UNIT IV

POLYNUCLEAR HYDROCARBONS

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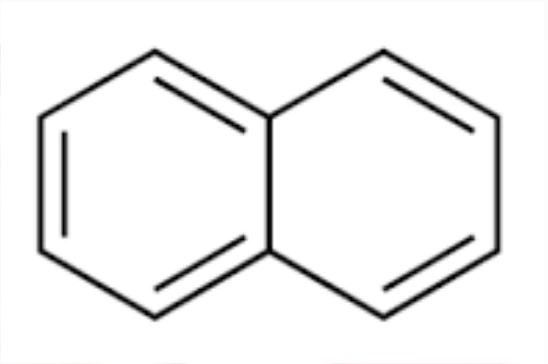
POLYNUCLEAR HYDROCARBONS

- Polynuclear aromatic hydrocarbon is a hydrocarbon made up of fused aromatic ring molecules. These rings share one or more sides and contain delocalized electrons. Another way to consider PAHs is molecules made by fusing two or more benzene rings.
- Polynuclear aromatic hydrocarbon molecules contain only carbon and hydrogen atoms.
- **Also Known As:** PAH, polycyclic aromatic hydrocarbon, polyaromatic hydrocarbon

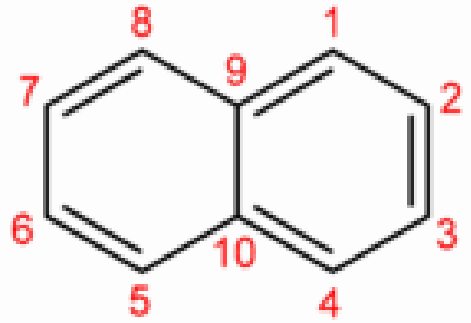
NAPHTHALENE



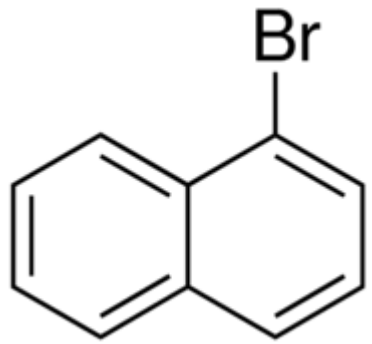
- **Naphthalene** is an organic compound with formula $C_{10}H_8$. It is the simplest polycyclic aromatic hydrocarbon.
- As an aromatic hydrocarbon, naphthalene's structure consists of a fused pair of benzene rings.
- A naphthalene molecule can be viewed as the fusion of a pair of benzene rings
- It is best known as the main ingredient of traditional mothballs.

Nomenclature

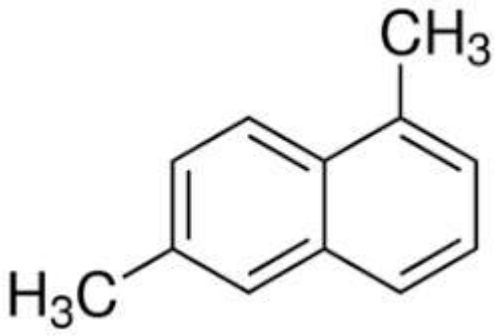
- For naming, following numbering system is used.
- Numbers selected to denote the position of a substituent on the naphthalene rings should be as small as possible.
- An alternative system occasionally used when one substituent is present.
- This system uses the Greek letters α (alpha) and β (beta) to designate the two possible orientations of the single substituent.



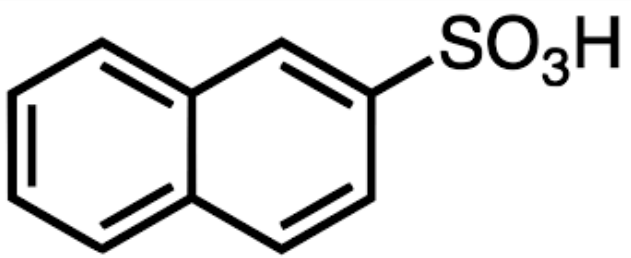
Naphthalene



1-Bromonaphthalene



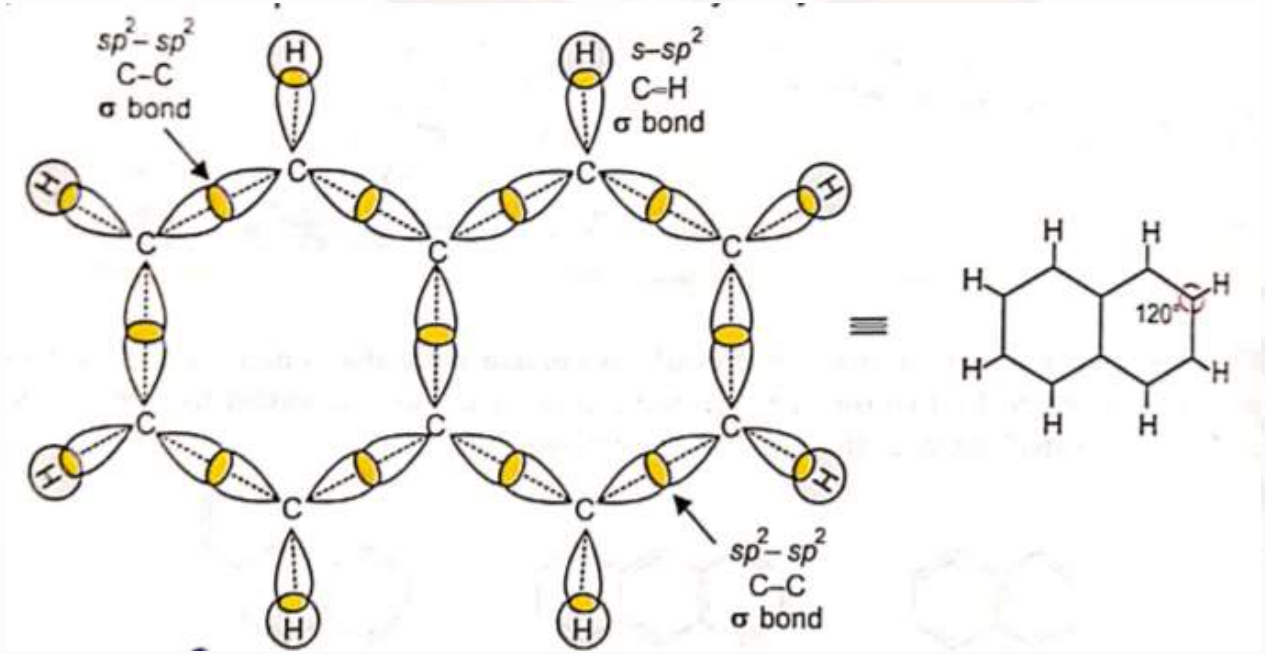
1,6-Dimethylnaphthalene



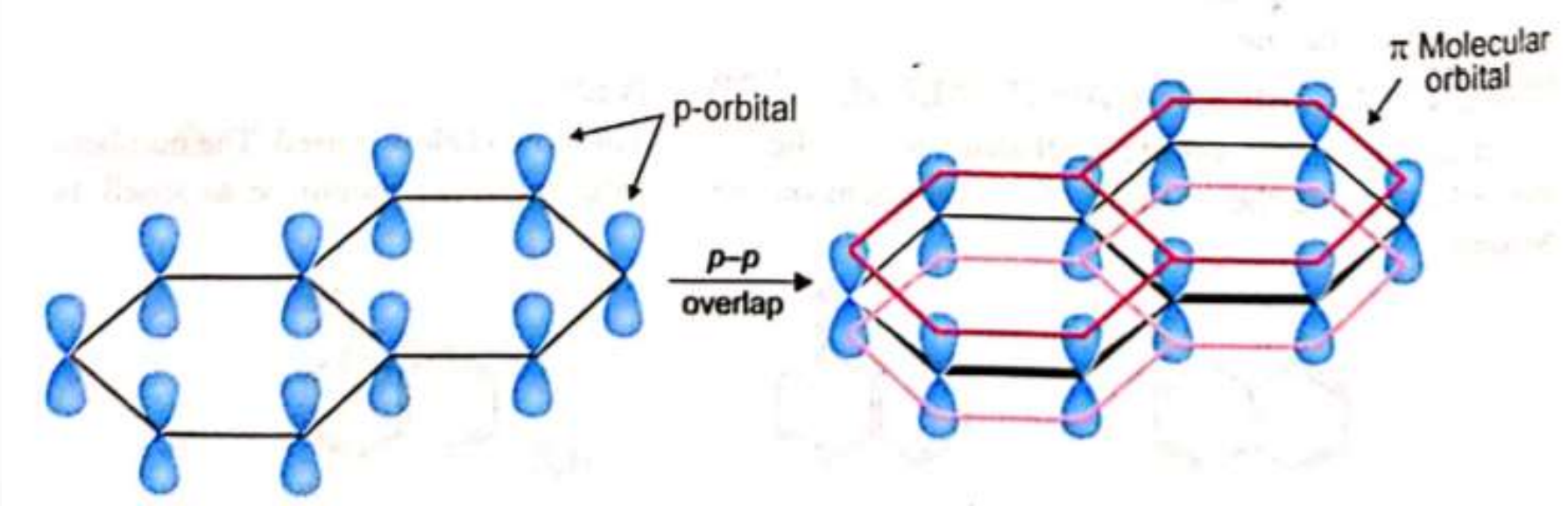
Naphthalene-2-sulphonic acid

Structure of naphthalene

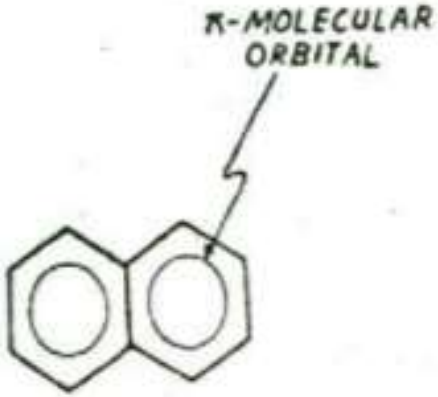
- All ten carbon atoms are sp^2 hybridized.
- The sp^2 hybrid orbitals overlap with each other and with s orbitals of the eight hydrogen atoms forming C-C and C-H σ bonds.
- Since the σ bonds result from the overlap of trigonal sp^2 orbitals, all C and H atoms lie in one plane.



- Each C atom in naphthalene also possesses an unhybridized p orbital containing one electron
- These p orbitals are perpendicular to the plane containing the σ bonds.
- The lateral overlap of the p orbitals produces a π molecular orbital containing ten electrons.
- One half of this π molecular orbital lies above and the other half lies below the plane of the bonds.
- Naphthalene shows aromatic properties because the resulting π molecular orbital satisfies the Huckel's rule (n=2, 4n+2).



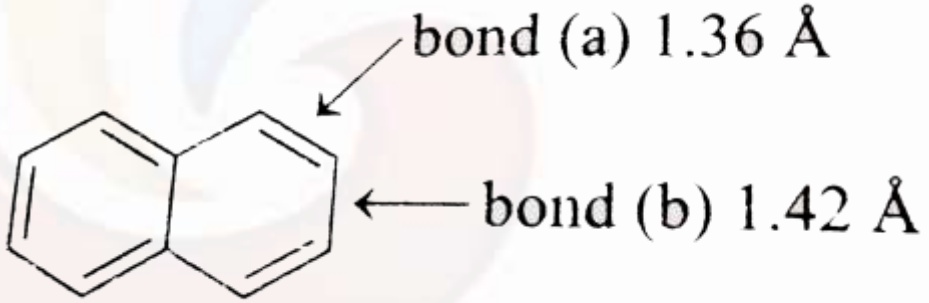
- A common shorthand representation of naphthalene is simply two fused hexagons with a circle inside each hexagon.
- The circle represent the π molecular orbital.



According to the resonance theory, naphthalene is considered to be a hybrid of the following *three* canonical forms.

