

# Unit-4

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## Pharmaceutical Organic-II

**Unit IV****8 Hours****Polynuclear hydrocarbons:**

Synthesis, reactions, Structure and medicinal uses of Naphthalene, Phenanthrene, Anthracene, Diphenylmethane, Triphenylmethane and their derivatives

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### Polynuclear Hydrocarbon:

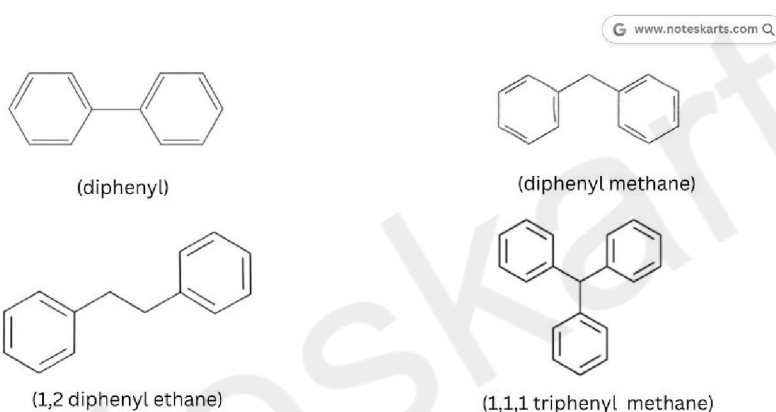
Polynuclear hydrocarbon are large group of hydrocarbon contains two or more fused aromatic ring, they have relatively low water solubility but lipophilic in nature (soluble in organic solvent).

Depending on the nature of linkage between rings they are classified into-

1. Isolated polynuclear hydrocarbon system.
2. Fused or condensed polynuclear hydrocarbon system.

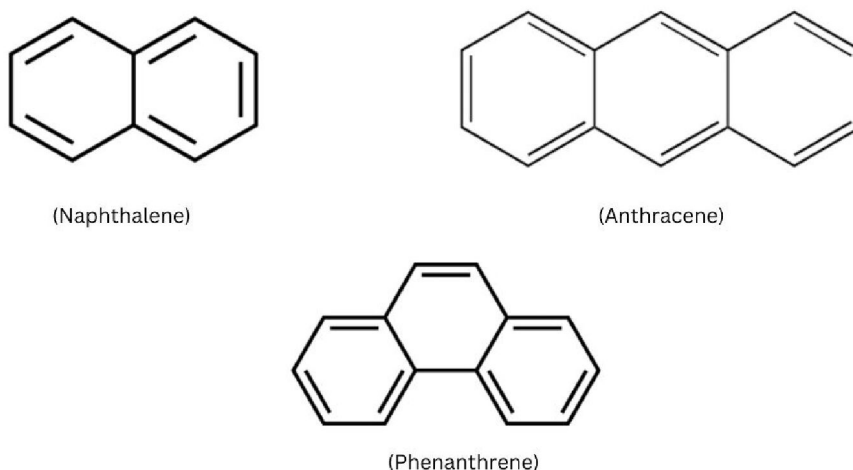
#### Isolated polynuclear hydrocarbon system:

In this system rings are isolated means benzene nuclei are either link directly to each other or thoroughly one or more carbon atom.



#### Fused or condensed polynuclear hydrocarbon system:

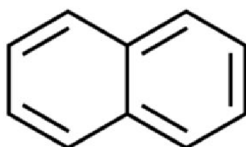
In this system, two or more rings are fused due to sharing of two or more carbon atoms by two or more rings.



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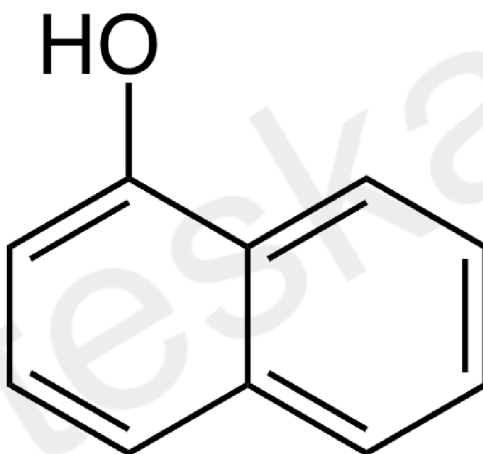
### Naphthalene:

- Naphthalene is the simplest example of polynuclear hydrocarbon containing benzene ring fused at other position.
- It is obtained from crude oil or coal tar it can be produced when the things burn naphthalene is found in smoke of forest fire, car exhaust etc.
- Poly nuclear hydrocarbon and their derivative such as naphthalene numbering should be start from carbon of fused carbon in the ring.

