Polynuclear Hydrocarbon

Naphthalene ($C_{10}H_8$)

Isolation :

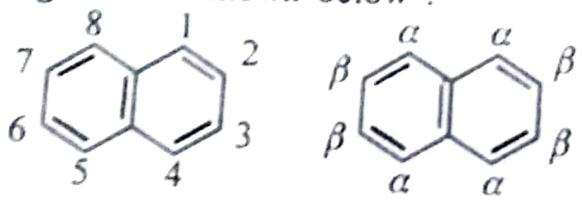
It is present to extent of 6-10% in coal tar and is isolated fro middle oil fraction.

i. The middle oil fraction of coal tar distillation is cooled. A maj portion of naphthalene crystallises out. It is separated b centrifugation or by pressing out the oil in a hydrolic press. Th crystals are washed with hot water and with aqueous sodiu hydroxide in a centrifugal machine to remove the adhering o and phenols. It is then washed with a little concentrate sulphuric acid to remove basic impurities. We get crud naphthalene. It is purified by sublimation.

ii. It is also made, now a days, synthetically from petroleum b passing petroleum fractions over heated copper catalyst at 95 K at atmospheric pressure. A mixture of naphthalene and methy naphthalene is obtained. The methyl naphthalene is heated with hydrogen under pressure in the presence of metal oxide catalyst. It is converted into naphthalene. This process is known as *hydrodealkylation*.

Nomenclature :

Naphthalene molecule contains ten carbon atoms which are numbered or designated as shown below :



It may be noted that 1,4,5 and 8 positions are equivalent and are designated as α-positions. Similarly 2,3,6 and 7 are equivalent and are termed β-positions. In naming monosubstituted derivatives the positions of substituents are indicated either by number or by letters. But in di and more highly substituted compounds, only number are used.

Properties

Naphthalene forms colourless crystalline plates, m.p. 80°C, b.p. 218°C, with a characteristic smell. It is insoluble in water; but readily soluble in hot alcohol, ether and other solvents.

Chemical properties :

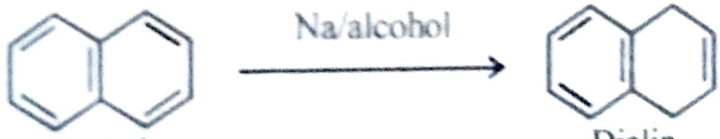
Naphthalene is aromatic. This is shown by the fact that the calculated heat of formation is less than the experimental value by about 255.2kJ $mole^{-1}$, suggesting that it is stabilised by resonance. It contains 10p electrons obeying Huckel's (4n + 2) rule. Here n = 2.

Chemically, naphthalene resembles benzene, but it is more active. Substitution products are formed more readily and the substituent is removed from the ring with less difficulty than in benzene. Nitration and chlorination of naphthalene yield a-derivatives. i.e., Nitration and chlorination occur in 1-position.

1. **Hydrogenation (Reduction) :**

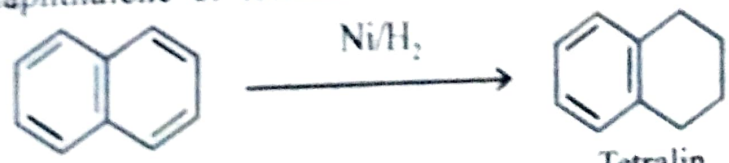
Naphthalene is reduced more readily than benzene.

When reduced with sodium and alcohol, it gives dihydronaphthalene (dialin).



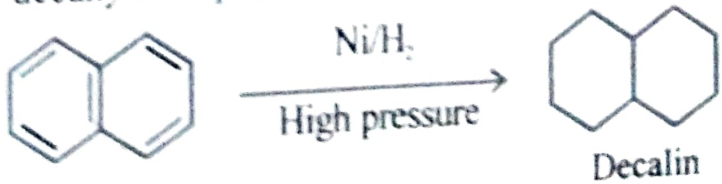
Naphthalene Dialin

When reduced with hydrogen in the presence of nickel gives tetrahydro naphthalene or tetralin.



