Name of Unit	Polynuclear Aromatic Hydrocarbons
Subject /Course	Pharmaceutical Organic Chemistry-II
Subject/Course ID	BP301T
Module No.	4
Class: B.Pharm.Semester	III
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Learning Outcome of Module-3

LO	Learning Outcome	Course Outcome Code
LO1	To understand the term polynuclear aromatic hydrocarbons and classification	BP301.3
LO2	To gain knowledge about different methods to prepare polynuclear aromatic hydrocarbons	BP301.3
LO3	To understand various physical and chemical properties	BP301.3
LO4	To gain the knowledge of uses of some compounds.	BP301.3

The Pioneer Pharmacy Institute of Punjab

Content Table

Topic
• Introduction of Polynuclear Hydrocarbons
• Synthesis of methods of preparation of Polynuclear Hydrocarbons
• Physical and Chemical properties
• Medicinal uses of Polynuclear Hydrocarbons Naphthalene, Phenanthrene, Anthracene,
• Structure and uses of Diphenylmethane, Triphenylmethane and their derivatives.

INTRODUCTION

A 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 considerPAHs is molecules made by fusing two or more benzene rings. Polynuclear aromatic hydrocarbon molecules contain onlycarbon and hydrogen atoms.

PROPERTIES

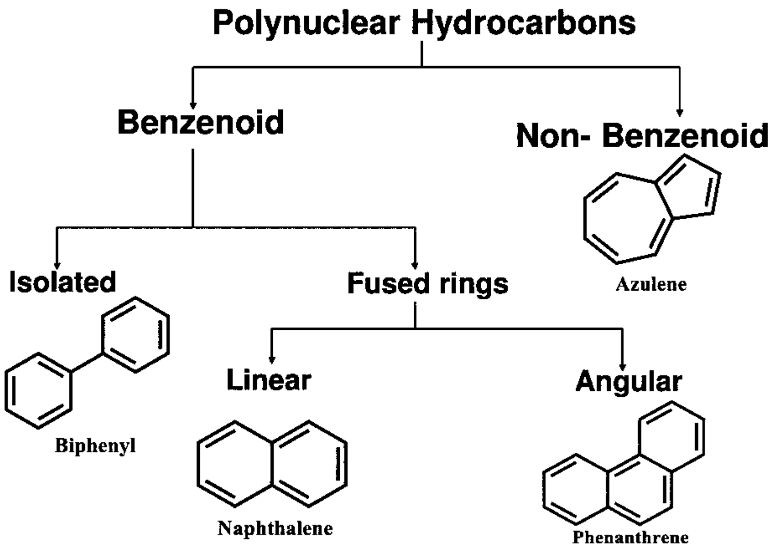
Polynuclear aromatic hydrocarbons are lipophilic, nonpolar molecules. They tend to persist in the environment because PAHs are not very soluble in water. While 2- and 3-ring PAHs are somewhat soluble in aqueous solution, the solubility decreases nearly logarithmically as molecular mass increases. 2-, 3-, and 4-ring PAHs are sufficiently volatile to exist in the gas phases, while larger molecules exist as solids. Pure solid PAHs may be colourless, white, pale yellow or pale green.

SOURCES

PAHs are organic molecules that form from a variety of natural and environmental pollutant reactions. Natural PAHs form from forest fires and volcanic eruptions. The compounds are numerous in fossil fuels, such as coal and petroleum.

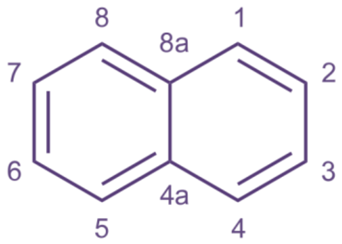
Man contributes PAHs by burning wood and by the incomplete combustion of fossil fuels. The compounds occur as a natural consequence of cooking food, particularly when food is cooked at a high temperature, grilled, or smoked. The chemicals are released in cigarette smoke and from burning waste.

CLASSIFICATION:



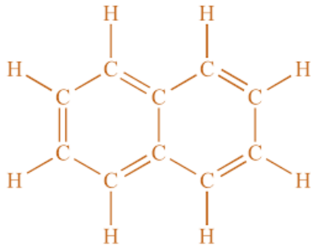
NAPTHALENE

Naphthalene ($\mathrm{C10H8}$) is an aromatic hydrocarbon in which two benzene rings are fused in ortho positions. For the purposes of naming its derivatives, the positions are indicated by figures.



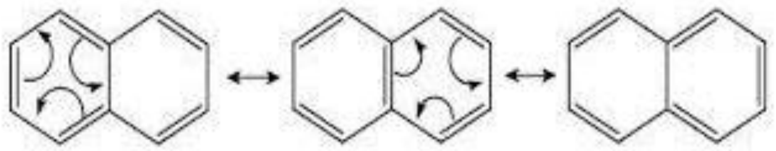
STRUCTIRE OF NAPTHALENE

All the carbons in naphthalene are sp^2 hybridized. The carbon atoms are joined by sp^2-sp^2 sigma bonds, while s-sp^2 bonds connect eight carbons with hydrogen atom.



Each of 10 carbons has an unused p-orbital containing an electron. These p-orbital of carbons of two rings overlaps to form a continuous pi-molecular orbital. One lobe is located above and one located below the two hexagons. The bond angle is 120^{0}C.As a result of delocalization of the 10 pi-electrons, the naphthalene ring became stable. Due to this stability it gives substitution reactions like benzene. Bond length between carbon and carbon is different at different position generally (C$_1$-C$_2$) 1.36 Å and (C$_2$-C$_3$) 1.40 Å.

According to the resonance theory naphthalene is considered to be the hybrid of three canonical form. The resonance energy ofnaphthalene is about 61 kcal/mole. This value is less than twice the amountof a single benzene ring (36 kcal/mole). As a result, naphthalene is somewhat less aromatic (morereactive) than benzene.

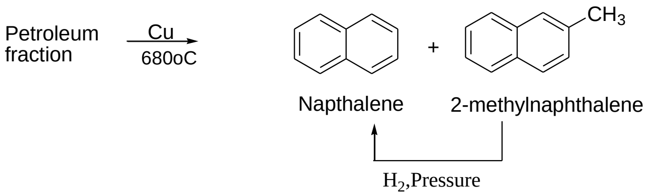


METHOD OF PREPARATION

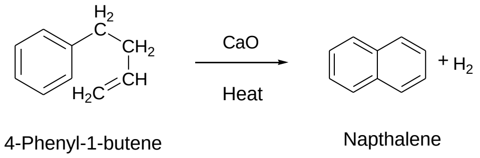
Naphthalene is the largest single component of coal-tar about (6-10 percent).The hydrocarbon wasfirst noticed as a deposit in the condensers during the distillation of naphtha fraction and hence itsname .It is obtained chiefly by cooling the middle oil fraction an(160-230°),where upon naphthalenecrystallisesout. The crude crystalsareremoved bycentrifuging.

Thesearemeltedandthentreatedsuccessivelywithconcentratedsulphuricacid(toremovephenols). Finallythenaphthaleneis sublimed to give thepure product.

