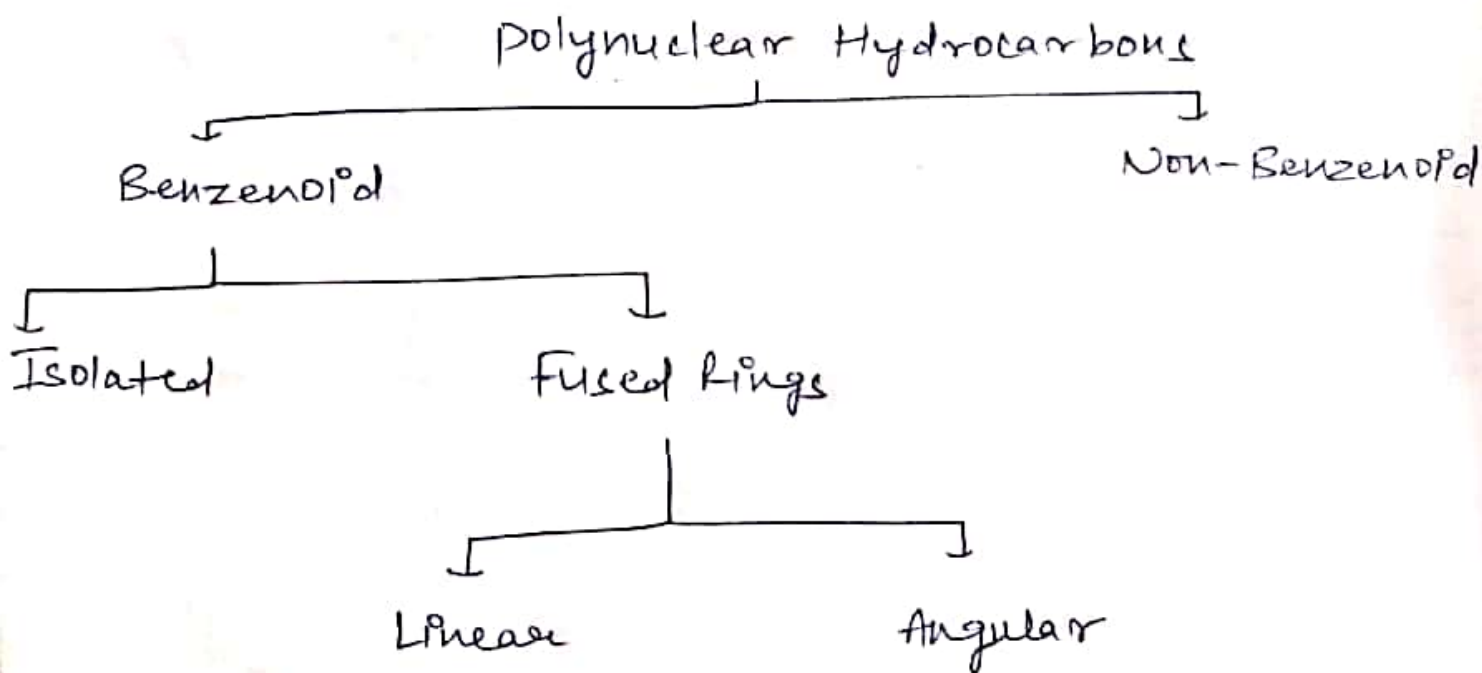


## UNIT-4

### Polynuclear Aromatic Hydrocarbons:-

A chemical compound containing Carbon and Hydrogen only and is composed of multiple Aromatic Rings.

### Classification of polynuclear Compounds:-



### A) Benzenoid polynuclear Hydrocarbons:-

- Hydrocarbons that contains benzene ring and follow the Huckel rule  $(4n+2)\pi$  electrons.

They are of 2 types:-

- 1) Isolated polynuclear compounds:- These compounds are isolated but are directly attached.

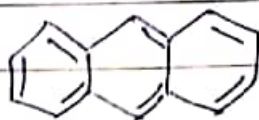
eg Diphenyl



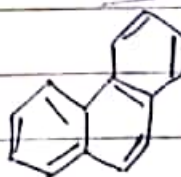
- 2) Fused polynuclear compounds:- In these compounds 2 or more than 2 rings are fused together.

eg Anthracene

Anthracene



Phenanthrene



### B) Non-Benzenoid polynuclear Hydrocarbons:-

The compounds which doesn't follow the Huckel rule  $(4n+2)\pi$  electrons.

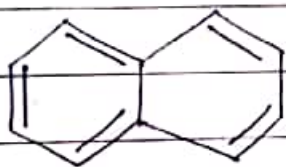
eg Azulene.

Teacher's Signature : \_\_\_\_\_

## Methods of preparation and rxns:-

### i) Naphthalene:-

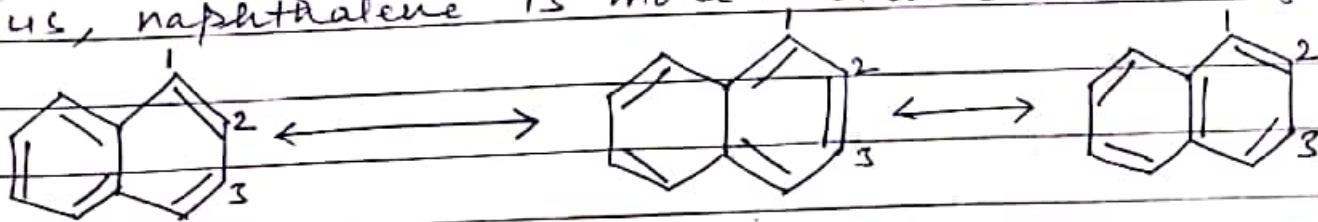
- Naphthalene is an organic compound with formula  $C_{10}H_8$ .
- It is the simplest polycyclic aromatic hydrocarbon, and is a white crystalline solid with a characteristic odour that is detectable at concentration 0.08 ppm by mass.



### Structure:-

Naphthalene exhibits resonance in its 3 Canonical forms. Thus, there is delocalization of  $\pi$  electrons, which decreases the electronic energy.

The resonance energy of naphthalene is 61 kcal/mole, which is less than twice of benzene (36 kcal/mole). Thus, naphthalene is more reactive than benzene.



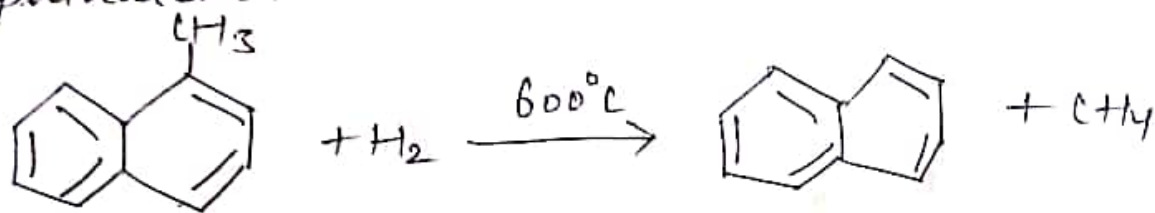


## Methods of preparation:-

### 1) From ~~pre~~ petroleum:-

Naphthalene is ~~also~~ prepared industrially from suitable petroleum fractions which on passing over a heated copper catalyst at  $680^{\circ}\text{C}$  give naphthalene and methyl naphthalenes.

Methyl naphthalenes are dealkylated by heating at about  $600^{\circ}\text{C}$  in the presence of  $\text{H}_2$  to give naphthalene.



