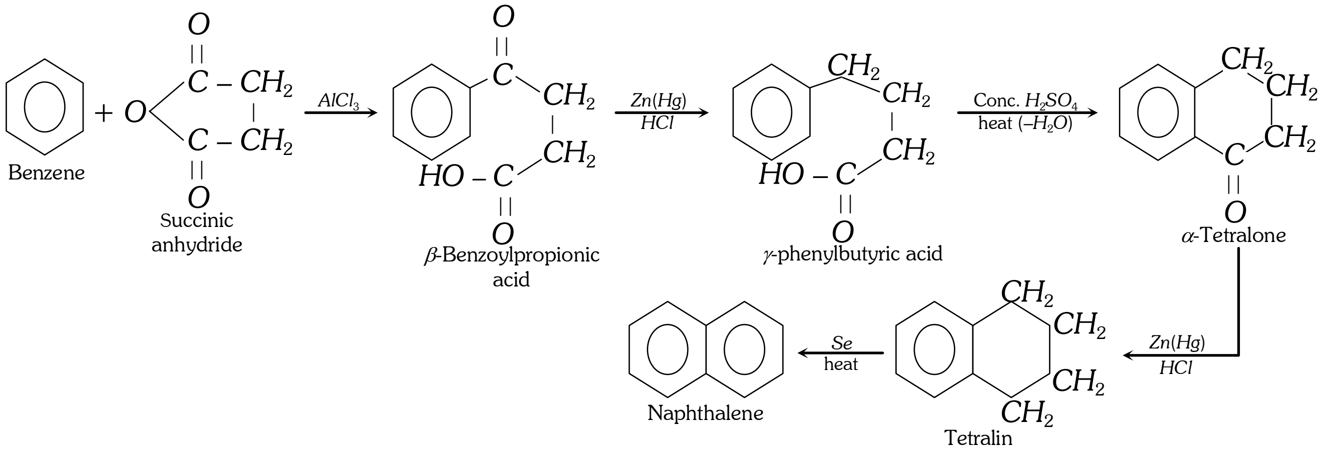
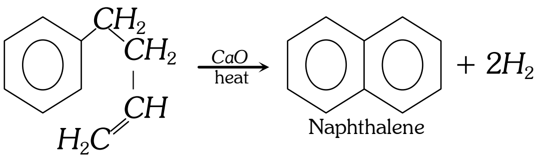
Aromatic Hydrocarbons Part 3

(i) ***Methods of preparation***

(a) *Haworth synthesis*



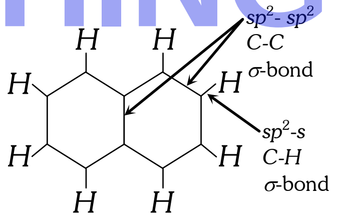
(b) *By 4-phenyl-1-butene* :



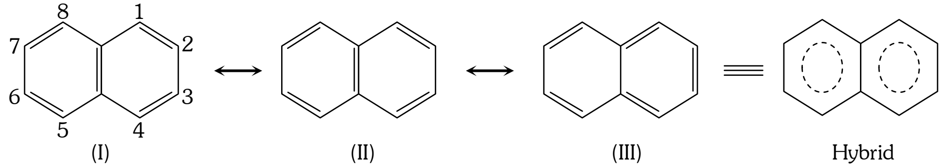
(ii) ***Structure***

(a) In naphthalene all carbon atoms are sp^2- hybridized. sp^2- hybrid orbital overlap with *s*- orbital of hydrogen atoms forming $C-C$ and $C-H$ sigma bond.

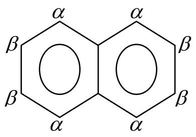
(b) All carbon and hydrogen atoms lie in one plane in naphthalene.

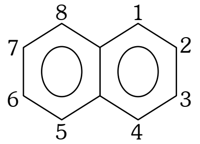


(c) According to resonance theory. It is a resonance hybrid.



(d) *Position* : 1,4,5,8 = α ;   2,3,6,7 = β



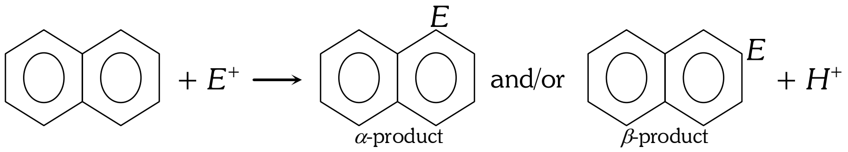


(e) Resonance energy of naphthalene is 61 *kcal/mol.* Which is less than of benzene. So that naphthalene is less aromatic *i.e.* more reactive than benzene.