Naphthalene Tetralin

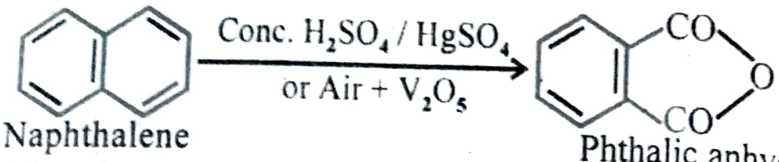
When hydrogenated under pressure with nickel leads to the formation of decahydronaphthalene or decalin.



Naphthalene Decalin

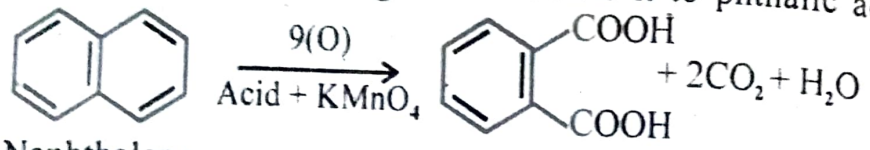
2. Oxidation :

a. When napthalene is oxidised with conc. H_2SO_4 and $HgSO_4$ or air in the presence of vanadium pentoxide it is oxidised to phthalic anhydride.



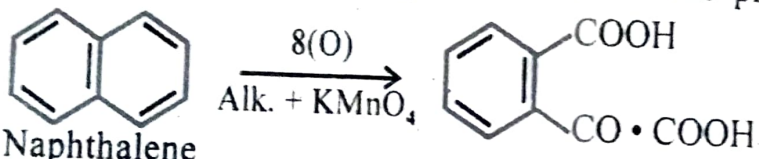
Naphthalene — Phthalic anhydride

b. Acid potassium permanganate oxidises it to phthalic acid.



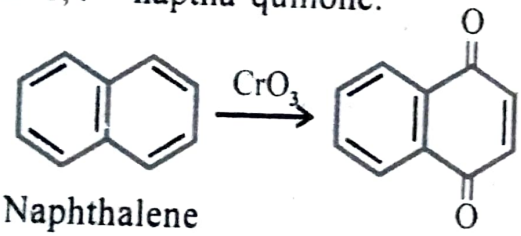
Naphthalene — Phthalic acid

c. Alkaline potassium permanganate oxidises it to phthalonic acid



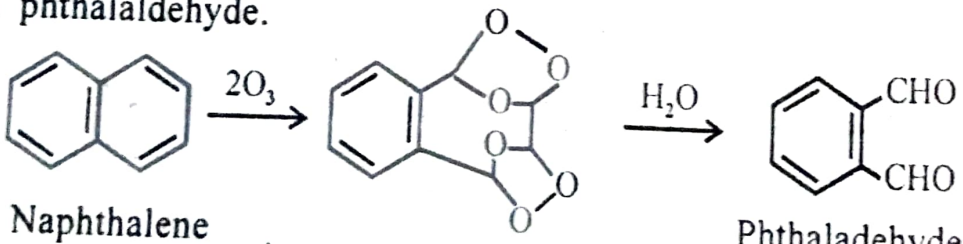
Naphthalene — Phthalonic acid

d. Chromic acid (in presence of acetic acid or acetic anhydride) oxidises it to 1,4 - naptha quinone.