1-methylnaphthalene

Naphthalene

### 2) Howarth synthesis:-

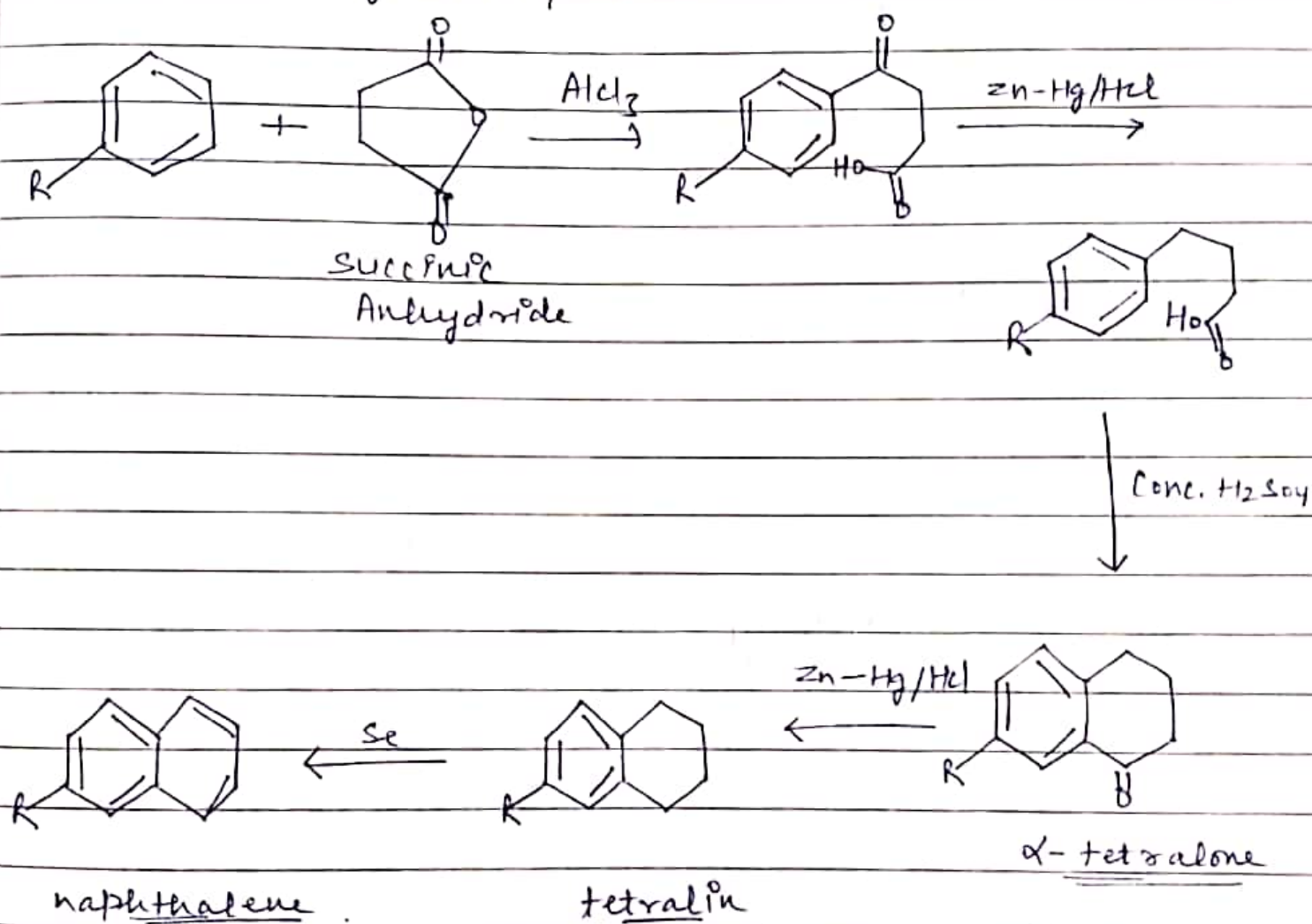
In this rxn, benzene is treated with Succinic Anhydride in the presence of  $\text{AlCl}_3$  to form  $\beta$ -benzoylpropionic Acid. This on Clemmensen Reduction gives gamma phenylbutyric Acid, which on heating with conc.  $\text{H}_2\text{SO}_4$  gives  $\alpha$ -tetralone by ring closure.  $\alpha$ -tetralone on Clemmensen reduction gives tetralin, which was heated with

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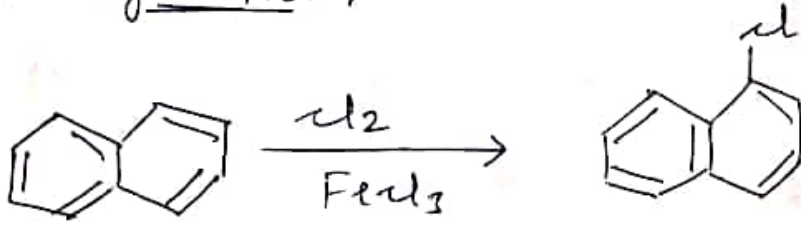
Page No. 5

selenium to give naphthalene.