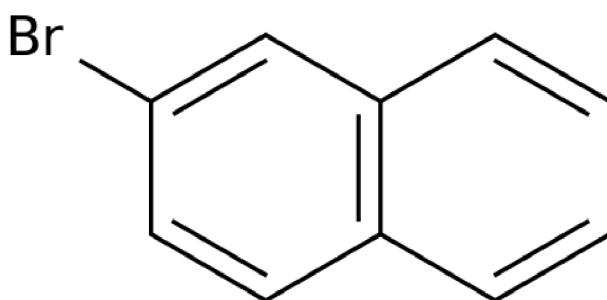


(Naphthalene)

- For mono substituted derivative of naphthalene the symbol  $\alpha$  and  $\beta$  is used for 1<sup>st</sup> and 2<sup>nd</sup> position of the ring.



$\alpha$ -naphthol



$\beta$  bromonaphthalene

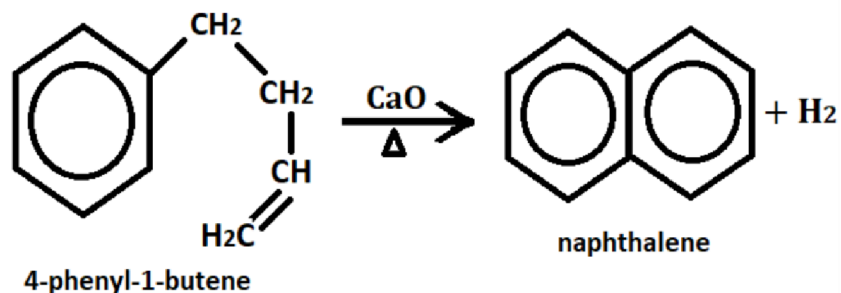


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### Synthesis of Naphthalene:

#### 1. From 4-phenyl-1-butene:

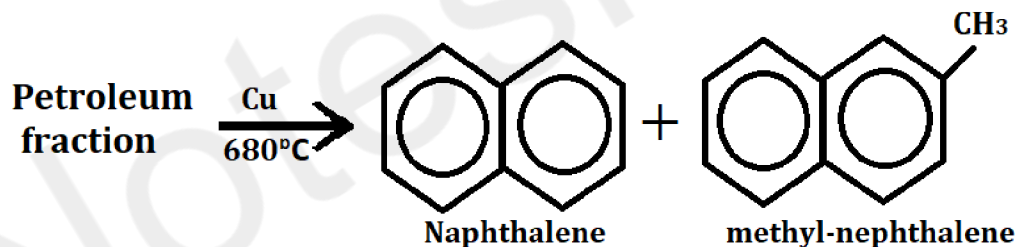
- If 4-phenyl-1-butene is passed over red hot calcium oxide naphthalene is obtained.



#### Preparation of naphthalene

#### 2. From Petroleum:

- Naphthalene and its derivatives obtained from petroleum fraction, when passed over copper catalyst 680°C Naphthalene and methyl naphthalene are formed.



#### Preparation of naphthalene

#### 3. From 4-phenyl-3-butenic acid

- When 4-phenyl-3-butenic acid is heated with concentration sulfuric acid(H<sub>2</sub>SO<sub>4</sub>) then 1 naphthol is formed after that it react with zinc dust then naphthalene produced.

#### Physical properties of naphthalene

- It is a colorless crystalline solid
- It is one of the largest constituents of coal tar.
- Melting point of naphthalene is 82°C.
- Boiling point of naphthalene is 218°C.
- It is the simplest fused ring system.
- It is insoluble in water but soluble in ether, benzene and hot ethanol.

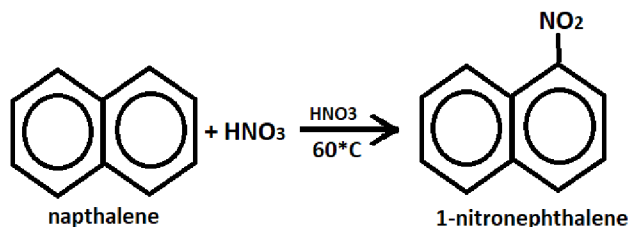


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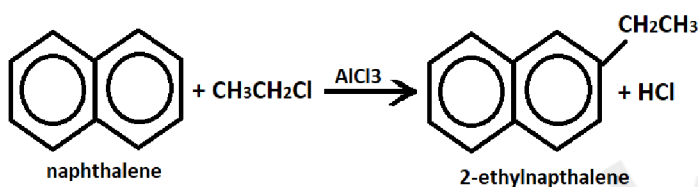
### Reaction of naphthalene

- Naphthalene also gives electrophilic substitution reaction, in this reaction electron attach on two different place and make two different structures.

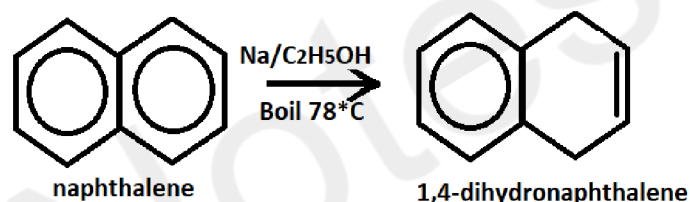
**1. Nitration:-** naphthalene undergoing nitration with concentrated nitric acid in the presence of sulphuric acid at 60°C to produce 1- nitronaphthalene.