Naphthalene — 1,4 - Naphthaquinone

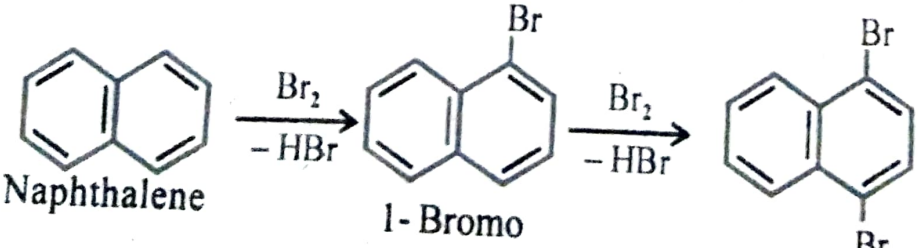
e. With ozone it gives a di - ozonide which on treatment with water gives phthalaldehyde.



Naphthalene — Diozonide — Phthaladehyde

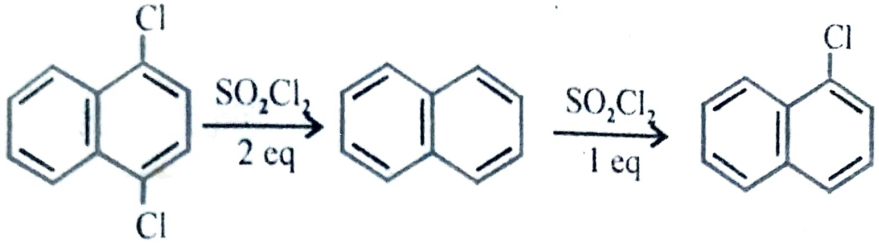
3. Halogenation :

On bromination in boiling carbon tetrachloride soultion, napthalene gives 1 - bromonaphthalene, on further bromination it gives mainly the 1,4 - dibromonaphthalene (with a little 1,2 - derivative).



Naphthalene — 1- Bromo naphthalene — 1,4 - Dibromo napthalene

Chlorination can be carried out with sulphuryl chloride in the presence of aluminium chloride. One equivalent of SO_2Cl_2 at 25°C gives 1 - chloronaphthalene, whereas, two equivalents of SO_2Cl_2 at 100 - 140°C give 1,4 - dichloronaphthalene.

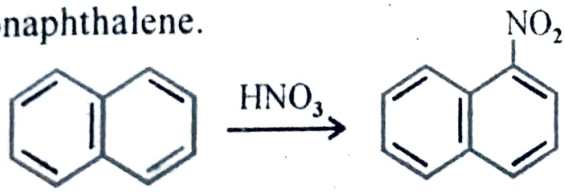


1,4 - Dichloro naphthalene

1 - chloro naphthalene

4. Nitration :

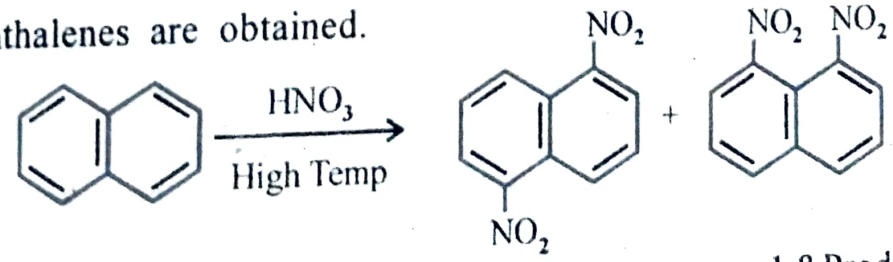
Nitration of naphthalane with nitrating mixture or cold nitric acid gives 1 - nitronaphthalene.



Naphthalene

1- Nitro naphthalene

At high temperature a mixture of 1, 5 and 1,8 - di nitro naphthalenes are obtained.