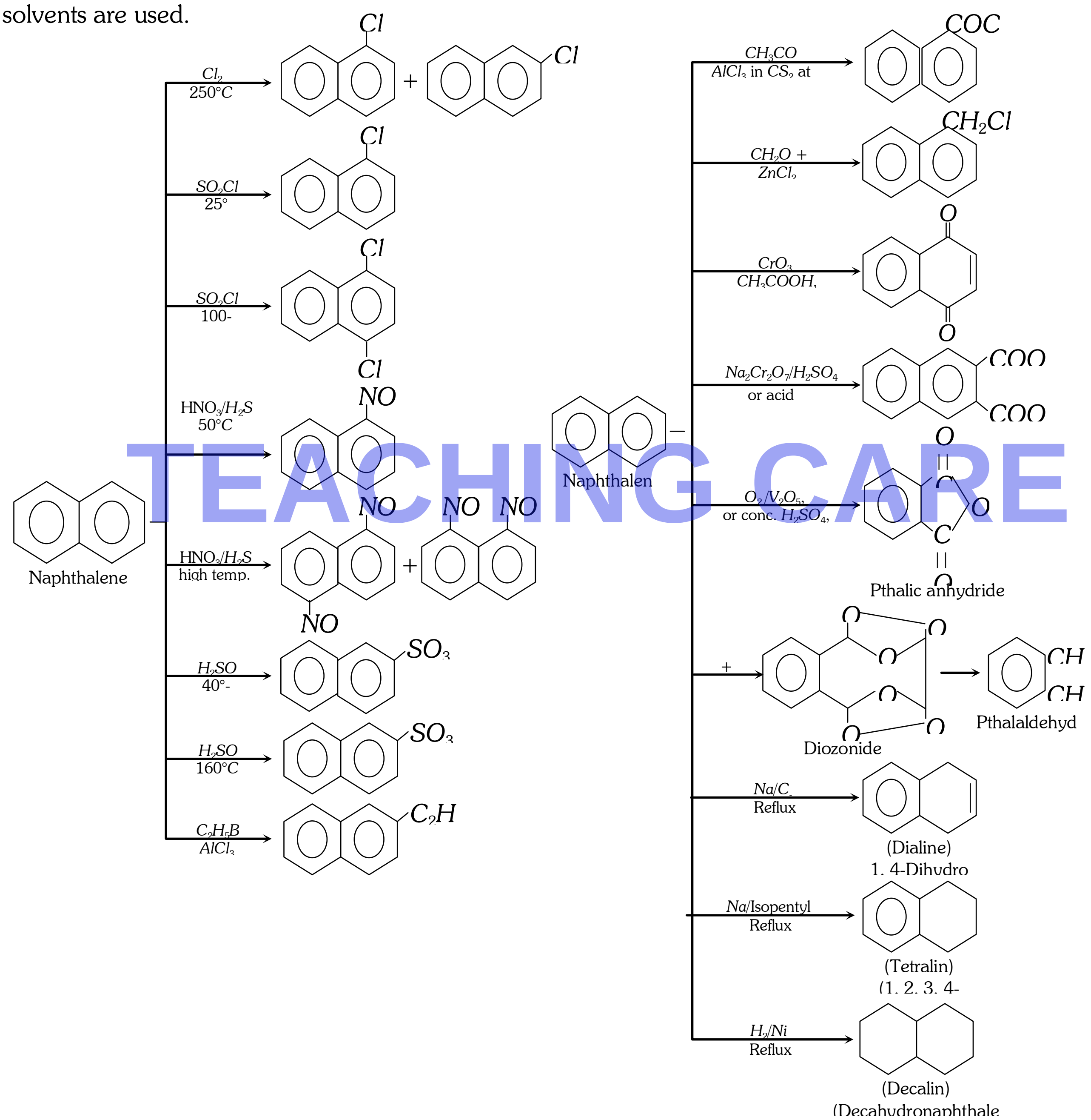
(f) In naphthalene C_1-C_2 bond length is shorter (1.36Å) *i.e.* $C=C$ and C_2-C_3 is 1.40Å *i.e.* single bond.

(iii) ***Physical properties :*** It is a colourless crystalline compound. It melts at 80.2°C. It is very volatile and sublimes slowly even at room temperature. It has strong characteristic odour. It is insoluble in water but very soluble in ether, benzene and hot alcohol. It burns with smoky flame.

(iv) ***Chemical properties*** **:** It undergoes usual aromatic electrophilic substitution reactions. The product of monosubstitution is either α or β -depending on conditions, but the α -product always predominates.



Substitution at β -position occurs only when the reaction is carried at high temperatures or when bulkier solvents are used.



(v) ***Uses***

(a) As moth repellent. It is, however, now being replaced by more powerful insecticides such as *p*-dichlorobenzene and DDT.

(b) For commercial production of phthalic anhydride, α-naphthol, β-naphthol, etc.

(c) For manufacture of dyes, explosives and synthetic resins.

(d) For increasing the illuminating power of coal gas.

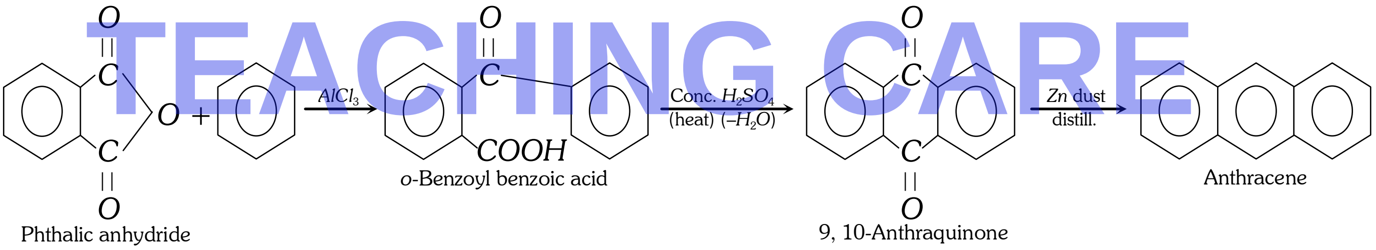
(2) Anthracene

The hydrocarbon derives its name from the world *anthrax* (Greek = coal) as coal is the chief source from which it is manufactured. It is present in coal-tar (Less than 0.5%) and is obtained from the anthracene oil or green oil fraction (because of its dark green fluorescence) formed during coal-tar distillation. This fraction is collected between 270 - 360°C.