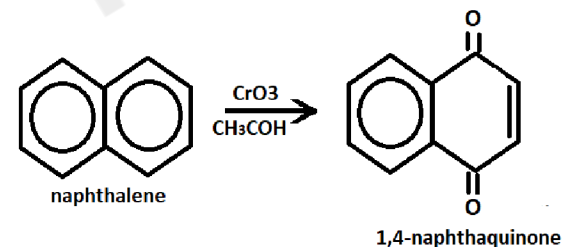
**2. Friedel craft alkylation:-** naphthalene undergoes alkylation with alkyl halides in the presence of aluminum chloride to give 2-alkylnaphthalene. (Methyl halides do not react.)



**3. Reduction:-** naphthalene undergoes reduction more readily than benzene when it reacts with sodium and ethyl alcohol it gives 1,4-dihydronaphthalene.



**4. Oxidation:-** naphthalene is much more easily oxidized than benzene when it reacts with chromium trioxide in acetic acid at room temperature it gives 1,4-naphthaquinone.



### Medicinal uses of naphthalene

- Naphthalene is used in manufacture of moth balls to protect wooden goods.
- In the production of pathetic anhydride.
- In the synthesis of dyes.
- Used to make plasticizers and natural rubber.

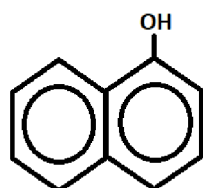


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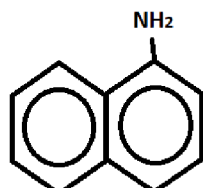
- Also used in leather industry.

### Derivatives of naphthalene

- Naphthalene is a hydrocarbon compound which has derivatives that are used in various industries.
- These derivatives of naphthalene have a wide range of applications, from being used as solvents and insecticides to being used in the production of dyes, plastics and pharmaceuticals.
- As like, naphthol's and naphthylamines.



Naphthols

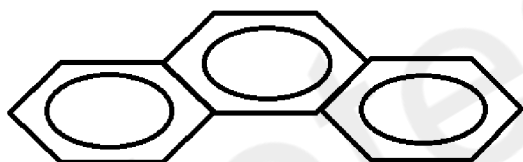


Naphthylamines

### Derivatives of naphthalene

### Phenanthrene:

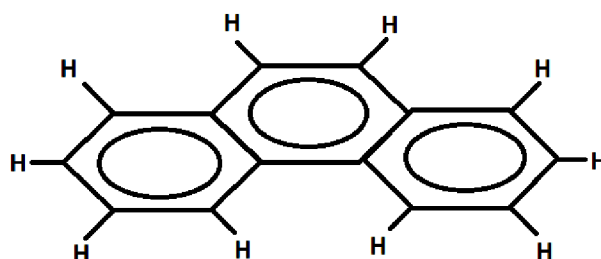
Phenanthrene is an isomer of anthracene. It may be obtained along with anthracene from the given oil fraction of coal tar.



Phenanthrene

### Structure of phenanthrene

- It is also a planar molecules like anthracene and phenanthrene. In the structure of phenanthrene all fourteen carbon atoms are  $Sp^2$  hybridized.
- The  $Sp^2$  orbitals overlap with each other and with S-orbital of ten hydrogen atom to form C-C and C-H pi bonds. Each carbon atom also passes a p-orbital and overlap of these p-orbital produce a pi molecular orbital.

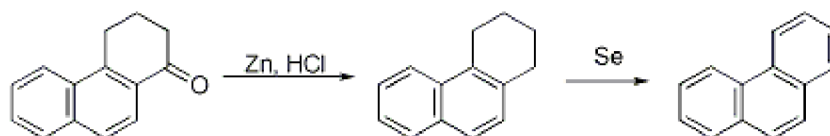
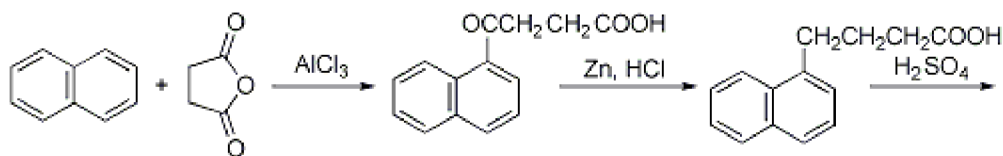


Structure of phenanthrene



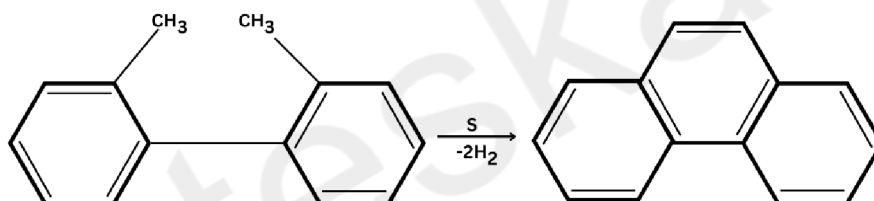
### Synthesis of phenanthrene

- Preparation of phenanthrenes from naphthalenes *via* a series of steps including a Friedel-Crafts acylation and two Clemmensen or Wolff-Kishner reductions, *q.q.v.*:



### From 2,2 dimethyl-diphenyl:

- Phenanthrene can also be obtained by cyclodehydrogenation of 2,2 dimethyl diphenyl using Sulphur.