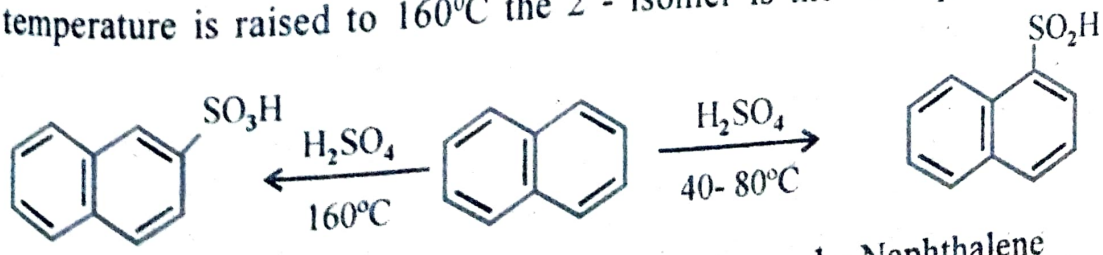
Naphthalene

1,5 Product

1,8 Product

5. Sulphonation :

When naphthalene is treated with conc. H_2SO_4 at 70 - 80°C 1 - naphthalene sulphonic acid is the main product. If the temperature is raised to 160°C the 2 - isomer is the main product.



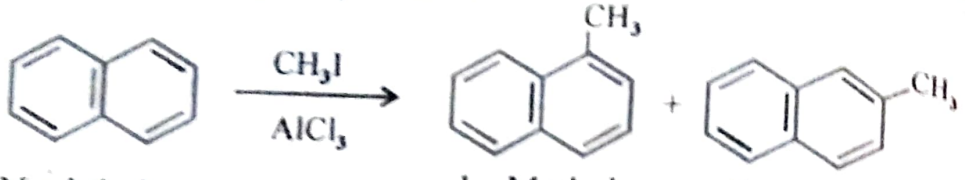
2 - Naphthalene sulphonic acid

Naphthalene

1 - Naphthalene sulphonic acid

6. Friedel - Crafts reaction :

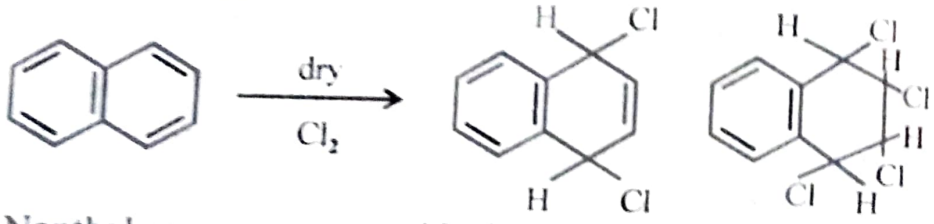
Methyl iodide reacts with naphthalene in presence of $AlCl_3$ yield 1 and 2 methyl naphthalenes.



Naphthalene — 1 - Methyl naphthalene — 2 - Methyl naphthalene

7. Addition of halogens :

Dry chlorine adds on to solid naphthalene to form naphthalene di and tetrachlorides.



Napthalene — Naphthalene dichloride — Naphthalene tetrachloride

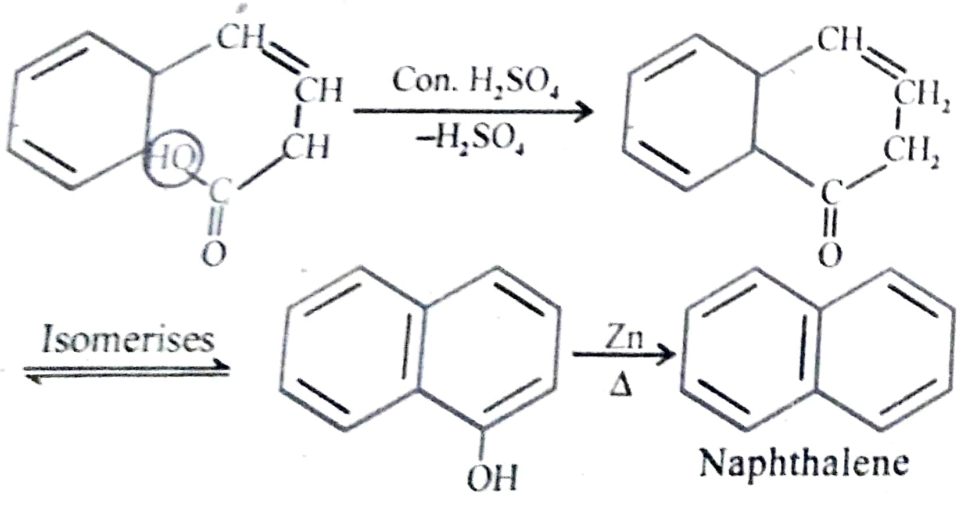
8. Formation of picrate :