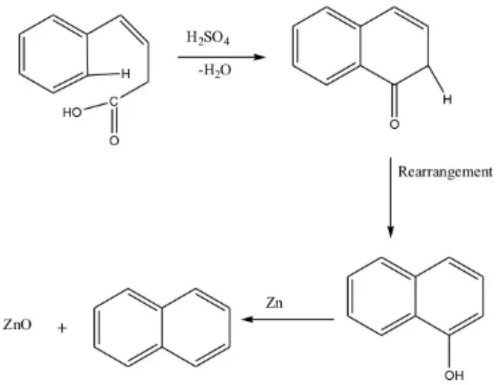
1. From petroleum- When petroleum fraction are passed over copper catalyst at 680^0C, naphthalene and methyl naphthalene are formed. The methylnaphthalene obtained is further converted into naphthalene by heating with hydrogen under reduced pressure.**(Dealkylation reaction).**



2. From 4-Phenyl-1-butene- When 4-phenyl-1-butene is passed over red hot calcium oxide, naphthalene is obtained.

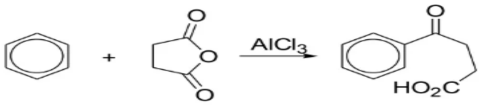


3. From 4-pheyl-3-butenoic acid- When 4-phenyl-3-butenoic acid is heated with conc. Sulphuric acid 1-napthol is formed, this on distillation with zinc dust gives naphthalene**.**

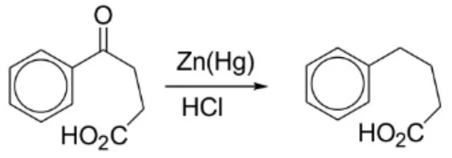


4. By Haworth synthesis- This reaction consists of 5 steps.

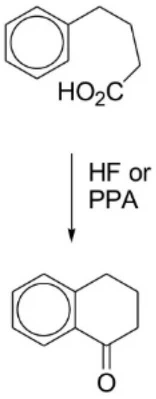
   Step-I (Friedal Craft acylation)- Benzene and succinic anhydride are heated in presence ofaluminium chloride to form β-benzoylpropionic acid.



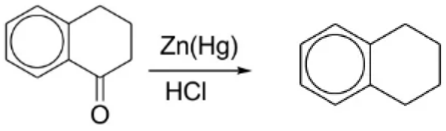
   Step-II(Clemmenson reduction)- β-benzoylpropionic acid is treated with amalgamated zinc in presence of hydrochloric acid to give γ-Phenylbutyric acid.



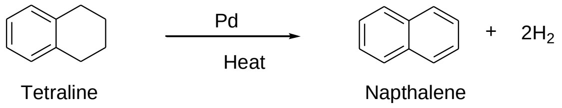
Step-III(Ring Closure reaction) γ-Phenylbutyric acid is heated with conc.sulphuric acid or polyphosphoric acid to form α-tetralone.



Step-IV(Clemmenson reduction) – α-tetralone is heated with amalgamated zinc or HCl to form tetraline.



Step-V(Aromatization)- Tetraline is heated with pallaium to yield naphthalene.



Physical:-

Naphthaleneisawhitesolidwhichcrystallisesinshiningplates.,m.p.-80°,b.p.-218°,havingastrongodour .Itisveryvolatileandsublimesreadilyonwarming. Naphthaleneisinsolubleinwater,but dissolves easilyinorganicsolvents, particularlyin ether andbenzene.

Chemical:-

The reactions of naphthalene are essentially the same as those of benzene. It undergoessubstitutionreadilyandformsadditionproducts.

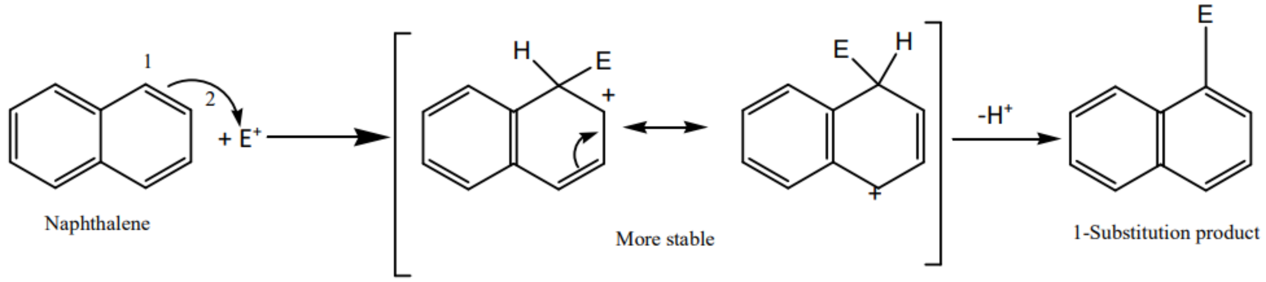
Howeveritissomewhatlessaromaticthanbenzene. Thus the double bonds in naphthalene exhibit in part the reactivity of alkenes and it formsaddition compounds more readily than does benzene. As soon as one of the ring is fully saturated byadditionof hydrogenor halogen.

REACTIONS OF NAPTHALENE

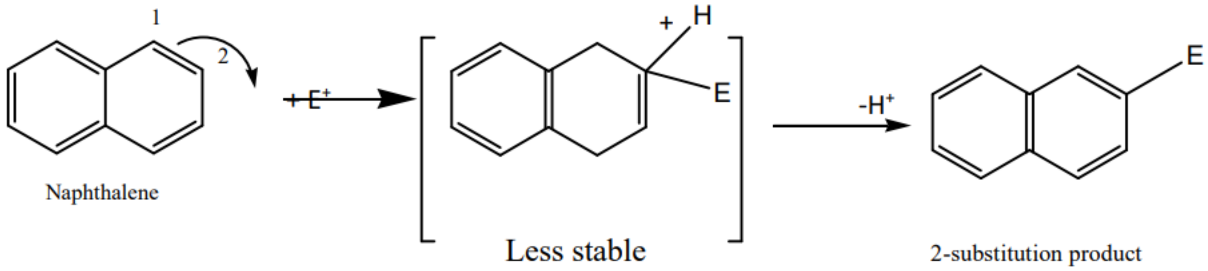
i) **Electrophilicsubstitutionreactions**:

Naphthalene, likebenzene,undergoeselectrophilicsubstitutionreaction. Substitutionoccursprimarily at C1(α-position).Thiscanbeunderstoodifweexaminetheintermediatecarbonium ion. Two resonance forms can be written for the intermediate carbonium ion obtained fromtheattackatC-1(withoutinvolvingtheotherring),where as onlysuchformispossibleforsubstitutionat C-2.E^+in the following equationsrepresentsan electrophile.

Attack at C_1

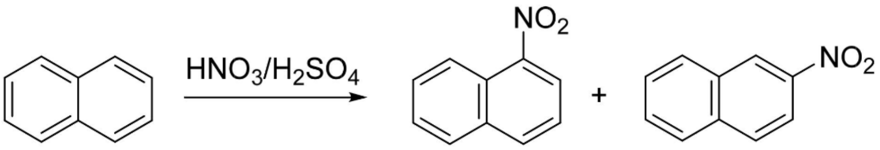


Attack at C-2

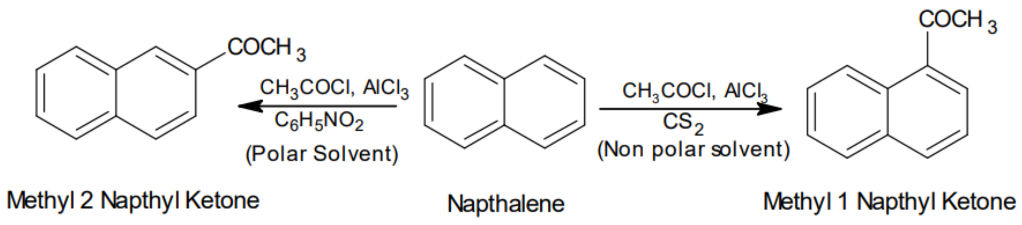


Consequently the former intermediate is more stable and the product with a substituent at C-1 predominates. Substitution at C-2 (ß-position) occurs only when the reactions are carried at higher temperatures or when bulkier solvents are used.