### Physical properties of Phenanthrene:

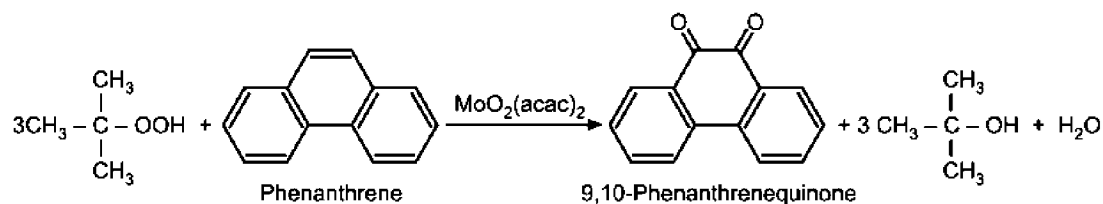
- It is a colorless solid.
- Melting point 100°C.
- It is insoluble in water, but dissolve readily in ethanol, benzene and ether.

### Reaction of Phenanthrene:

It undergoes oxidation reduction, addition and electrophilic substitution reaction.

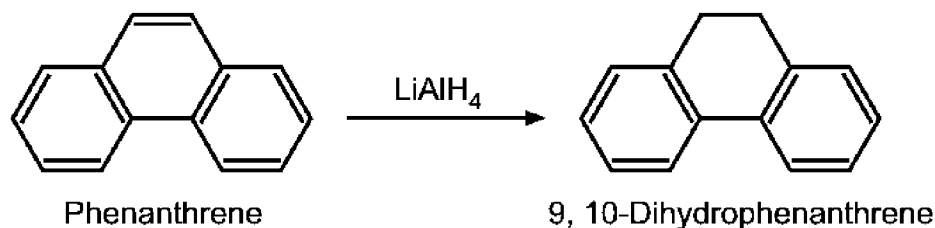
As with anthracene these reaction preferentially occur at the C-9 and C-10 position.

(1) **Oxidation:** Using, tert-butyl hydroperoxide and molybdenum acetylacetonate [MoO<sub>2</sub>(acac)<sub>2</sub>] it can be oxidized to phenanthrenequinone.

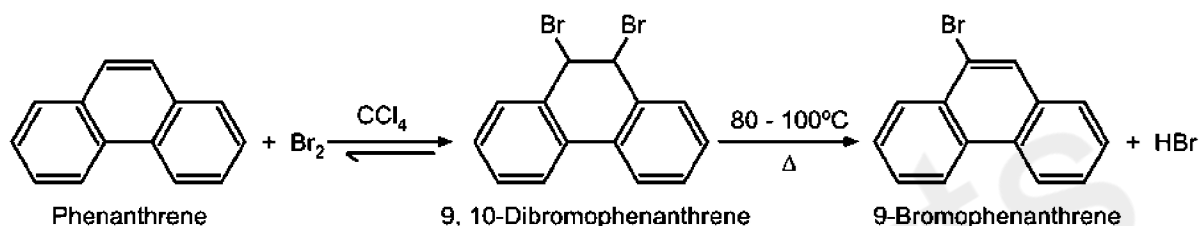


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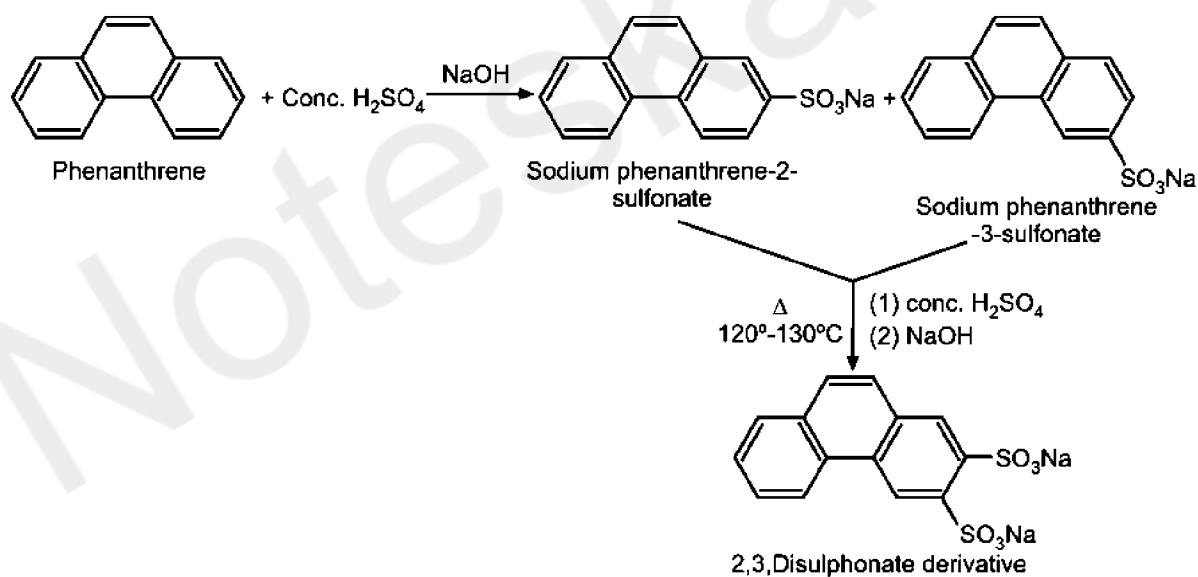
(2) **Reduction:** When the solid lithium aluminium hydride is vigorously shaken with molten phenanthrene at high temperature, phenanthrene is reduced to 9, 10 dihydrophenanthrene.