Bond length

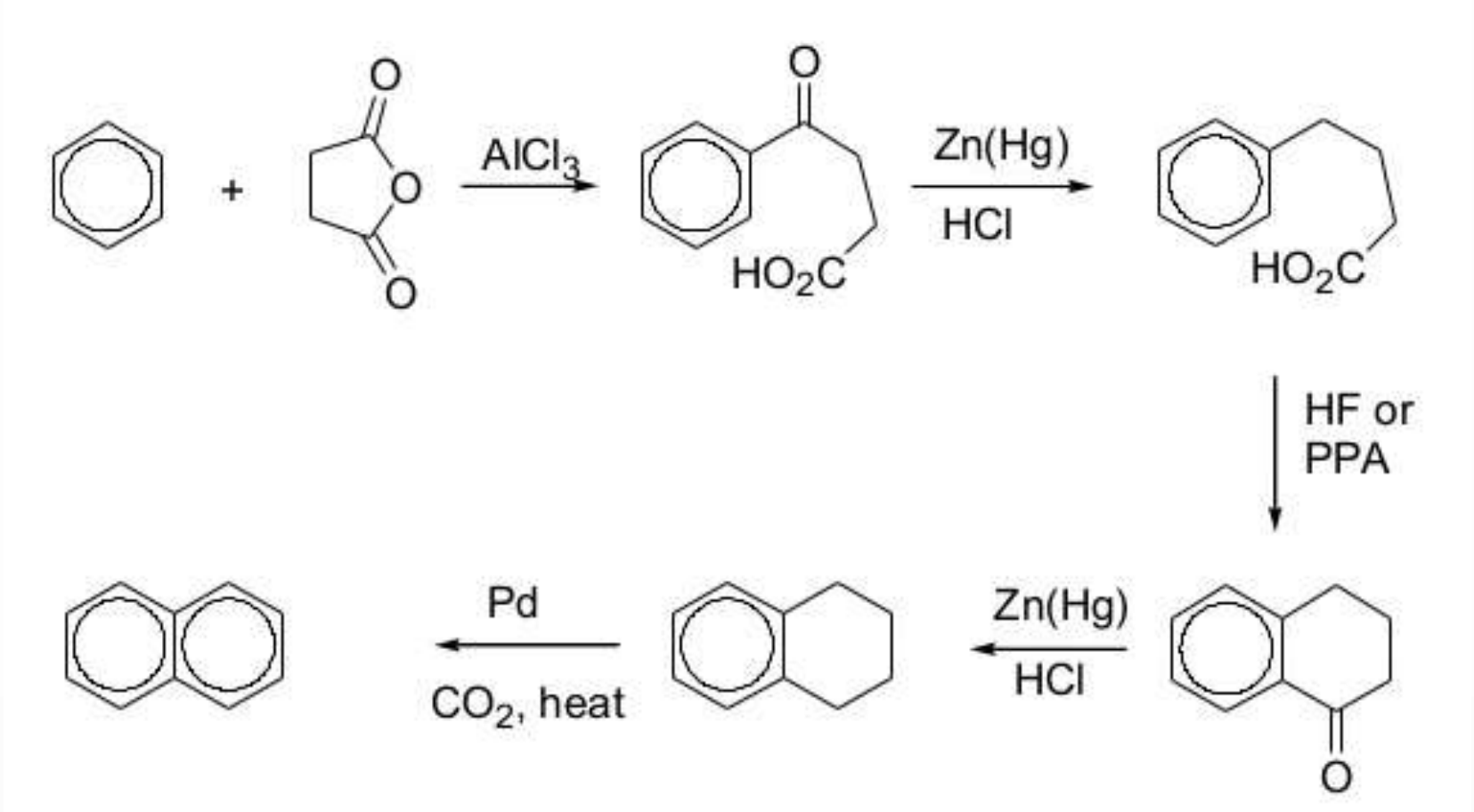
- Unlike benzene, the carbon–carbon bonds in naphthalene are not of the same length. The bonds C1−C2, C3−C4, C5−C6 and C7−C8 are about 1.37 Å (137 pm) in length, whereas the other carbon–carbon bonds are about 1.42 Å (142 pm) long.



- C1-C2 bond is double in two structure and single in only one; whereas the C2-C3 bond is single in two structures and double in only one.
- Thus, C1-C2 bond have more double-bond character and the C2-C3 bond have more single bond character.

Synthesis of naphthalene

1. Haworth synthesis



Synthesis of naphthalene

1. Haworth synthesis

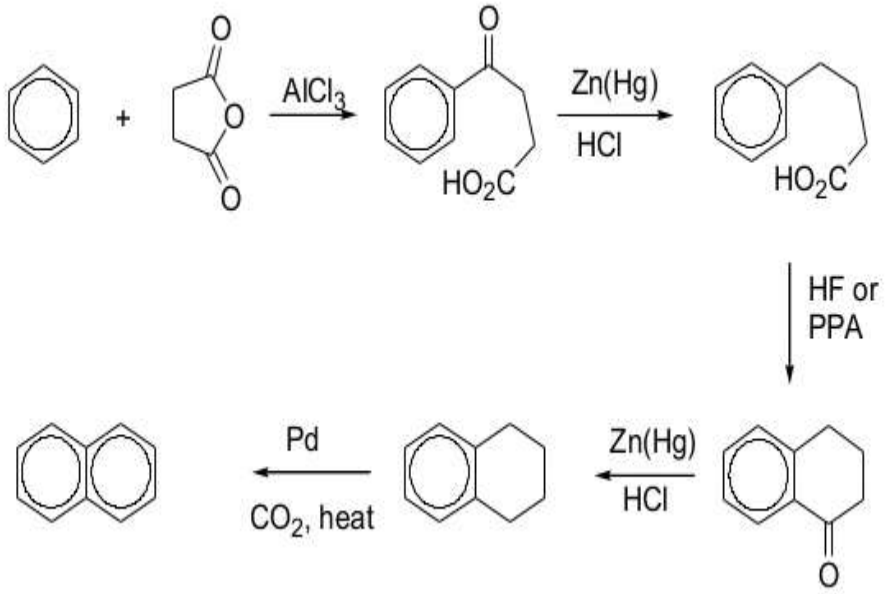
I. **Friedel-Crafts Acylation:** Reaction of benzene with succinic anhydride in presence of AlCl3 – 1-Benzoyl propanoic acid.

II. **Clemmensen Reduction:** Reaction of 1-Benzoyl propanoic acid with amalgamated zinc in presence of HCl – 4-Phenylbutanoic acid

III. **Ring-closure Reaction:** Heating 4-Phenylbutanoic acid with conc. Sulphuric acid or polyphosphoric acid - Tetralone.

IV. **Clemmensen Reduction:** Heating Tetralone with amalgamated zinc in presence of HCl – Tetralene.

V. **Aromatization:** Heating Tetralin with palladium – **NAPHTHALENE.**



Physical properties

- Naphthalene is a white crystalline solid.
- Have a characteristic ‘moth ball’ odor.
- Insoluble in water.
- Soluble in ether, benzene, hot ethanol.
- Sublimes readily when warmed and is volatile with steam.

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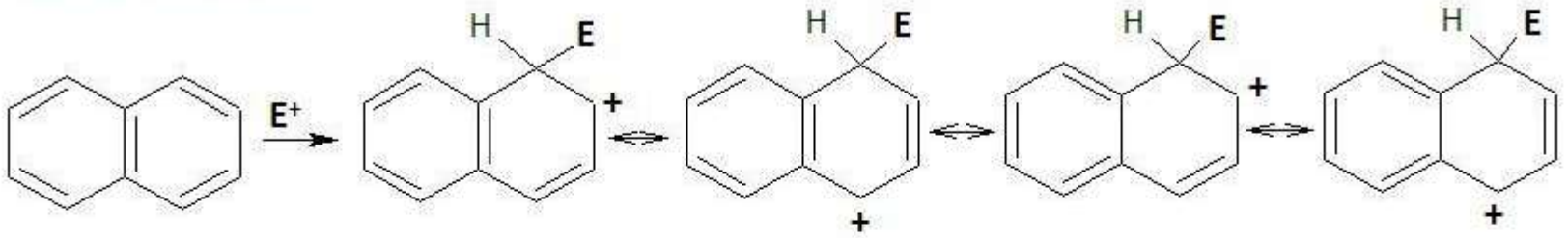
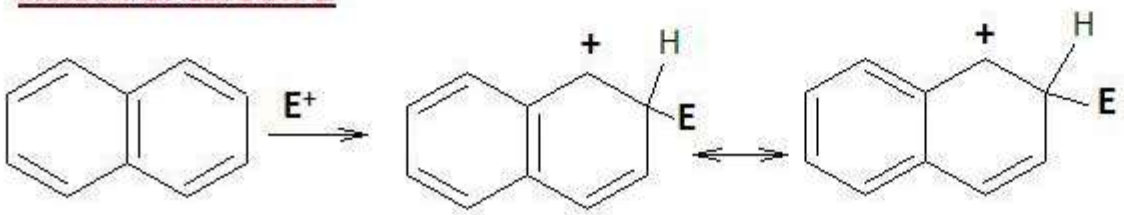
ELECTROPHILIC SUBSTITUTION REACTION

- Substitution occurs at C1 (α position).
- The carbonium ion obtained by attack of an electrophile (E) at C1 has four resonance forms making it more stable.
- The carbonium ion obtained by attack of an electrophile (E) at C2 has two resonance forms making it less stable. It takes place at higher temperature or when bulkier solvents are used.

Attack at carbon-1

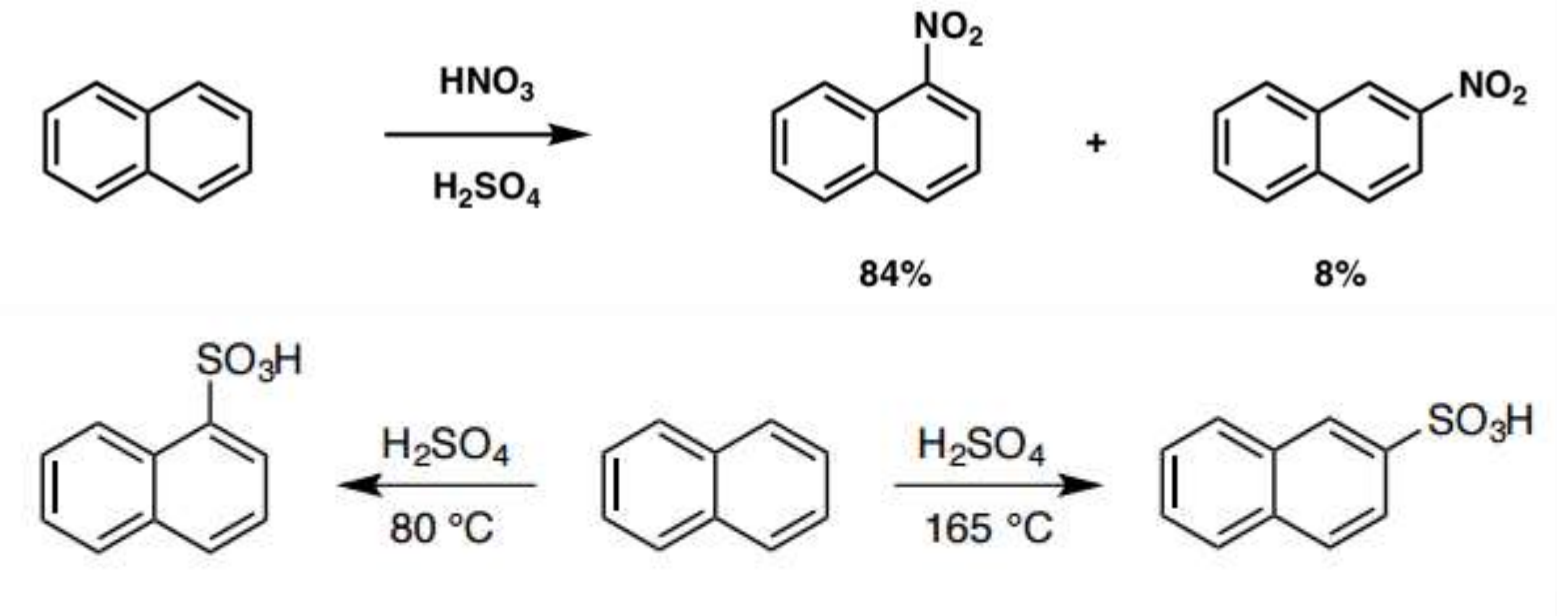


Attack at carbon-2

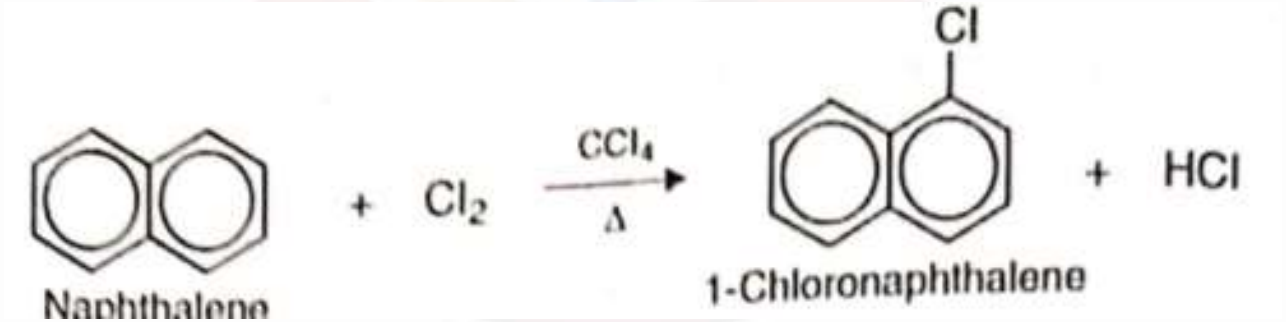


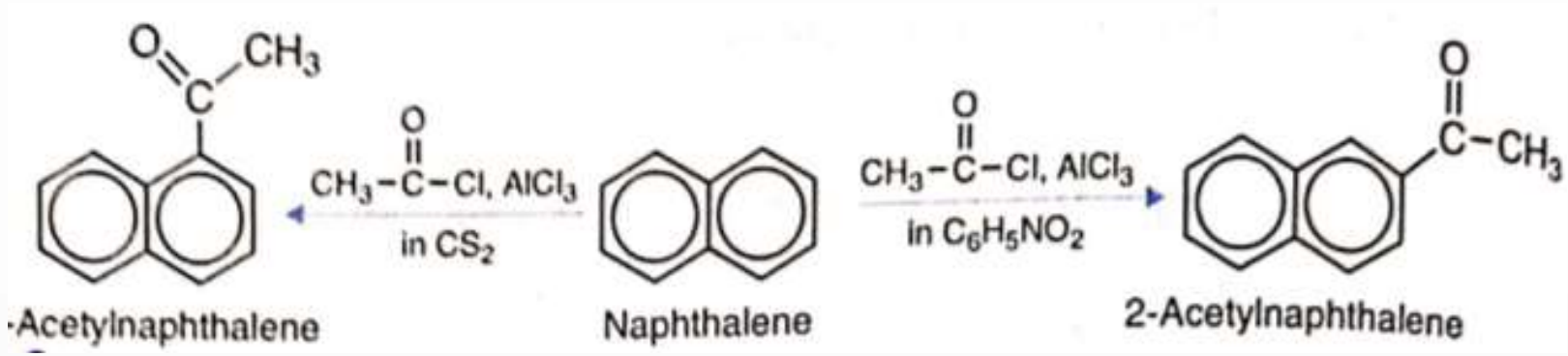
ELECTROPHILIC SUBSTITUTION REACTION

1. **Nitration:** Reaction with HNO3 in presence of H_2SO_4 at 60^0C to form 1-nitronaphthalene.
2. **Sulphonation:** Reaction with sulphuric acid at 80^0C – 1-naphthalenesulphonic acid. At 165^0C - 2-naphthalenesulphonic acid.