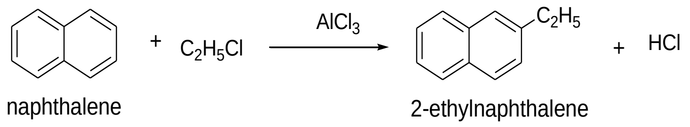
1. **Nitration-** Naphthalene nitrates with a mixture of nitric acid and sulphuric acid at low temperature to form mainly the α-nitronaphthalene.



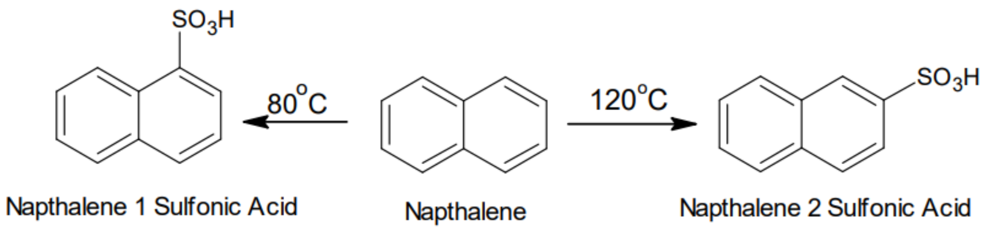
2. **Friedal Craft Acylation-** Naphthalene undergoes Friedel-crafts reaction with acetyl chloride to form the α or β products depending on the conditions.



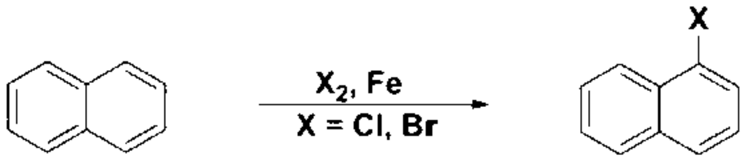
3. **Friedal Craft Alkylation-**Napthalene undergoes friedal craft alkylation with alkyl halide in the presence of aluminium chloride to give 2-alkylnapthalene.

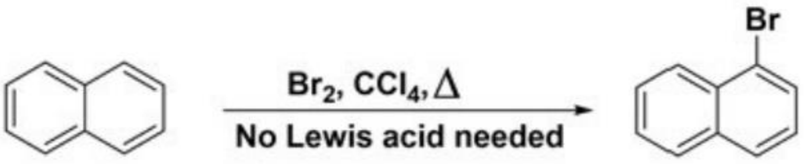


4. **Sulphonation-** Sulphonation of Napthalene at low temperature (80°C) produces naphthalene-1-sulfonic acid while at higher temperature (120°C) it produces naphthalene -2-sulfonic acid.

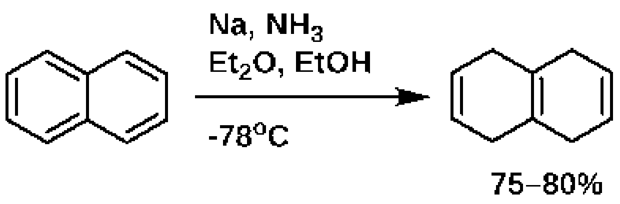


5. **Halogentaion-** Naphthalene reacts with halogen to give the 1-halo derivative of naphthalene.

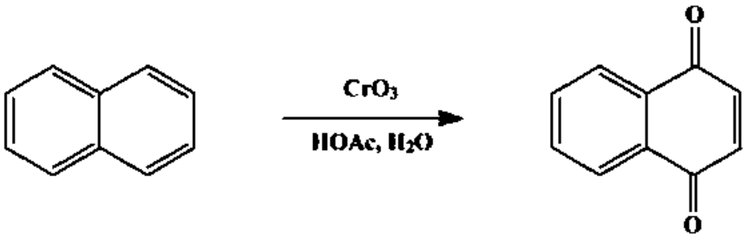




6. **Reduction-** Naphthalene undergoes reduction more readily than benzene, when it react with sodium or ethylalcohol , it gives 1,4-dialin



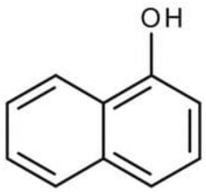
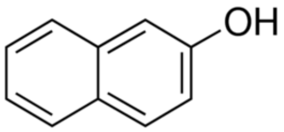
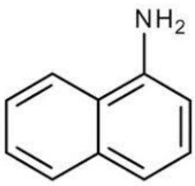
7. **Oxidation** -Naphthaleneon oxidation with chromium trioxide in acetic acid it gives 1,4-Naphthaquinone.



MEDICINAL USES OF NAPHTHALENE

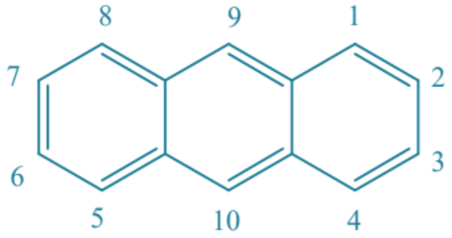
1. It is used in manufacturing of ‘moth balls’ to protect woolen clothes, recently *p*-dichlorobenzene replaced it due to its less obnoxious odour.
2. It is used in manufacturing of phthalic anhydride.
3. It is also used in some dyes and medicinal products.
4. It is used as dusting powder in veterinary medicines.
5. Polyethylene naphthalene is used to prepare plastic bottles.
6. Naphtahlene sulphonic acid is used to prepare plasticizer and natural rubber etc.

DERIVATIVES OF NAPHTHALENE

Naphthols (Hydroxy derivatives of Naphthalene)	 
Naphthylamine (Amine derivative of Naphtahtene)	

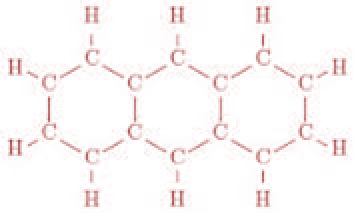
ANTHRACENE

Anthracene is present is coal-tar to the extent of 0.3 to 3.5 percent hence its name Greek anthrac-meaning coalon distillation of tar , it passes over in the high boiling fractions anthracene oil.The molecule of anthracene is made of three benzene nuclei fused in ortho positions . It is a colorless solid polycyclic aromatic hydrocarbon

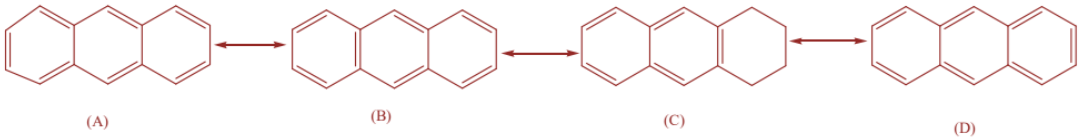


Anthracene

STRUCTURE OF ANTHRACENE



- ✓ It has sp^2hybridization, the sp^2 hybrid orbital overlaps each other and with s orbital of the ten hydrogenatoms forming C-C and C-H σ bonds.
- ✓ All carbon bonds in anthracene are not of the same length. in particular, the C1-C2 bond is considerably shorter(1.37A°) than the (C2-C3)bond. (1.42A°). this difference in bond lengths can be understood if we examine the four resonance forms given above.Notice that the C1-C2 bond is double in three structures (A,B and C), and single in only one (D);whereas the C2-C3 bond is single in three structures(A,B andC) and double in only one (D). we would, therefore,expect the C1-C2 bond to have more double-bond character (shorter bond length), and the C2-C3 bond to have more single-bond character(longer bond length).
- ✓ The resonance energy of anthracene is 84 kcal/mole. This averages to 28 kcal/mole per ring,which is substantially lower than that of benzene (36 kcal/mole).As a result, anthracene is much less aromatic than benzene and behaves more like an unsaturated aliphatic hydrocarbon.