Reactions:- \* Electrophilic Aromatic Rxn:-

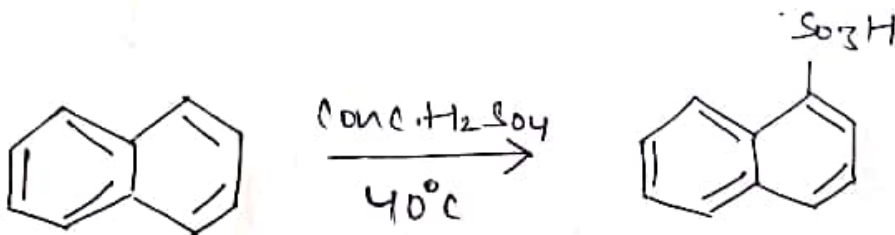
1) Halogenation:-



naphthalene

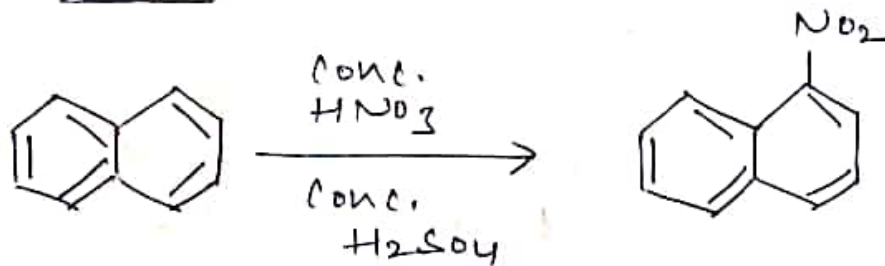
1-chloronaphthalene

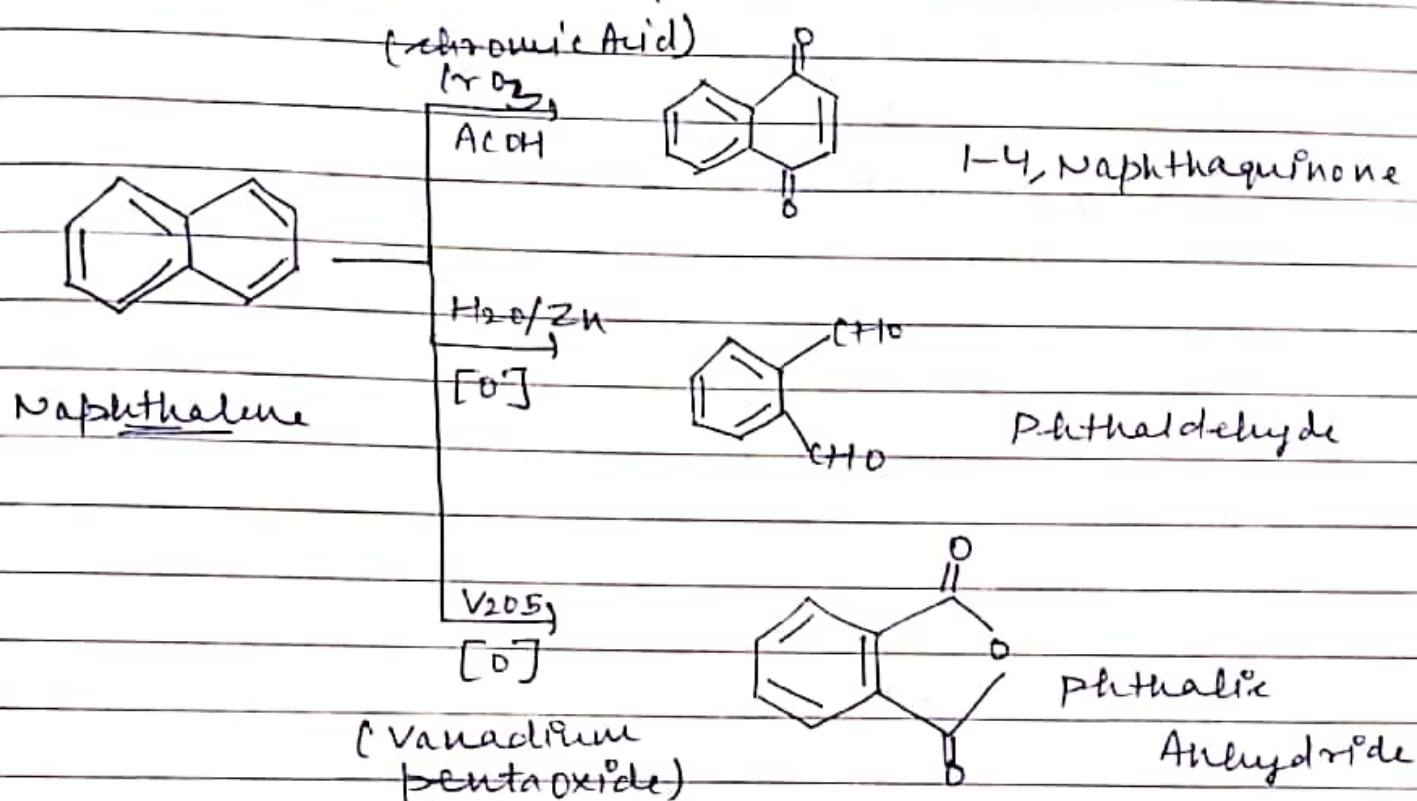
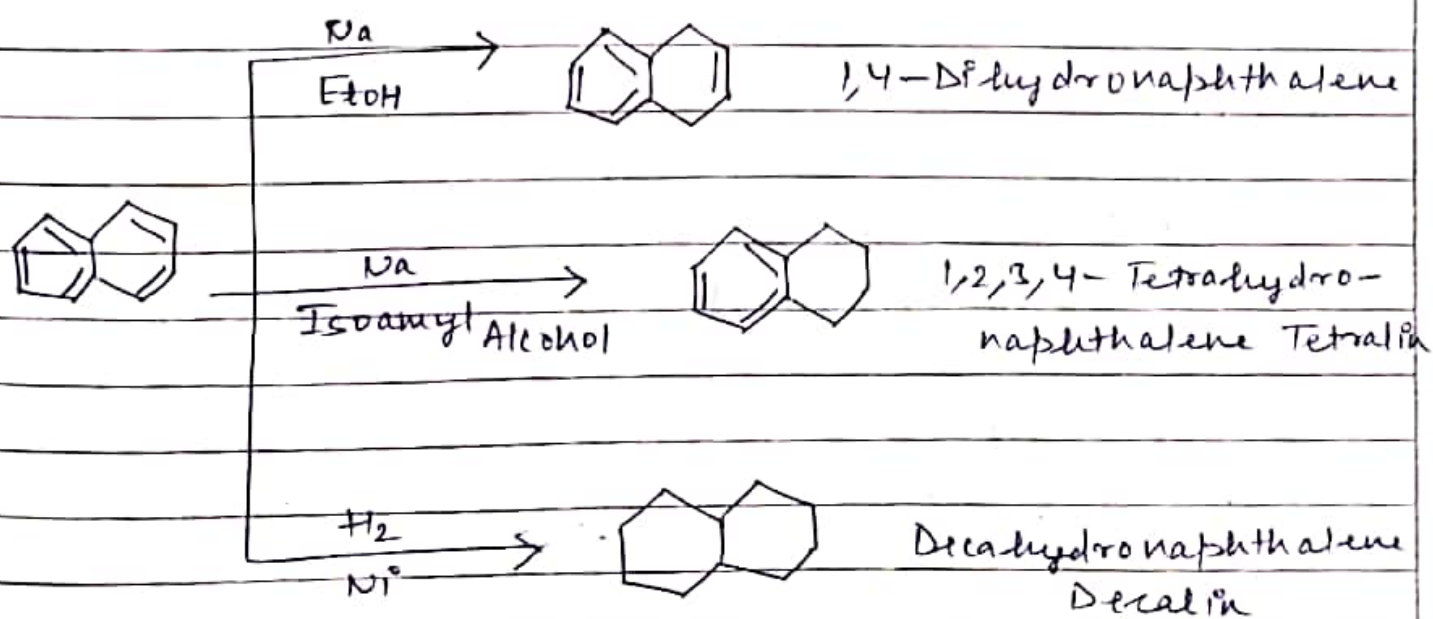
2) Sulfonation:-



Naphthalene -1-sulfonic acid

3) NO<sub>2</sub>ration:-



\* oxidation Rxn. of Naphthalene:-\* Reduction Rxns. of Naphthalene:-

Teacher's Signature : \_\_\_\_\_



\* Uses of Naphthalene:-

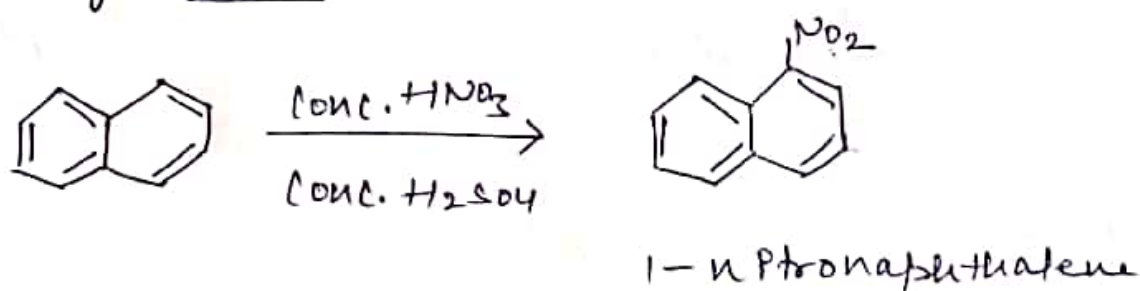
- 1) It is used as a moth-repellant, dyes and synthetic resin.
- 2) It is used in the manufacturing of  $\beta$ -naphthols (tanning Agent) and  $\alpha$ -naphthols (insecticides).