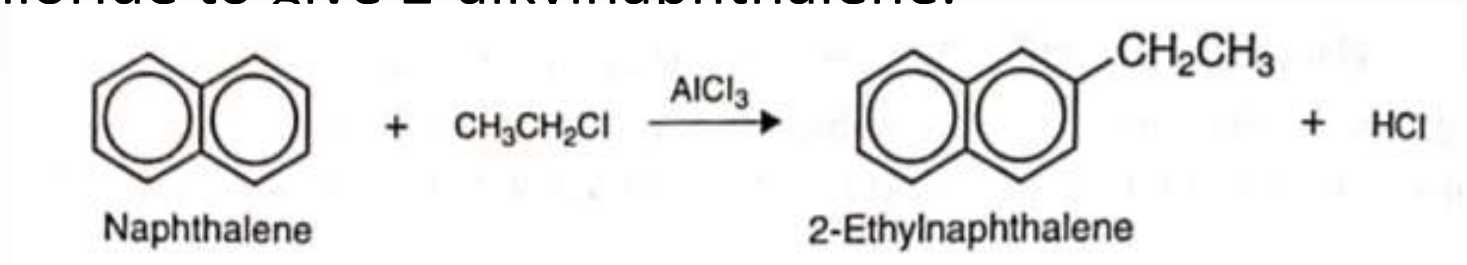


3. **Halogenation**: Chlorination or bromination in boiling CCl_4 – 1-chloronaphthalene.
4. **Friedel-Crafts Acylation:** Reaction with acetyl chloride and AlCl3 – In carbon disulphide (CS2): 1- acetylnaphthalene and in nitrobenzene: 2-acetylnaphthalene obtained.





5. **Friedel-Crafts Alkylation:** Reaction with alkyl halides in presence of aluminium chloride to give 2-alkylnaphthalene.

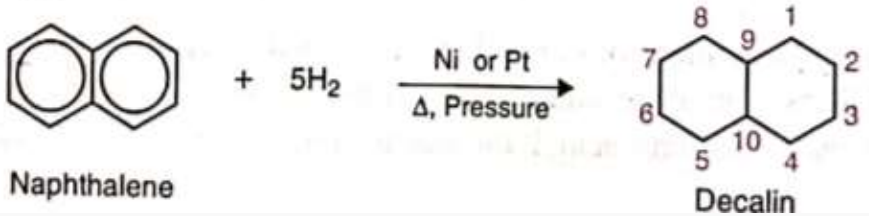


OTHER REACTIONS

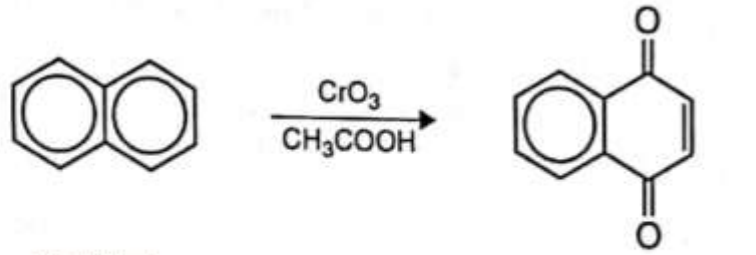
Reduction: With sodium and ethyl alcohol (78^0C) it gives 1,4-dialin or 1,4-dihydronaphthalene.

With sodium and isopentanol (130^0C) it gives tetralin or 1,2,3,4-tetrahydronaphthalene.

Catalytic reduction completely hydrogenates both rings and produces decalin or decahydronaphthalene.

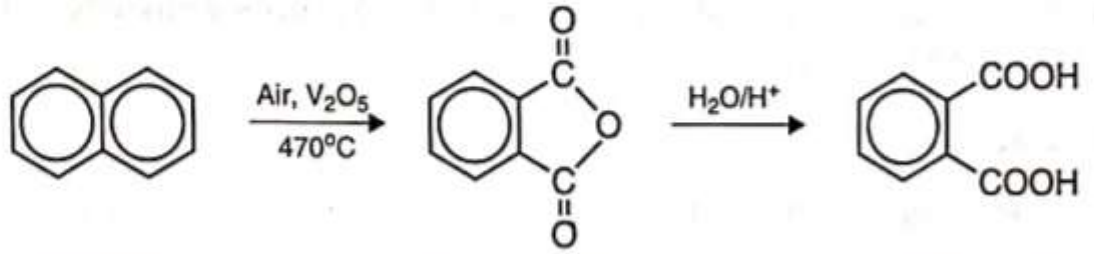


7. **Oxidation:** Oxidation with chromium trioxide in acetic acid at room temperature gives 1,4-naphthaquinone.



Naphthalene 1,4-Naphthaquinone

Oxidation of naphthalene with oxygen and vanadium pentoxide at 475°C yields phthalic anhydride. This method is used industrially.



Naphthalene Phthalic anhydride Phthalic acid

Phthalic acid is an important industrial material. It is used in the manufacture of resins, paints, dyes and plastics.

Uses of naphthalene

- As ‘moth balls’ , it is used to protect woolen goods from moths for many years. (Now replaced with p-dichlorobenzene).
- It is used for increasing the illuminating power of coal gas.
- It is used in the manufacture of phthalic anhydride, carbaryl for insecticides, 2-naphthol for dyes and several medicinal products.

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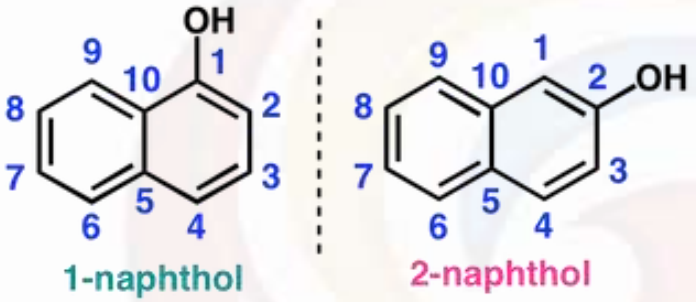
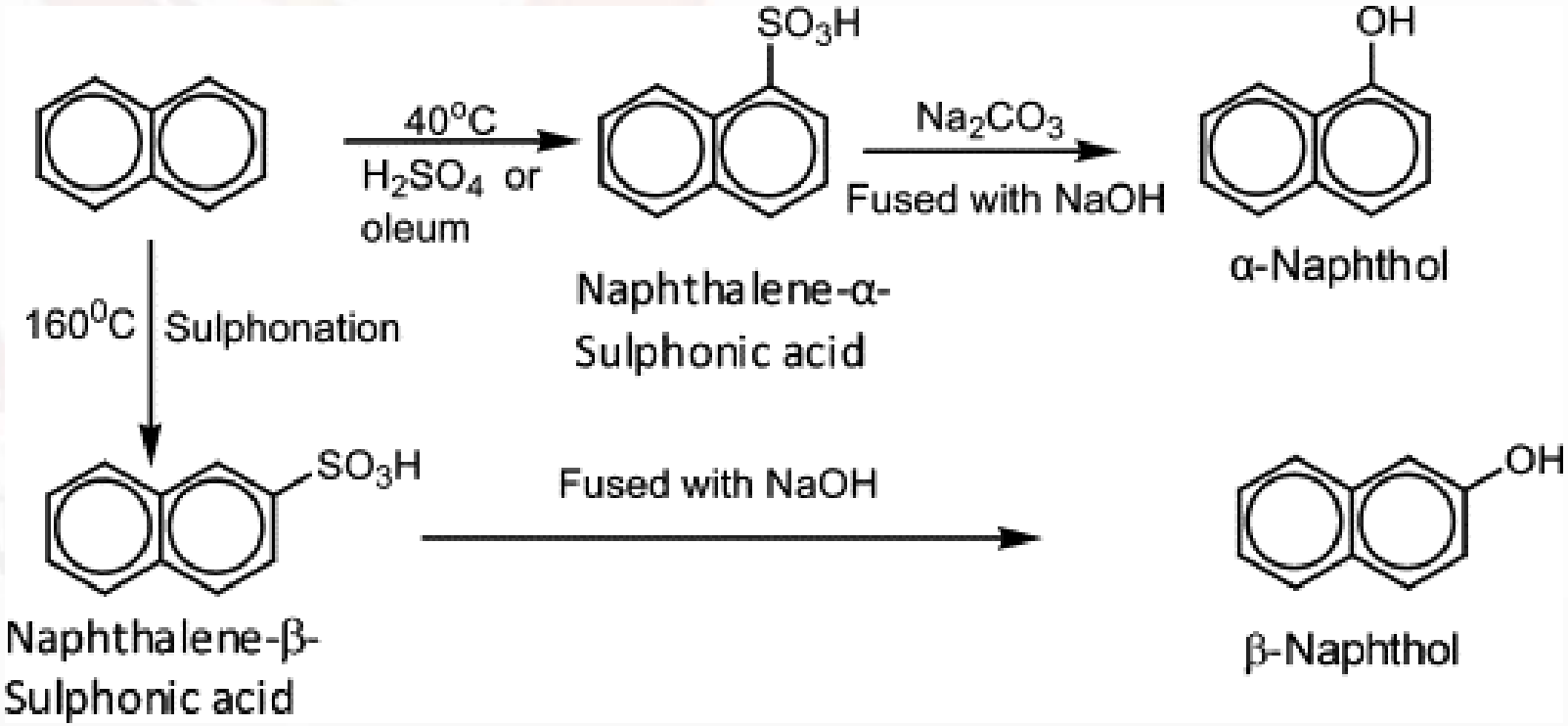
NAPHTHOLS

Monohydroxy derivatives of naphthalene are called NAPHTHOLS.



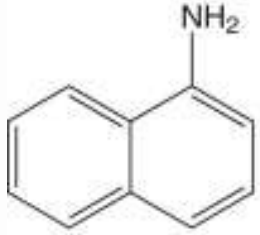
Uses: They are used
As insecticides and for making dyes.
Ethers of beta-naphthol are used in perfumery.

Preparation

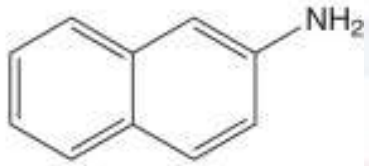


NAPHTHYLAMINES

Monoamino derivatives of naphthalene are called NAPHTHYLAMINES.



1-Naphthylamine



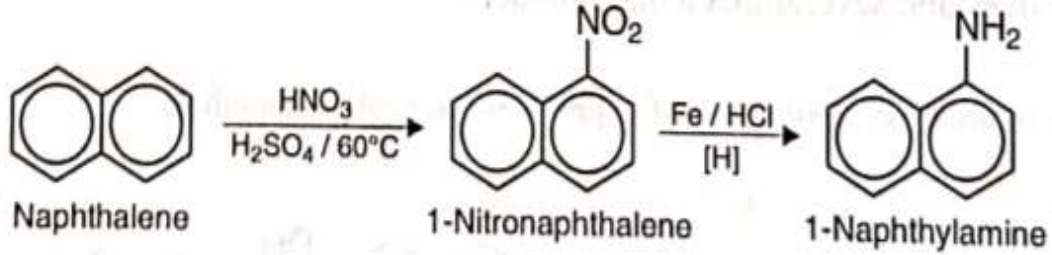
2-Naphthylamine

Properties: Colourless solids,
mp- 500C and 1130C,
Soluble in alcohol, ether.

Uses: They are used
for making dyes.

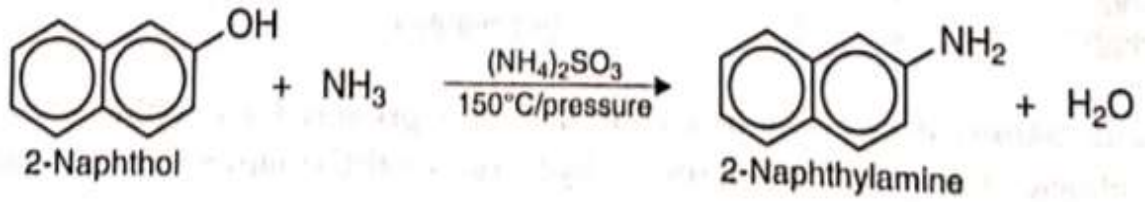
Preparation

Preparation. α-Naphthylamine is prepared by the reduction of the corresponding nitronaphthalene.



Naphthalene — 1-Nitronaphthalene — 1-Naphthylamine

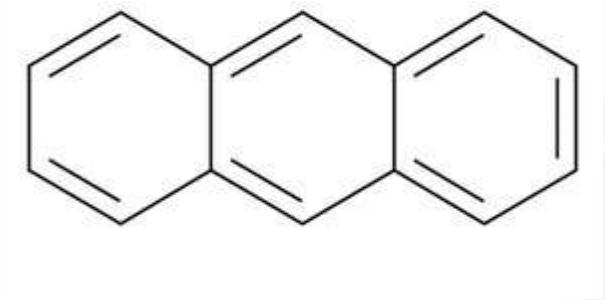
2-Naphthylamine is prepared by the reaction of 2-naphthol with ammonia and ammonium bisulfite at high temperature and pressure. (**Bucherer Reaction**)

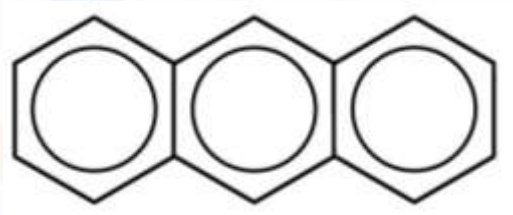


2-Naphthol — 2-Naphthylamine

ANTHRACENE

Anthracene is a solid polycyclic aromatic hydrocarbon (PAH) of formula $C_{14}H_{10}$, consisting of three fused benzene rings. It is a component of coal tar.