The anthracene oil fraction is cooled when crude anthracene crystallizes out. The crude product consists phenanthrene and carbazole as impurities. The crude product is successively washed with solvent naphtha as to remove phenanthrene and pyridine to remove carbazol. Finally, the solid is sublimed to get pure anthracene.

(i) ***Methods of preparation***

Haworth synthesis

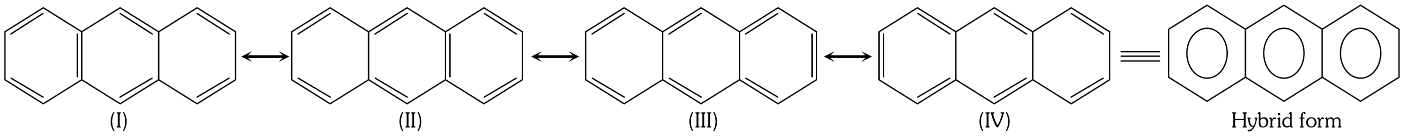


(ii) ***Structure***

(a) Anthracene is tricyclic aromatic hydrocarbon.

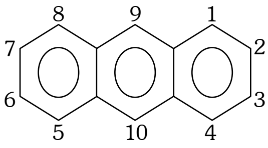
(b) All carbon atoms in anthracene are sp^2 hybridized.

(c) resonance hybrid are as follows

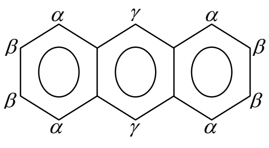


(d) It gives both addition and electrophilic substitution reaction.

(e) In anthracene the numbering of carbon atom is



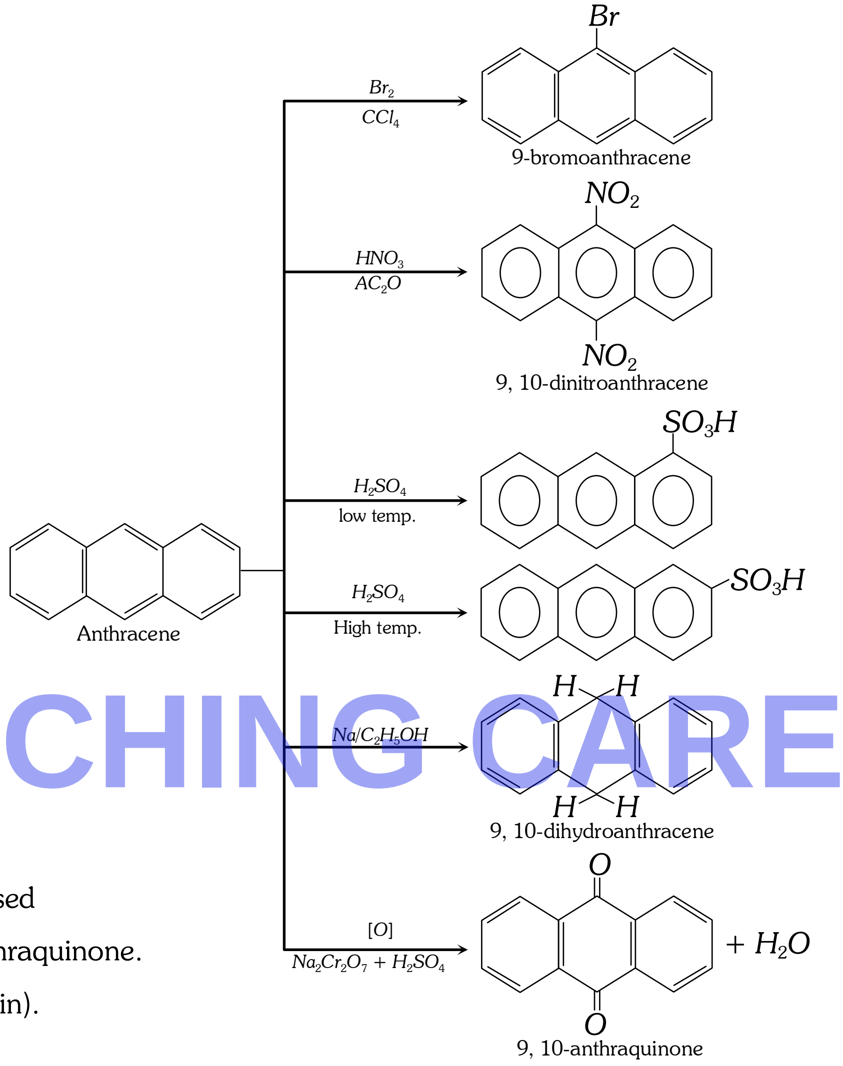
Anthracene



Anthracene

(iii) ***Physical properties* :** Anthracene is a colourless solid. It melts at 217°*C*. It is insoluble in water but soluble in alcohol and ether in small amounts. It is comparatively more soluble in hot benzene. With picric acid, it forms a red colour picrate.