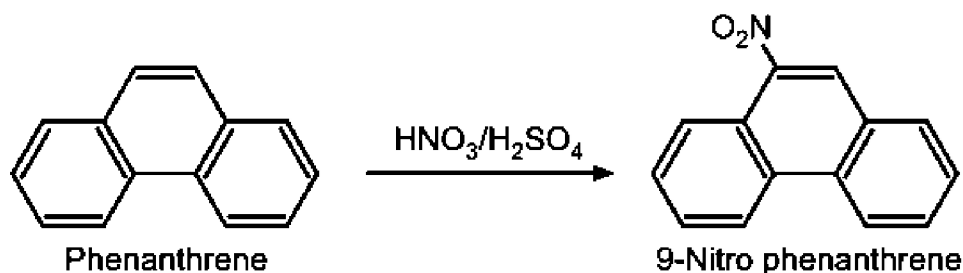
(3) **Halogenation:** Phenanthrene forms a crystalline dibromide which is sufficiently stable to be isolated. The dibromide can be converted further to mono Bromo product by gentle heating.



(4) **Sulfonation:** When phenanthrene is treated with conc. H<sub>2</sub>SO<sub>4</sub>, the following two products are obtained after neutralization with NaOH.



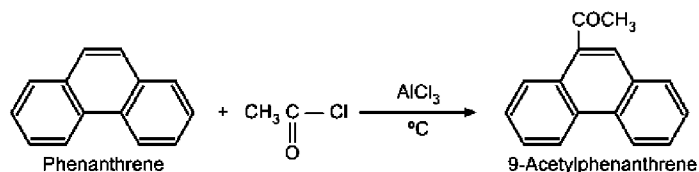
(5) **Nitration:** Upon treatment with a nitrating mixture, phenanthrene gives 9-nitro derivative.





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(5). **Fridal craft acylation:** Phenanthrene undergoes acylation with acetyl chloride in the presence of aluminium chloride at 0°C to give 9-acetylphenanthrene acetyl.



### Medicinal Use of Phenanthrene:

- It is used to make dyes, Plastic and pesticides also used in explosives and drugs.
- Also used to make bile acids, cholesterol and steroids.

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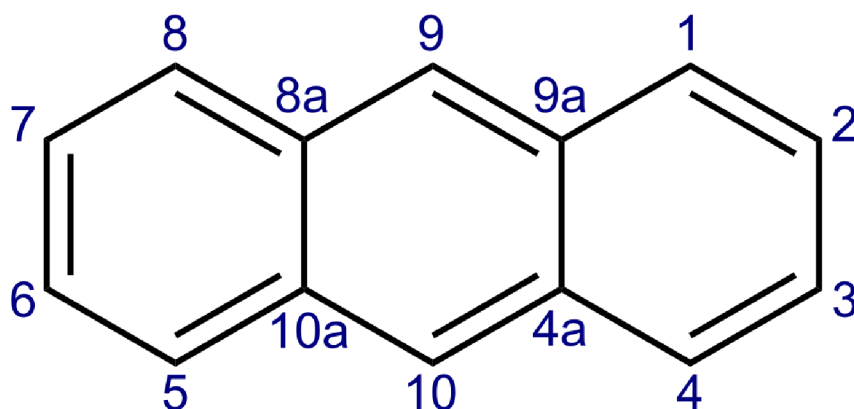
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### Anthracene:

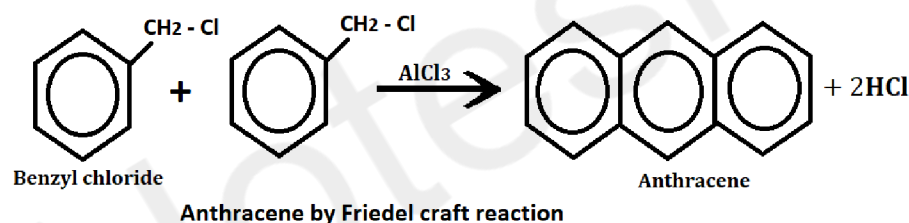
Chemical Formula:  $C_{14}H_{10}$



- Anthracene occurs in coal tar, This can be obtained from fractional distillation of coal tar as anthracene oil or as green oil. It has dark green fluorescence. It is obtained from high boiling at  $270^{\circ}C$  to  $350^{\circ}C$  of fraction of coal tar distillation.
- Anthracene has three dependent positions for the substituents to give three isomeric mono-substitution, product  $\alpha$ - (1 position),  $\gamma$ - ( $9^{th}$  position), mesoform.