DERIVATIVES OF NAPHTHALENE:-

1) 1-Nitronaphthalene:-

Preparation:-

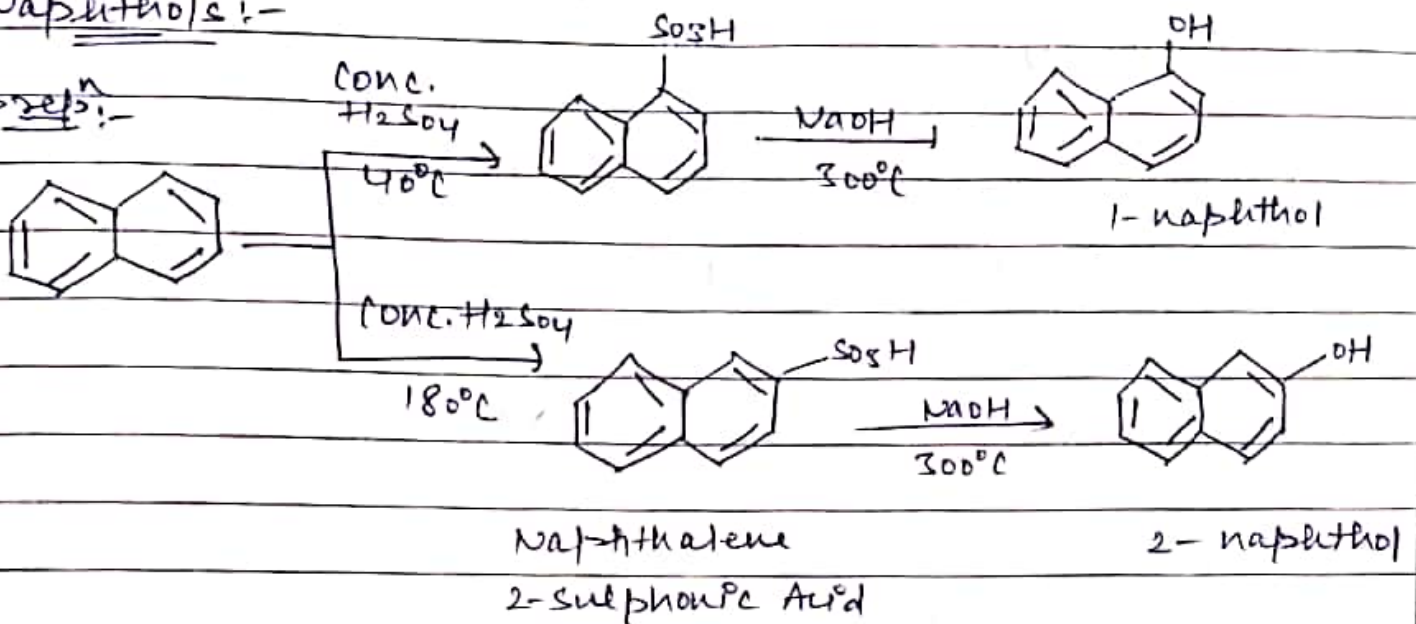
→ By nitration:-



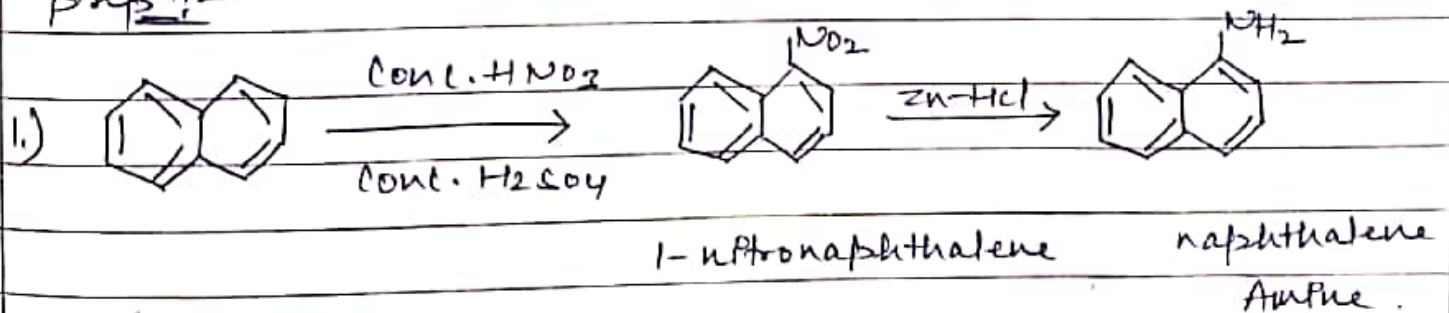
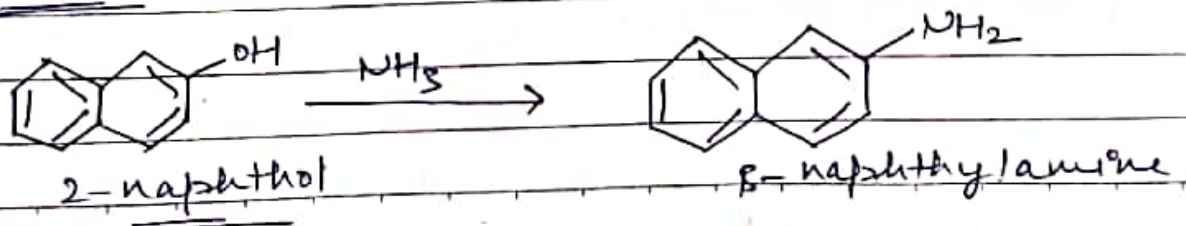
Uses:-

- 1) In production of dyes.
- 2) Used as industrial intermediate.



2) Naphthols:-Prep<sup>n</sup>:-

Uses:- 1) Naphthols are used as insecticides.  
 2) Also used in dyes and perfumery.

3) Naphthylamine:-Prep<sup>n</sup>:-2.) Bucherer Rxn:-

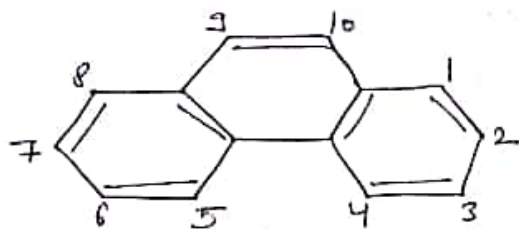
Teacher's Signature : \_\_\_\_\_

uses:- 1.) used in manufacturing of dyes.

## # ② PHENANTHRENE:-

phenanthrene is a polycyclic Aromatic Hydrocarbon composed of 3 fused benzene rings.

Structure:-



→ The three benzene rings are fused in Angular fashion.

## Synthesis of phenanthrene:-

1.) from coal-tar:- phenanthrene, along with

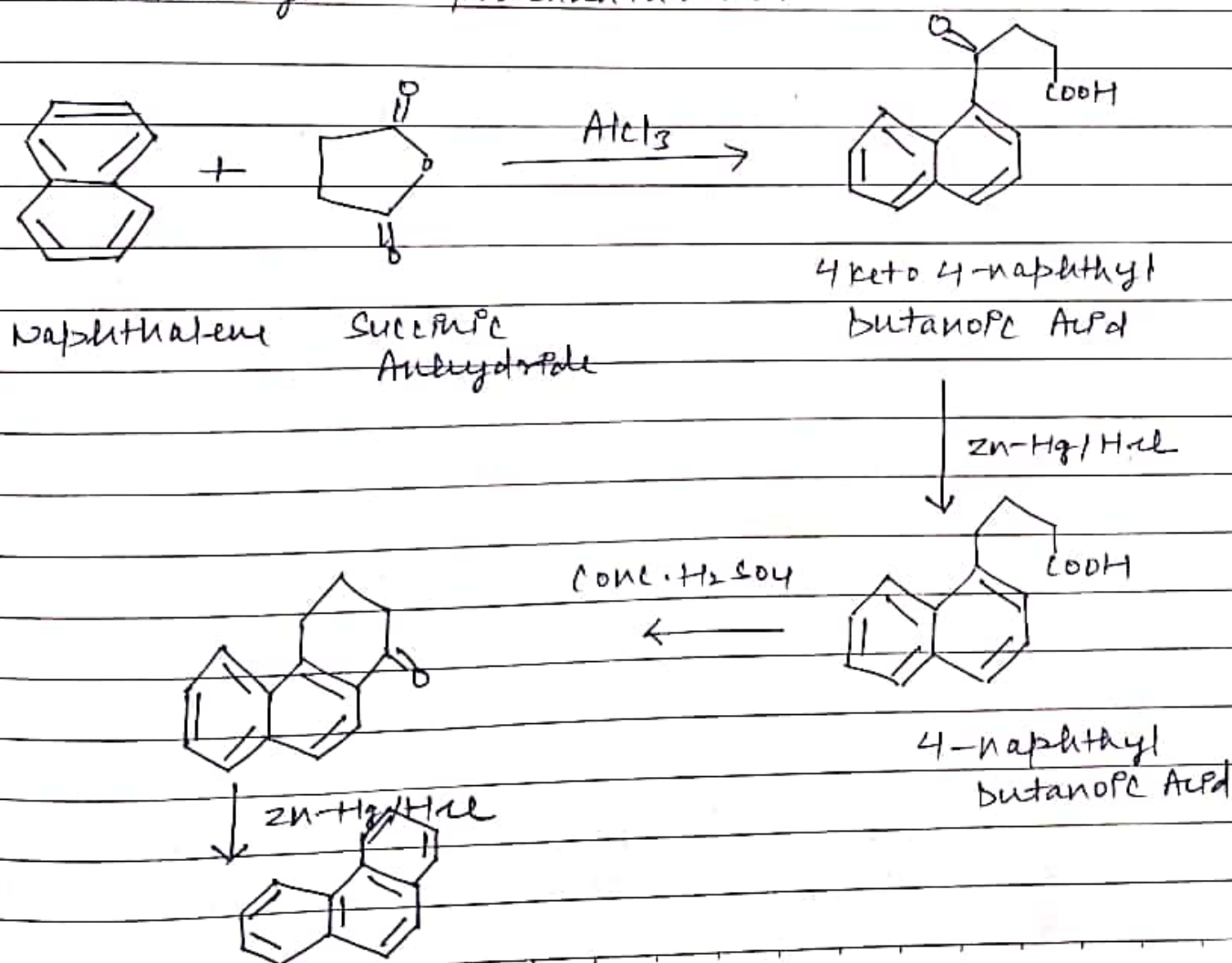
anthracene, occurs in the green oil fraction of coal tar.