(4) Chemical properties



(v) ***Uses* :** Anthracene is used

(a) For manufacture of anthraquinone.

(b) For making dyes (Alizarin).

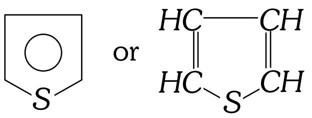
(c) In smoke screens.

Heterocyclic compounds.

These are cyclic compounds in which the ring includes in addition to carbon atoms at least one atom of another element (*Hetero* = other, different). The common hetero atoms present in the carbon rings are *O*,*N* and *S*.

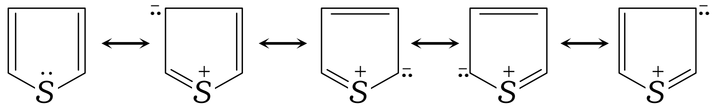
(1) Thiophene

It is found in the benzene fraction of coal-tar and petroleum. The benzene fraction is shaken with cold concentrated sulphuric acid. Thiophene present in the fraction combines with sulphuric acid more readily than benzene to form thiophene sulphonic acid which is separated with water being soluble. Thiophene sulphonic acid is treated with super-heated steam to recover thiophene.

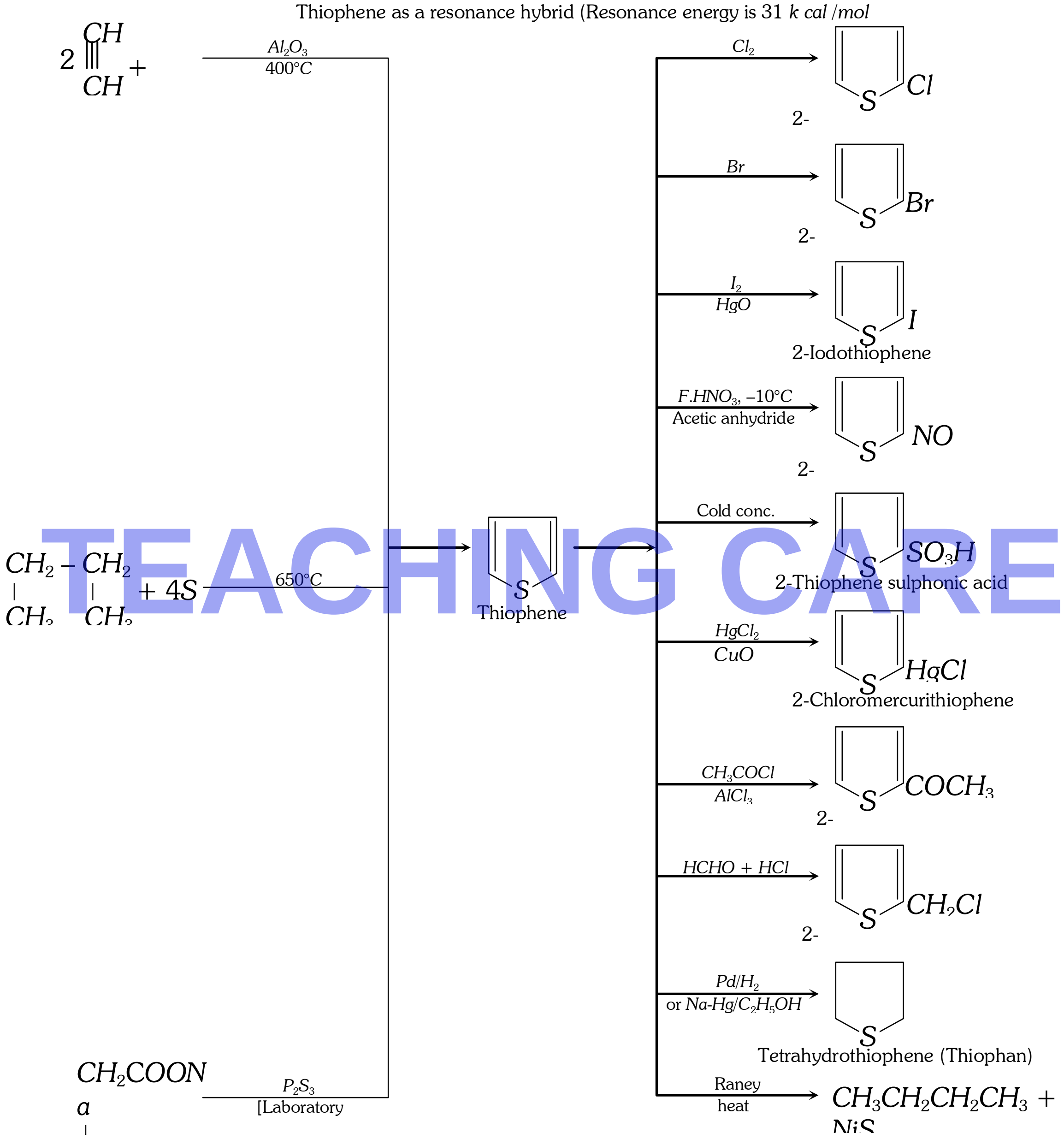


Properties : It is a colourless liquid. Its boiling point is 84°*C*. Its odour is similar to that of benzene. It is insoluble in water but soluble in organic solvents. It is flammable and toxic in nature.