Naphthalene forms an addition compound, naphthalene picrate, when concentrated solution of naphthalene picric acid in benzene are mixed and evaporated. This reaction is used to identify naphthalene.

Synthesis

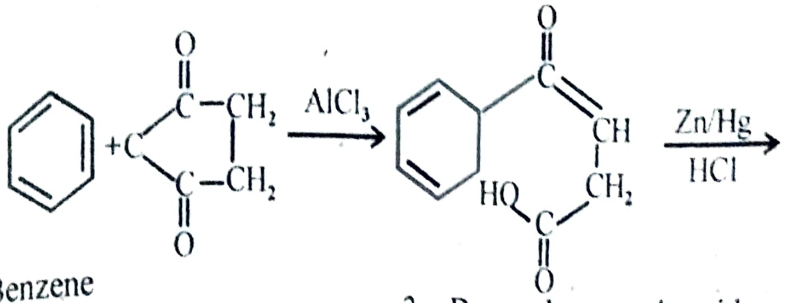
a. Fittg's Synthesis :

From phenyl isocrotonic acid.



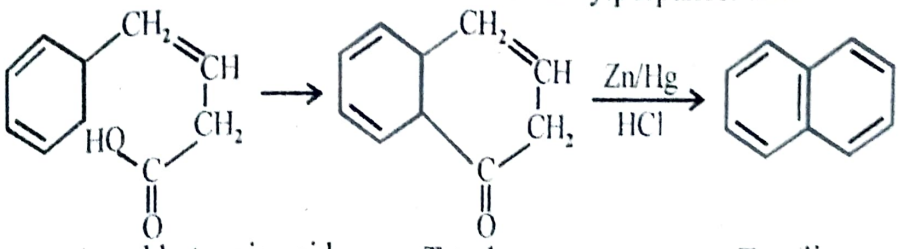
Haworth's synthesis :

By Friedel Crafts acylation reaction using succinic anhydride.



Benzene

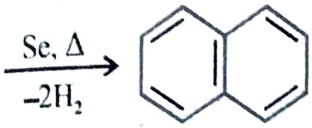
3 – Benzoylporpanoic acid



4 – Phenyl butanoic acid

Tetralone

Tetralin

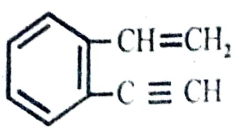


Naphthalene

From the above synthesis it is clear that naphthalene contains two benzene nuclei fused in ortho - position.

Structure :