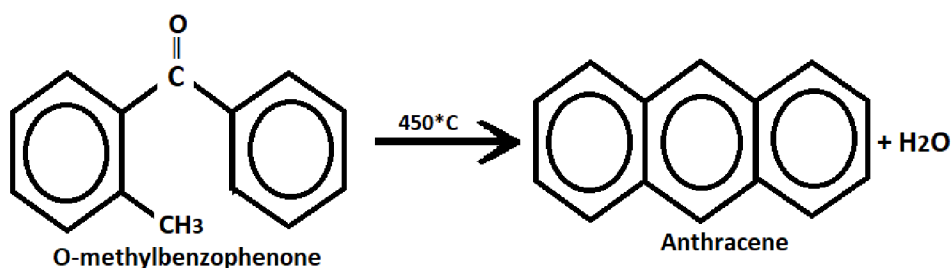
### Preparation of Anthracene:

**1. By Friedel craft reaction:-** Anthracene is prepared by condensation of two molecules of benzyl chloride in the presence of aluminum trichloride ( $AlCl_3$ ).



**2. By Haworth synthesis:-** This involves the treatment of benzene with phthalic anhydride in the presence of aluminum chloride to form *O*-benzoyl benzoic acid. Then *O*-benzoyl benzoic acid heated with concentrated sulphuric acid ( $H_2SO_4$ ) to give 9,10-anthraquinone. Note distillation of the anthraquinone with zinc dust yield anthracene.

**3. By Elb's reaction:-** The conversion of a di-aryl ketones containing a methyl or methylene group to the carbonyl function is known as the Elbs reaction.

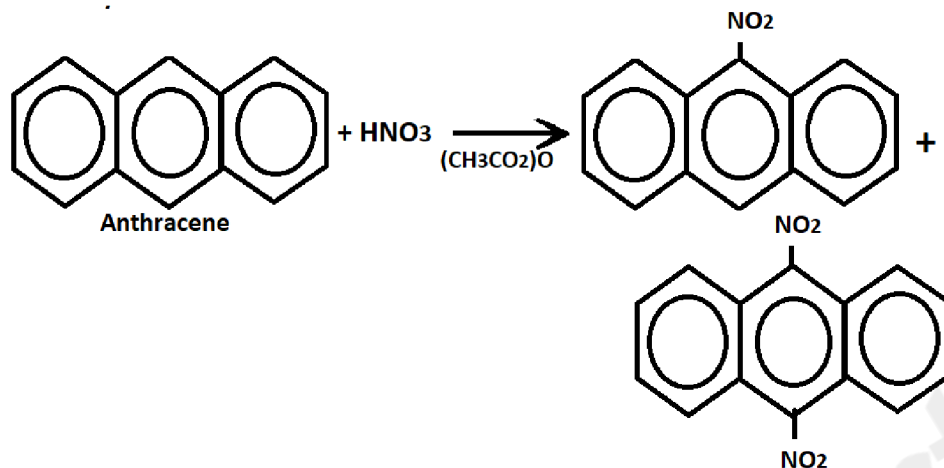


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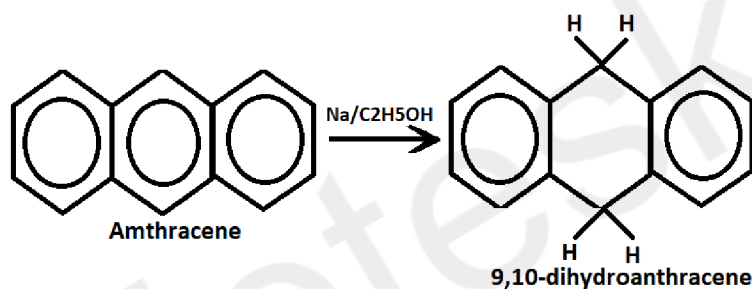
### Chemical reaction of anthracene

There are some important reactions of anthracene-

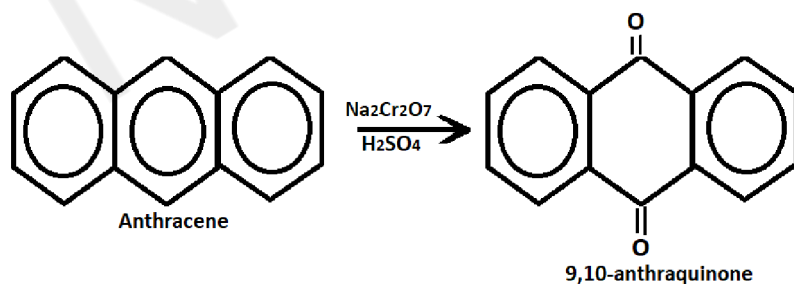
**1. Nitration:-** Anthracene react with concentrated nitric acid in acetic anhydride( $\text{H}_2\text{SO}_4$  not used here) at room temperature to yield a mixture of 9-nitroanthracene and 9,10-dinitroanthracene.