Its resonance energy is $31\,k\,cal\,mol^{-1}$. Hence, it is more stable and resembles benzene more closely than furan $(23\,k\,cal\,mol^{-1})$ and pyrrole $(25\,k\,cal\,mol^{-1})$. It does not show basic properties and does not undergo **Diels-Alder reaction.**



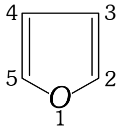
Thiophene as a resonance hybrid (Resonance energy is 31 $k\ cal\ /mol$

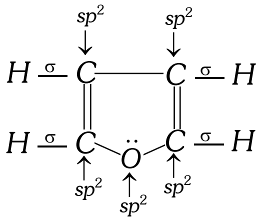


(2) Furan

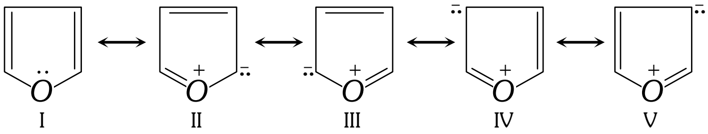
Furan derives its name from furfur meaning bran in Greek which is the source of its aldehyde, furfural. It is present in pine-wood tar and may be extracted from it.

Furan shows aromatic behaviour because resulting π-molecular orbital satisfies the Huckel rule $((4n+2)\pi$ where, $n=1$.





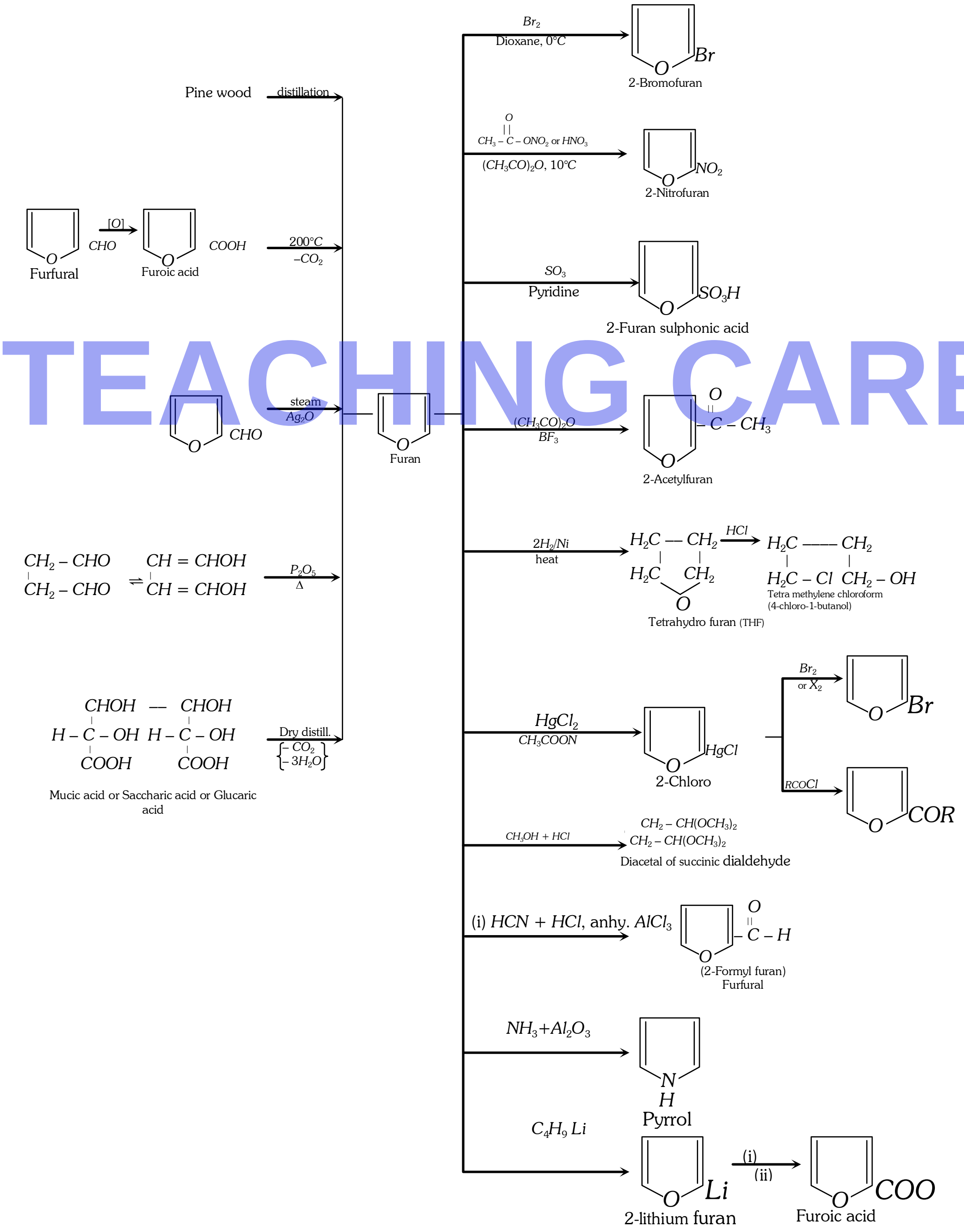
Furan is also considered as a resonance hybrid of the canonical forms. Out of which the first three are the main contributing structures.