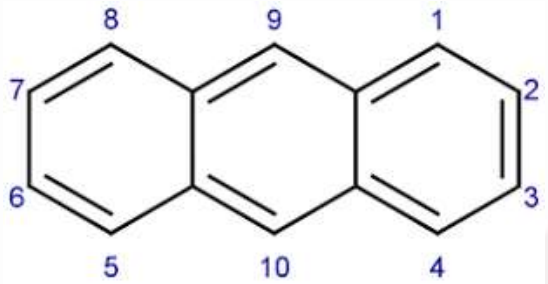




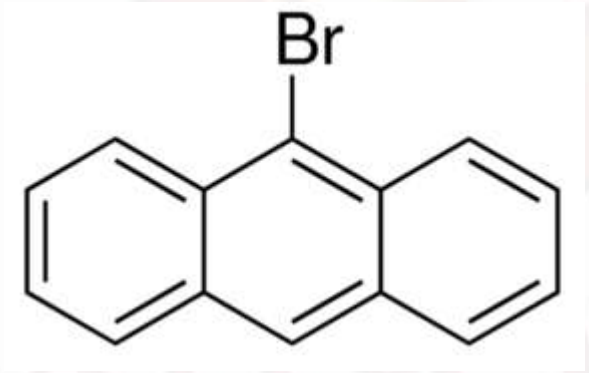
- **Occurrence and production**
- Coal tar, which contains around 1.5% Anthracene, remains a major source of this material.
- It contains phenanthrene and carbazole as impurities.
- It is purified by washing successively wity solvent naphtha (to remove phenanthrene) and pyridine(to remove carbazole).
- Purified by sublimation.

Nomenclature

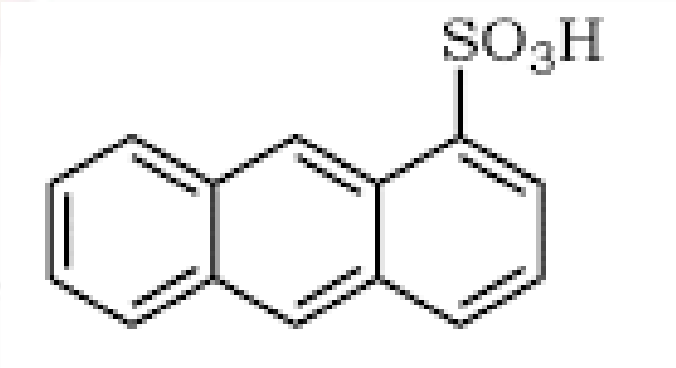
- For naming, following numbering system is used.
- Numbers selected to denote the position of a substituent on the anthracene rings should be as small as possible.



Anthracene



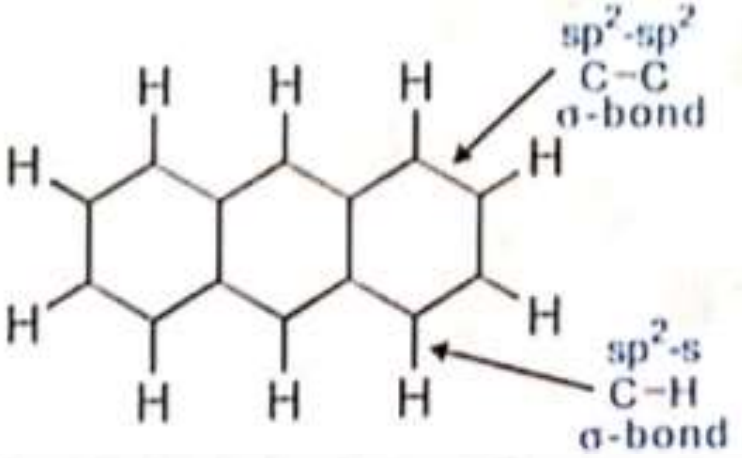
9-Bromoanthracene



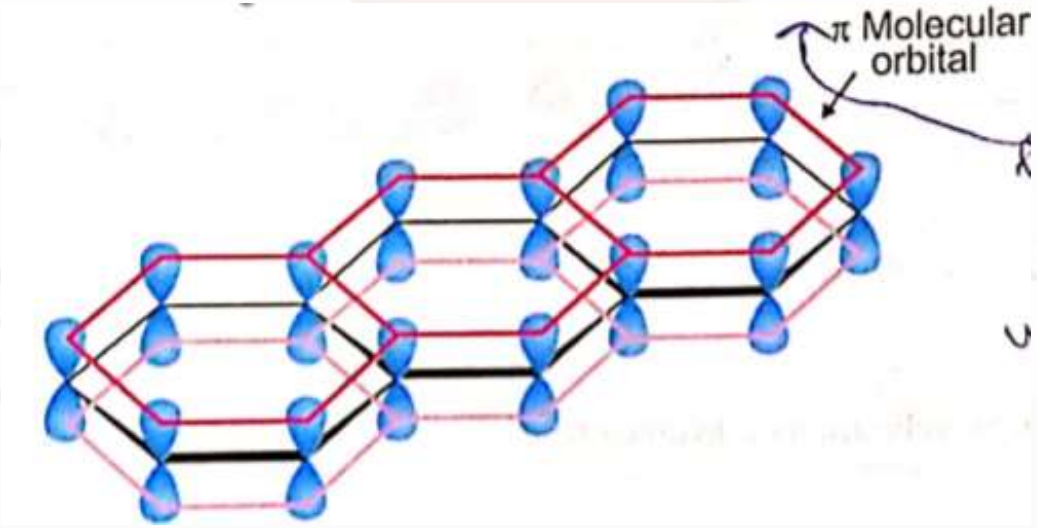
1-Anthracenesulfonic acid

Structure of anthracene

- All fourteenen carbon atoms are sp^2 hybridized.
- The sp^2 hybrid orbitals overlap with each other and with s orbitals of the eight hydrogen atoms forming C-C and C-H σ bonds.
- Since the σ bonds result from the overlap of trigonal sp^2 orbitals, all C and H atoms lie in one plane.

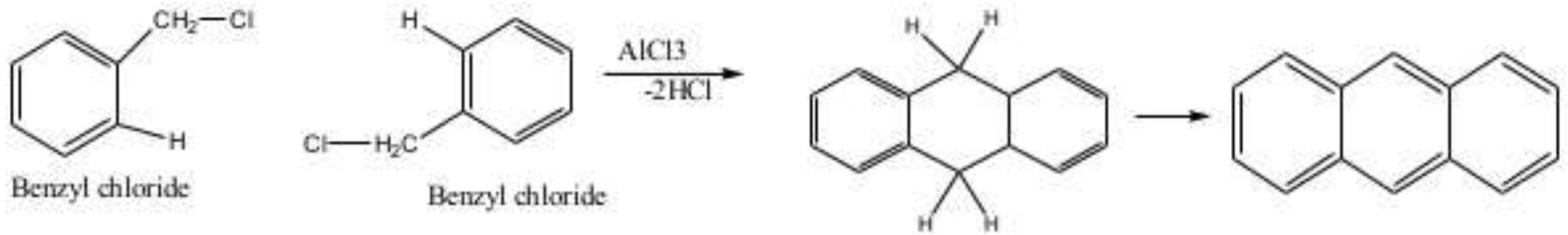


- Each C atom in naphthalene also possesses an unhybridized p orbital containing one electron
- These p orbitals are perpendicular to the plane containing the σ bonds.
- The lateral overlap of the p orbitals produces a π molecular orbital containing fourteen electrons.
- One half of this π molecular orbital lies above and the other half lies below the plane of the bonds.
- Naphthalene shows aromatic properties because the resulting π molecular orbital satisfies the Huckel's rule (n=3, 4n+2).

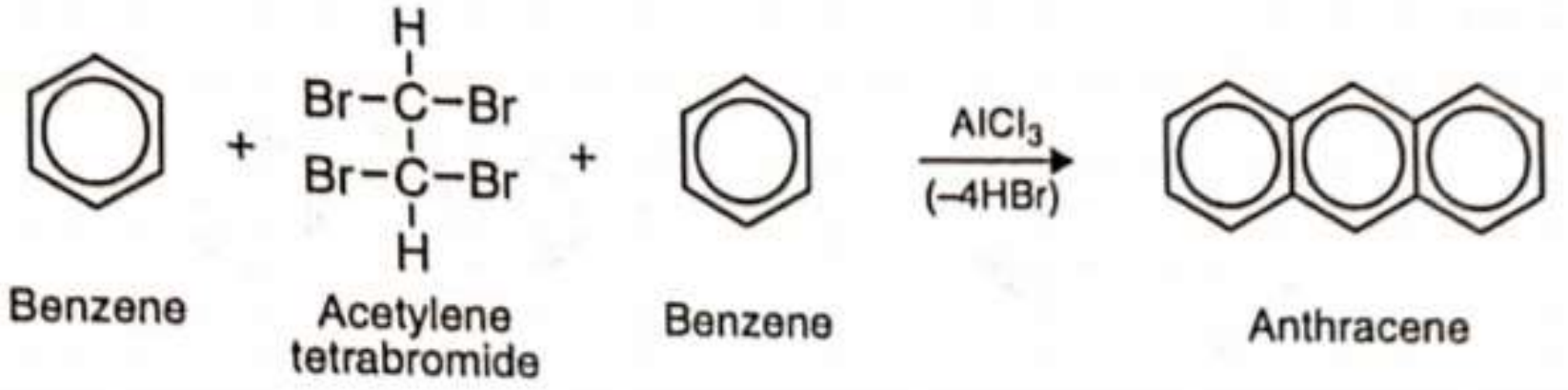


Synthesis of anthracene

1. **Friedel-Crafts Reaction:** (i) Reaction of 2 molecules of benzyl chloride in presence of aluminium chloride.



(ii) Reaction of benzene with 1,1,2,2-tetrabromoethane.

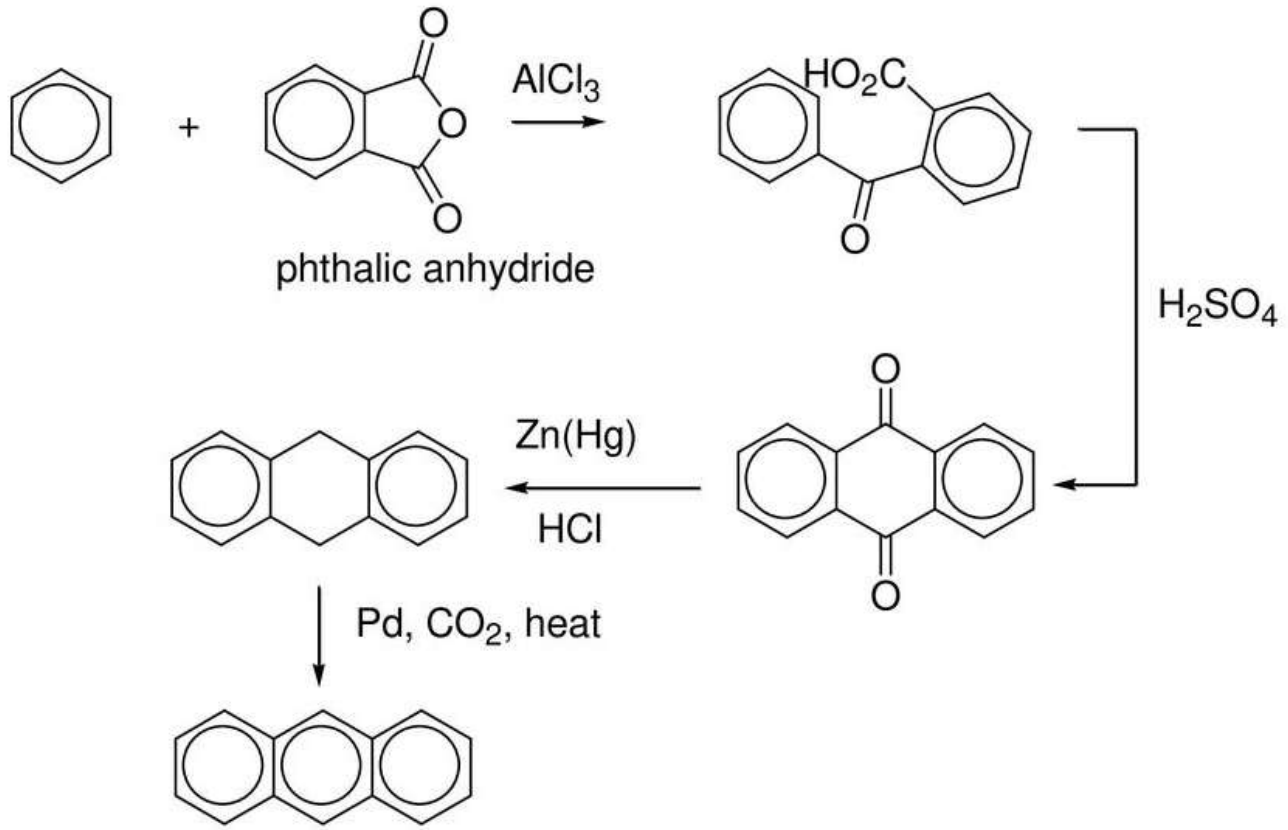


2. Haworth synthesis

I. **Friedel-Crafts Acylation:** Reaction of benzene with phthalic anhydride in presence of AlCl3 – o-Benzoyl benzoic acid.