**2. Reduction:-** Anthracene undergoes reduction with sodium and ethyl alcohol to form 9,10-dihydroanthracene.



**3. Oxidation:-** Anthracene undergoes oxidation with sodium dichromate and sulfuric acid to form 9,10-dioxoanthracene.



### Physical properties of anthracene

- It is colorless solid.
- It has melting point of  $218^\circ\text{C}$ .
- It has a boiling point of  $340^\circ\text{C}$ .
- Insoluble in water and soluble in benzene.
- Chemical formula is  $\text{C}_{14}\text{H}_{10}$ .

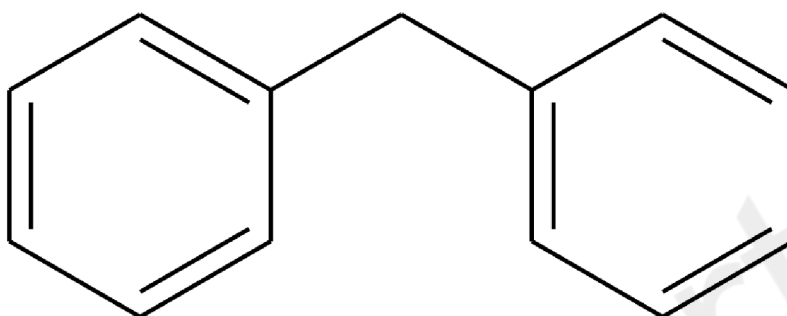


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### Uses of anthracene

- Used in the manufacture of alizarin and several other dyes.
- Used as a preservative in wood
- Used as an insecticide for crops
- Also used in anti-cancer agent.
- It is used as scintillator.

### Diphenylmethane:

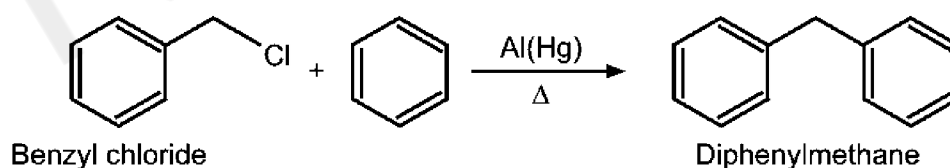


- Diphenylmethane is an organic compound with molecular formula  $(C_6H_5)_2CH_2$
- The compound contain methane and 2-phenyl ring the diphenyl methane group is also known as benzhydryl.
- Diphenylmethane can be prepared by Friedel crafts acylation of benzyl chloride with benzyne in presence of  $AlCl_3$ .

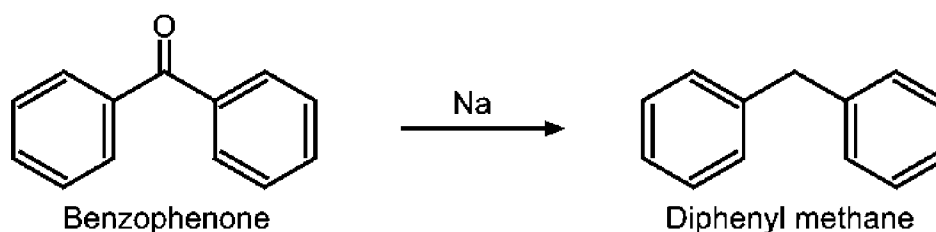


### Synthesis of Diphenylmethane:

1) Diphenylmethane can be synthesized by Friedel Crafts' alkylation of benzyl chloride with benzene in presence of amalgamated aluminum turning.



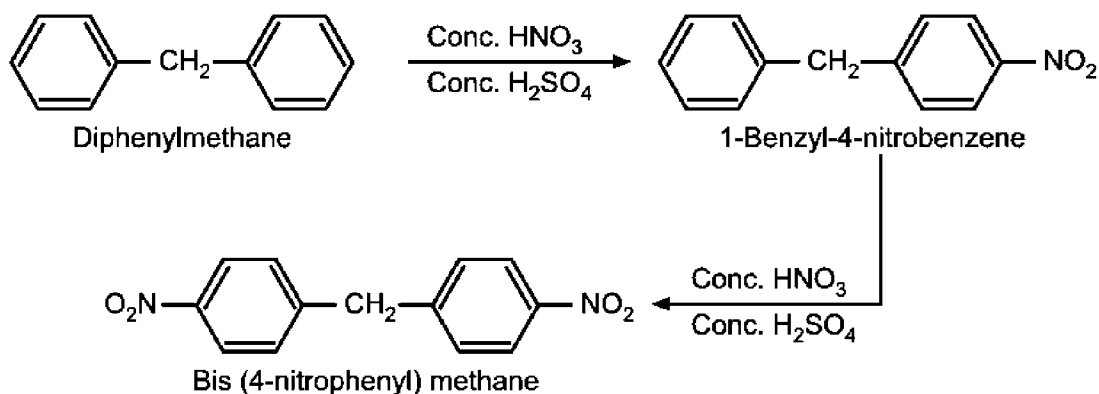
2) Diphenylmethane can be synthesized by reduction of benzophenone using metallic sodium.



