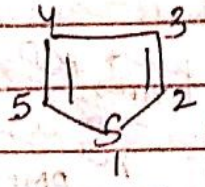
DATE

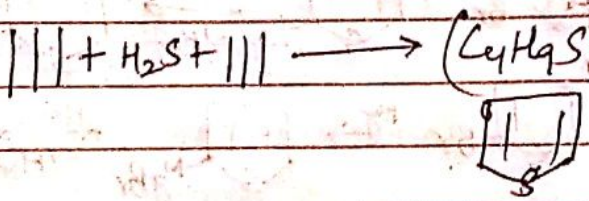
Thiophene

Thiophene occurs in Coal-tar and Shale oils. Its boiling point is 84°C. It is miscible water but soluble in most organic Solvents



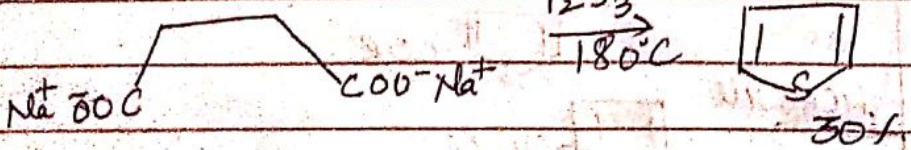
Preparation

1) Prepared by passing a mixture of acetylene & hydrogen Sulphide through a tube Containing alumina at 400°C

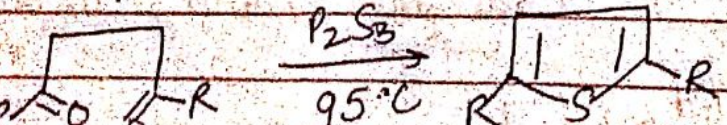


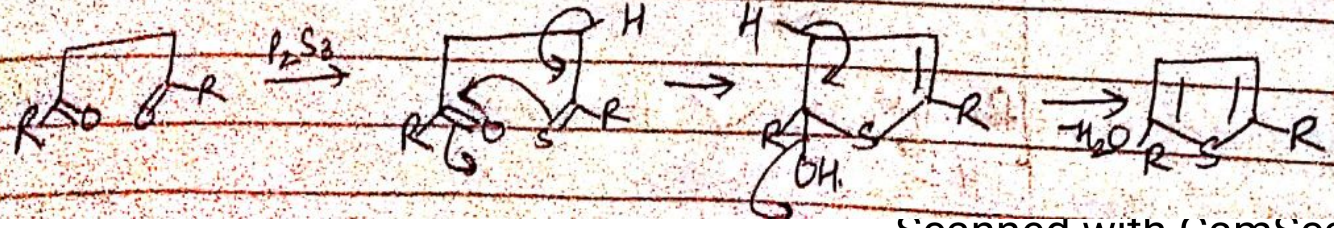
This method is used Commercially.