Canonical forms of furan

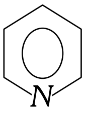
Furan has resonance energy about $23\,k\,cal\,mol^{-1}$ which is less than benzene. However it is less aromatic and more reactive than benzene.

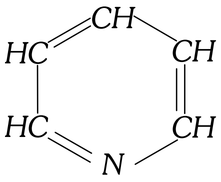
Properties : Furan is a colourless liquid. Its boiling point is 32°C. It is insoluble in water but soluble in orgainic solvents. It is a reactive compound. It is a weak base. In Furan electrophilic substitution reactions take place preferably at 2 and 5 position where electron density is high. If these positions are occupied, substitution occurs at 3 and 4 positions. It undergo **Diels-Alder reaction.**

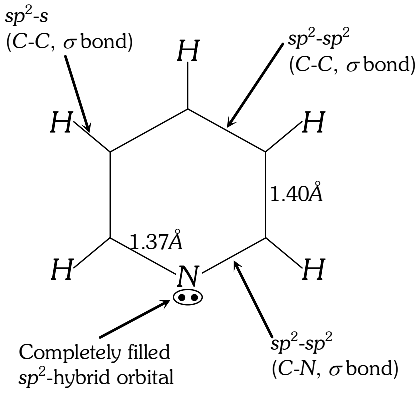


(3) Pyridine

Pyridine is a six membered aromatic heterocycle with one nitrogen atom in the ring. It may be supposed to have been derived by replacement of $=CH-$ group of benzene by $=N-$. Hence, it is isoster of benzene. Its systematic name is **azabenzene.** (Prefix aza stands for nitrogen). The hybrid structure of pyridine is represented as:



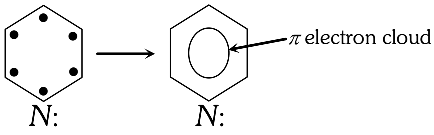




(i) ***Properties :*** It is a colourless liquid having an unpleasant odour. It boils at 115°C. It is miscible with water and is hygroscopic. It is a good solvent for many organic compounds and inorganic salts.

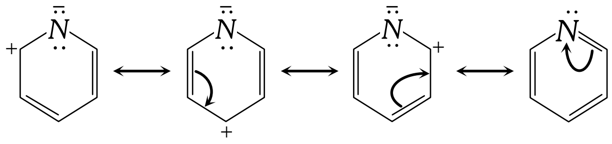
(ii) ***Aromatic character :*** Each carbon atom and nitrogen atom in the ring have sp^2 hybridized and one unhybrid *p*-orbital containing one electron. These orbitals overlap to form π molecular orbital consisting six electrons. The π molecular orbital satisfies Huckel's rule $(4n+2)$ and thus aromatic properties are observed in pyridine.

The resonance energy is 43 *k cal/mol* and bond length of $C-C$ bond is 1.40 Å and $C-N$ 1.39 Å.



$4n+2=6;\ n=1$

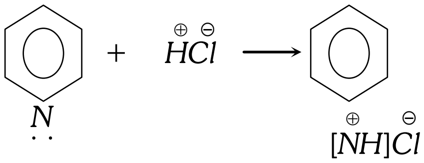
(iii) ***Resonance structure :***



Canonical form of pyridine

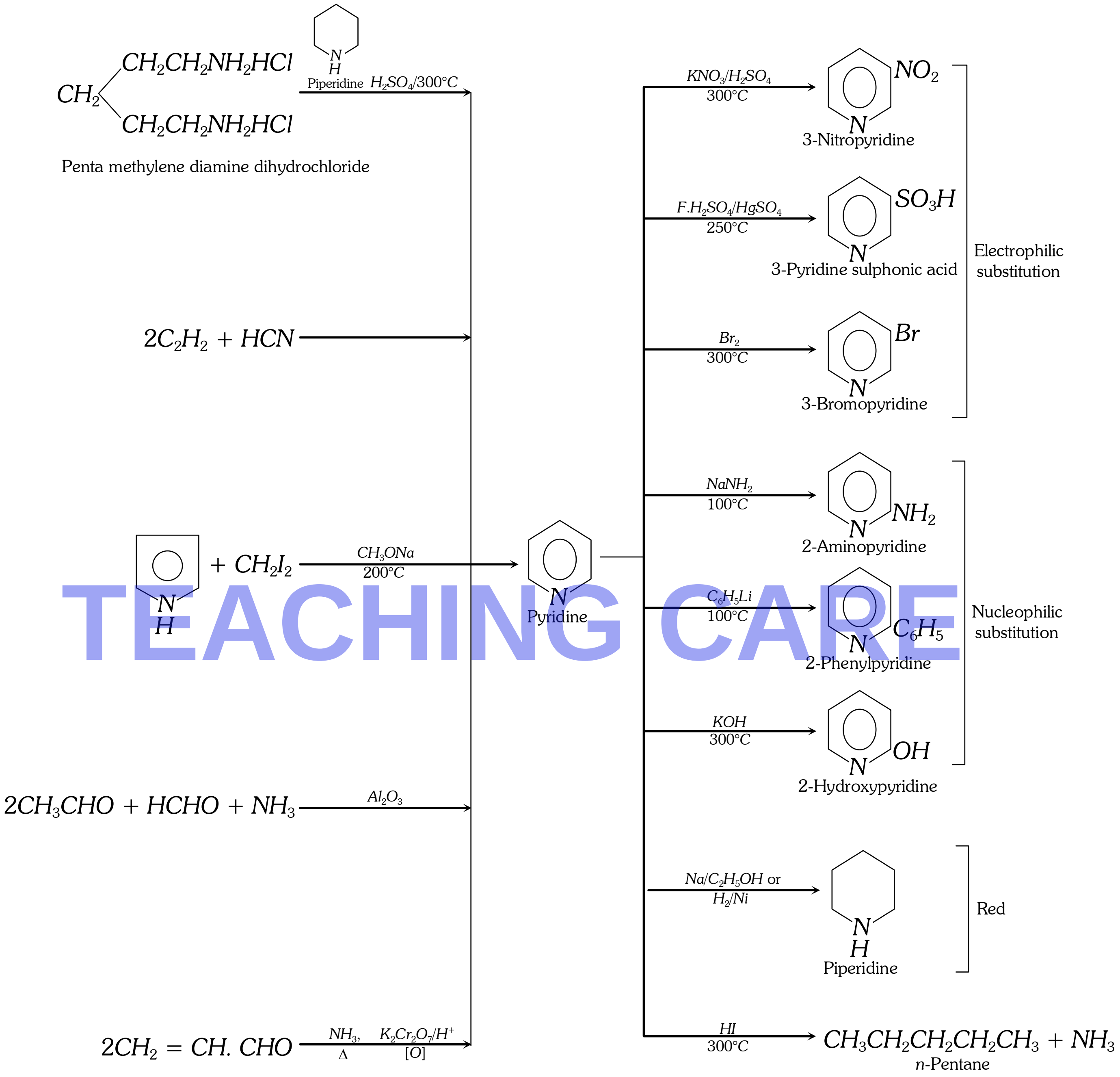
(iv) ***Basic nature :*** Pyridine is basic in nature due to presence of lone pair nitrogen atom. It is more and more basic than pyrrole and less basic than aliphatic amine.

