UNIT-IV - POLYNUCLEARHYDROCARBONS

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 consider PAHs is molecules made by fusing two or more benzene rings.Polynuclear aromatic hydrocarbon molecules contain only carbon 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.

Health Effects

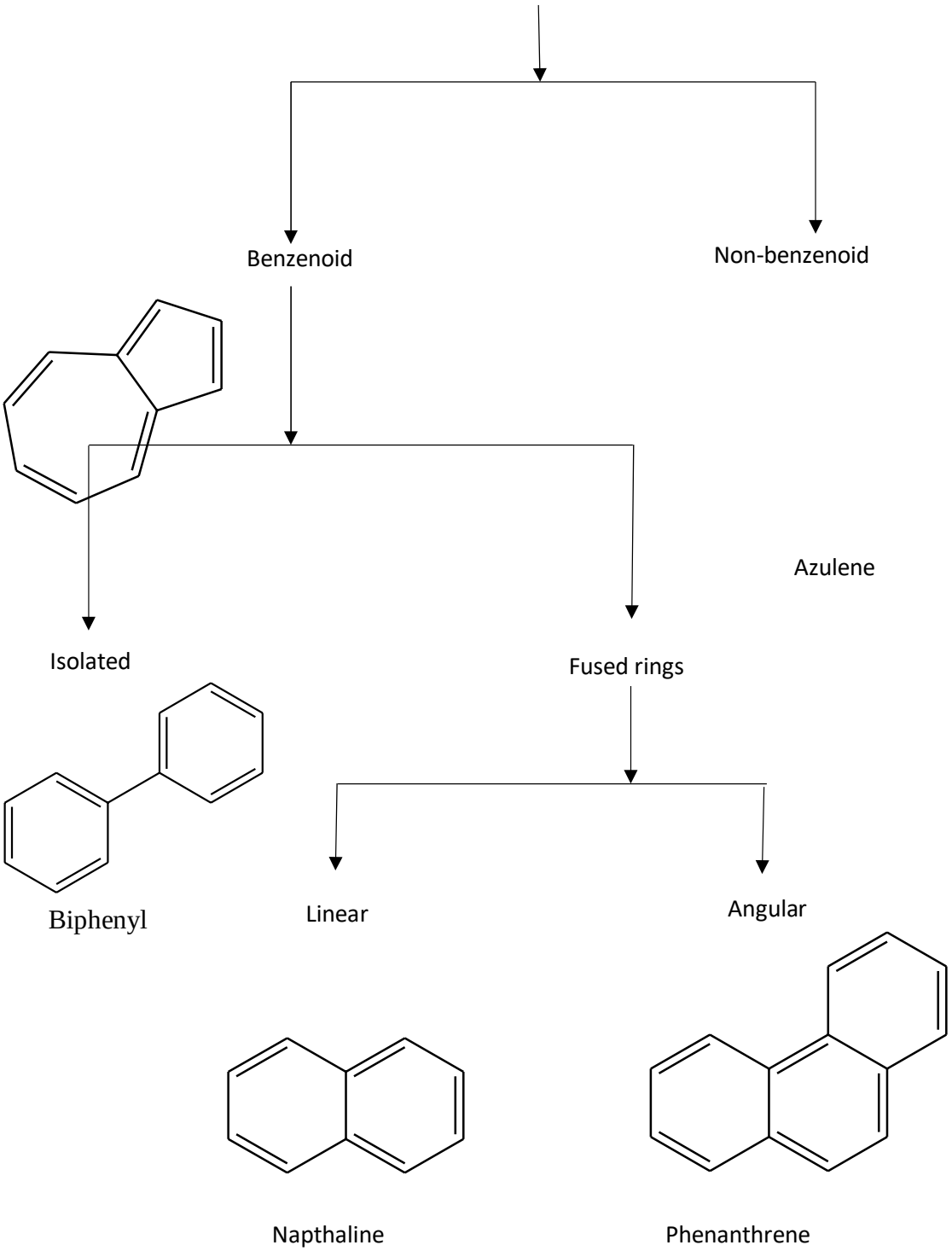
Polynuclear aromatic hydrocarbons are extremely important because they are associated with genetic damage and diseases. Also, the compounds persist in the environment, leading to increased problems over time. PAHs are toxic to aquatic life. In addition to toxicity, these compounds are often mutagenic, carcinogenic, and teratogenic. Prenatal exposure to these chemicals is associated with lowered IQ and childhood asthma.

People get exposed to PAHs from breathing contaminated air, eating food that contains the compounds, and from skin contact. Unless a person works in an industrial setting with these chemicals, exposure tends to be long-term and low-level, so there aren't medical treatments to address the effects. The best defence against health effects from PAH exposure is to become aware

of situations that elevate risk: breathing smoke, eating charred meat, and touching petroleum products.

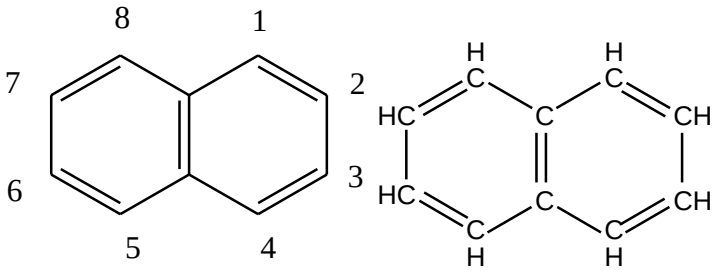
CLASSIFICATION:

Polyneuclear hydrocarbons



Napthalene:

Naphthalene ($C_{10}H_8$) is an aromatic hydrocarbon in which two benzene rings are fused in ortho positions. For the purposes of naming its derivatives,the positions are indicatedby figures.



Isolation from coal-tar:

Napthalene is the largest single component of coal-tar aboute (6-10 percent).The hydrocarbon was first noticed as a deposit in the condensers during the distillation of naphtha fraction and hence its name .It is obtained chifly by cooling the middle oil fraction an(160-230°),where upon naphthalene crystallises out.The crude crystals are removed by centrifuging.

These are melted and then treated successively with concentrated sulphuric acid (to remove phenols).Finally the naphthalene is sublimed to give the pure product.

Properties:

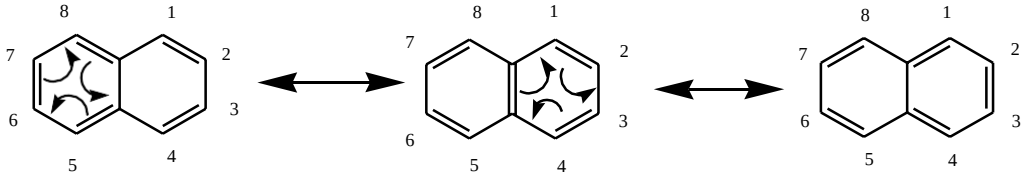
Physical:-Naphthalene is a white solide which crystallises in shining plates., m.p.-80°,b.p.-218°,having a strong odour.It is very volatile and sublimes radily on warming.Naphthalene is insoluble in water, but dissolves easily in organic solvents, particularly in eather and benzene.

Chemical:-The reactions of naphthalene are essentially the same as those of benzene .It undergoes substitution readily and forms addition products.however it is somewhat less aromatic than benzene.Thus the double bonds in naphthalene exhibit in part the reactivity of alkenes and it forms addition compounds more readily than does benzene.As soon as one of the ring is fully saturated by addition of hydrogen or halogen.

Resonance structure of naphthalene:

x-ray diffraction studies show that ,unlikebenzene,all carbon –carbon bonds in naphthalene are not of the same length.In particular the C1-C2 bond is considerably shorter (1.36A°) than the C2-X3 bond (1.40A°).This difference can be understood if we examine the three resonance forms given above.Notice that the C1-C2 bond is double in two structures (A and B) and single in only one (C) ; wherw as the C2-C3 bond is single in two structures (A and B) and double in only one (C). 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 lenghth).

The resonance energy of naphthalene is about 61 kcal/mole.This value is less than twice the amount of a single benzene ring (36 kcal/mole).As a result, naphthalene is somewhat less aromatic (more reactive) than benzene.

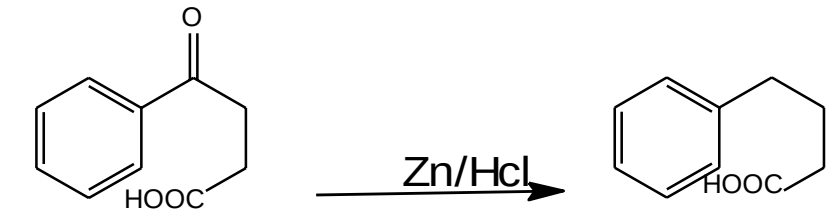


(A) (B) (C)

Preparation of Napthalene:

i) From 3-Benzoyl propanoic acid:

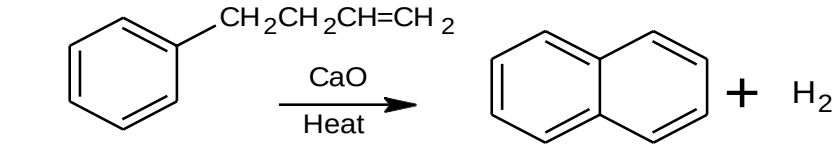
When 3-benzoyl propanoicacid is heated with sulphuric acid, α napthol is formed, which on distillation with zinc dust forms naphthalene.



3- Benzoyl propanoic acid 4-Phenyl butanoic Acid

ii) From 4-phenyl-1-butene:

When 4-phenyl 1 butene is passed over red hot calcium oxide naphthalene is formed.