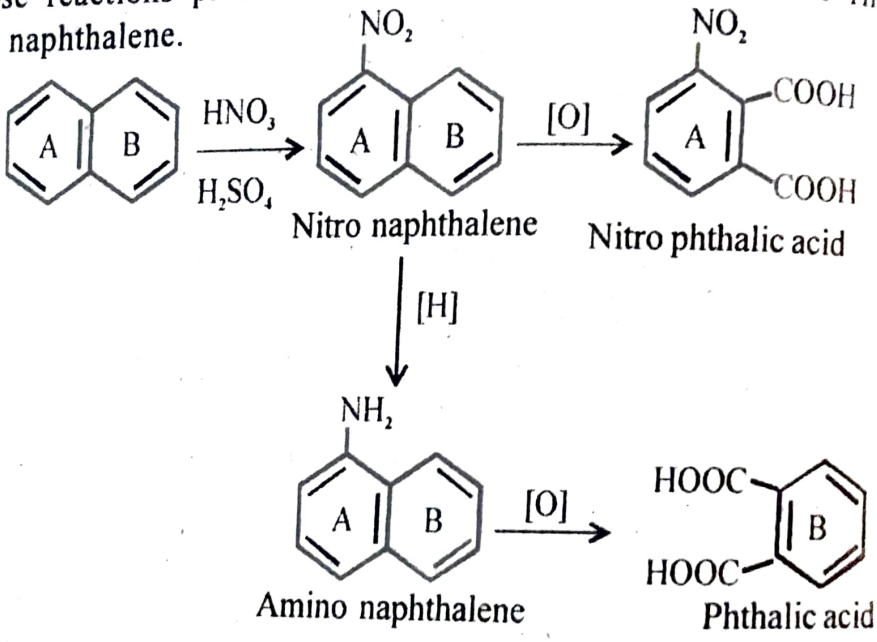
1. The molecular formula of naphthalene is $C_{10}H_8$.
2. Naphthalene resembles benzene in its chemical reactions. It can be nitrated, sulphonated and halogenated like benzene. Its hydroxyl derivatives (naphthols) resemble phenol. Naphthalene is very stable. All these suggest a ring structure as for benzene.
3. Oxidation of naphthalene yields phthalic acid (benzene dicarboxylic acid). Therefore naphthalene molecule must contain one benzene ring with two ortho side chains or a closed chain linked to ortho position.
4. If were represent napthalene with the side chains, the possible structure is.



But such structure having two unsaturated side chains - could not explain the observed reactions of naphthalene.

5. Naphthalene on nitration gives nitronaphthalene, which on oxidation yields nitrophthalic acid. This shows that the benzene ring A containing the nitrogroup remains unaffected during oxidation. If nitronaphthalene is reduced to aminonaphthalene and if the aminonaphthalene is oxidised, the product is phthalic acid. This shows that the benzene ring A to which amino group is attached is destroyed during oxidation. Therefore nitronaphthalene contains another benzene ring B apart from the one carrying the nitro group. These reactions may be represented as follows:

These reactions prove that there are two fused benzene rings in naphthalene.

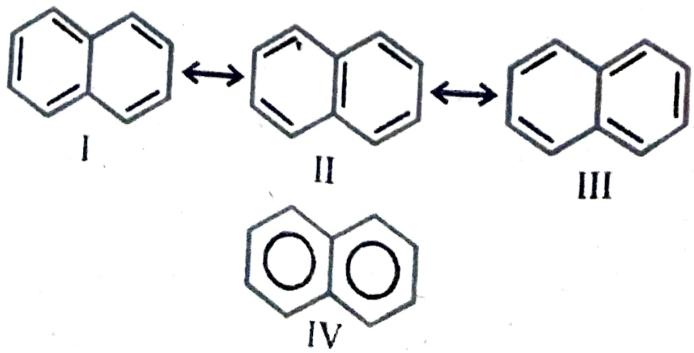


6. The condensed ring structure of naphthalene is established by its synthesis.

[For a question on structure of napthalene, write the synthesis of napthalene here]

7. **Resonance Concept :**

Napthalene is considered to be a resonance hybrid of three contributing structures I, II and III.



It may be noted that the number of electrons in cyclic p electron cloud of naphthalene is 10. It is in accordance with Huckel's 4n + 2 rule. This showe that naphthalene is a typical aromatic compound. In actual practice, naphthalene is generally represented as IV.

Uses :

Naphthalene has great industrial importance.

1. It is used as an insecticide and for destroying moths (used as moth balls)
2. It is used in dye industry for manufacturing various dyes such as azodyes, cosin and indigo.
3. It is used in the manufacture of phthalic acid, phthalic anhydride and phthalimide. These compounds, in turn, have great industrial importance.
4. Natural gases are carburetted with naphthalene to increase their illuminating power.