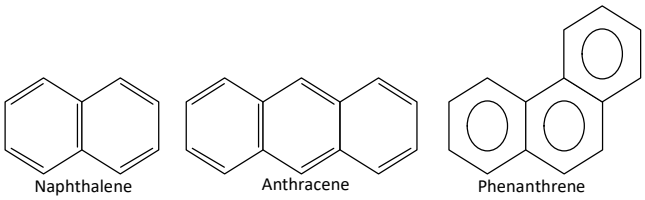
Polynuclear hydrocarbons.

Compounds having two or more benzene rings fused together in ortho positions are termed as fused polynuclear hydrocarbons. These hydrocarbons also called fused ring hydrocarbons.

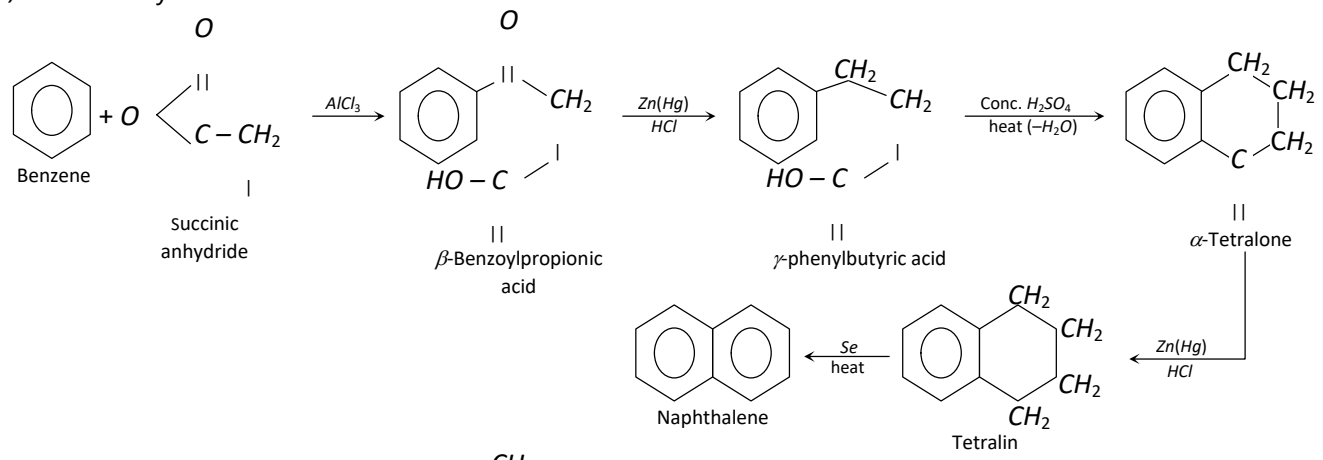


(1) **Naphthalene**

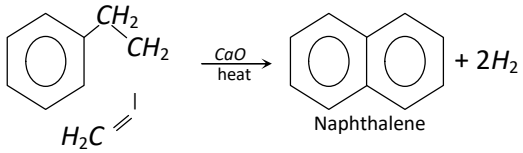
Naphthalene is the largest single constituent of coal-tar (6-10%). It is obtained in the middle oil fraction of coal-tar distillation. It is recovered as crude product when the middle oil fraction is cooled. The crude crystalline product is separated by centrifugation and purified by washing successively with dilute H_2SO_4 (to remove basic impurities), sodium hydroxide solution (to remove acidic impurities) and water. Finally, the solid is sublimed to get pure naphthalene.

(i) **Methods of preparation**

(a) Haworth synthesis



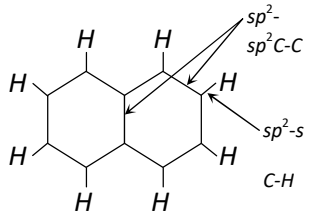
(b) By 4-phenyl-1-butene **:**



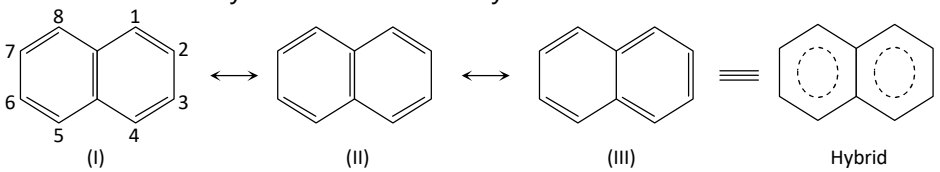
(ii) **Structure**

(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.

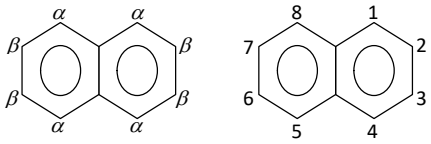
(b) All carbon and hydrogen atoms lie in one plane in naphthalene.



