_4 , thiophene gives blue colour.

Use :- in industrial use (resins, medicines, rubber, dyes etc.)