On cooling the oil, a solid mass crystallises out. It contains Anthracene & phenanthrene. These crystals are treated with solvent naphtha when phenanthrene goes into solution. Evaporation of this solution yields phenanthrene.

2.) Haworth synthesis:-

In the 1<sup>st</sup> step naphthalene is treated with succinic Anhydride in the presence of Aluminium chloride, which gives 4-keto, 4-naphthyl, butanoic Acid.

In the next step it is reduced to 4-naphthyl butanoic Acid in the presence of reducing agents (Zn-Hg/HCl). Then on Acid catalysed cyclisation, it gives 4-keto-1,2,3,4-tetrahydronaphthalene, which on Clemmensen reduction gives phenanthrene.

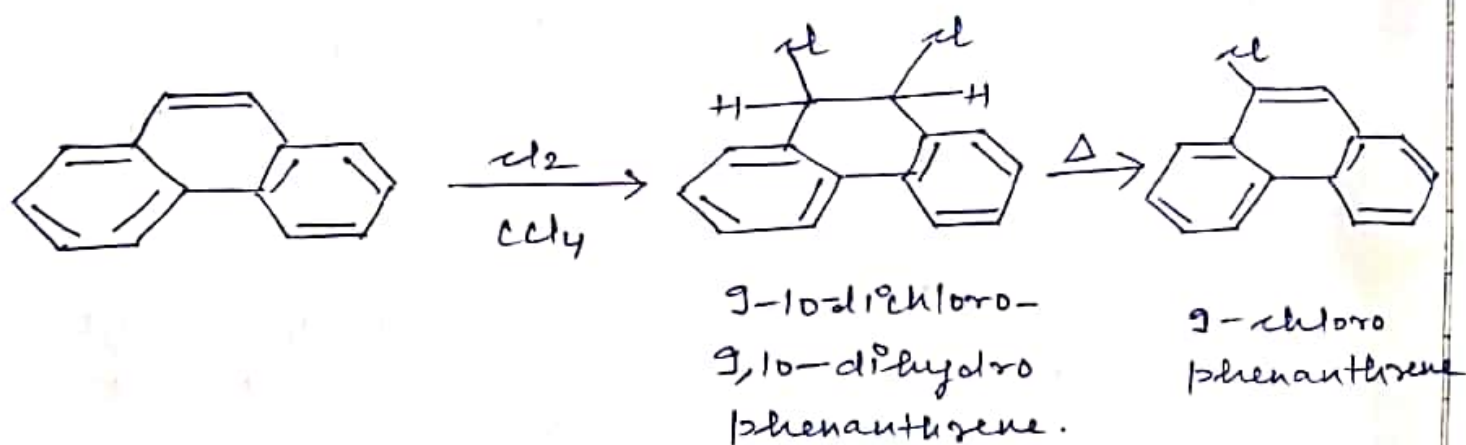


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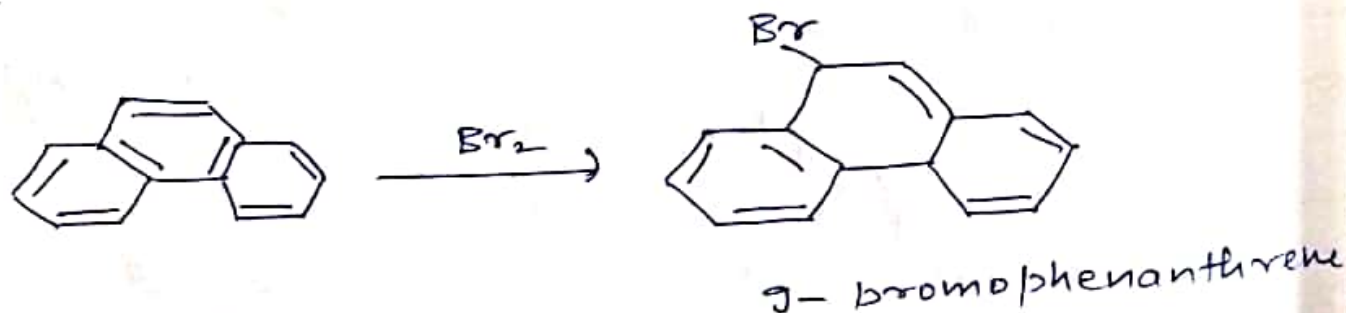


## Rxns. of phenanthrene:-

- 1) Halogenation:- phenanthrene reacts with halogen (Cl, Br, I) in  $CCl_4$  to give 9,10-dichloro-9,10-dihydrophenanthrene.

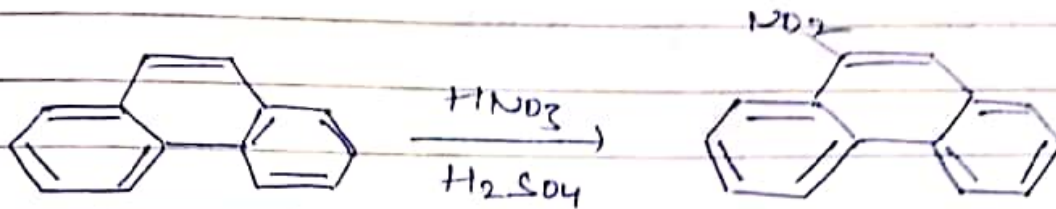


- 2) Bromination:- Bromination of phenanthrene is carried out by bromine in the presence of ferric salt to give 9-bromophenanthrene.



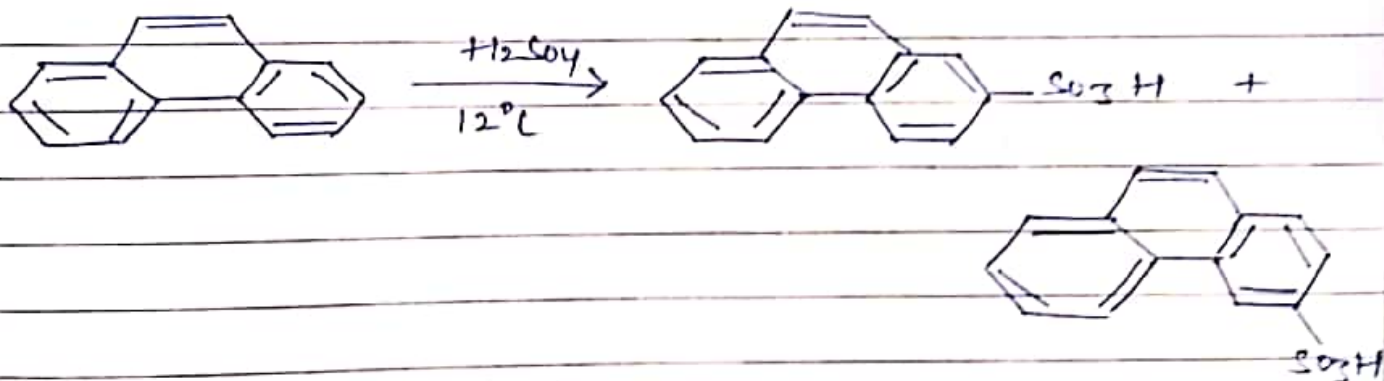


- 3) Nitration:- phenanthrene undergoes nitration with nitrating mixture to give 9-nitrophenanthrene.