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



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

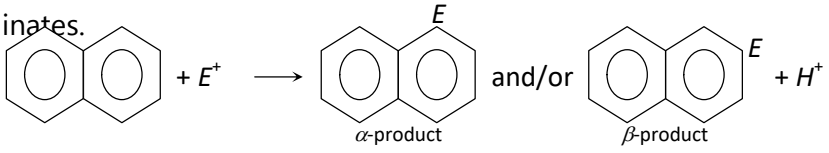


(e) Resonance energy of naphthalene is 61 kcal/mol. Which is less than of benzene. So that naphthalene is less aromatic i.e. more reactive than benzene.

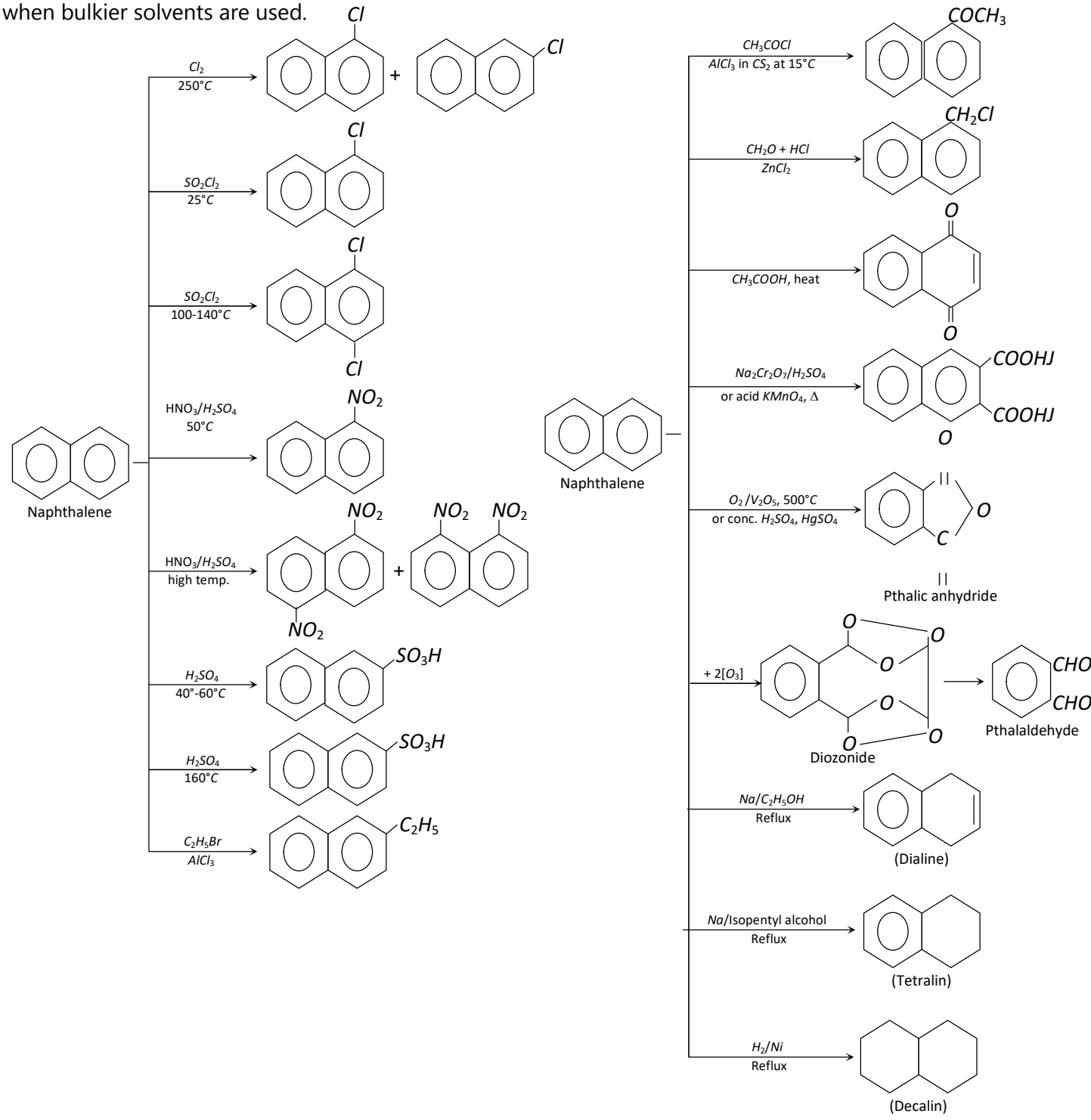
(f) In naphthalene C_1-C_2 bond length is shorter (1.36Å) i.e. $C=C$ and C_2-C_3 is 1.40Å i.e. single bond.

(iii) **Physical properties:** It is a colorless 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) **Chemicalproperties:**It undergoes usual aromatic electrophilic substitution reactions. The product of monosubstitution is either · or · -depending on conditions, but the · -product always predominates.



Substitution at · -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, · -naphthol, · -naphthol, etc.