II. **Ring-closure Reaction:** Heating o-benzoyl benzoic acid with conc. Sulphuric acid - 9,10-anthraquinone.

III. **Reduction:** Distillation with zinc dust – **ANTHRACENE**.



Physical properties

- Naphthalene is a colourless solid.
- Insoluble in water.
- Soluble in benzene.
- Melting point 218^0C.
- It shows strong fluorescence when exposed to UV light, which is useful in cruminal detection work.
- Sublimes readily when warmed and is volatile with steam.

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ELECTROPHILIC SUBSTITUTION REACTION

- Substitution occurs at C9 and C10 position.
- The carbonium ion obtained by attack of an electrophile (E) at C9 contains two benzene rings intact, whereas at C-1 or C-2 yields an intermediate in which a naphthalene system is retained.
- The former intermediate is more stable and its formation favored because the resonance energy of two benzene rings (2 x36= 72 kcal) exceeds that of naphthalene (61 kcal).
- This carbonium ion intermediate can lose a proton to give the corresponding substitution product, or it can react wih a nucleophile to form the 9,10-addition product.

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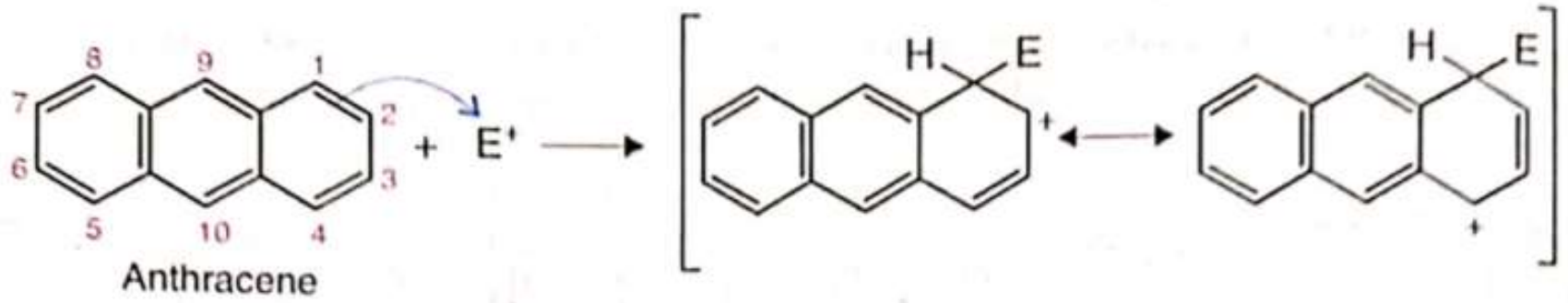
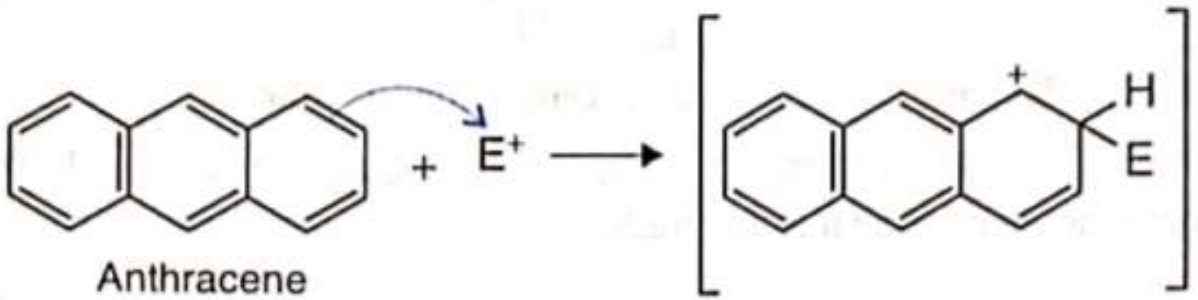
Attack at C-1



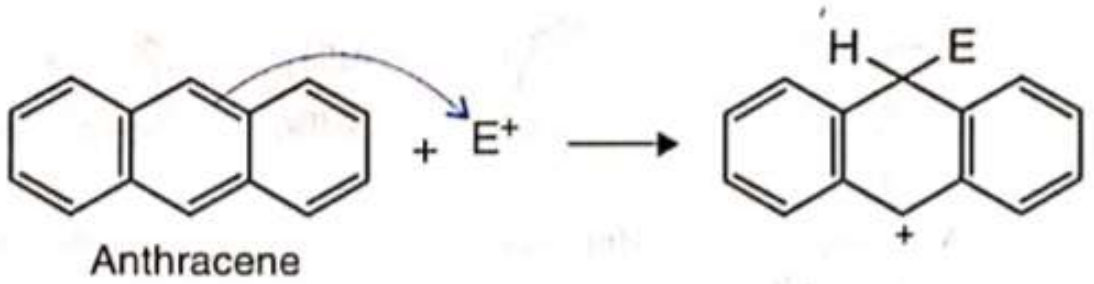
Anthracene

Attack at C-2



Anthracene

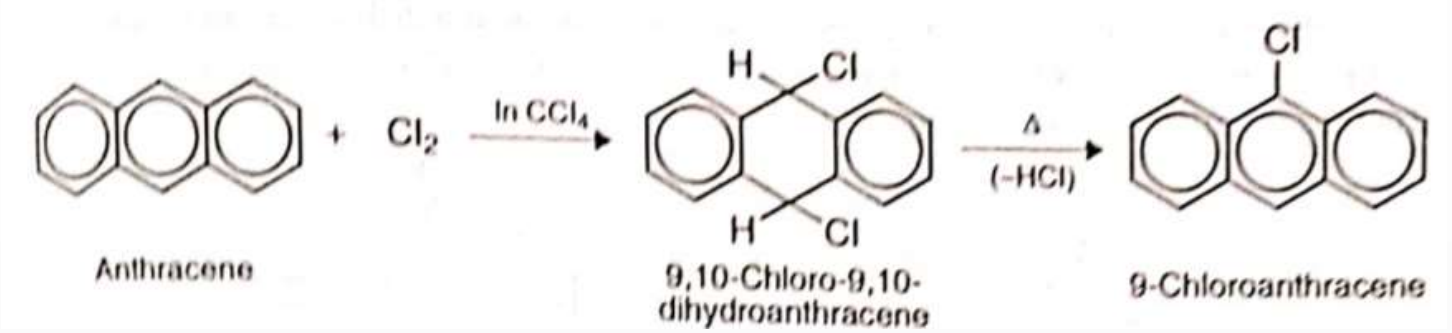
Attack at C-9



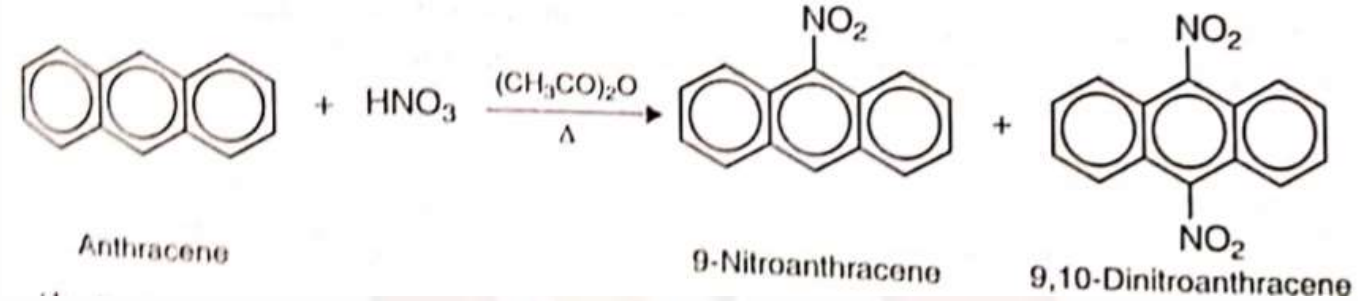
Anthracene

1. **Reaction with halogens:** Reaction with chlorine in carbon tetrachloride at room temp. togive 9,10-dichloro-9,10-dihydroanthracene (an addition product). on heating this addition product loses a molecule of hydrogen chloride by 1,4-elimination to form 9-chloroanthracene (a substitution product).

2. **Friedel-Crafts Acylation:** Upon reaction wity acetyl chloride and aluminium chloride it forms 9-acetylanthracene.

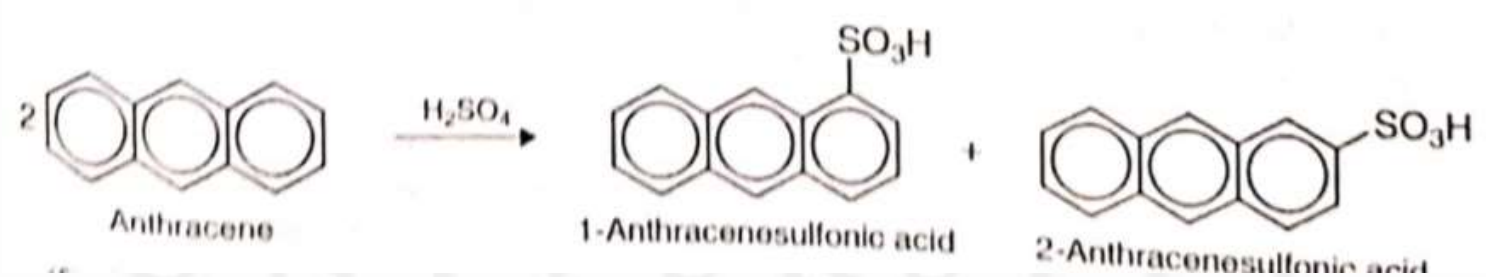


3. **Nitration:** Reaction with HNO3 in acetic anhydride at room temp to form mixture of 9-nitroanthracene and 9,10-dinitroanthracene. Usual nitrating agent is not used because it leads to the formation of 9,10-anthraquinone due to oxidation.

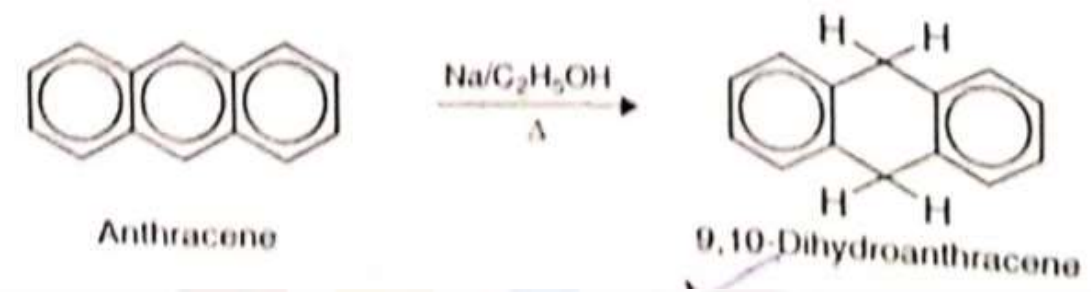


4. **Sulphonation:** Reaction with conc. H2SO4 forms a mixture of 1-anthracenesulfonic acid and 2-anthracenesulfonic acid.

At lower temp 1-anthracenesulfonic acid is the major produce, where as at higher temp, 2-anthracenesulfonic acid is the major product.

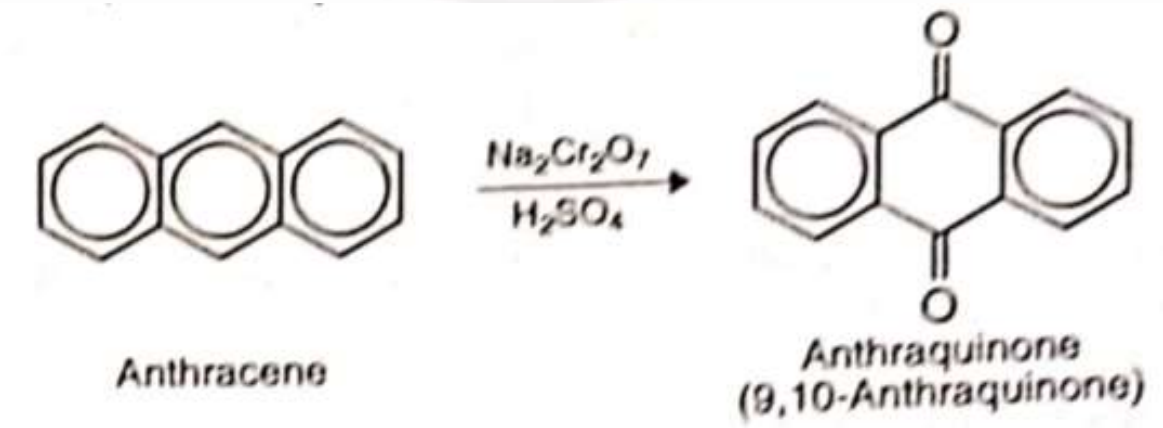


5. **Reduction:** Reduction wity sodium and ethyl alcohol to form 9,10-dihydroanthracene.



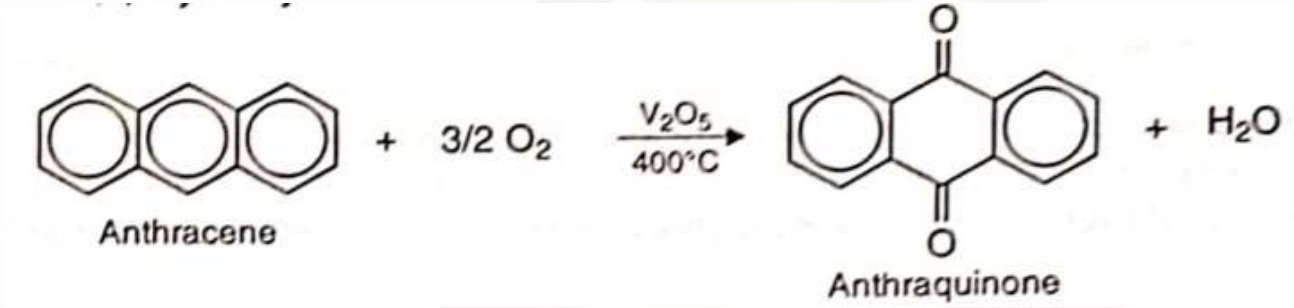
6. **Oxidation:** Oxidation with sodium dichromate and H2SO4 forms 9,10-anthraquinone

oxidation with nitric acid and air in presence of V2O5 also lead to the formation of 9,10-anthraquinone.