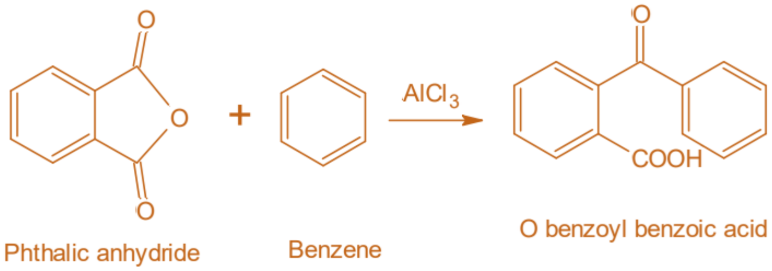


METHOD OF PREPARATION

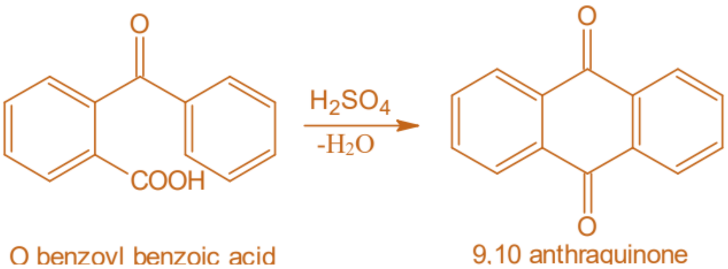
1. **By Friedal Craft reaction-** Two molecules of benzyl chloride is condensed in presence of $AlCl_3$ to produce Anthracene.

2. By Haworth Synthesis-

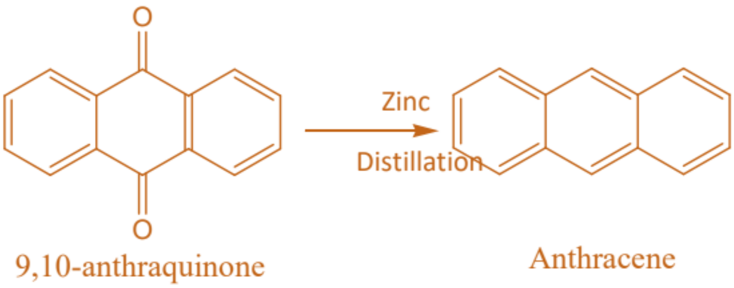
Step I: Benzene on reaction with phthalic anhydride in presence of AlCl3 produces O-Benzoyl benzoic acid.



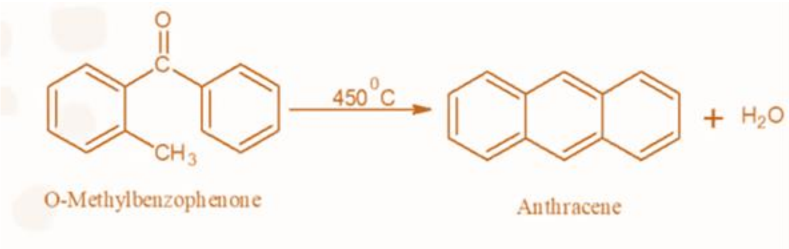
Step II: O-benzoyl benzoic acid is heated with conc. H_2SO_4 to give 9.10-anthraquinone.



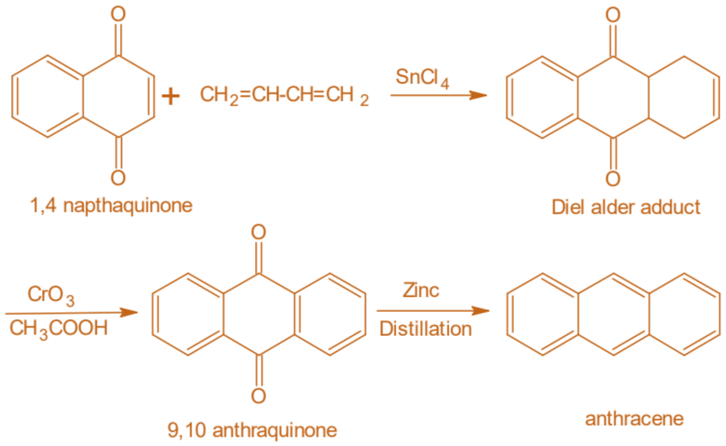
Step III: Distillation of 9,10-anthraquinone with zinc dust will produce anthracene.



3. **By Elbs Reaction-** Intermolecular condensation of diaryl ketone containing a methyl or methylene substituent ortho to the carbonyl group leading to the formation of aronmatic compound is referred to as Elbs reaction.



4. **By Diels Alder reaction-** This involve the reaction of napthaquinone with 1,3-butadiene. The product of this reaction is oxidized with chromium trioxide in glacial acetic acid to form 9, 10 anthraquinone. Distillation of Anthraquinone with Zinc dust yields Anthracene.



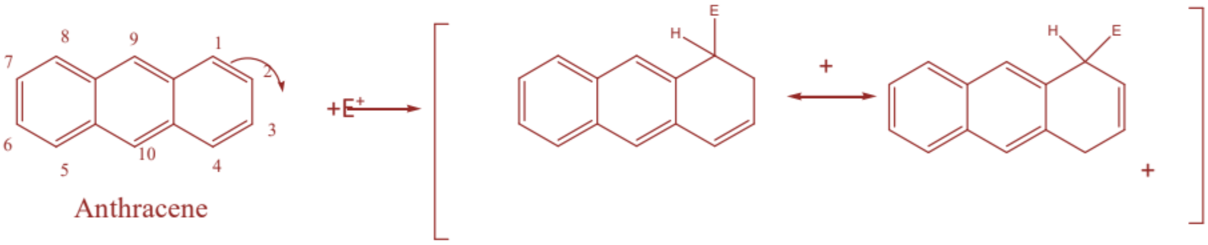
PHYSICAL PROPERTIES

Anthracene is a colorless solid. It melts at 218°C and boils at 340°C.Anthracene is insoluble in water,but dissolves in benzene. It shows a strong blue fluorescence when exposed to ultraviolet light.This fluorescent property of anthracene is used in criminal detection work,since a small amount of finely powder anthracene on clothing,skin,money, etc.,is not detected under ordinary light but easily noticed when exposed to ultraviolet light

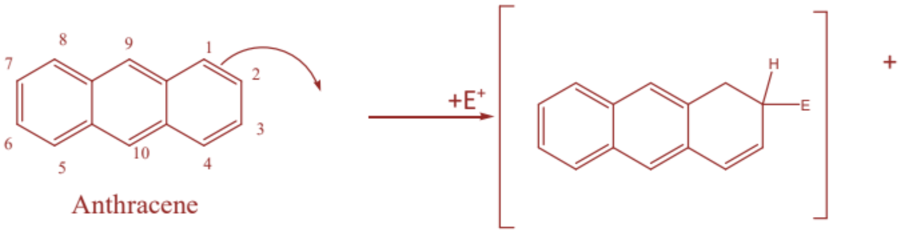
CHEMICAL REACTION

Chemical anthracene undergoes addition and electrophilic substitution reactions These reactions preferentially occur at the C-9 and C-10 positions.This can be understood if we examine the intermediate carbonium ions obtained from attack at C-1,C-2, and C-9(all other positions are equivalent to either 1 or 2 or 9 by symmetry).E+ in the following equations represents an electrophile.