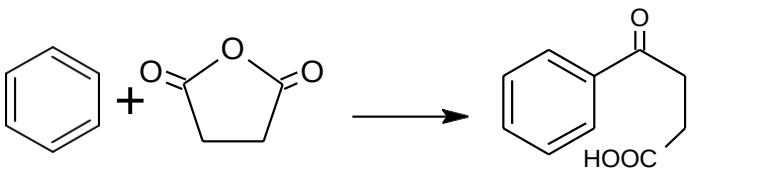


4 Phenyl 1 Butene Napthalene

iii) Haworth synthesis:

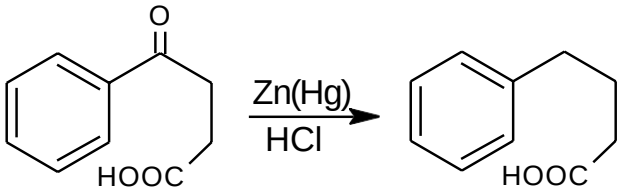
It involves five steps.

Step I: Formation of 3-benzoyl propanoic acid by the treatment of benzene with succinic anhydride.



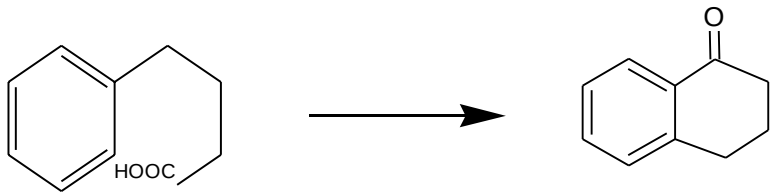
Benzene Succinic Anhydride 3 Benzoyl Propanoic Acid

Step II: 3 benzoyl propanoic acid is treated with amalgamated zinc to produce 4-phenyl butanoic acid.



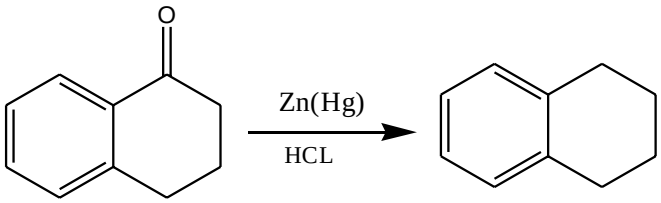
3 Benzoyl Propanoic Acid 4 Phenyl Butanoic Acid

Step III: 4- phenyl butanoic acid is heated with conc. Sulphuric acid to form Tetralone (ring closer reaction).



4-Phenyl Butanoic Acid Tetralone

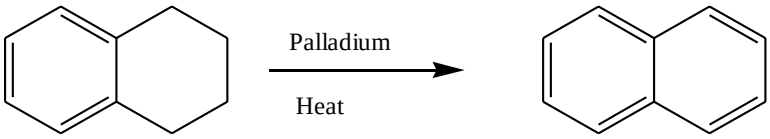
Step IV: Tetralone is again heated with amalgamated zinc and HCl to give tetraline.



3,4-Dihydro-2H-naphthalen-1-one 1,2,3,4-tetrahydronaphthalene

Tetralone Tetraline

Step V: Tetraline is heated with palladium to yield naphthalene.

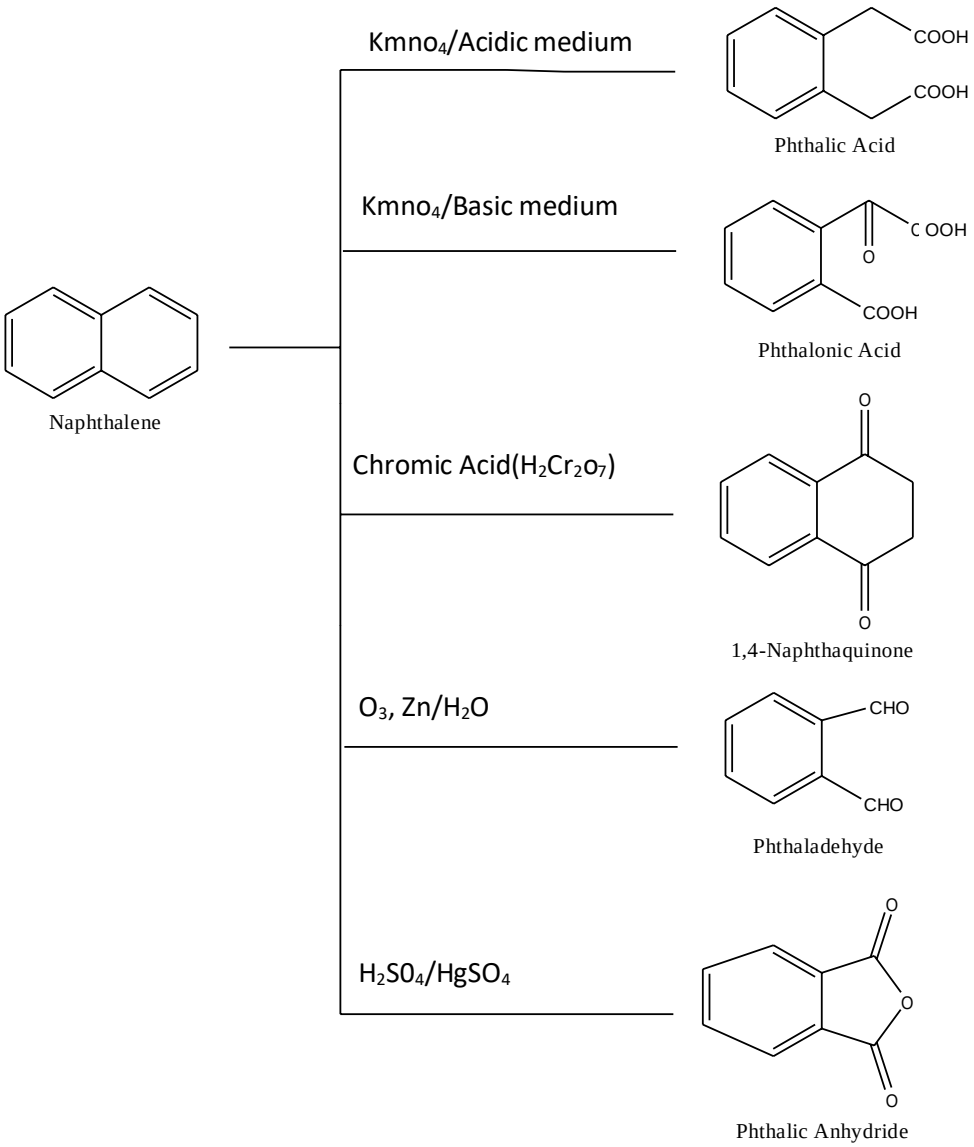


Tetralin Naphthalene

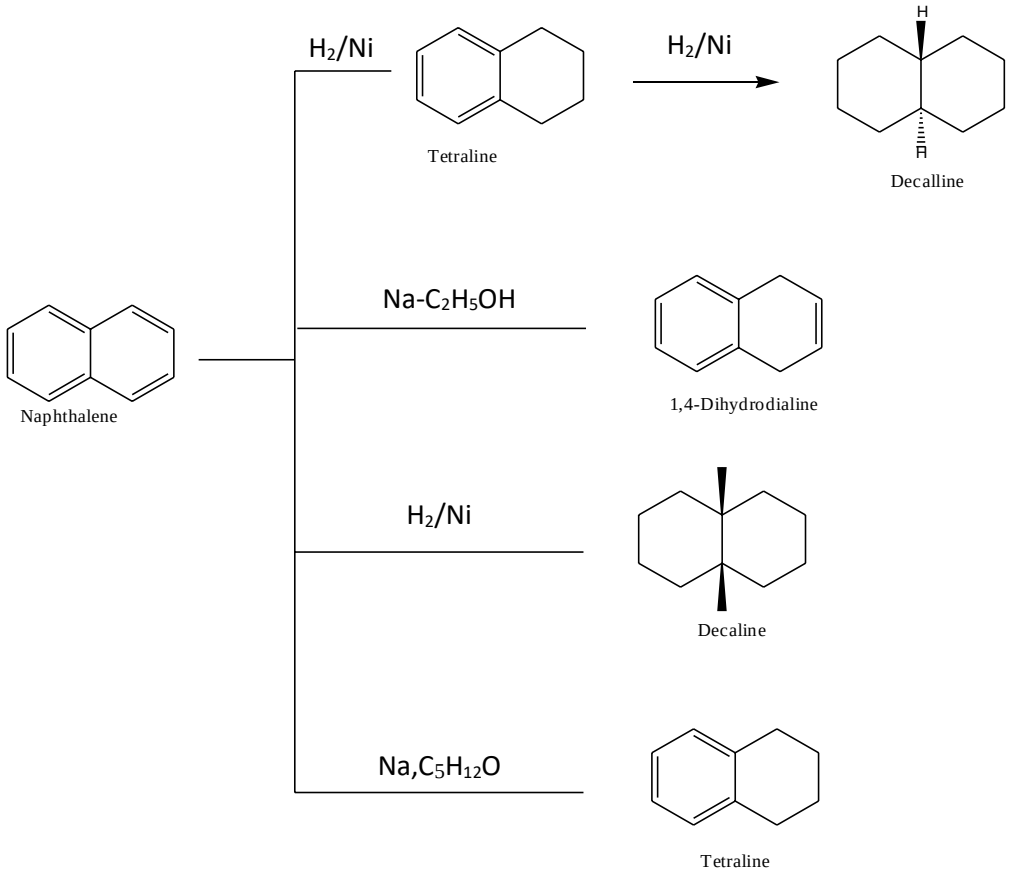
Reactions of Naphthalene:

Naphthalene is more reactive than benzene. It undergoes several reactions like oxidation, reduction, addition, nitration, halogenations, acylation etc.

i. Oxidation of Naphthalene:

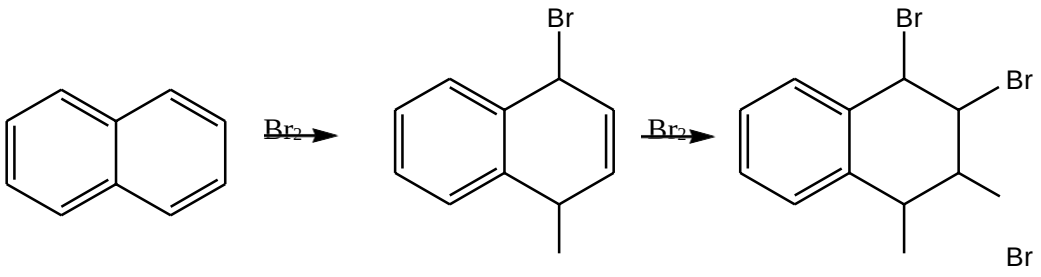


ii.Reduction of Naphthalene:



iii. Addition Reaction:

Addition of bromine or chlorine to naphthalene gives naphthalene dibromide or naphthalene dichloride. Further addition of bromine or chlorine results in formation of naphthalene tetra bromide or naphthalene tetra chloride.