② Prepared by heating Sodium Succinate with P_2S_3

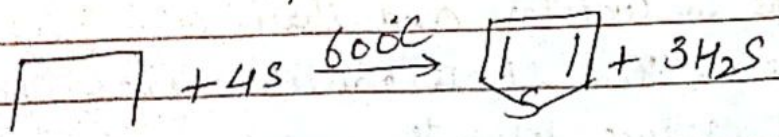


③ Paal knor Synthesis

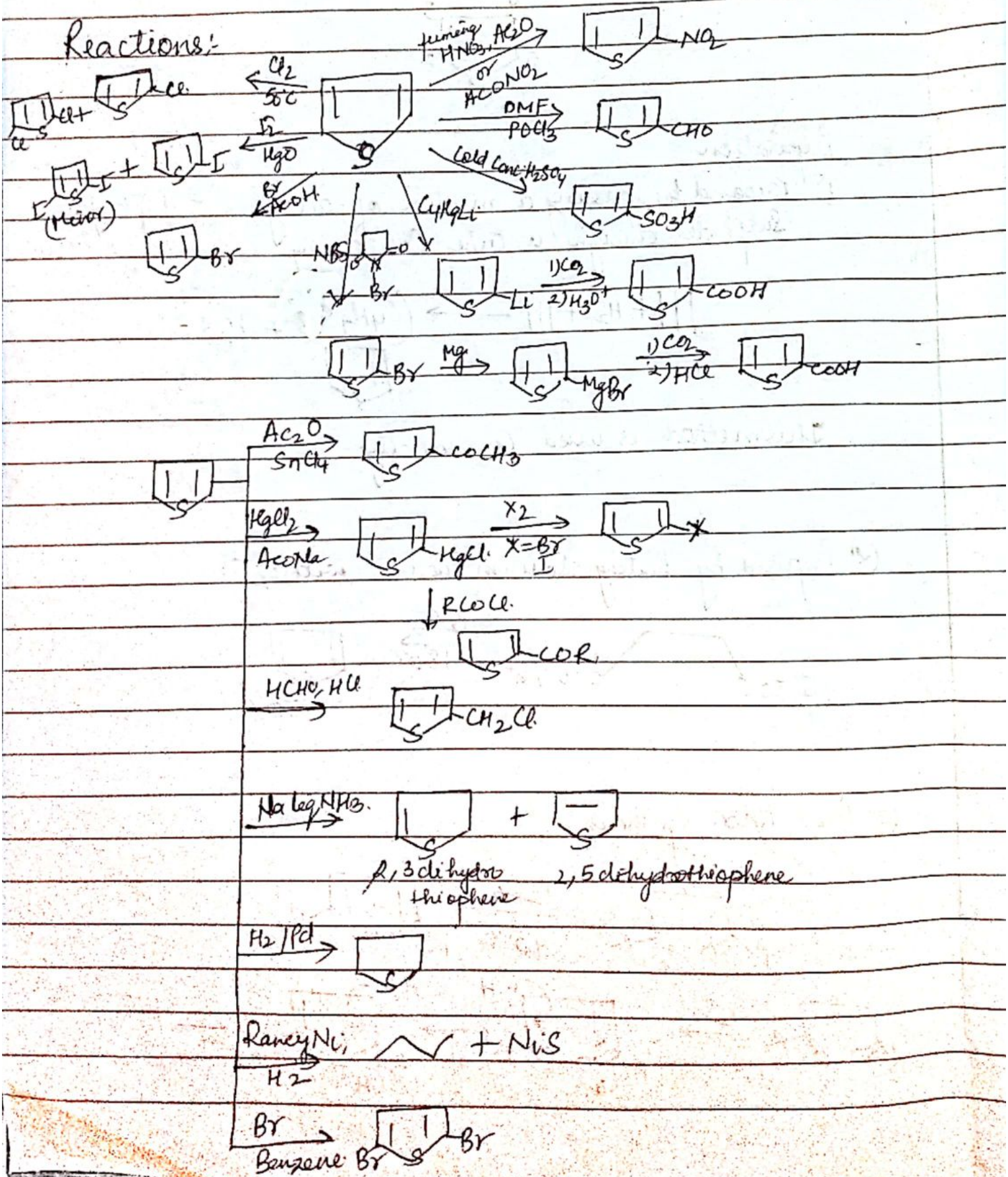




4. It is also manufactured by reaction between n-butane & Sulphur in the vapour phase



Reactions:-



Aromaticity Order

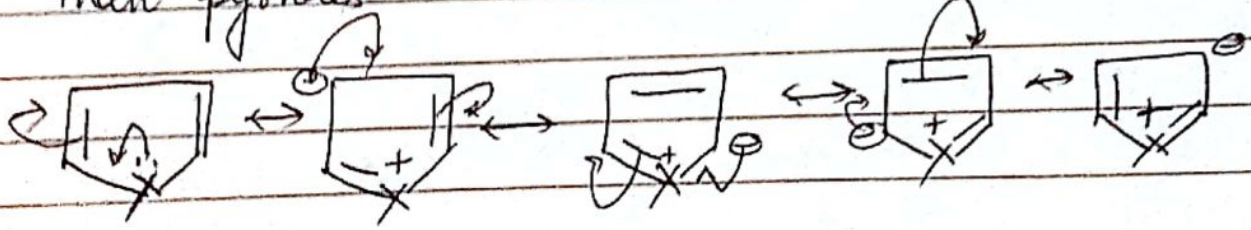
Thiophene > Pyrrole > Furan

29 Kcal/mol 21.6 Kcal/mol 16 Kcal/mole

Thiophene is more aromatic than Pyrrole and furan.

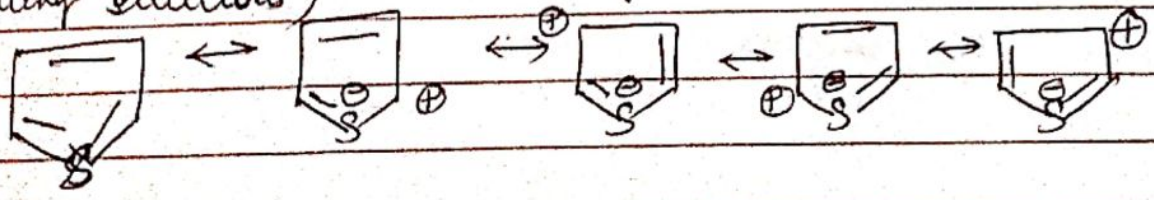
(1) Sulphur is less electronegative than nitrogen and oxygen so its lone pairs are readily do participate in delocalisation (in ring)

(2) In Sulphur 3d orbitals are available which are not present in case of N & O. Due to less electronegativity of S the e⁻ on Sulphur readily participate in delocalisation and this process 3d orbitals are used and as a result no. of Contributing structure are more in case of thiophene than pyrroles



5 Resonating Structure in Case pyrrole & furan

in Case of Thiophene (5 Resonating structure + more Contributing Structure)



Reactivity towards Electrophilic Substitution

Pyrrole > furan > Thiophene

* High reactivity of pyrrole is due to the ease with which nitrogen accomodate the positive charge Compared to oxygen

and sulfur, which result in an increase in the electron density of the ring. Thus nucleophilic character of ring increases.

In case of ethiophene sulphur uses 3d orbitals in delocalisation and as a result ring bears the +ve charge and reactivity towards electrophilic substitution ↓s