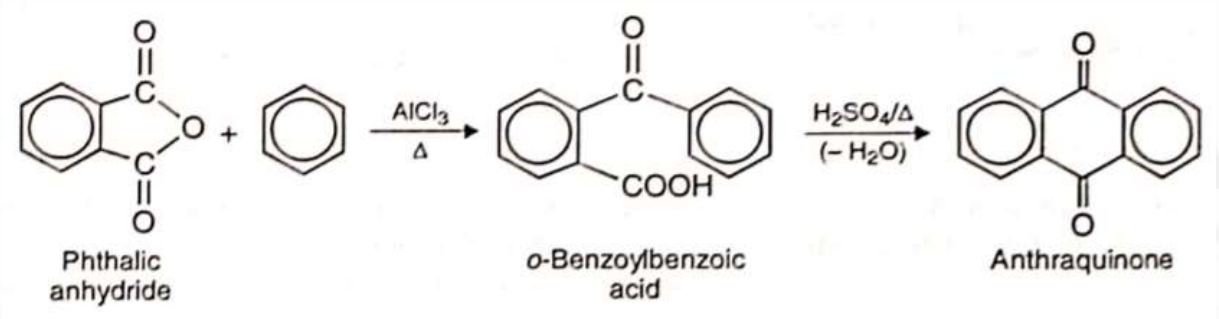


9,10-Anthraquinone

- **Manufacture:** 1) By catalytic oxidation of anthracene derived from coal-tar.



2) By Friedel-Crafts acylation between phthalic anhydride with benzene, and dehydration of the product with conc. sulfuric acid.



Physical properties

- Anthraquinone is yellow needle like crystals..
- Insoluble in water.
- Soluble in alcohol, ether, acetone, benzene.
- Melting point 286^0C.
- Sublimes readily when warmed and is volatile with steam.

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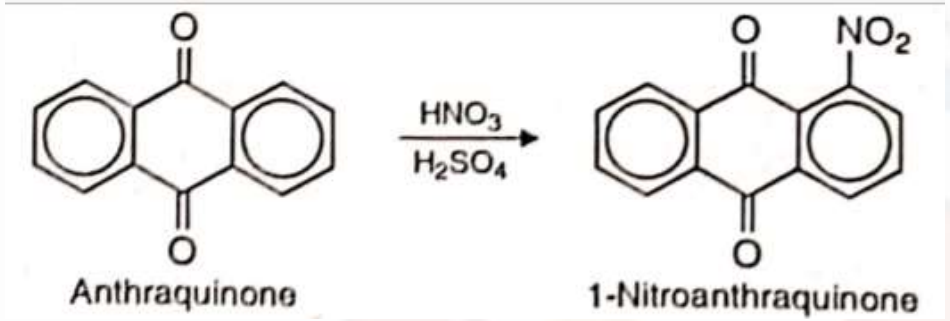
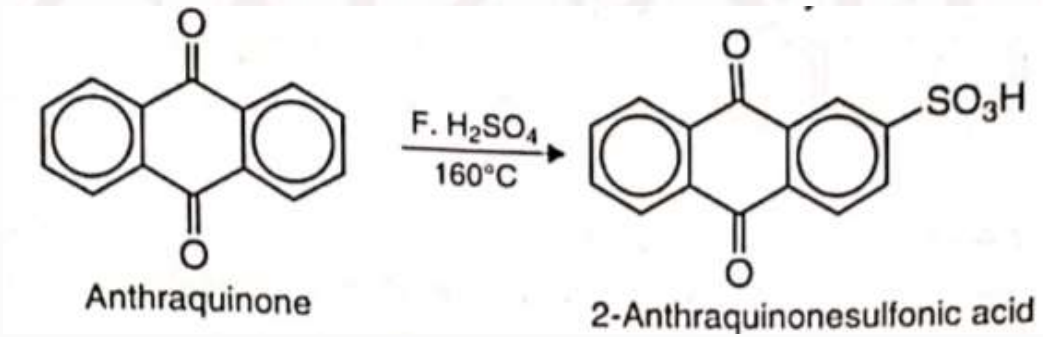
Chemical properties

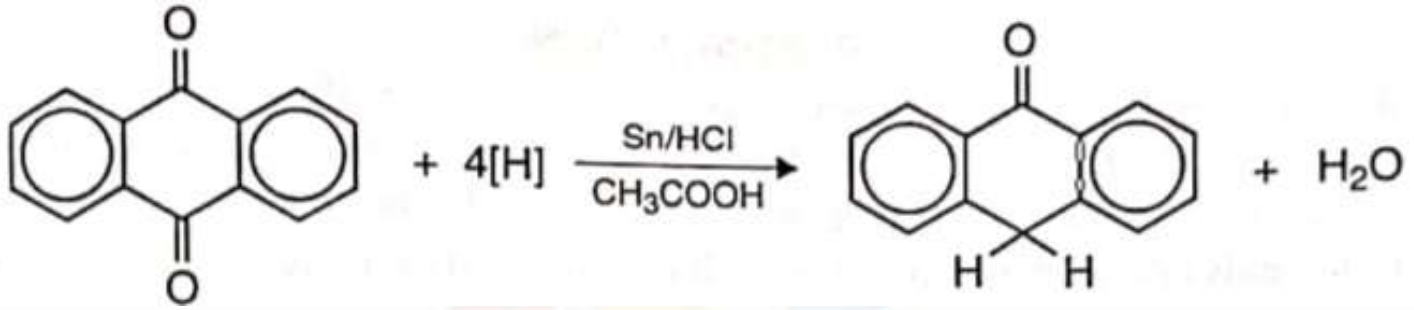
1. **Nitration:** Upon reaction with HNO3 and H2SO4, it forms 1-nitroanthraquinone.



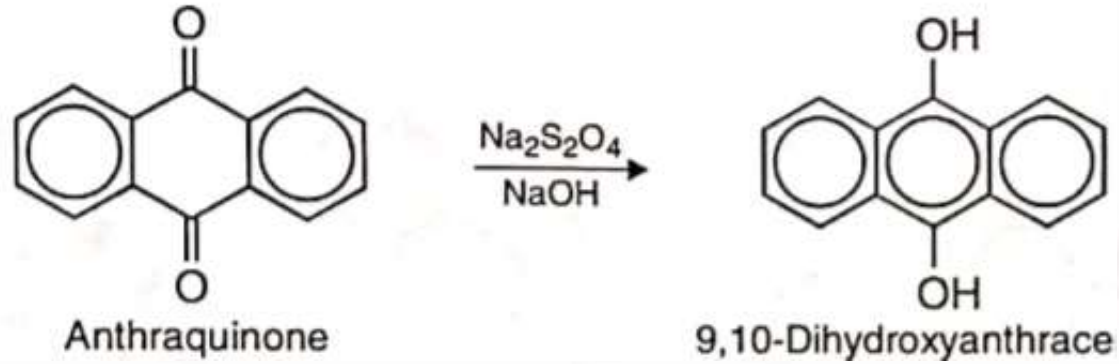
2. **Sulfonation:** Upon reaction with fuming sulfuric acid at 1600C, it forms 2-anthraquinone sulfonic acid (an intermediate in synthesis of alizarin).



3. Reduction: a) With tin and HCl in acetic acid, anthrone is obtained.

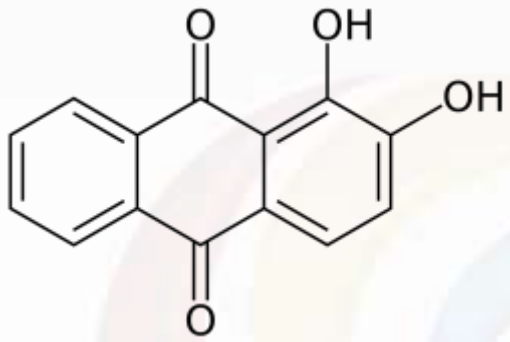


b) With sodium hydrosulfite (Na2S2O4) and alkali, 9,10-dihydroxyanthracene.



Uses: Anthraquinone is used in the manufacture of alizarin and several other dyes

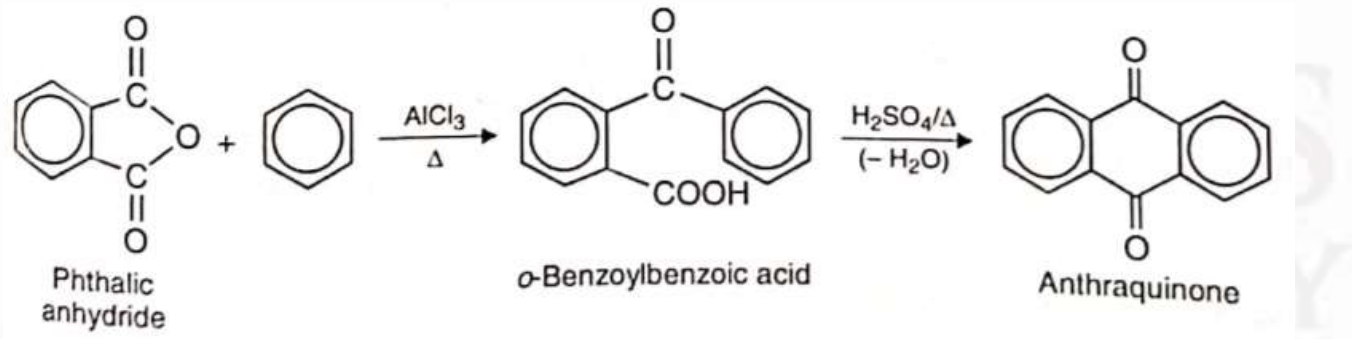
ALIZARIN

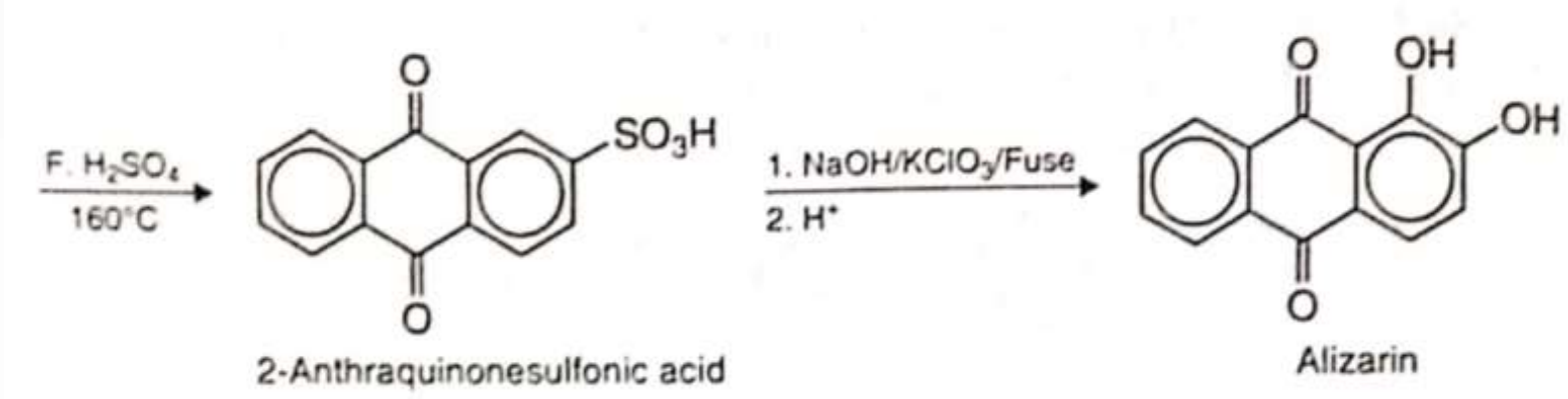


- **Preparation:** 1) Friedel-Crafts acylation – Reaction of benzene with phthalic anhydride , followed by dehydration with conc. H2SO4.

2) Sulfonation with fuming sulfuric acid to form 2-anthraquinonesulfonic acid.

3) Fusion with NaOH and Potassium chlorate, followed by acidification.





2-Anthraquinonesulfonic acid

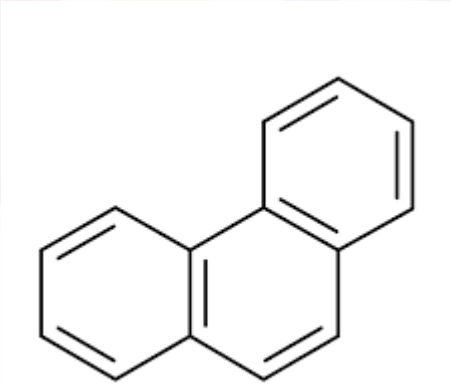
Alizarin

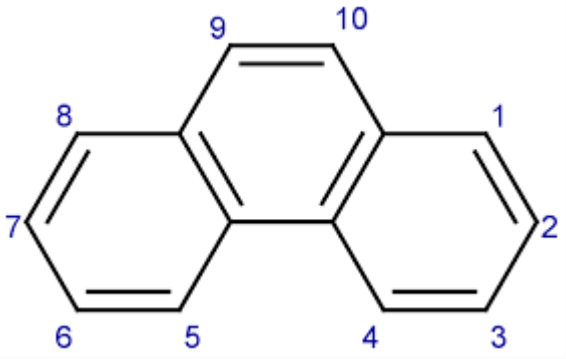
Properties:

- Ruby red crystals
- Melting point- 290^0C.
- Sparingly soluble in water, soluble in alcohol and ether.
- It is a typical mordant dye, its aluminium mordant gives bright red colour.
- Rarely used now.
- It is a parent of many other dyes and pigments in current use.