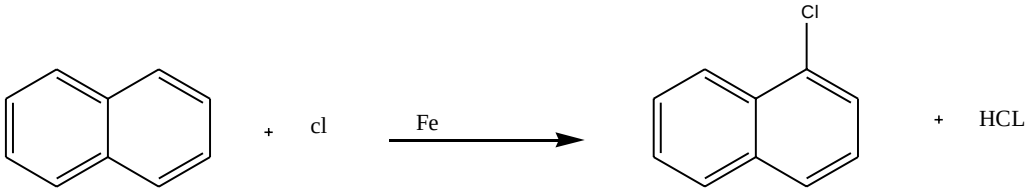
Naphthalene

Br

1,4- Dibromo naphthalene

Br

1,2,3,4-Tetrabromo naphthalene



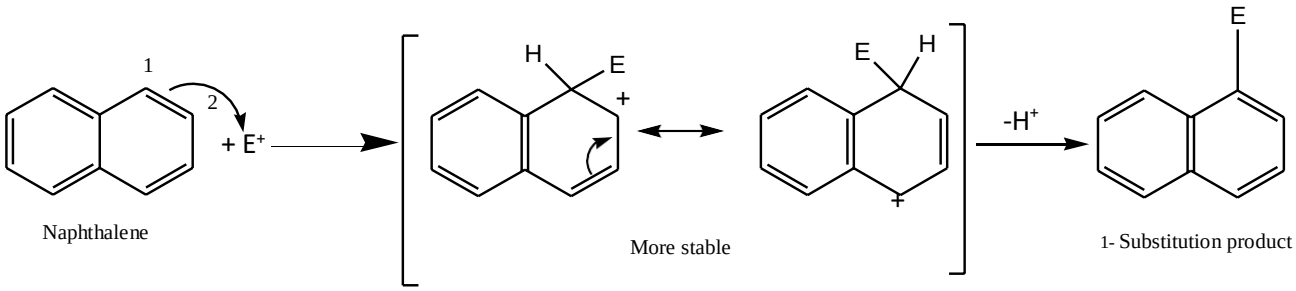
Naphthalene

a-chloronaphtalene

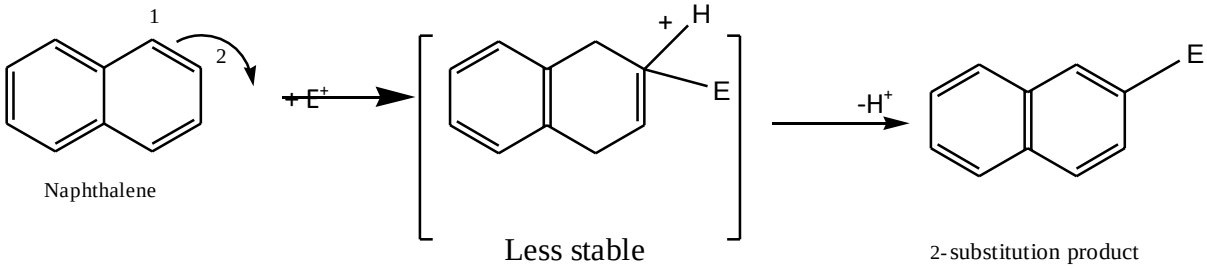
iv)Electrophilic substitution reactions:

Naphthalene ,like benzene, undergoes electrophilic substitution reactions.substitution occurs primarilyatC1(α-position). This can be understood if we examine the intermediate carboniumion.Tworesonsnce forms can be written for the intermediate carbonium ion obtained from the attack at C-1(without involving the other ring), whereas only such form is possible for substitution at C-2.E^+in the following equations represents an electrophile.

Attack at C-1



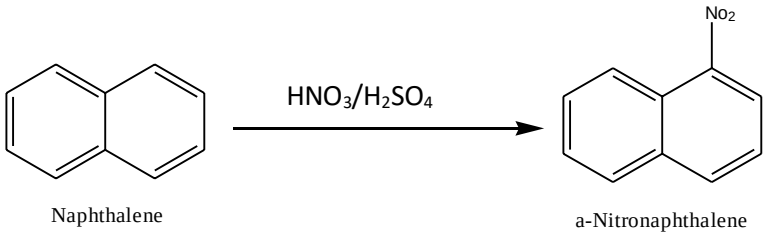
Attack at C-2



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.

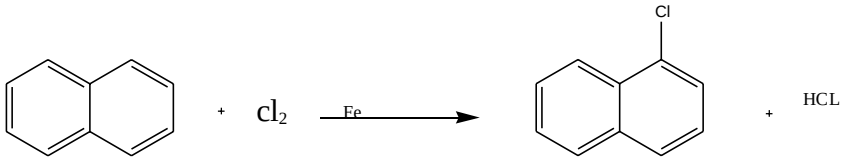
ii.Nitration reaction:

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



iii. Halogeantion reaction:

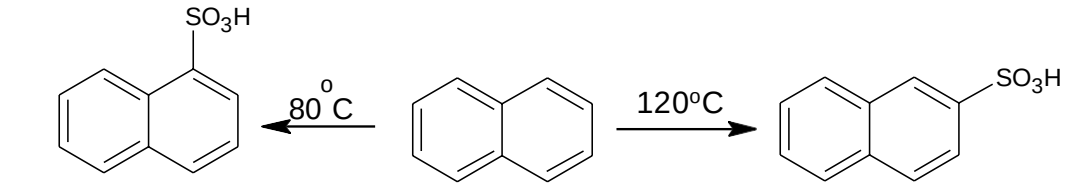
Naphthalene in presence of iron catalyst reacts with halogen to form α-substituted naphthalene.



Naphthalene a-chloronaphtalene

iv. Sulphonation:

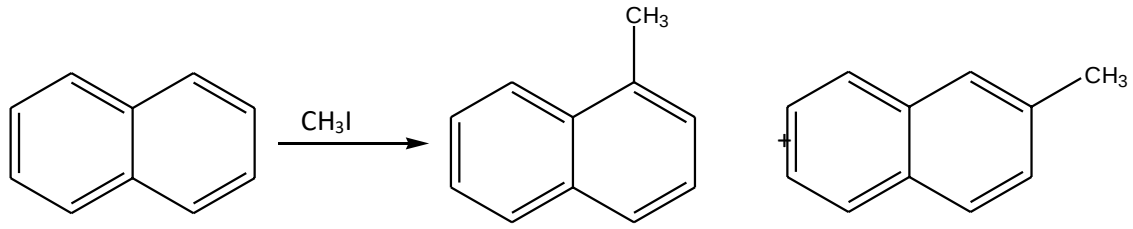
Sulphonation of Napthalene at low temperature (80°C) produces naphthalene-1-sulfonic acid while at higher temperature (120°C) it produces naphthalene -2-sulfonic acid.



Napthalene 1 Sulfonic Acid Napthalene Napthalene 2 Sulfonic Acid

v. Friedel-craft alkylation:

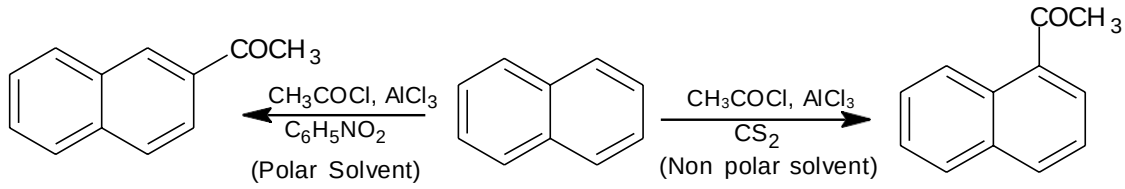
Friedel craft alkylation at low temperature is carried out for naphthalene, which reacting with iodomethane to produce 1-methyl naphthalene as major product and 2-methyl naphthalene as minor product.