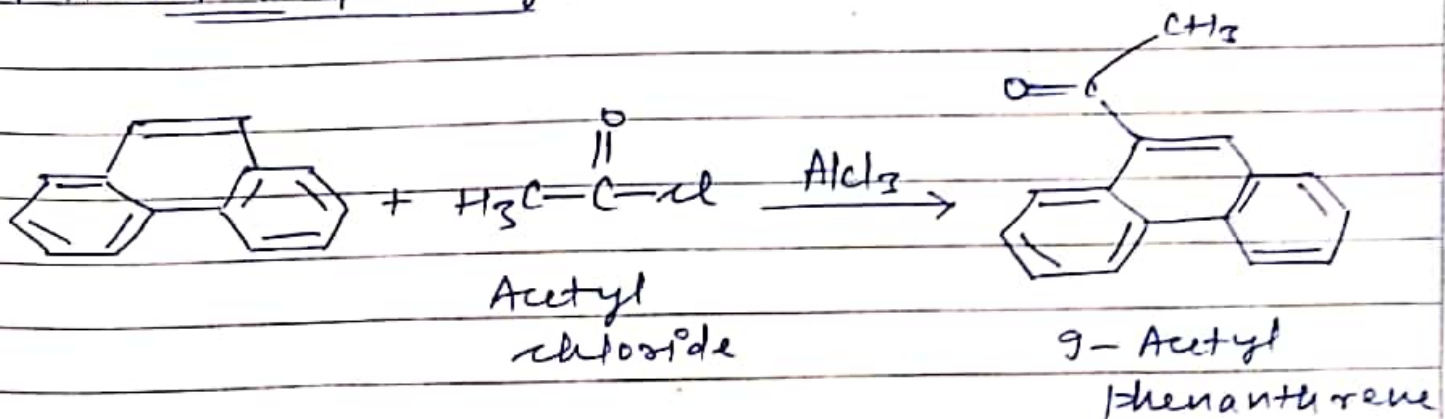


9-Nitrophenanthrene

- 4) Sulphonation:- phenanthrene reacts with  $H_2SO_4$  at  $120^\circ C$  to give a mixture of 2-phenanthrene sulphononic Acid and 3-phenanthrene sulphononic Acid.



- 5) Friedel Craft Acylation:-



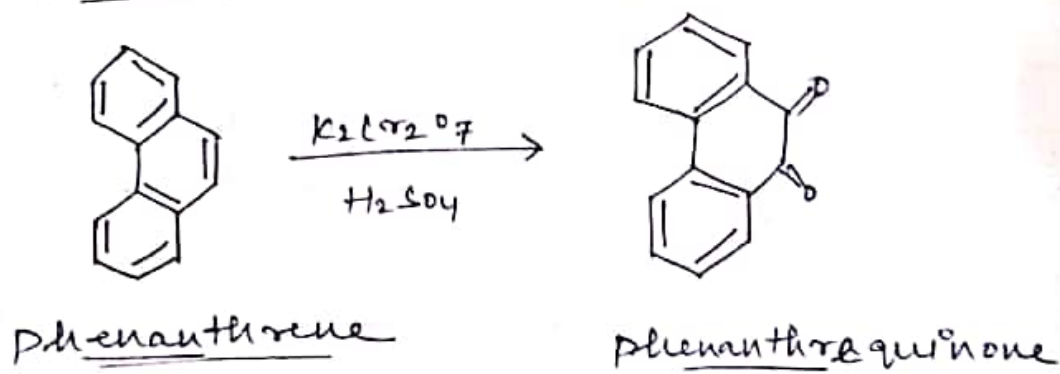
Teacher's Signature : \_\_\_\_\_

## Uses of phenanthrene :-

- 1) It is used in the preparation of phenanthraquinone, synthetic resin, pesticides and preservatives.
- 2) It is also used as Antifogging Agent.
- 3) Also used to make steroids, Bile Acids and Sex Hormones.

## Derivatives of phenanthrene :-

1) phenanthraquinone :- By oxidation of phenanthrene.

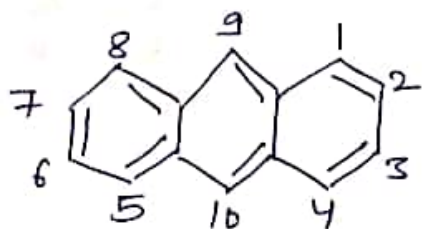


## Uses :-

- 1) used in synthesis of dyes, explosives, and drugs.
- 2) Also used in preservatives.

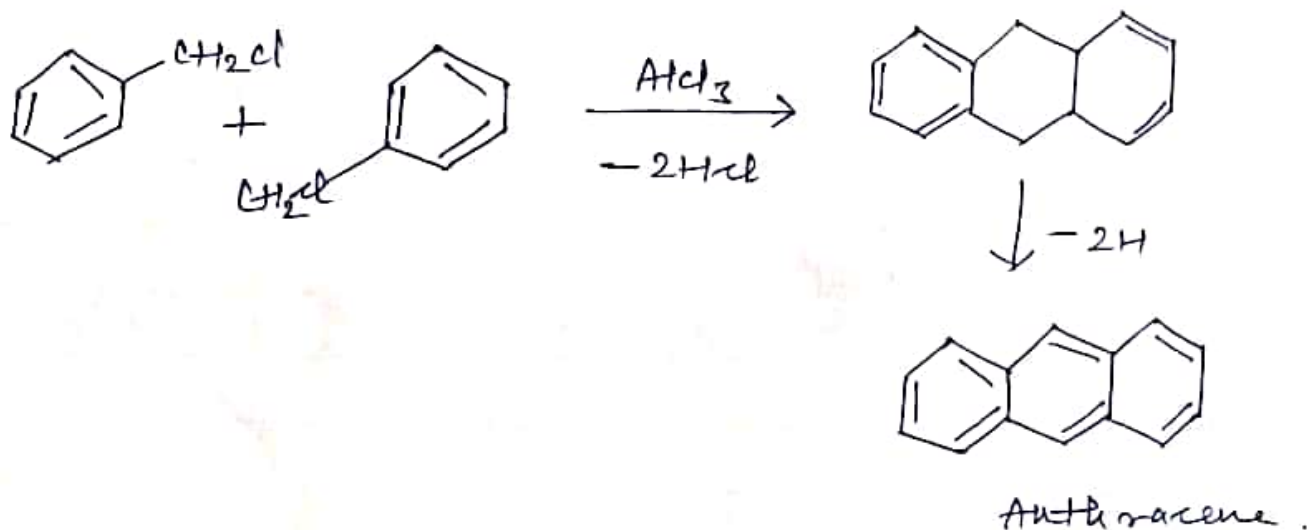
## # ⑤ Anthracene:-

It is a tricyclic system containing 3 benzene rings fused together in a linear pattern.