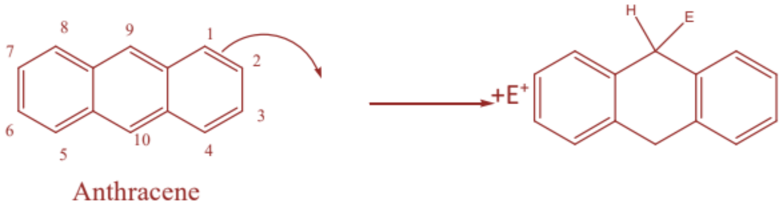
Attack at C-1



Attack at C-2



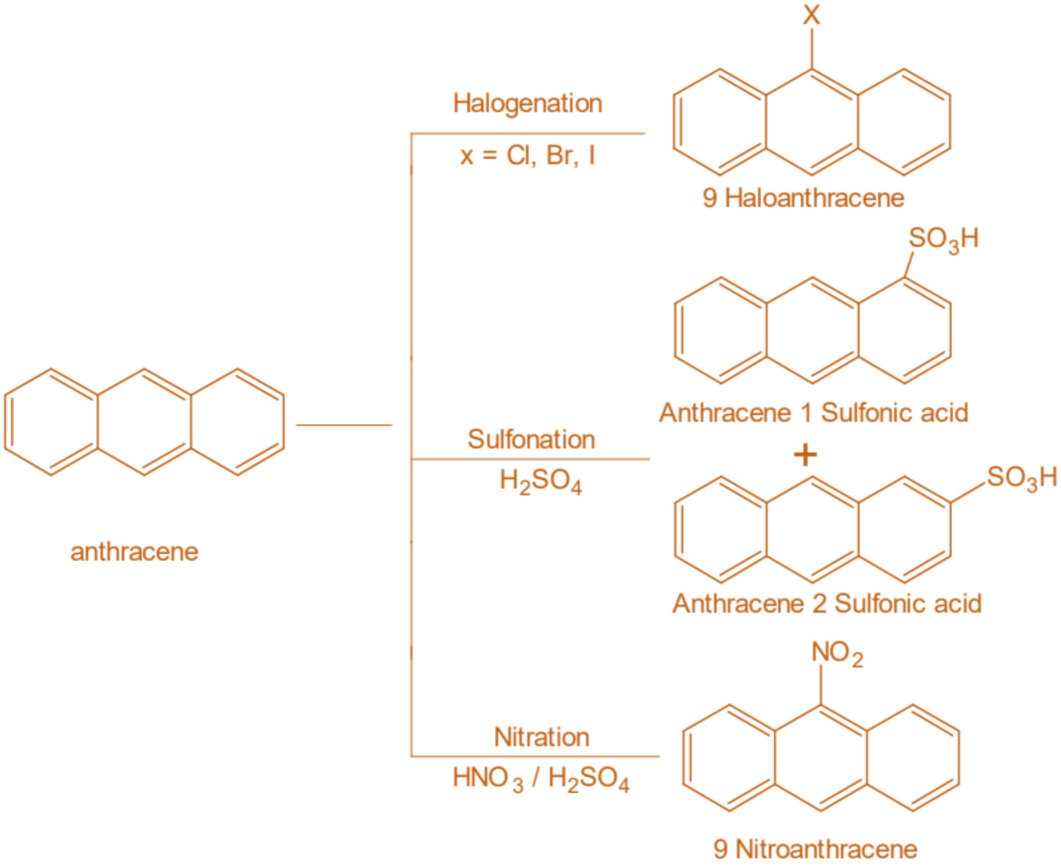
Attack at C-9

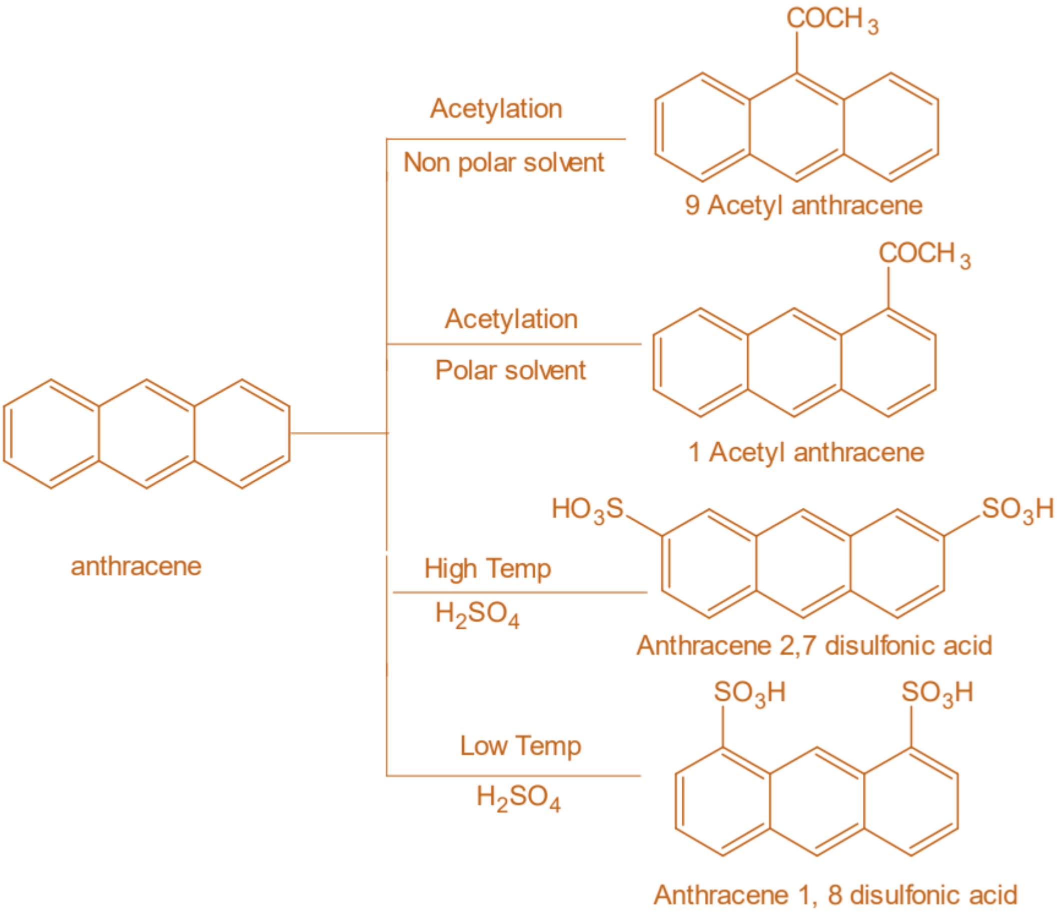


Attack at C-9 yields a carbonium ion intermediate in which two benzene rings are retained; whereas attack C-1 or C-2 yields an intermediate in which a naphthalene system is retained. The former intermediate is more stable and its formation is favoured because the resonance energy of two benzene rings (2 * 36 =72 kcal) exceeds that of naphthalene (61kcal).