Naphthalene 1-methyl naphthalene(major) 2-methyl naphthalene (minor)

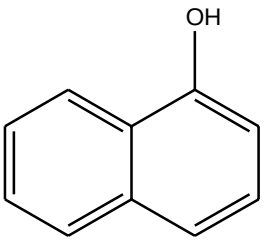
vi. Friedel-craft acylation:

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

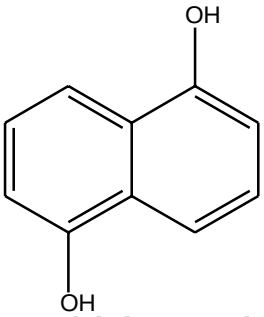


Methyl 2 Napthyl Ketone Napthalene Methyl 1 Napthyl Ketone

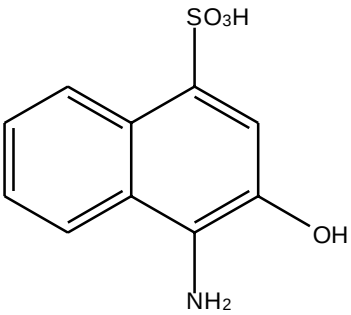
Derivatives of naphthalene :



Naphthalene-1-ol



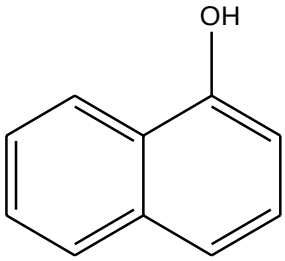
Naphthalene-1,5- diol



4-Amino-3-hydroxynaphthalene-1-sulphonic acid

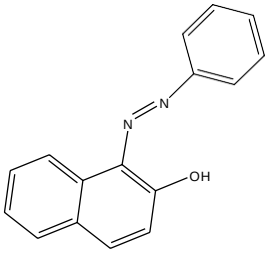
Medicinal uses of Napthalene:

1.Production of Napthols.



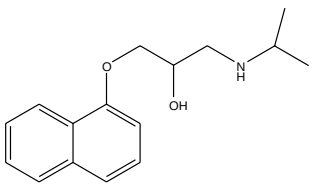
alpha-Napthol

2.Production of Dyes.



Phenyl azo-beta-napthol red dye

3.Preparing of beta blocker drugs.



Propranolol

4.To synthesize synthetic dyes.

5.Useful insecticide.

6.Veterinary medicine – dusting powder.

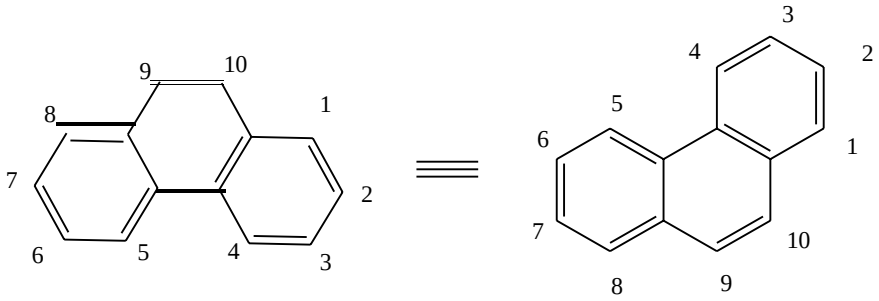
7.Polyethylene naphthalene to prepare plastic bottles.

8.Naphthalene sulfonic acids are used to prepare plasticizers, natural rubbers etc.

9.Naphthalene drugs to cure cough, urine infection, eye trouble etc.

Phenanthrene

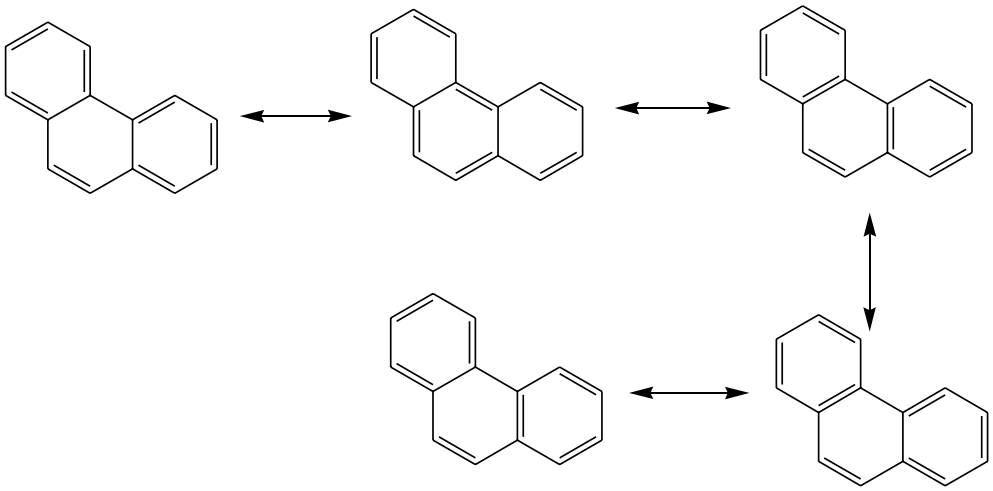
Phenanthrene is apolycyclic aromatic hydrocarboncomposed of three fusedbenzenerings. In its pure form, it is found incigarette smokeand is a knownirritant,photosensitizingskin to light. Phenanthrene appears as a white powder having bluefluorescence.Phenanthrene is the backbone of morphine.



Phenanthrene

Resonance structure of phenanthrene:

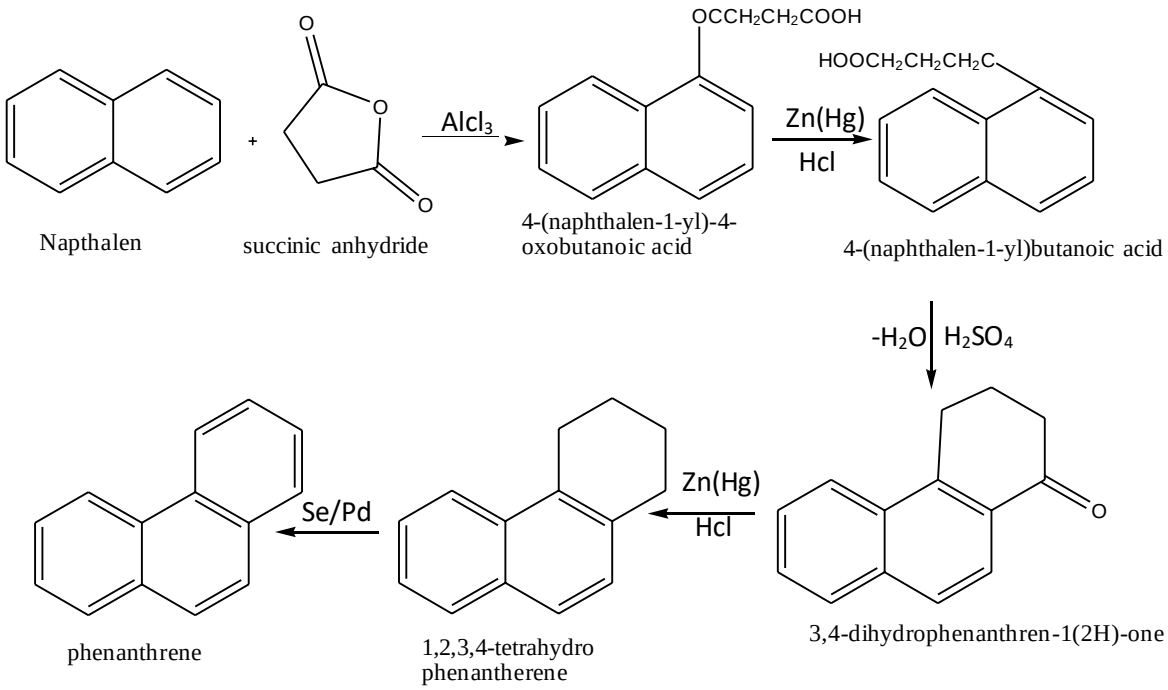
Like anthracen ,phenanthrene is aplanar molecule. All fourteen carbone atoms are sp2 hybridized.The sp2 orbitals overlap with each other and with s orbitals of ten hydrogen atoms to C-C and C-H σ bonds.Each carbon atom also possesses a p orbital and these are perpendicular to the plane containing the bonds. The lateral overlap of these p orbital produces a π molecular orbital containing ten electrons.Phenanthrenen shows aromatic properties because the resulting π molecular orbital satisfies the Huckel`s rule (n=3 in 4n+2).



Resonance energy=91Kcal/mole

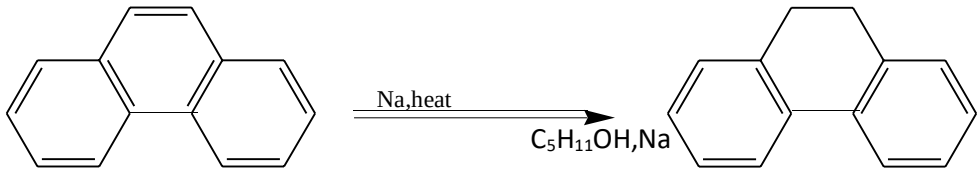
Preparation of phenanthrene:

(i) Haworth phenanthrene synthesis:

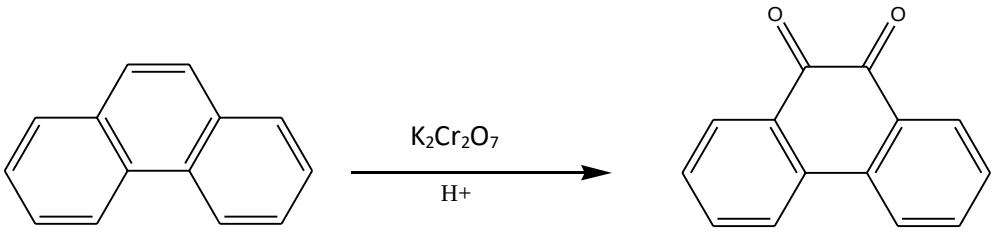


Reaction of phenanthrene:

Reduction:



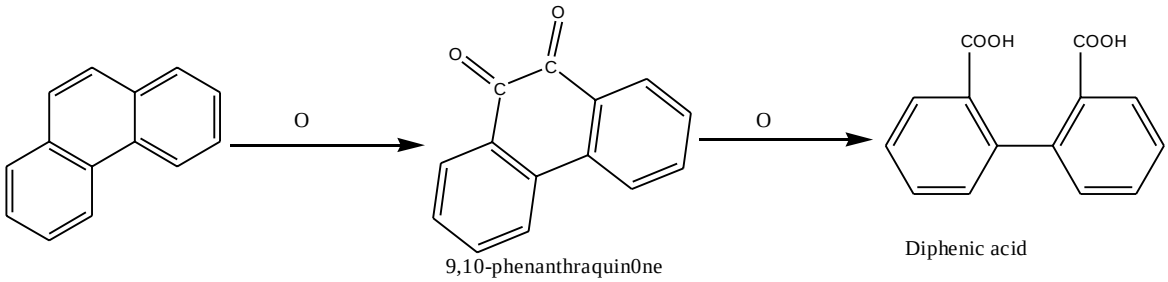
Oxidation:



Phenanthrene

9,10-phenanthrone

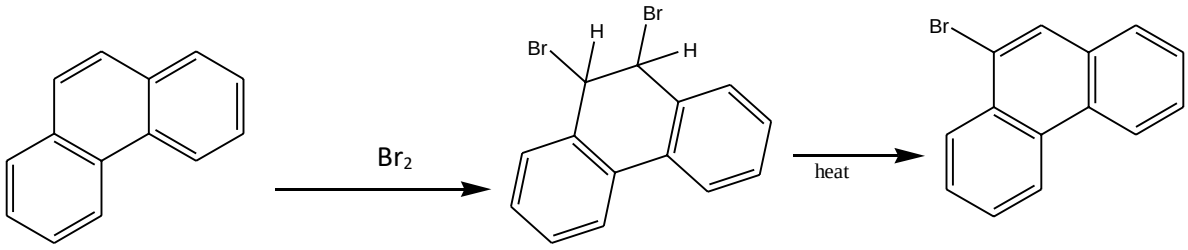
When oxidised with chromic acid in acetic acid phenanthrene yields a diketone,phenantraquinone which upone further oxidation gives diphenic acid.



9,10-phenanthraquin0ne

Diphenic acid

Bromination:

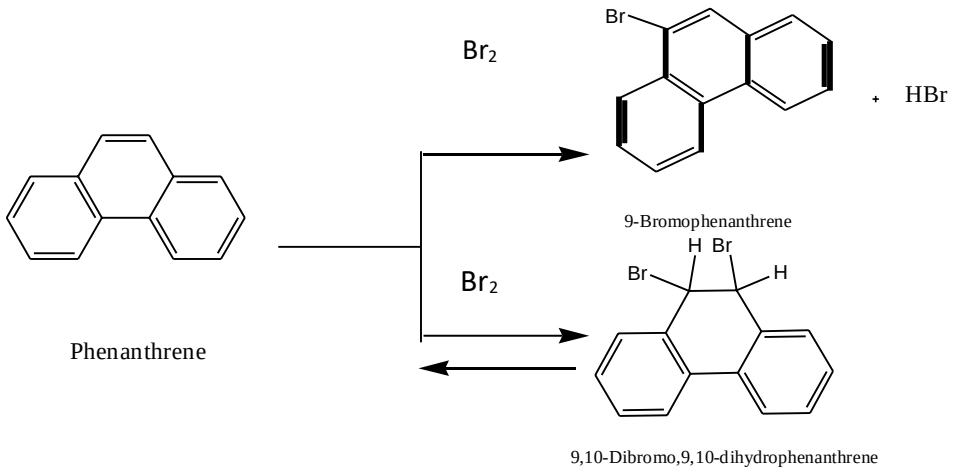


phenanthrene

Phenanthrene9,10dibromide

9-bromophenanthren

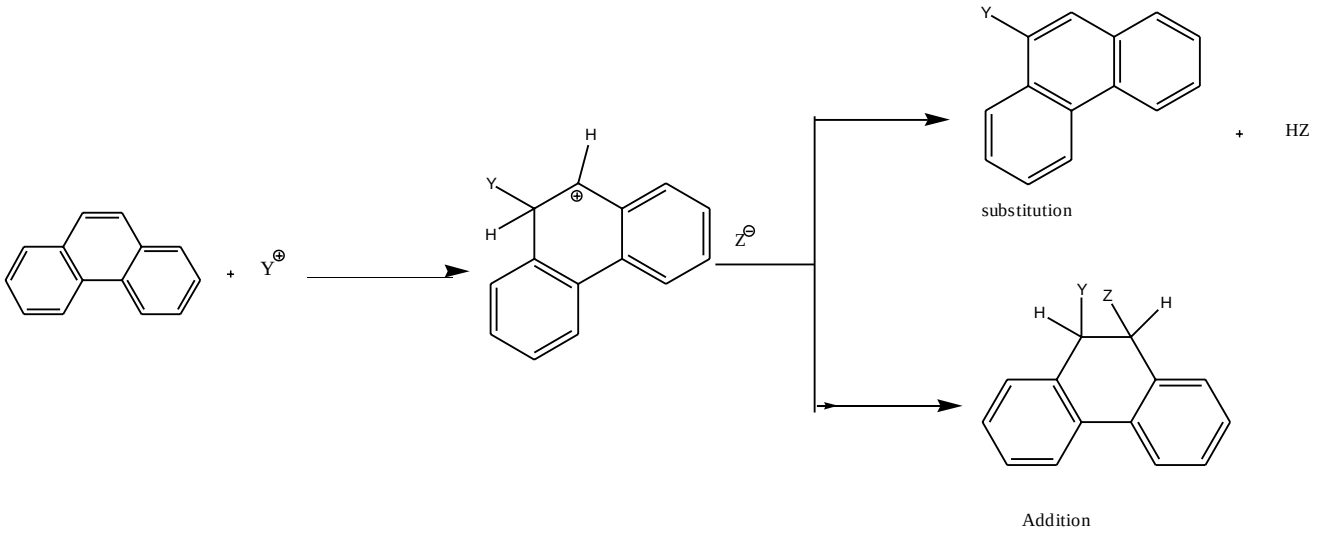
Electrophilic addition versus electrophilic substitution

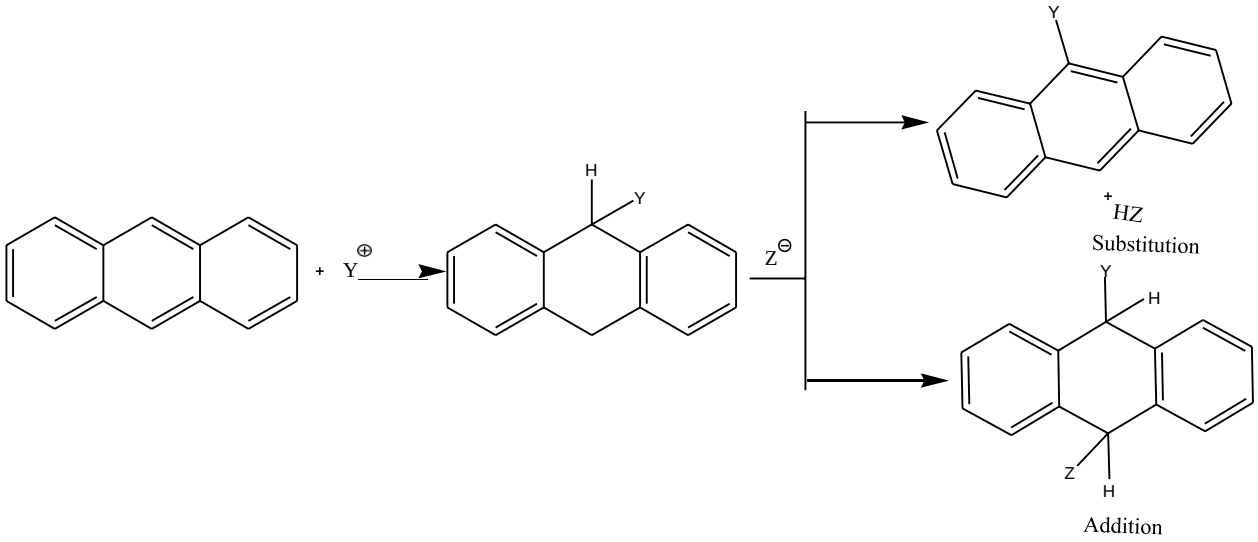


Phenanthrene

9-Bromophenanthrene

9,10-Dibromo,9,10-dihydrophenanthrene



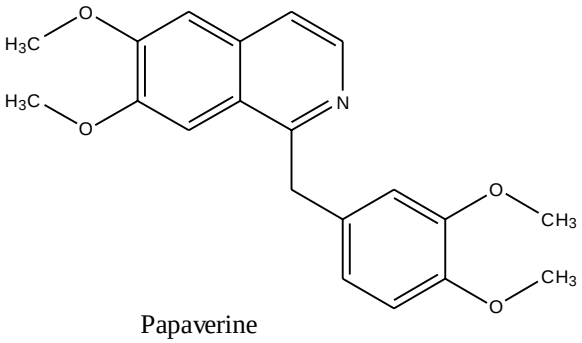


The reactivity of the 9- and 10-positions toward electrophilic attack, whether reaction leads to substitution or addition, is understandable since the initially formed carbocation is the most stable one, in which aromatic sextets are preserved in two of the three rings.

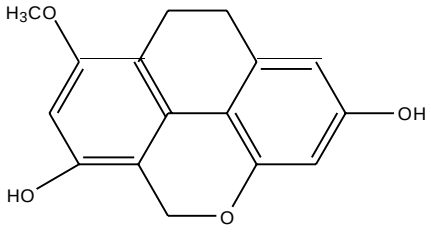
This carbocation can then either (a) give up a proton to yield the substitution product, or (b) accept a nucleophile to yield the addition product.

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).