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

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

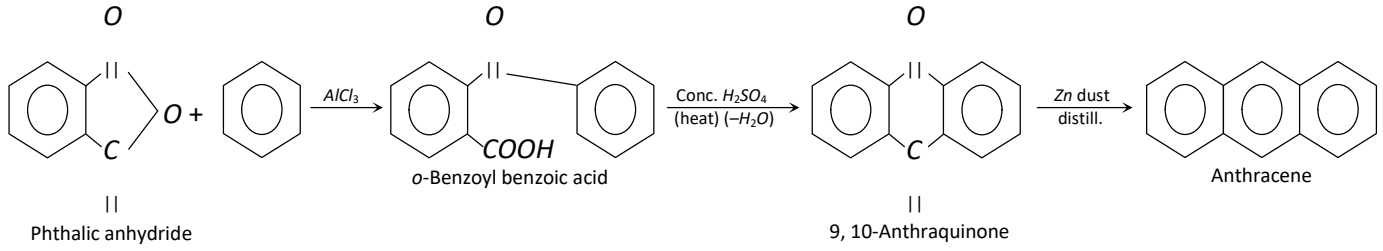
(2)**Anthracine**

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

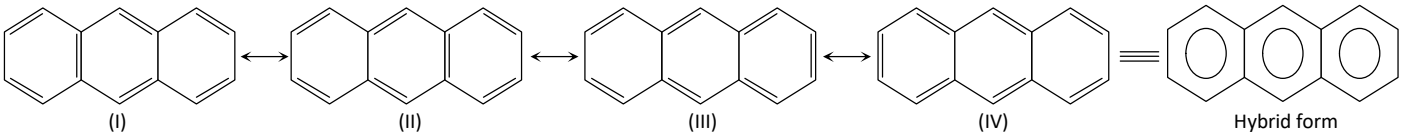


(ii) **Structure**

(a) Anthracine is tricyclic aromatic hydrocarbon.

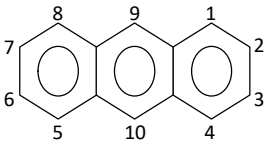
(b) All carbon atoms in anthracene are sp^2 hybridized.

(c) resonance hybrid are as follows

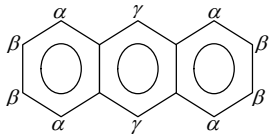


(d) It gives both addition and electrophilic substitution reaction.

(e) In anthracene the numbering of carbon atom is



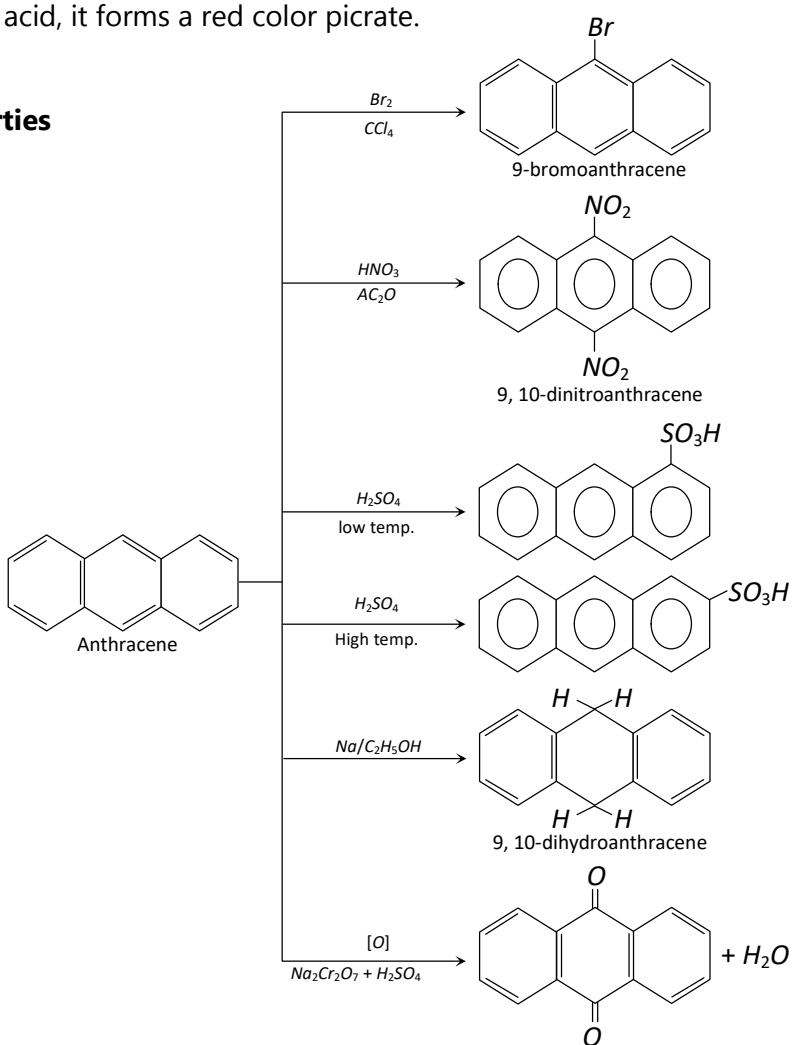
Anthracene



Anthracene

(iii) **Physical properties:**Anthracene is a colorless 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 color picrate.

(4) **Chemical properties**



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

(a) For manufacture of anthraquinone.

(b) For making dyes (Alizarin).

(c) In smoke screens.