PHENANTHRINE

Phenanthrene is a an isomer of anthracene. It is solid polycyclic aromatic hydrocarbon (PAH) of formula $C_{14}H_{10}$, consisting of three fused benzene rings. It is a component of coal tar.





- **Occurrence and production**
- Coal tar is a major source of this material.
- Upon cooling the green oil fraction, it forms a solid mass containing anthracene, phenanthrene, carbazole.
- Treated with solvent naphtha to dissolve phenanthrene and then evaporated the solvent to form phenanthrene, followed by purification using ethanol.

Synthesis of phenanthrene

- **Haworth synthesis**

I. **Friedel-Crafts Acylation:** Reaction of naphthalene with succinic anhydride in presence of AlCl3 – 1-naphthoyl propanoic acid.

II. Clemensen reduction: Reaction with amalgated zinc and HCl- 1-naphthyl butanoic acid.

III. **Ring-closure Reaction:** Heating with conc. Sulphuric acid.

IV. **Clemensen reduction:** Reaction with amalgated zinc and HCl.

V. **Reduction:** Reaction with palladium – **PHENANTHRENE**.

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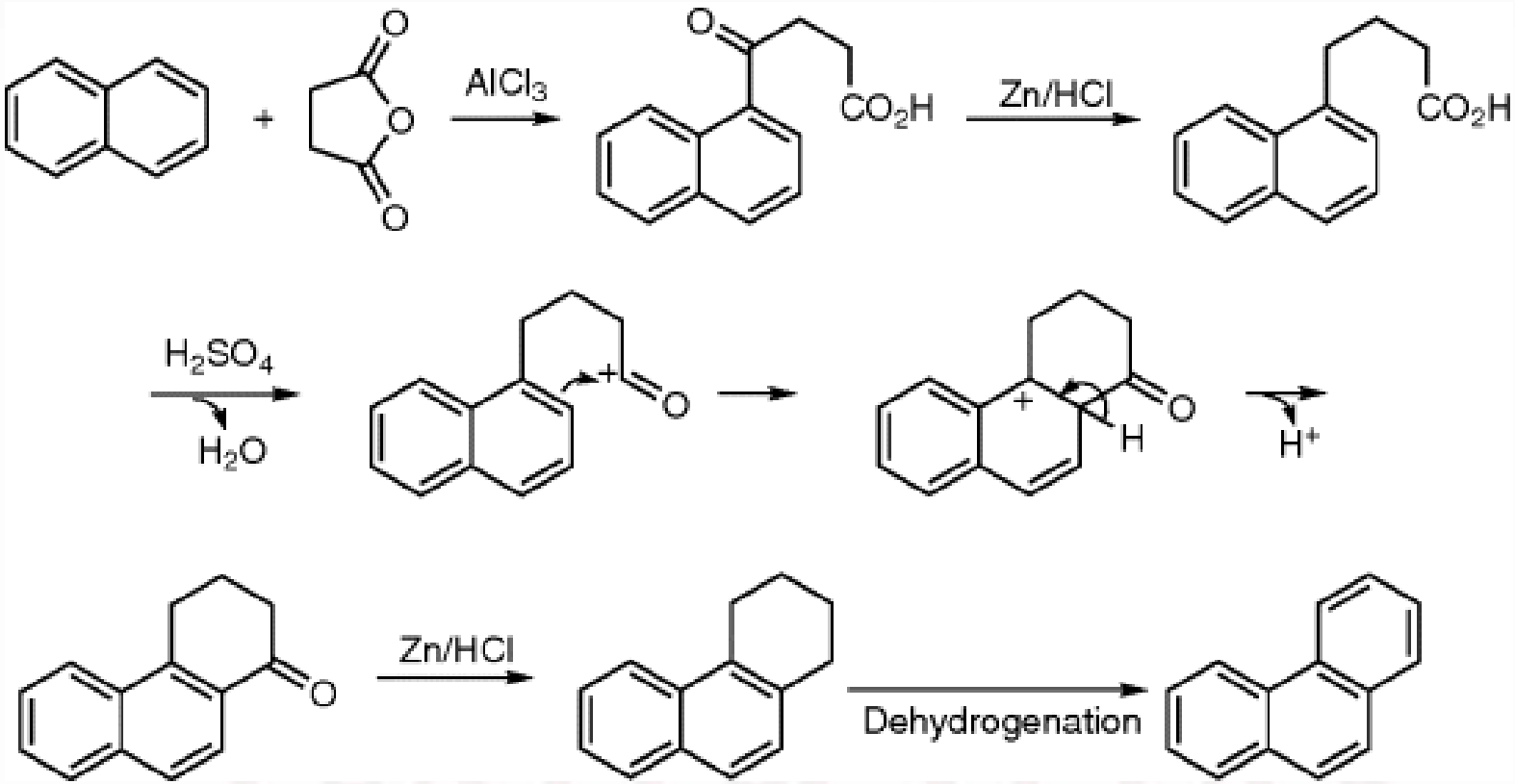
Haworth synthesis of phenanthrene



Physical properties

- Phenanthrene is colourless solid.
- Insoluble in water.
- Soluble in alcohol, ether, acetone, benzene.
- Melting point 100^0C.
- It gives blue fluorescence in benzene solution.
- Sublimes readily when warmed and is volatile with steam.

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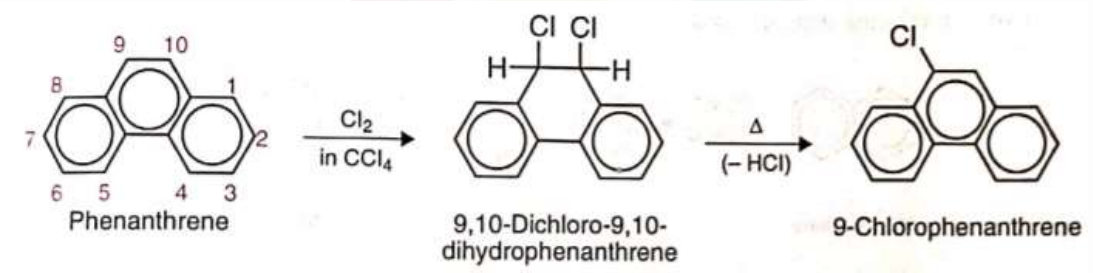
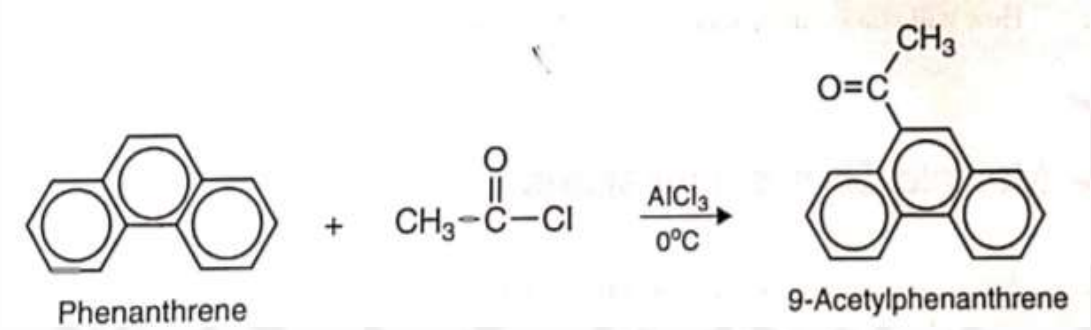
Chemical reactions

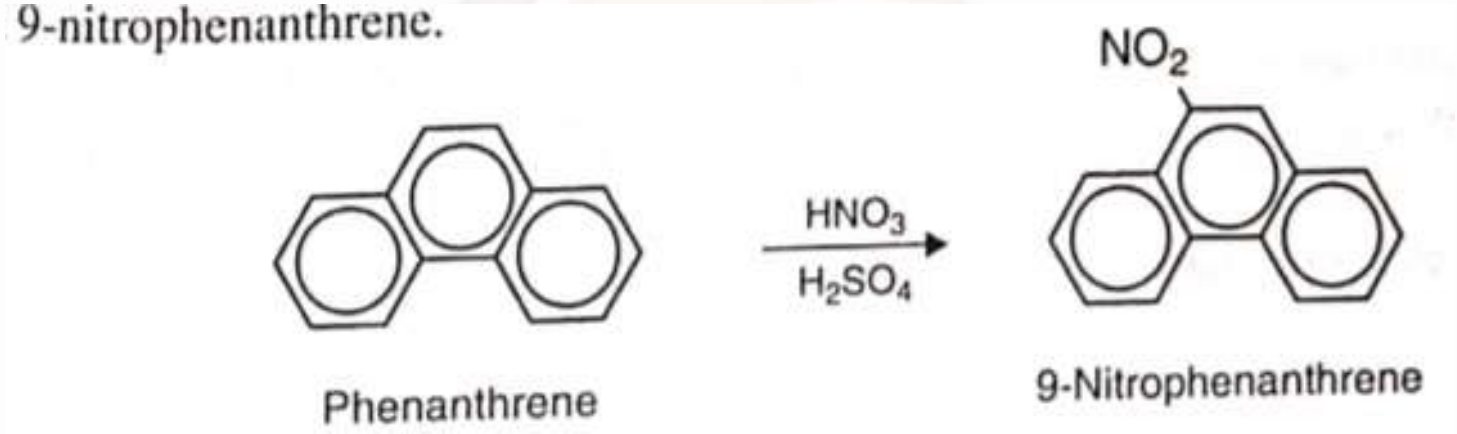
1. Reaction with halogens. Reaction with chlorine in CCl4 at room temp to give 9,10-dichloro-9,10-dihydrophenanthrene (an addition product). This upon heating loses HCl to yield 9-chlorophenanthrene (a substitution product).



2. Friedel-Crafts acylation: Reaction with acetyl chloride in presence of AlCl3 at 0^0C gives 9-acetylphenanthrene.



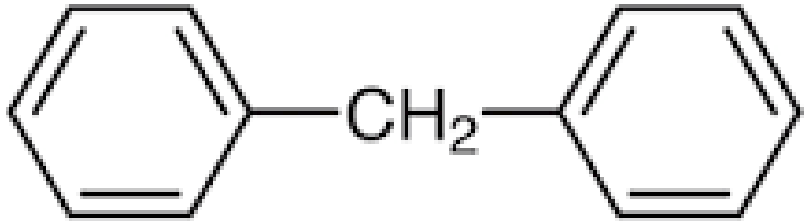
3. Nitration: Reaction with conc. HNO3 and sulfuric acid gives 9-nitrophenanthrene.



Uses: It is of little industrial importance, but this ring system is widely distributed in natural compds e.g. carcinogenic hydrocarbons, bile acids, sex hormones, morphine alkaloids, cholesterol.

DIPHENYLMETHANE

- **Diphenylmethane** is an organic compound with the formula $(C_6H_5)_2CH_2$
- The compound consists of methane wherein two hydrogen atoms are replaced by two phenyl groups. It is a white solid.

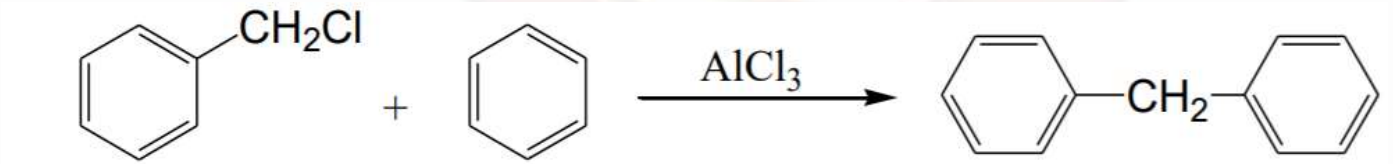


Preparation of diphenylmethane

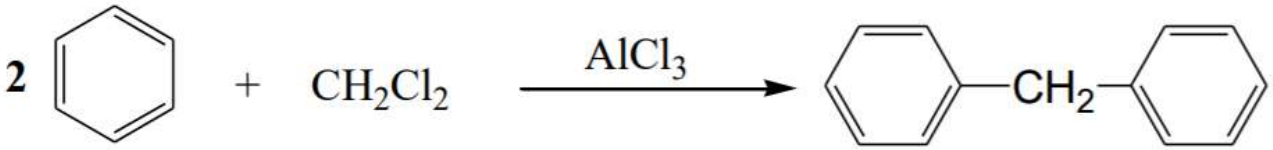
I. Friedel Craft alkylation

a) When benzene is treated with benzyl chloride in presence of $AlCl_3$, it gives diphenylmethane.

b) Reaction of benzene with dichloromethane in presence of $AlCl_3$ gives diphenylmethane