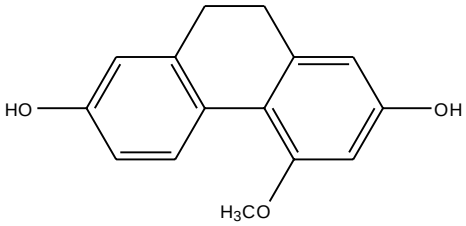
Derivatives of phenanthrene:



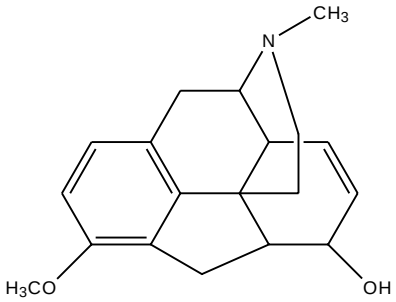
Papaverine



Parviflorin



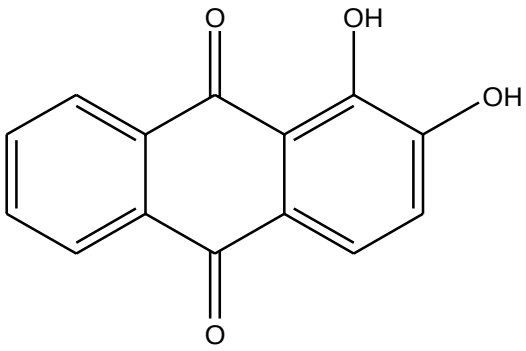
Coelonin



Codeine

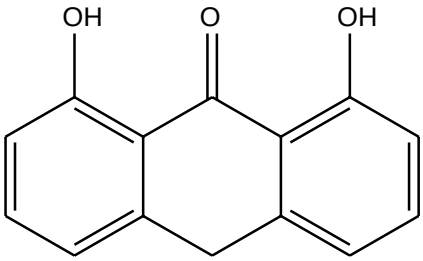
Medicinal uses of phenanthrene:

1.Anthraquinone is used in the manufactutre of alizarin and several other dyes.



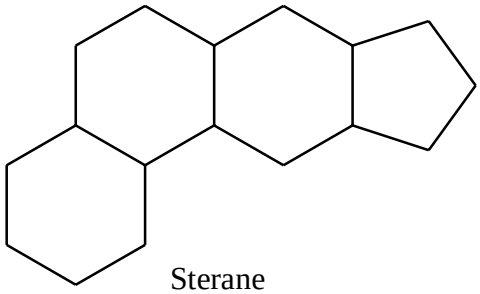
Alizarin

2. Dithranol antifungal



Dithranol

3.steroid moiety contain phenanthrene nucleus.



Sterane

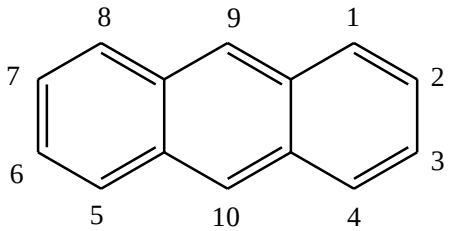
4.sex hormones and bile acids.

5.steroid used as oral contraceptive and antiinflamatory agent.

6.Cardiac glycosides,morphine, codeine

Anthracene

Anthracene is present is coal-tar to the extent of 0.3 to 3.5 perecent hence its name Greek anthrac- meaning coal.on 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.

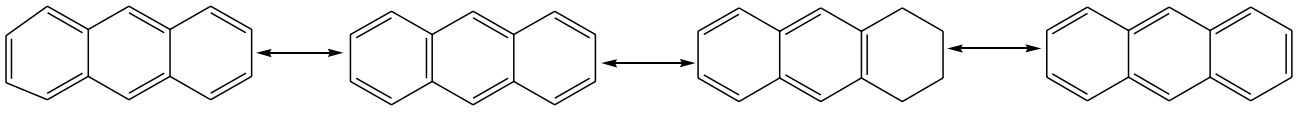


Anthracene

Resonance structure of anthracene:

x-ray diffraction studies show that,like naphthalene ,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 andC), 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.

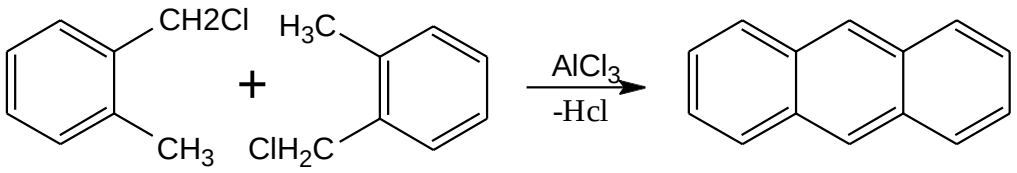


(A) (B) (C) (D)

Preparation of Anthracene:

i.ByFriedel-Craft Reaction:

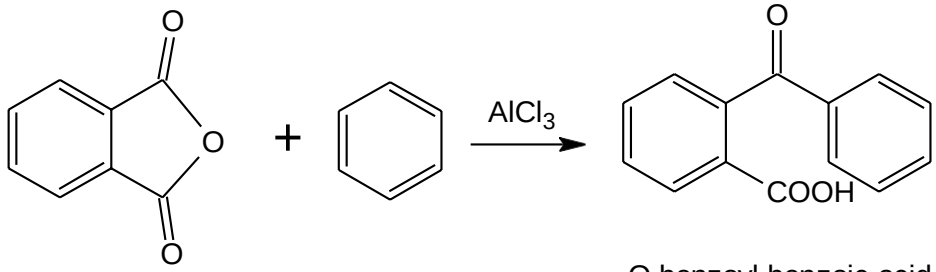
Two molecules of benzyl chloride is condensed in presence of $AlCl_3$ to produce Anthracene.



Benzyl Chloride Anthracene

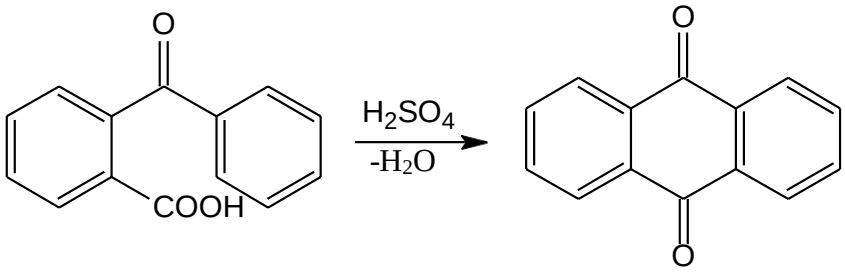
ii.By Haworth Synthesis:

Step I: Benezene on reaction with phthalic anhydride in presence of $AlCl_3$ produces O-Benzoyl benzoic acid.



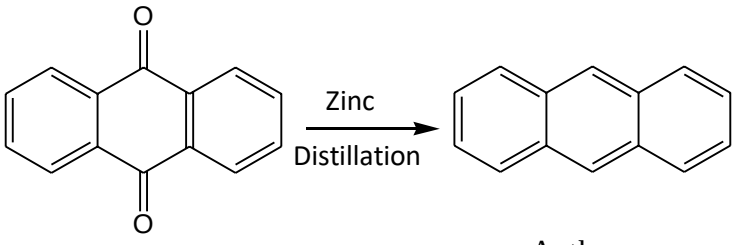
Phthalic anhydride Benzene O benzoyl benzoic acid

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



O benzoyl benzoic acid 9,10 anthraquinone

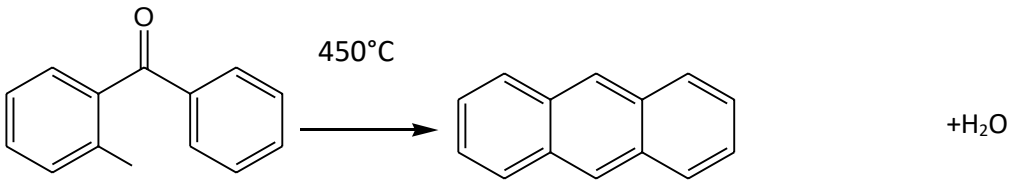
Step III: Distillation of 9,10-anthraquinone with zinc dust will produce anthracene.



9,10-anthraquinone Anthracene

iii. Elbs Reaction:

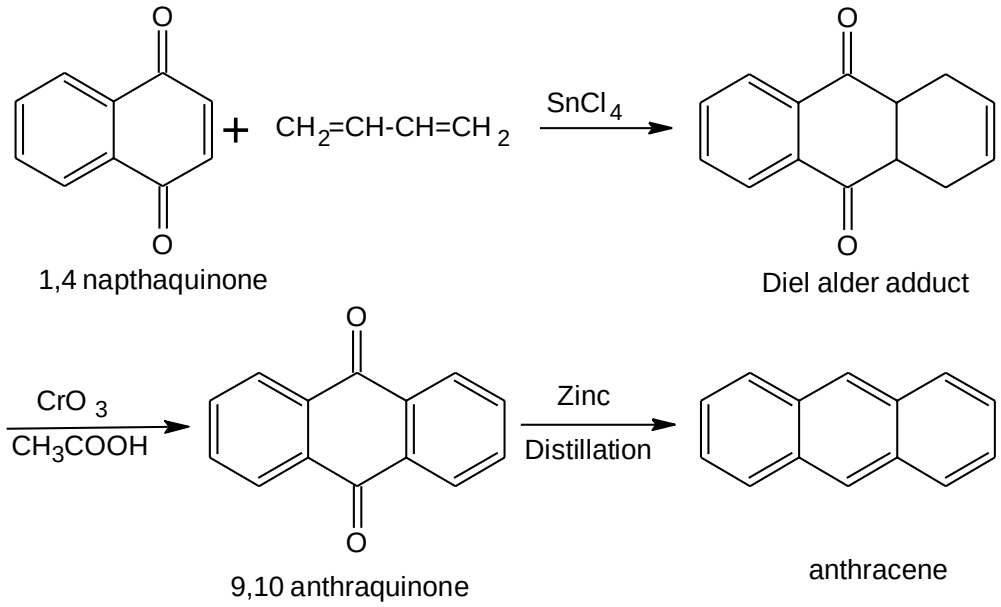
Pyrolysis of O-methylbenzophenone at 450°C can produce anthracene.



o-Methylbenzophenone Anthracene

iv. By Diel-Alder Reaction:

This involves the reaction of 1, 4 napthaquinone with 1, 3 butadiene. The product is oxidized with chromium trioxide in GAA to form 9, 10 anthraquinone, which on distillation (Zn) produce anthracene.