### Synthesis:-

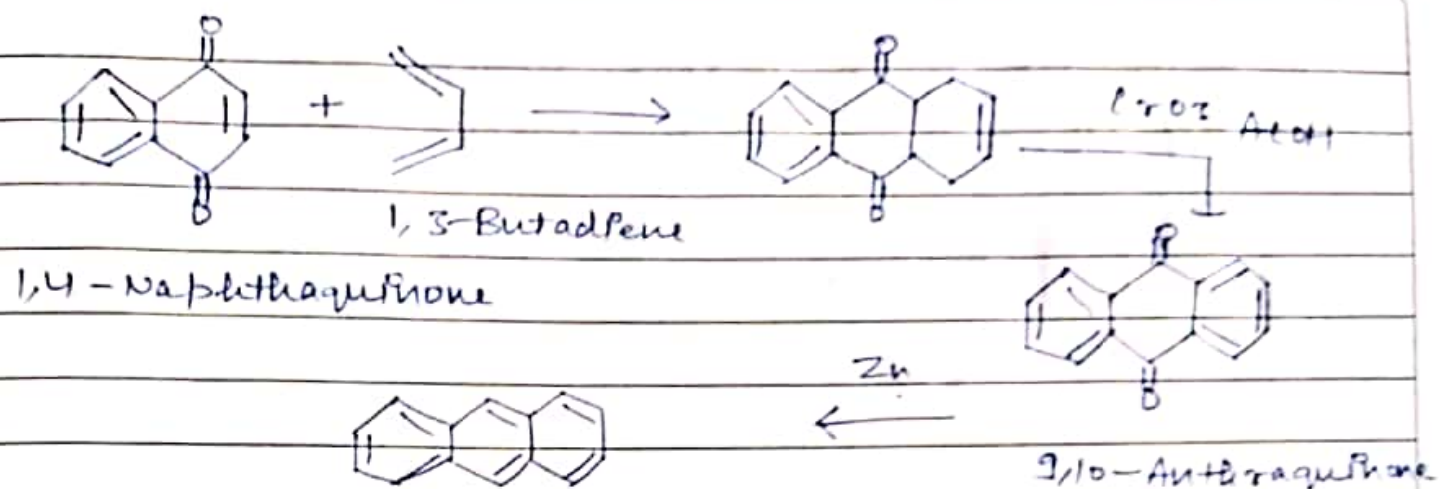
1) By Friedel-Craft's Rxn:- Anthracene is synthesized from benzyl chloride by Friedel-Craft's rxn.



2) By Diels-Alder rxn:-

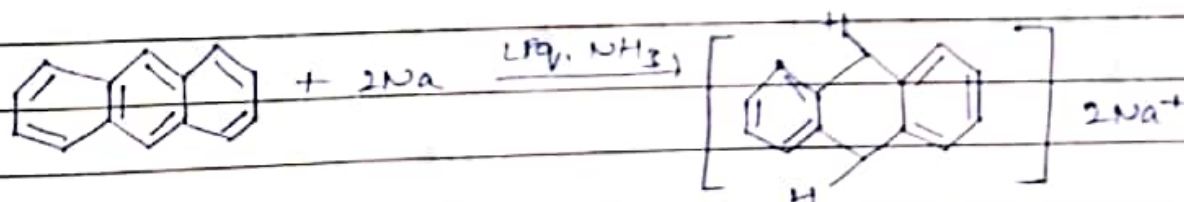
Anthracene is also synthesized from 1,4-naphthoquinone by Diels-Alder rxn.



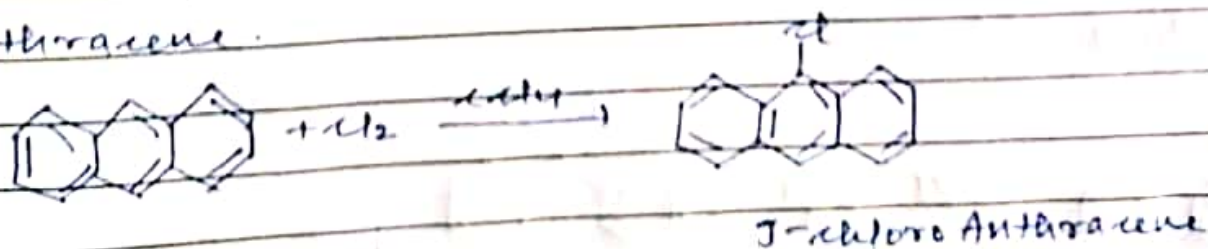


### CHEMICAL RXNS:-

- 1) Reaction with sodium:- Anthracene is treated with metallic sodium in liquid ammonia, gives deep blue 9,10-disodiumanthracene.



- 2) Halogenation rxn:- Anthracene reacts with chlorine in the presence of catalytic  $\text{FeCl}_3$  to give 9-chloro Anthracene.

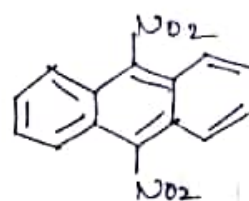
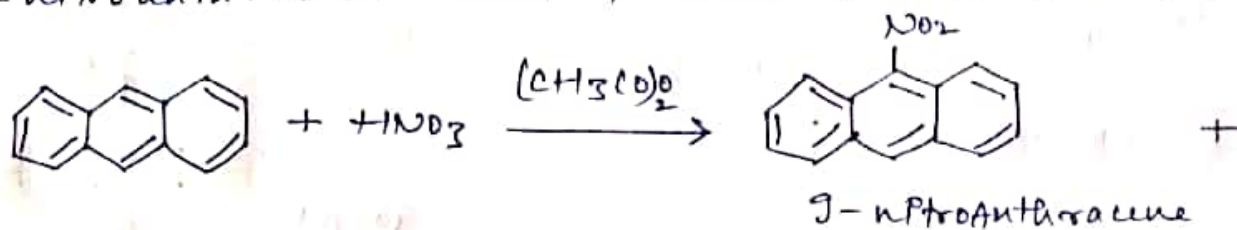


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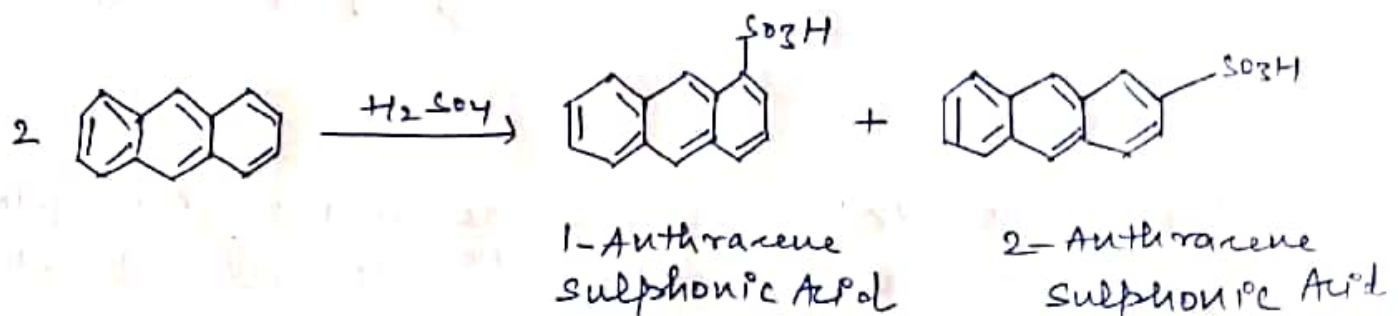
### 3) Nitration:-

Anthracene is treated with  $\text{HNO}_3$  in the presence of Acetic Anhydride to give a mixture of 9-nitroanthracene and 9,10-dinitroanthracene.

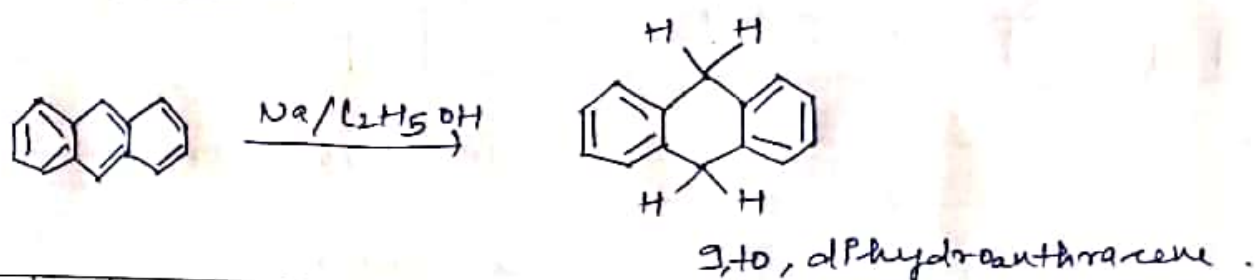


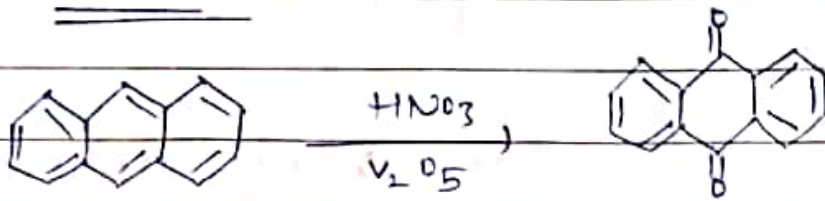
9,10-dinitroanthracene

4) Sulphonation:- Anthracene undergoes sulphonation with concentrated  $\text{H}_2\text{SO}_4$  to give a mixture of 1-Anthracene sulphonic Acid and 2-Anthracene sulphonic Acid.