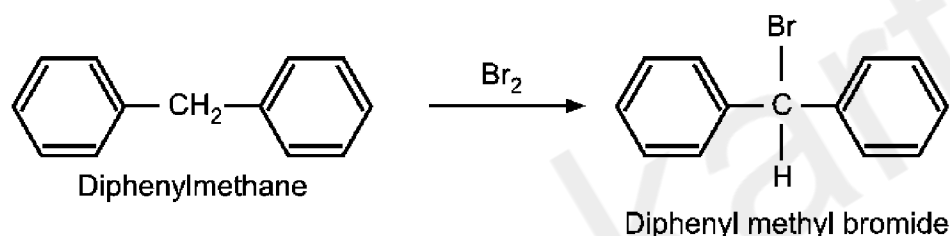
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### Chemical reactions of Diphenylmethane:

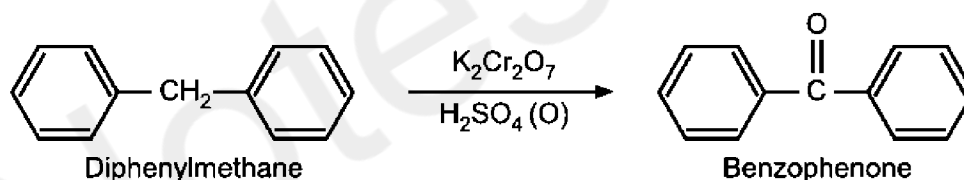
(i) **Nitration:** It undergoes nitration when heated with conc.  $\text{HNO}_3$ /conc.  $\text{H}_2\text{SO}_4$ , mixture.



(ii) **Halogenation:** When treated with liquid bromine, it undergoes bromination at methane carbon.



(iii) **Oxidation:** Upon oxidation, diphenylmethane gives benzophenone.



#### Uses:

- It is used in the preparation of polymerization initiator diphenyl methyl potassium.
- It is also used as masking agent in cosmetic preparation.
- They are also used as surface active agent.

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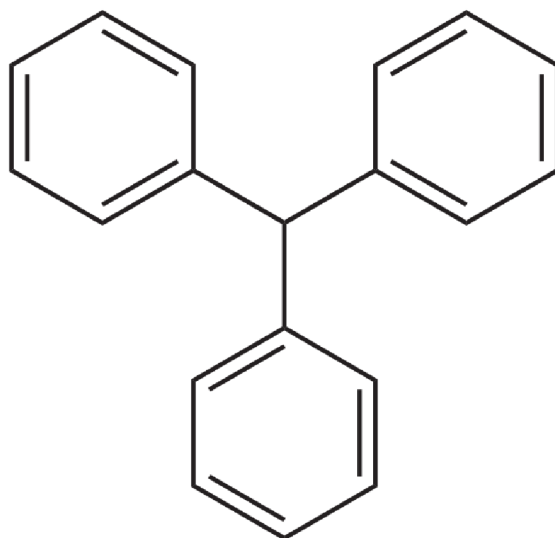
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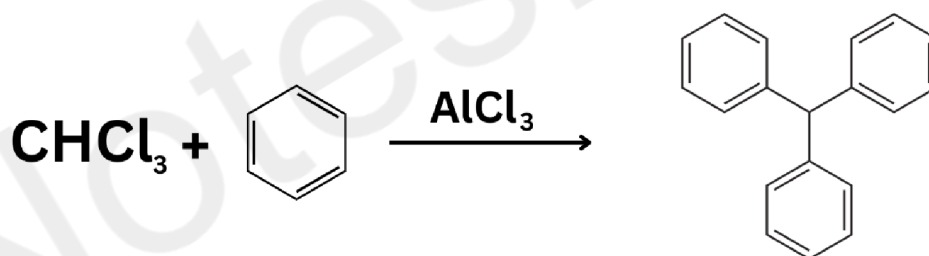
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### Triphenylmethane:

Structure:



- Triphenylmethane is the polynuclear hydrocarbon with the formula  $C_{19}H_{16}$ .
- This is colorless solid, which is insoluble in water.
- This can be prepared by reaction between benzene and trichloromethane in presence of  $AlCl_3$  to form tri-phenyl methane.



Uses:

- Triphenylmethane is the basic skeleton of many synthetic dyes called tri-aryl methane dye.
- These dyes are used as pH indicator and some.
- They are used as antiseptic and antibiotic in skin disease.

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