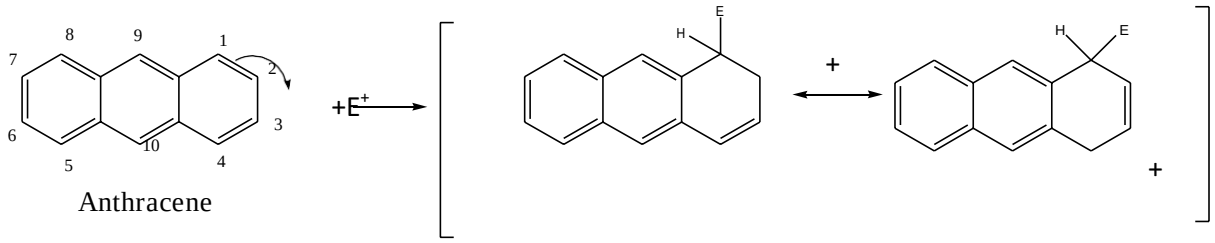


Properties of anthracene:

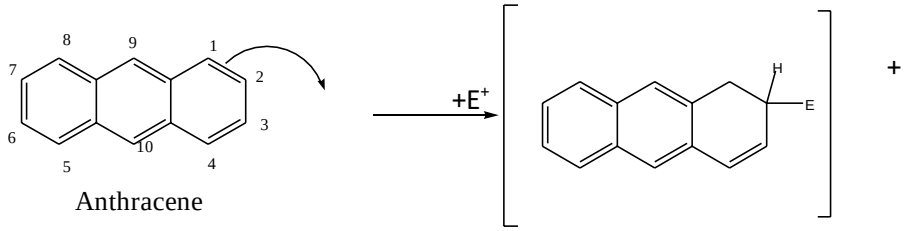
Anthracene is a colorless solid. It mealts at 218°C and boils at 340°C.Anthracene is insoluble in water,but dissolves in benzene. It shows a strong blue flurescence when exposed to ultraviolet light.This fluorescent property of anthracene is used in criminal detection work,since a small amount of finely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

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

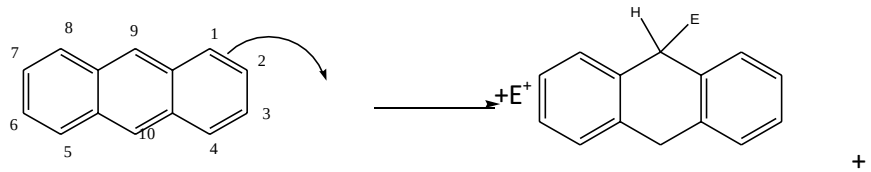
Attack at C-1



Attack at C-2



Attack at C-9

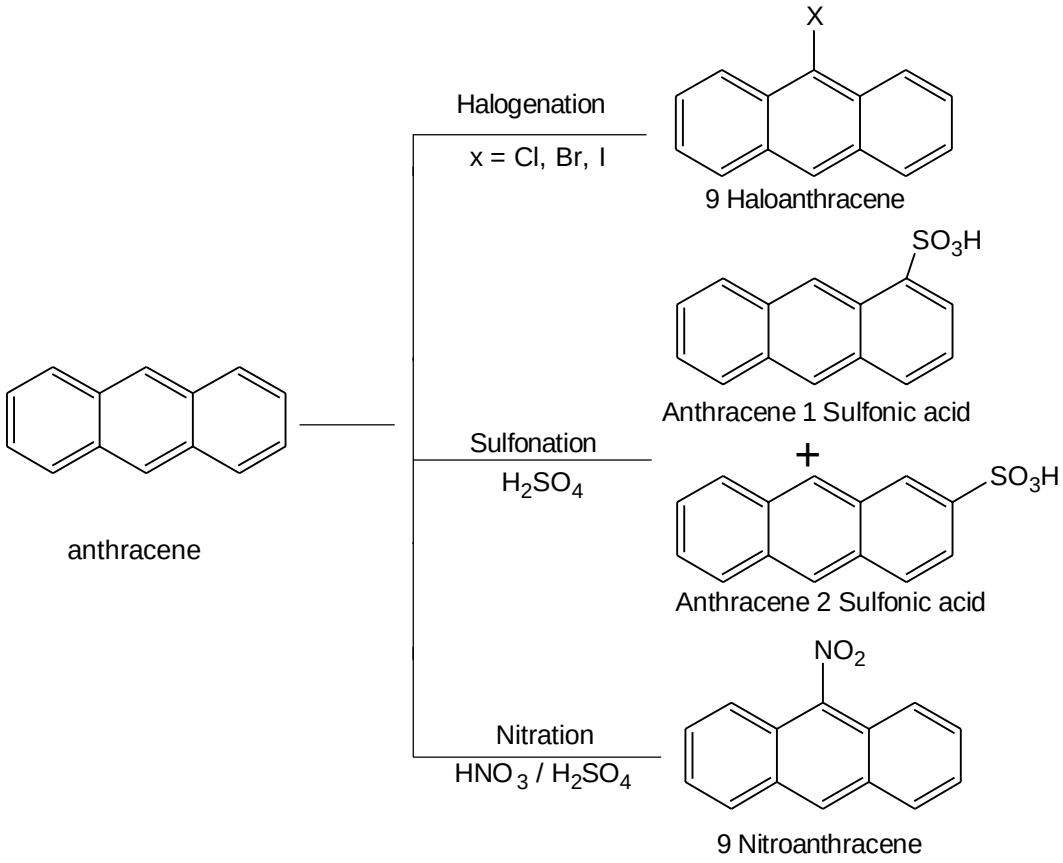


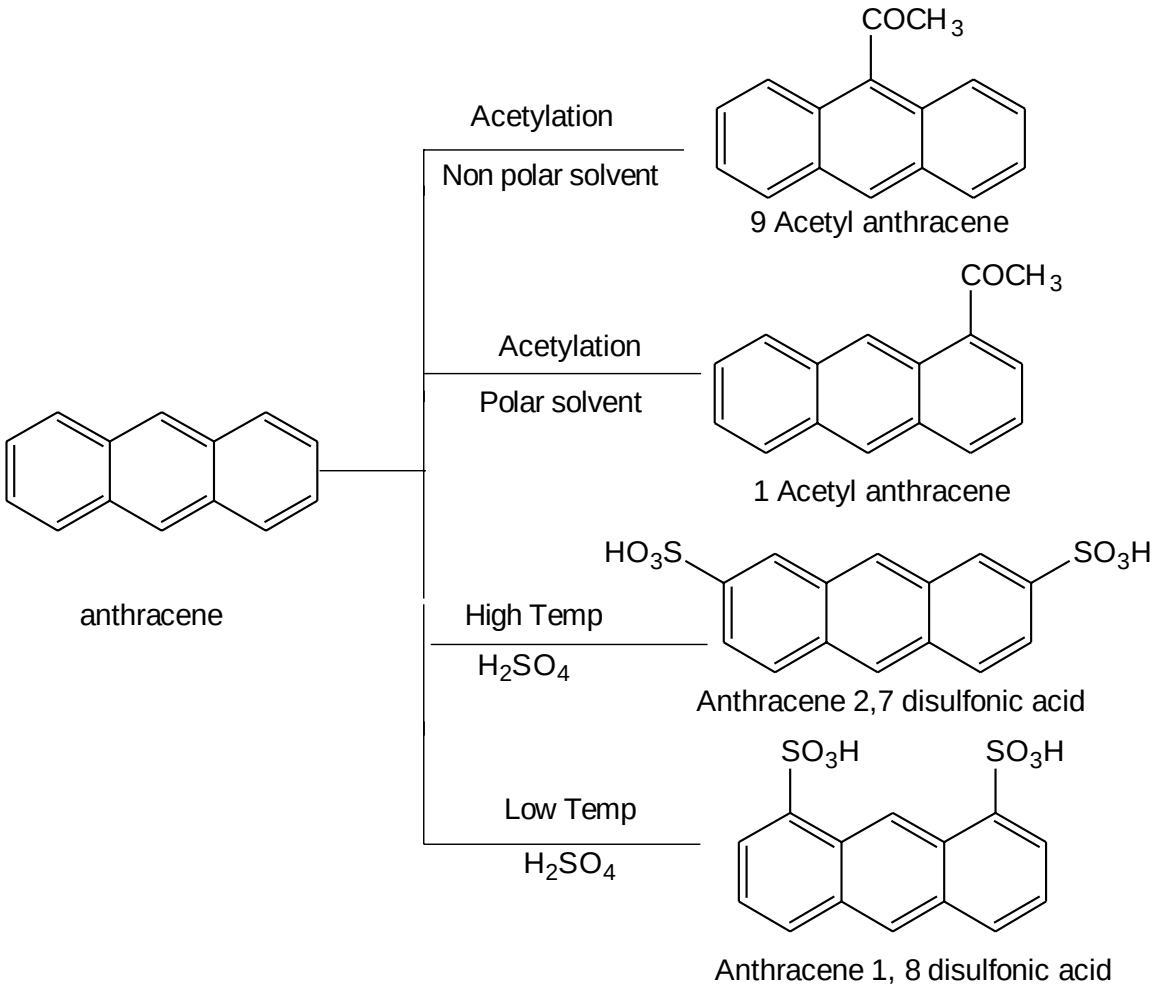
Anthracene

Attack at C-9 yields a carbonium ion intermediate in which two benzene rings are retained; where as 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 favoured because the resonance energy of two benzene rings (2 * 36 =72 kcal) exceeds that of naphthalene (61kcal).