### 5) Reduction rxn:-



c) Oxidation Rxn:-

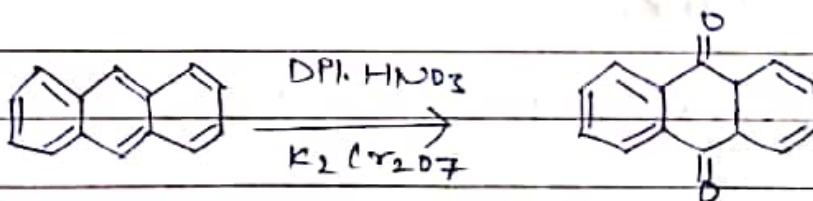
9,10-Anthraquinone

USES:-

- i) In manufacturing of Anthraquinone dyes (Alizarin) and in smoke screens.

Derivatives:-

- i) Anthraquinone:-

Preparation:-

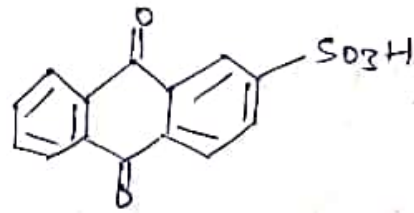
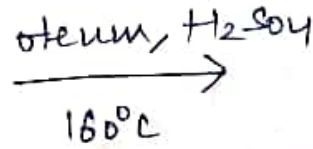
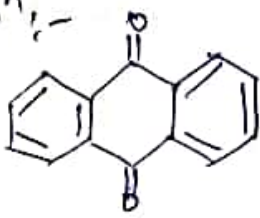
9,10-Anthraquinone .

USES:- i) Anthraquinone is used in the manufacturing of Alizarine and several other dyes.

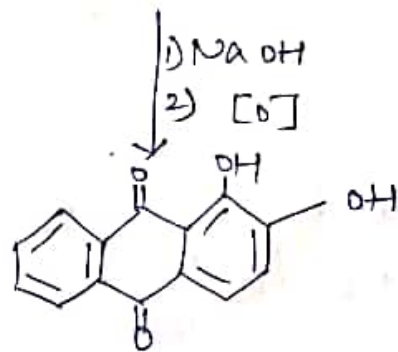
Teacher's Signature \_\_\_\_\_

## 2) Alizarine:-

Prep<sup>n</sup>:-



9,10-Anthraquinone - 2-sulphonic  
Acid

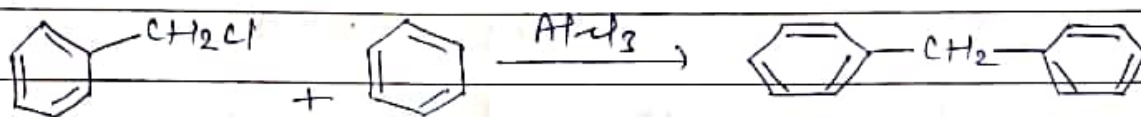


Alizarine

Uses:-

1) Used as a mordant dye.

2) It is also used for dyeing wool by blue colour.

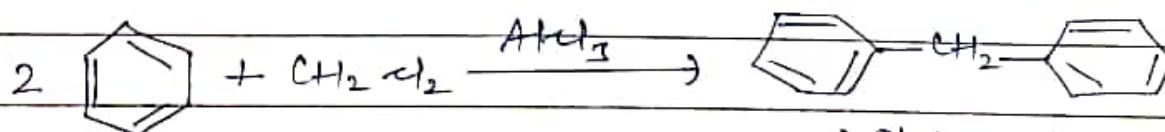
# (4) Diphenyl methane :-Preparation :-(p) Friedel-Craft's Rxn :-

Benzyl chloride

Diphenyl methane

(ii) From benzene :-~~Reaction~~

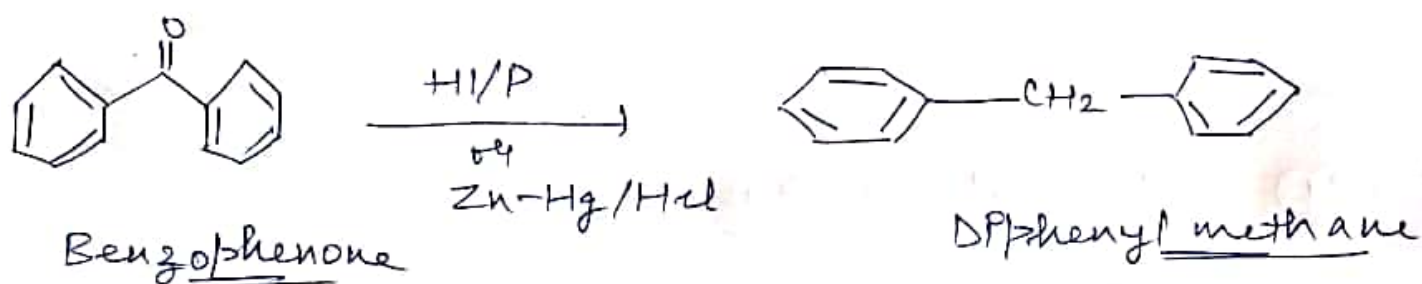
Diphenyl methane is prepared from benzene and dichloroethane in the presence of  $AlCl_3$ .



Diphenyl methane

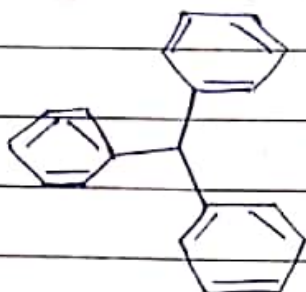
(iii) From benzophenone :- Diphenyl methane is prepared from benzophenone, which is reduced to diphenyl methane in the presence of red hot phosphorous and hydriodic acid.





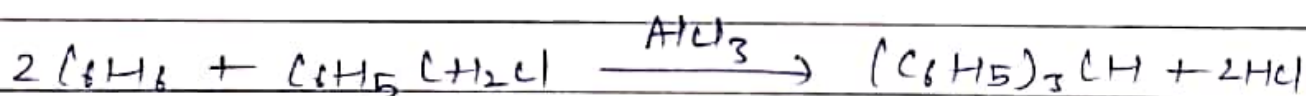
Uses:-

- 1) It is used in the preparation of various polymers, dyes, steroids, Benzophenone and diphenyl carbinol.

# TRIPHENYL METHANE :-

Preparation :-

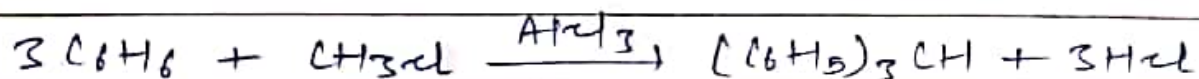
1) Friedel-Craft's method :-



Benzyl chloride

Triphenyl  
methane

2) The condensation between benzene and chloroform gives triphenyl methane.



Triphenyl methane

~~Triphenyl~~

USES:-

- 1) Triphenyl methane is used in the preparation of various dyes like malachite green, crystal violet and other dyes.