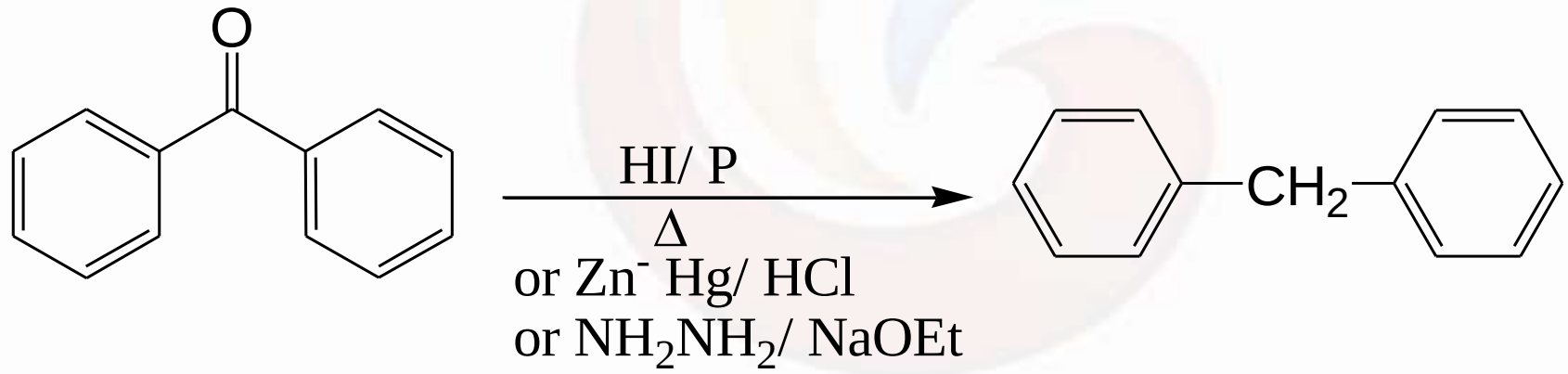
Benzyl chloride **Diphenyl methane**



Diphenyl methane

Preparation of diphenylmethane

II. **Reduction** of benzophenone in presence of HI and phosphorus gives diphenylmethane



Benzophenone **Diphenyl methane**

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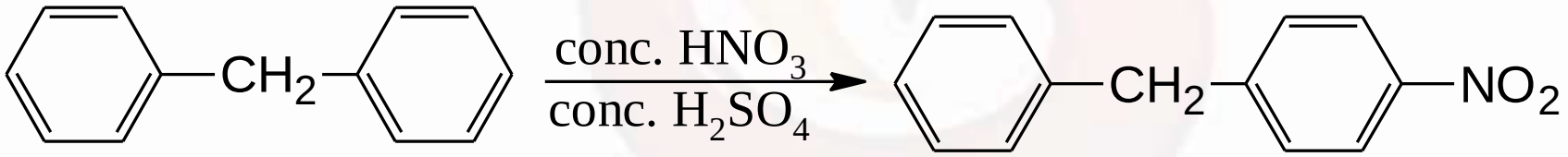
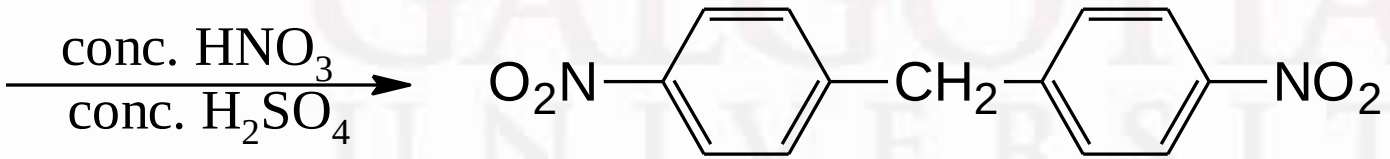
Reactions of diphenylmethane

I. **Nitration**: Diphenylmethane upon reaction with conc. HNO_3 and conc. H2SO4 forms 1-benzyl-4-nitrobenzene which upon further nitration gives bis-4-nitrophenylmethane



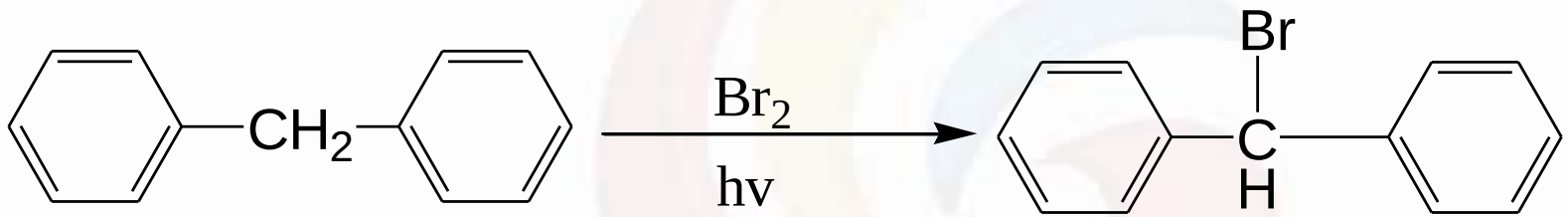
Diphenyl methane **1-benzyl-4-nitrobenzene**



bis(4- nitrophenyl)methane

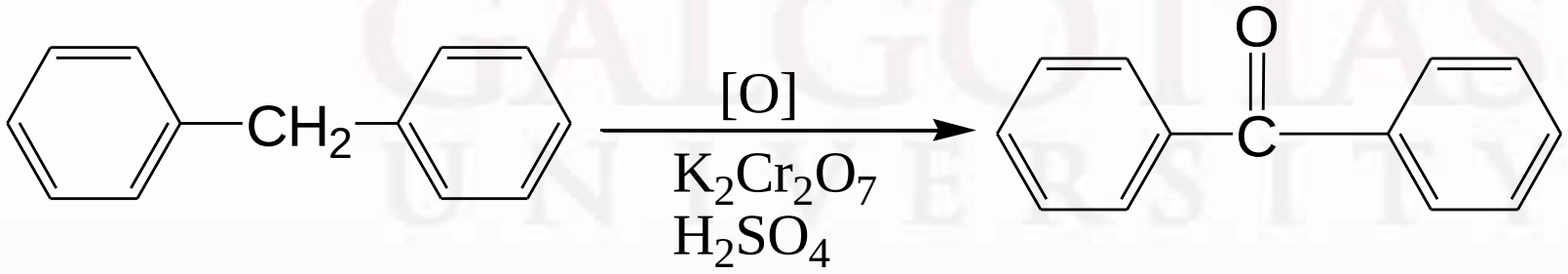
Reactions of diphenylmethane

II. **Halogenation**: Diphenylmethane upon bromination gives diphenylmethyl bromide



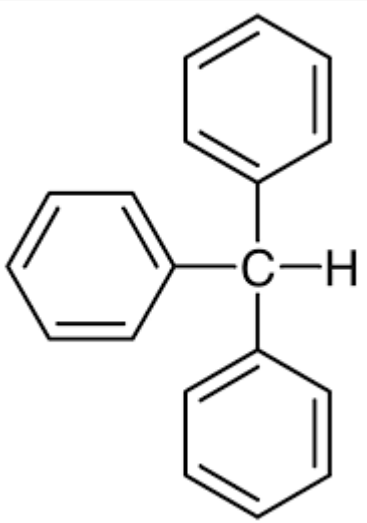
Diphenyl methane **Diphenylmethylbromide**

III. **Oxidation**: Reaction of biphenylmethane with $K_2Cr_2O_7$ in presence of H_2SO_4 gives benzophenone



Diphenyl methane **benzophenone**

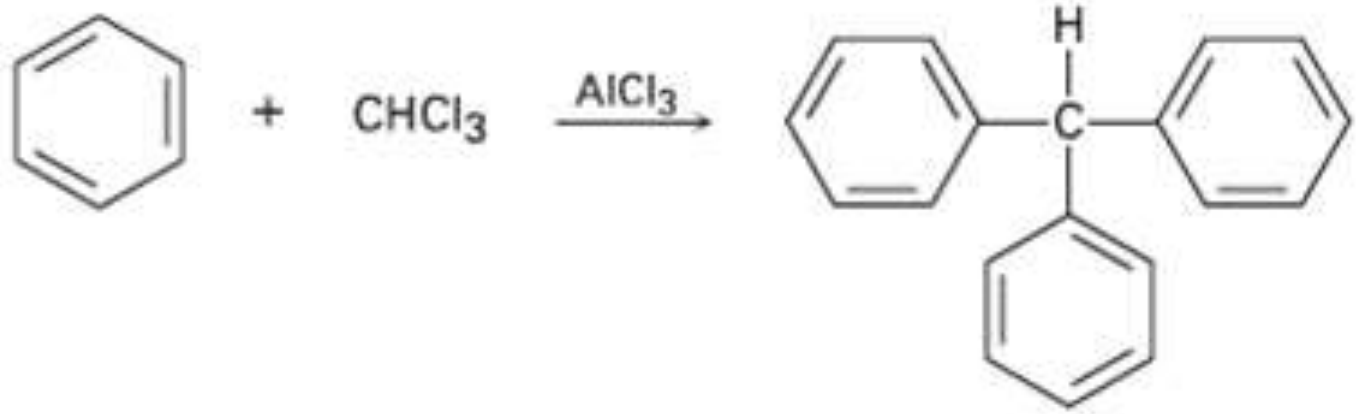
TRIPHENYLMETHANE



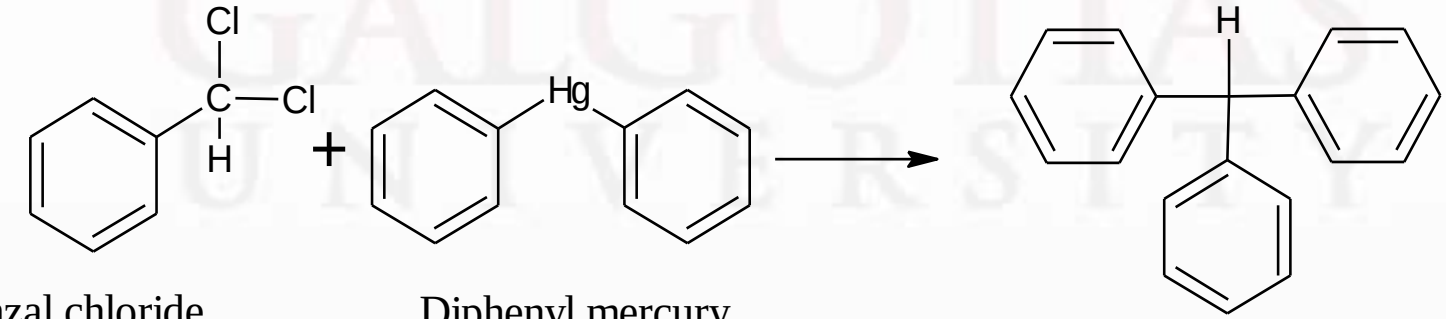
- **Diphenylmethane** is an organic compound with the formula $(C_6H_5)_3CH$.
- The compound consists of methane wherein three hydrogen atoms are replaced by three phenyl groups.
- It is a white solid, soluble in non-polar solvents.
- It is the basic skeleton of many synthetic dyes called triarylmethane dyes.
- Many of them are pH indicators

Preparation of triphenylmethane

I. **Friedel Craft alkylation:** Three moles of benzene react with chloroform in presence of $AlCl_3$, to form triphenylmethane



II. By reaction of diphenyl mercury on benzal chloride

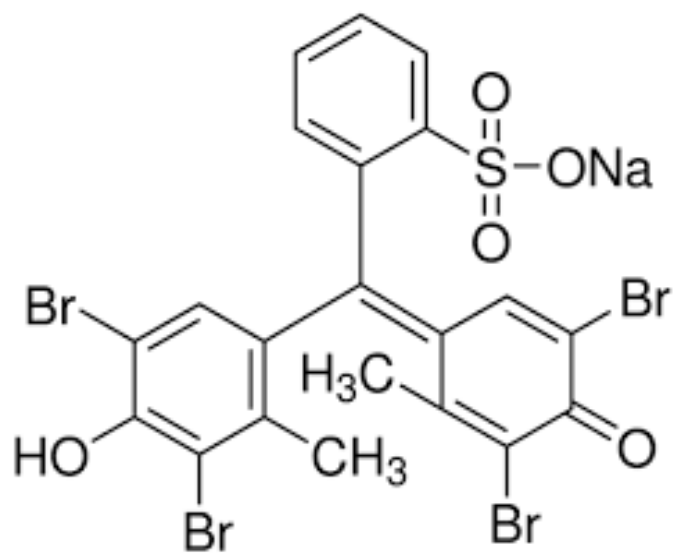


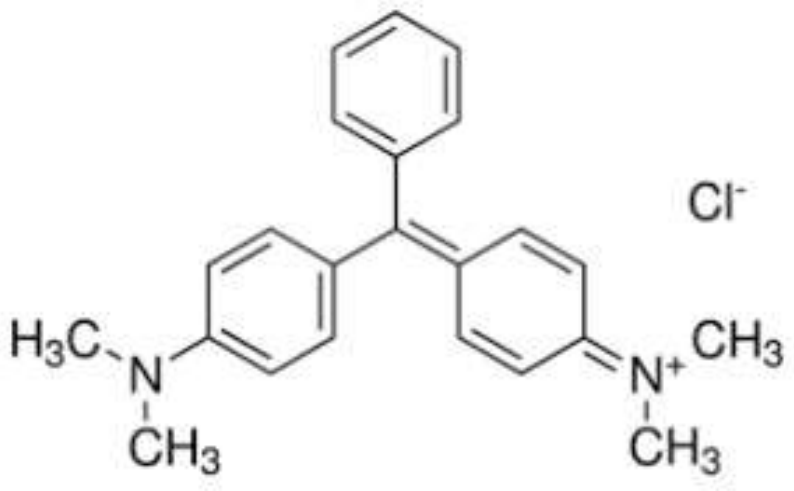
Benzal chloride Diphenyl mercury Triphenylmethane

Uses

Diphenylmethane is widely used in the synthesis of luminogens for aggregation-induced emission (AIE). It is used in the preparation of a polymerization initiator, diphenylmethyl potassium (DPMK)

Triphenylmethane is utilized in synthesis of triarylmethane dyes, e.g. bromocresol green, malachite green





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2. Organic Chemistry, R. T. Morrison, R. N. Boyd, Pearson Education Pvt. Ltd.
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