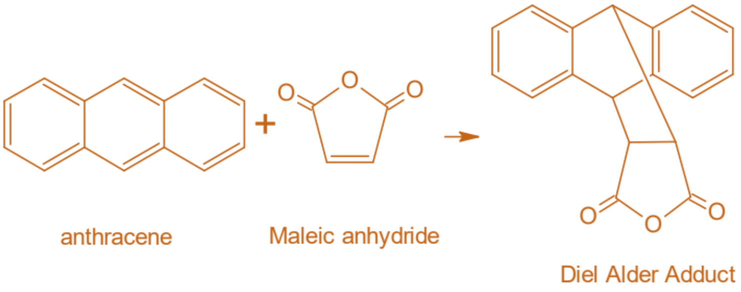
CHEMCAL REACTIONS

1. **Electrophilic substitution reaction-** Anthracene undergoes different type of electrophilic substitution reactions like halogenation, sulphonation, nitration etc.

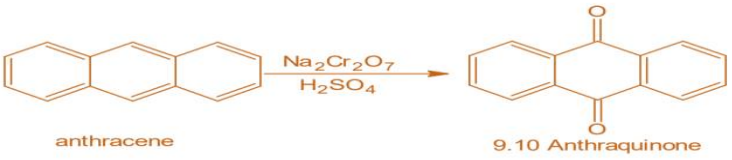




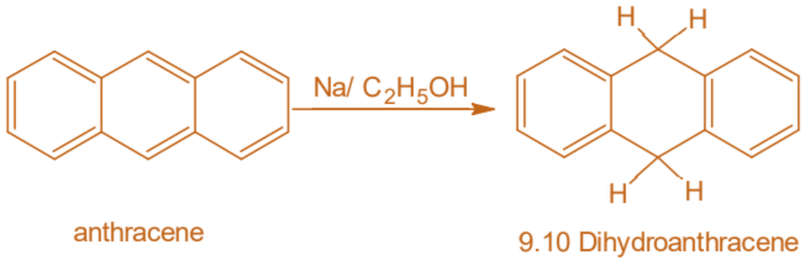
2. **Diels-Alder Reaction-** Anthracene undergoes Diels-Alder reaction at 9, 10 positions and forms endo anthracene maleic anhydride.



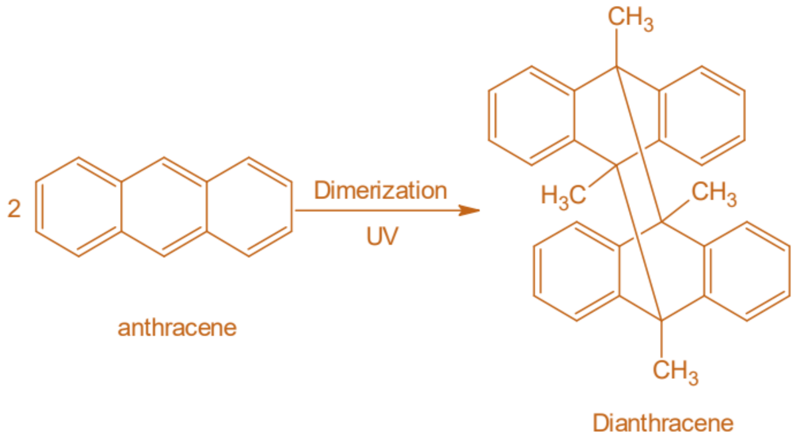
3. **Oxidation-** Anthracene undergoes oxidation with sodium dichromate and sulfuric acid to form 9, 10 anthraquinone.



4. **Reduction-** Anthracene on reduction with sodium and ethyl alcohol produces 9, 10 dihydroanthracene.



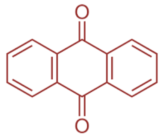
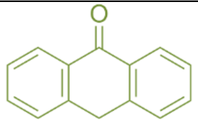
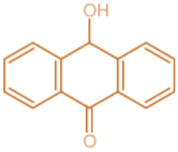
5. **Dimerisation-** Dimerization of anthracene in UV light produces dianthracene.



USES OF ANTHRACENE

1. Anthracene glycosides are oxygenated derivatives of pharmacological importance that are used as laxatives or catharatics,antineoplasticagent,polycystic kidney.
2. It is used in manufacturing of Anthraquinone, alizarin and several other dyes.
3. Used as preservative in wood and used in insectisides.

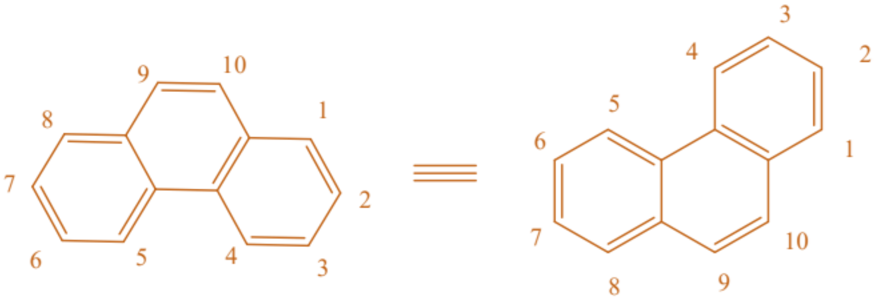
DERIVATIVES OF ANTHRACENE

Anthraquinone	
Anthrone	
Oxanthrone	

PHENANTHRENE

Phenanthrene is apolycyclic aromatic hydrocarbon composed of three fusedbenzenerings. In its pure form, it is found incigarette smokeand is a knownirritant,photosensitizingskin to light.

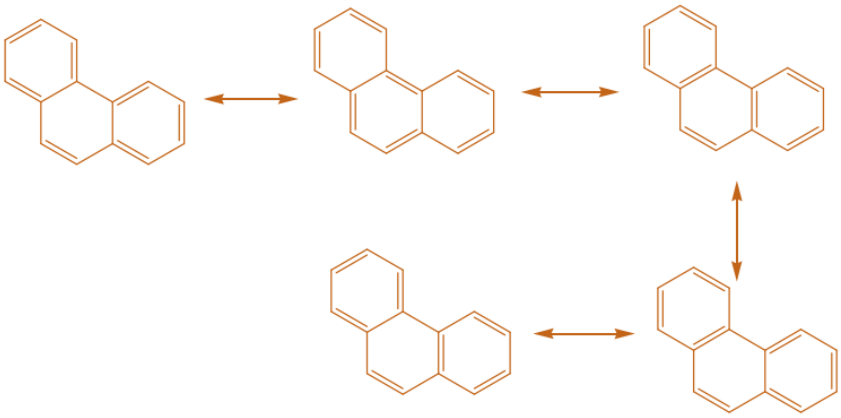
Phenanthrene appears as a white powder having bluefluorescence.Phenanthrene is the backbone of morphine.



STRUCTURE

It is also a planar molecule like anthracene.All 14 carbons are sp^2 hybridized. The sp^2 hybrid orbitals overlap each other and with s orbital of 10 hydrogen atom to formC-C and C-H σ bonds.Each carbon atom possess a p orbital, and overlap of these p orbital produce a π molecular orbitals.Phenanthrenen shows aromatic properties because the resulting π molecular orbital satisfies the Huckel`s rule (n=3 in 4n+2).