Example :



Pyridinium hydrochloride

(v) Chemical properties :



(vi) ***Uses***

(a) To denature alcohol.

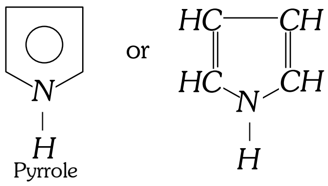
(b) As a basic solvent in organic reactions.

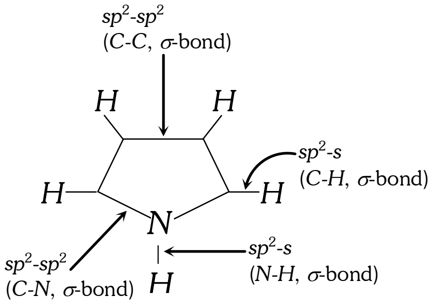
(c) For preparing sulpha-pyridine and vitamin B_6.

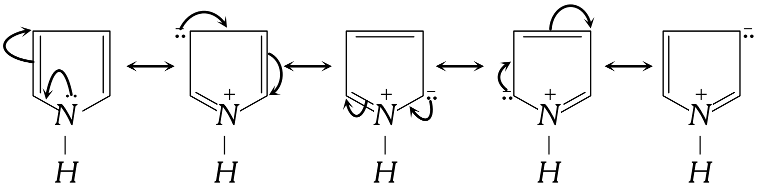
(d) As a catalyst in many reactions, *e.g.*, in the formation of Grignard reagent, in Perkin and Knoevenagel reactions.

(4) **Pyrrole**

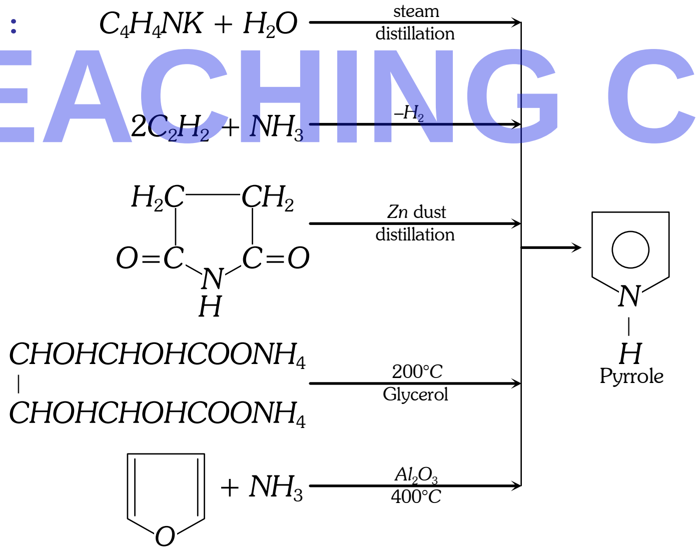
It occurs in coal-tar and bone oil and is found in many natural products including chlorophyll, haemoglobin and alkaloids.







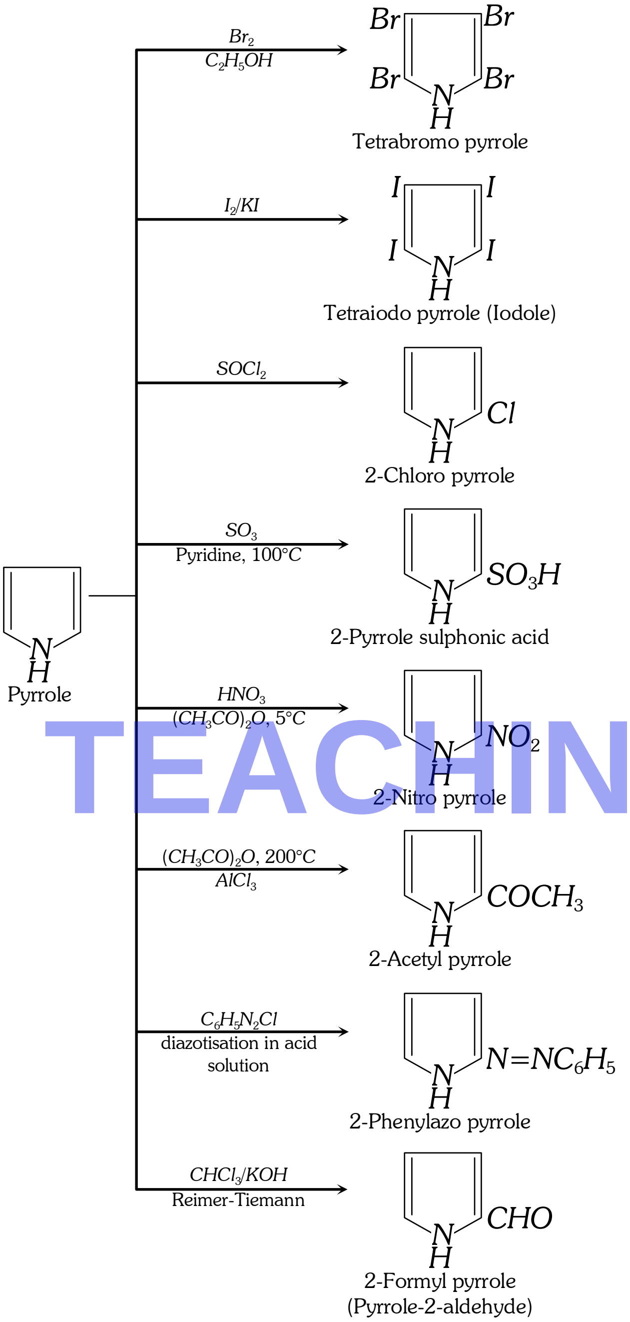
(i) ***Preparation :***

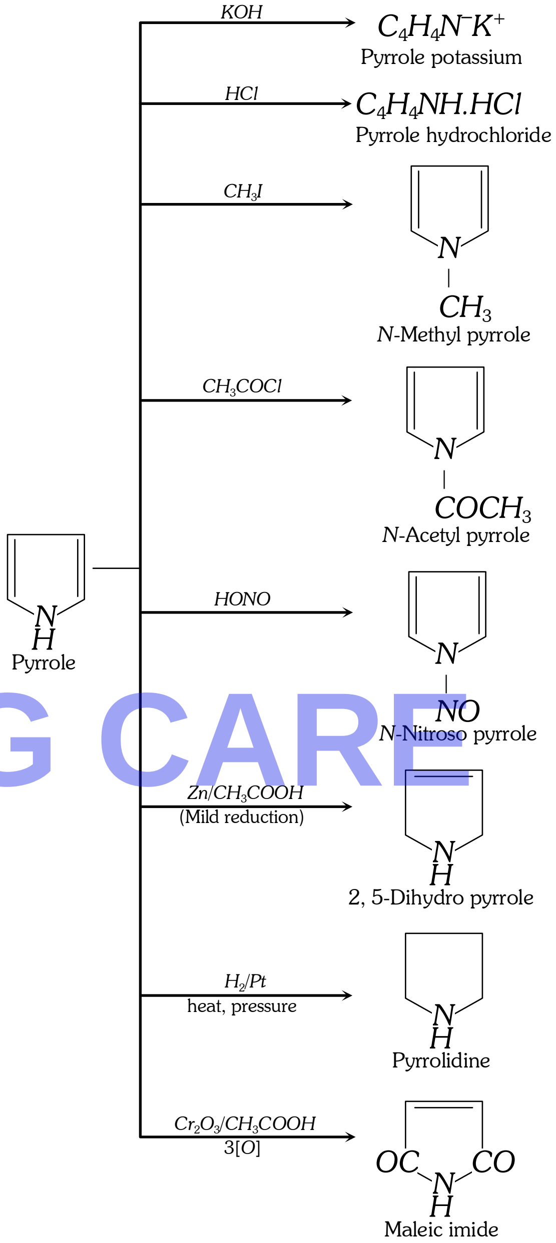


Note : ✹ Furan needed for the process is obtained from agricultural waste materials which are rich in pentosans. The pantosans on acid hydrolysis yields furfural which is decarbonylated.

(ii) ***Properties :*** Pyrrole is a colourless liquid. Its boiling point is 131°C. It is slightly soluble in water but highly soluble in alcohol and ether. Its odour is similar to chloroform. It rapidly becomes brown when exposed to air. Vapours of pyrrole turn a pine splint moistened with HCl red. Pyrrole derives its name from this property.

Chemical properties :





(iii) ***Uses*** **:** It is used as a commercial solvent, as an intermediate in the production of nylon and for making pharmaceuticals.