Resonance energy=91Kcal/mole



METHOD OF PREPARATION

1. By Haworth Synthesis- This involves 5 steps

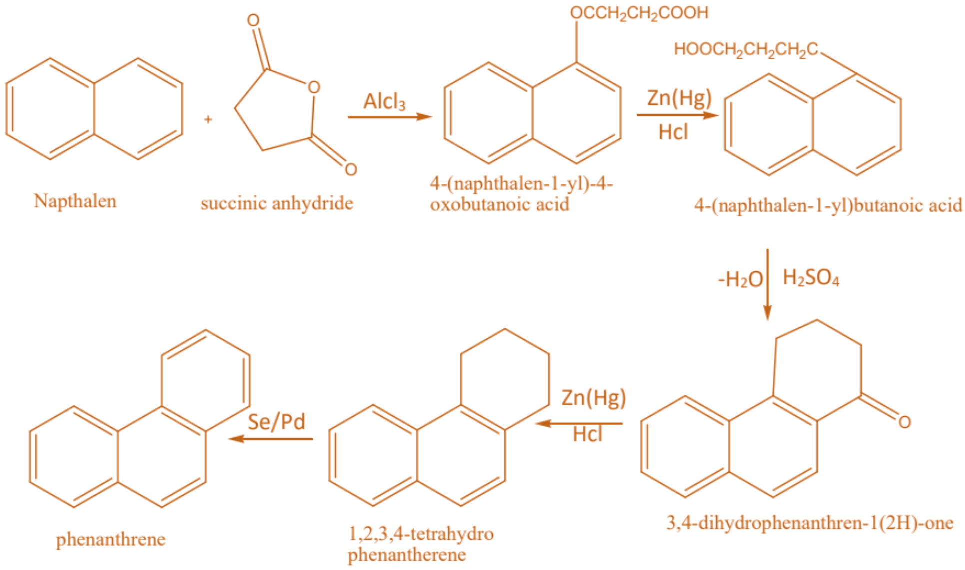
Step-1 This involve the treatment of naphthalene with succinic anhydride in the presence of aluminium chloride to form napthoylpropionic acid (Friedal craft acylation).

Step-2 Napthoylpropionic acid treated with amalgamated Zinc in the presence of HCl to give napthobutyric acid (clemmenson reduction).

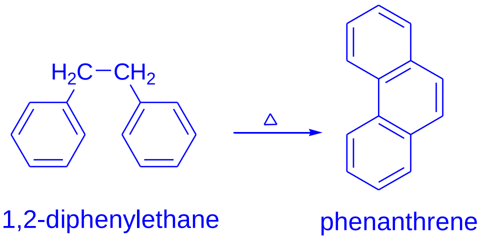
Step-3 Napthobutyric acid heated with sulphuric acid to give 1-keto-1,2,3,4-tetrahydrophenanthrene(Ring closure reaction).

Step-4 1-keto-1,2,3,4-tetrahydrophenanthrene reacted with amalgamated zinc in the presence of HCl to give 1,2,3,4-Tetrahydrophenanthrene (clemmenson reduction).

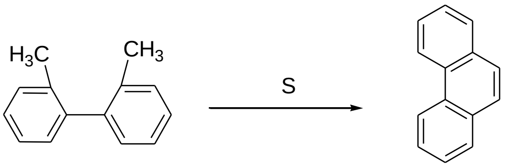
Step5-1,2,3,4-Tetrahydrophenanthrene heated with palladium to yield phenanthrene.



2. **By Dibenzal-** Phenanthrene can be obtained by passing dibenzal over red hot tube.



3. **From 2,2-Dimethyldiphenyl-** Phenanthrene can be obtained by cyclodehydrogenation of2,2-Dimethyldiphenylusing sulfur.

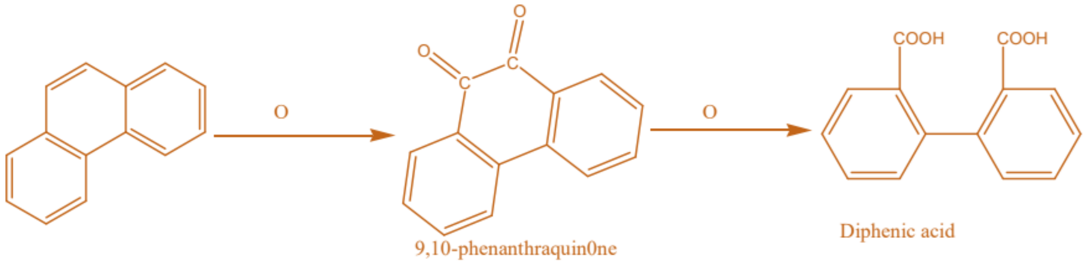


PHYSICAL PROPERTIES

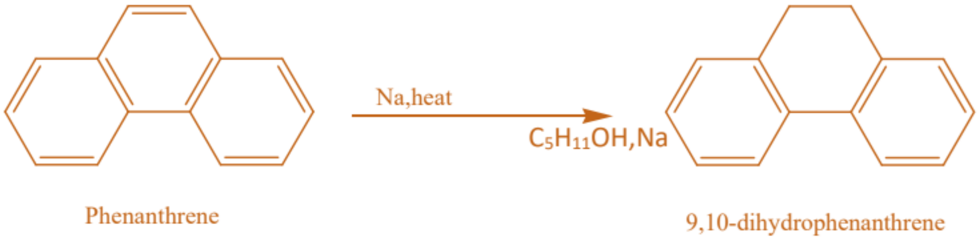
It is colorless solid having a melting point of 100ºC. It is insoluble in water but dissolves readily in organic solvents like ethanol, benzene, and ether.

CHEMICAL REACTIONS

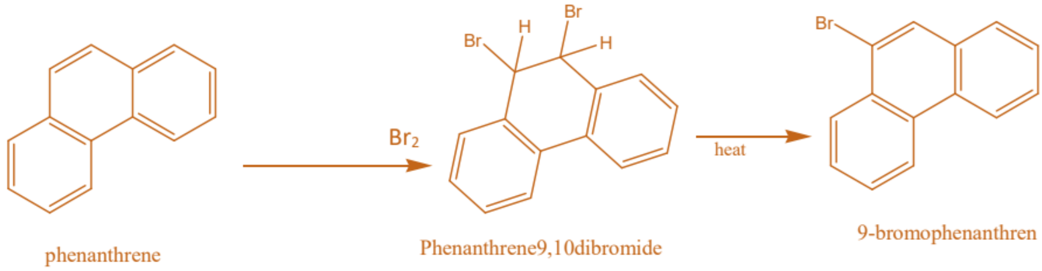
1. Oxidation-When oxidized with chromic acid in acetic acid phenanthrene yields a diketone,phenantraquinone which upon further oxidation gives diphenic acid.



2. Reduction- Phenanthrene undergoes reduction with sodium and isopentanol to form 9.10-dihydrophenenthrene.



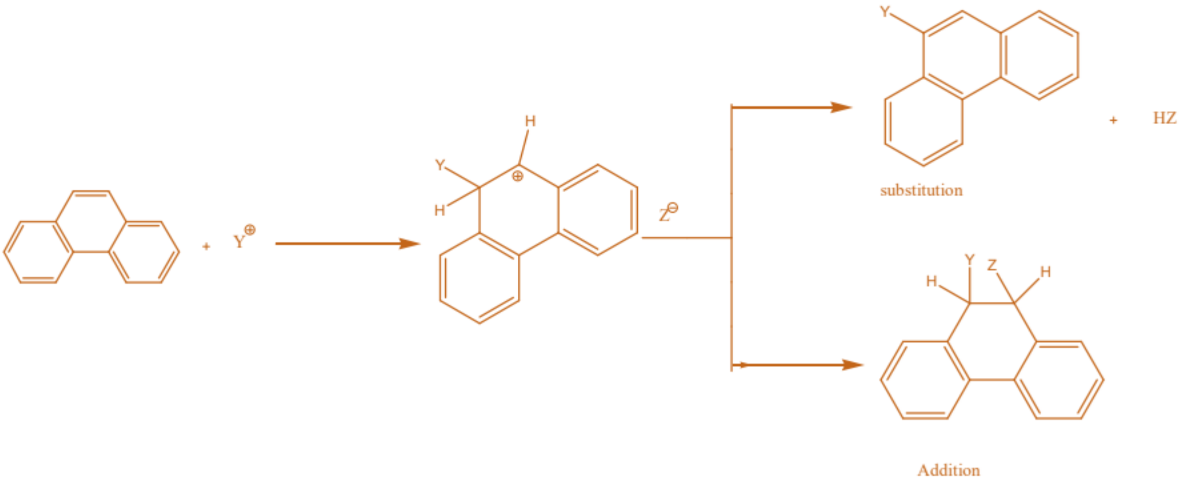
3. Bromination- Phenanthrene reacts with bromine to give 9-Bromophenanthrene.

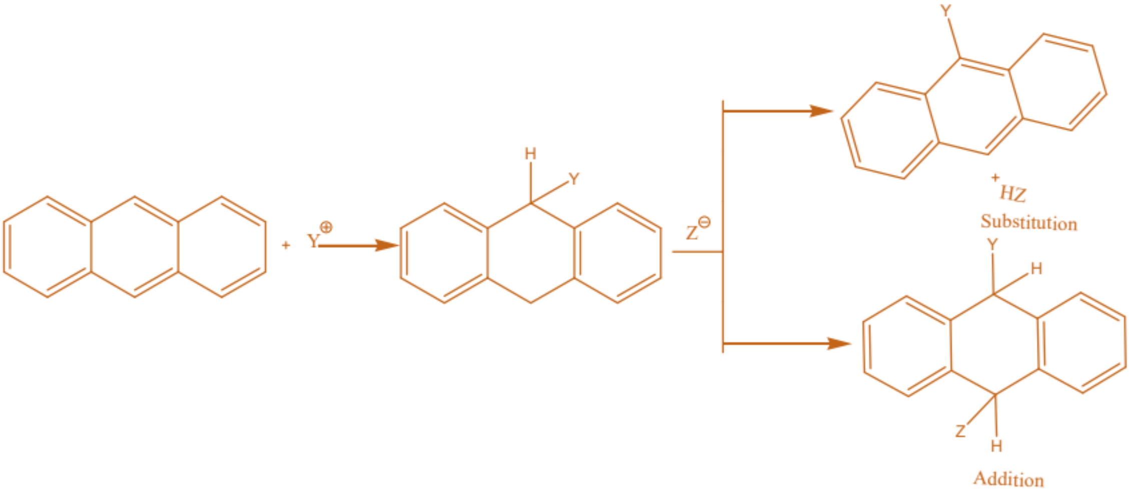


The reactivity of the 9- and 10-positions toward electrophilic attack, whether reaction leads to substitution or addition, is understandable since the initially formed carbocation is the most stable one, in which aromatic sextets are preserved in two of the three rings.

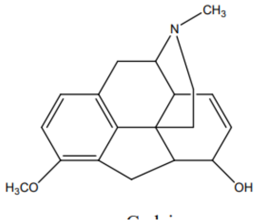
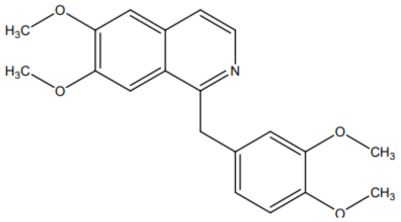
This carbocation can then either (a) give up a proton to yield the substitution product, or (b) accept a nucleophile to yield the addition product.

The tendency for these compounds to undergo addition is due to the comparatively small sacrifice in resonance energy (12 kcal/ mol for anthracene, 20 kcal/ mol or less for Phenanthrene).





DERIVATIVES OF PHENANTHRENE

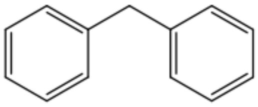
Codein	
Papaverine	

USES

1. It is used to make dyes, plastic and pesticides, also used in explosive and drugs.
2. It is also used to make bile acid, steroids, cholesterol, cardiac glycosides.

DIPHENYLMETHANE

Diphenylmethane is an organic compound with the formula$(C_6H_6)_2CH_2$ abbreviated by (CH_2Ph_2).The compound consists of methane where in two hydrogen atoms are replaced by two phenyl groups.It is a white solid.



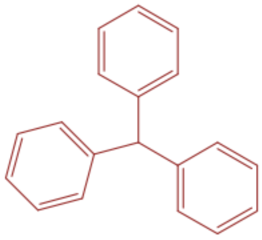
USES

1. Diphenylmethane is widely used in the synthesis of luminogens for aggregation induced emission.
2. Diphenylmethyl potassium used in the preparation of polymerization.
3. It is used in the synthesis of methylene diphenyl diisocyanate, which is used in the manufacturing of polyethene as an industrial strength adhesive.

TRIPHENYLMETHANE

Triphenylmethane (C6H6)3CH is the chromogen of a large number of dyes.The common chromophore is the p-quinoid structure and the auxochromes are OH,NH_2 and NR_2.

Triphenylmethane dyes are very brilliant intense colours but fade quickly in light. Therefore,they are no longer much used on textiles. However, they are used in large quantities for coloring paper and typewriter ribbons where pastness to light is not so important.



Triphenylmethane

USES

1. It is used as backbone of various synthetic dyes.
2. Triphenylmethane has also been shown to inhibit neoplastic transformation of loti cells.

IMPORTANT QUESTIONS

2 MARKS QUESTION

1. What happens when anthracene is treated with sodium and ethyl alcohol?
2. What arenaphthols?
3. How many monosubstituted derivatives are possible for anthracene?
4. Give chemical reaction and uses of Triphenylmethane.
5. Give chemical reaction and uses of diphenylmethane.
6. What are polynuclear hydrocarbons? Write down the oxidation and reduction reaction of naphthalene.
7. Enlist various physical properties of Naphthalene.
8. Give the preferential position of naphthalene, and anthracene for electrophilic reaction.

5 OR 10 MARKS QUESTION

1. Write the synthesis, reactions, and uses of naphthalene and phenanthrene.
2. Give an account of Triphenylmethane and its derivatives.
3. Writedown chemical reactions of naphthalene.
4. Explain in detail method of preparation of anthracene and give its physical properties.
5. Write a detail note on Naphthalene.
6. Enlist the commonsteps involved in the Haworth synthesis of anthracene and phenanthrene.
7. Describe in detail the structure of Anthracene and Naphthalene.
8. Draw the structure of Derivatives of Phenanthrene and anthracene.