Reactions of Anthracene:

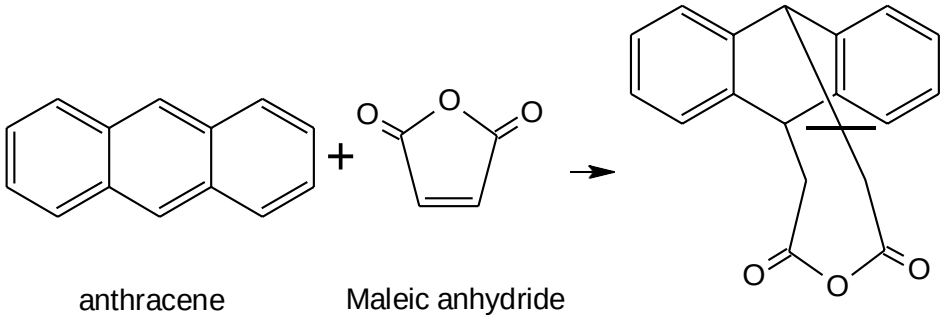
i.Electrophillic substitution reactions:





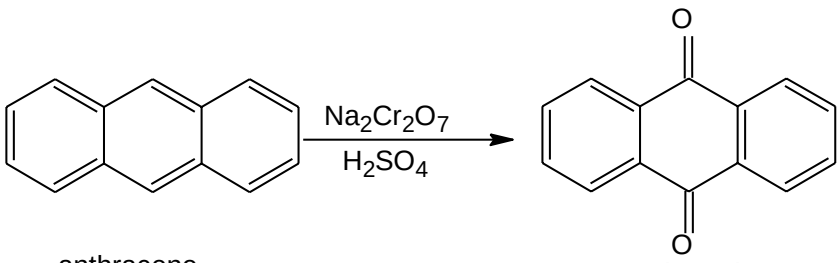
ii.Diels-Alder Reactions:

Anthracene undergoes Diels-Alder reaction at 9, 10 positions and form endo anthracene maleic anhydride.



v.Oxidation:

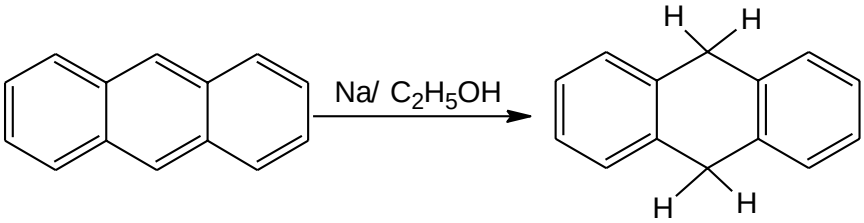
Anthracene undergoes oxidation with sodium dichromate and sulfuric acid to form 9, 10 anthraquinone.



anthracene 9.10 Anthraquinone

Reduction:

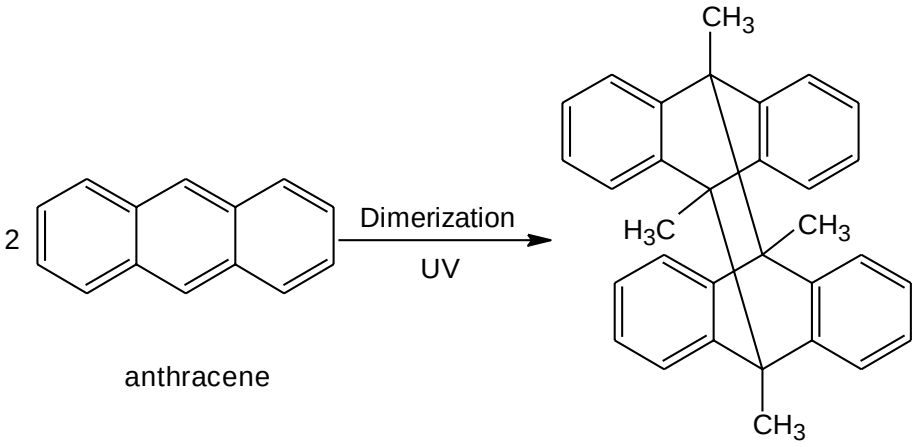
Anthracene on reduction with sodium and ethyl alcohol produces 9, 10 dihydroanthracene.



anthracene 9.10 Dihydroanthracene

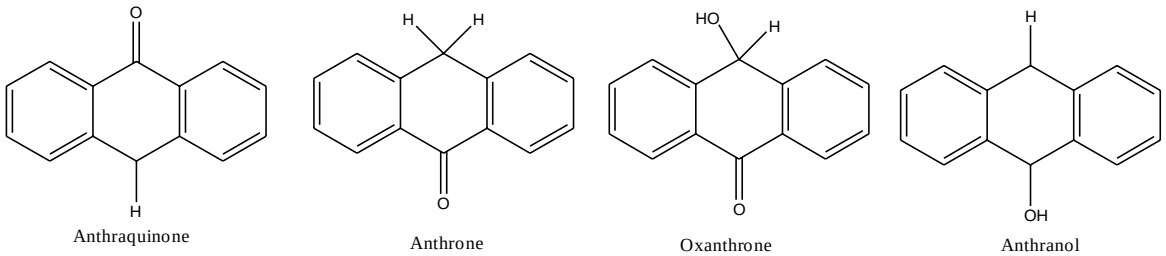
Dimerization:

Dimerization of anthracene in UV light produces dianthracene.



anthracene Dianthracene

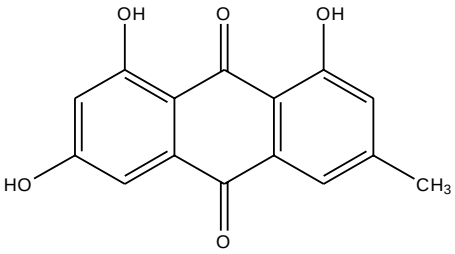
Derivatives of anthracene:



Anthraquinone Anthrone Oxanthrone Anthranol

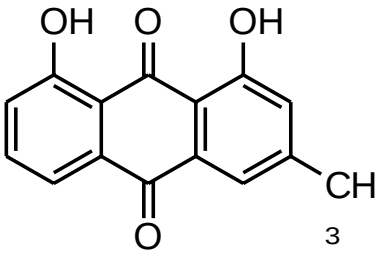
Medicinal uses of anthracene:

1.Anthracene glycosides are oxygenated derivatives of pharmacological importance that are used as laxatives or catharatics,antineoplasticagent,polycystic kidney.

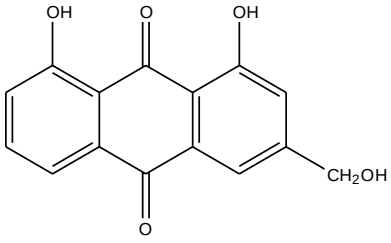


Emodin

2.Anti-inflamatory, antibacterial, antifungal andantiproliferative activity.



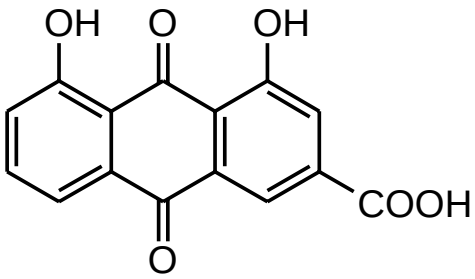
Chrysophanol



Aloe-emodin

3.As natural dyes.

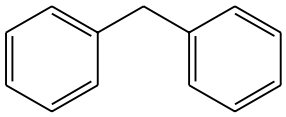
4.Hepatoprotective,nephroprotrctive,antioxidant.



Rhein

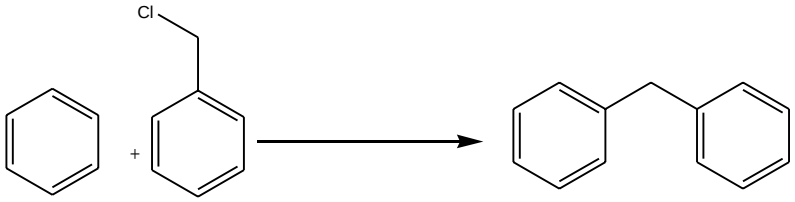
Diphenylmethane:

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.

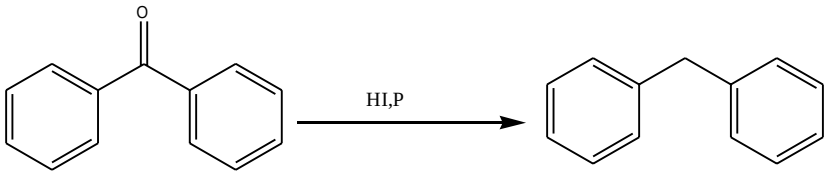


Diphenylmethane

Preparation of diphenylmethane:

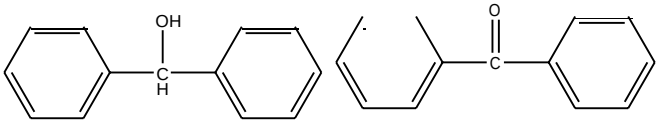


Diphenylmethen



Diphenylmethane

Derivatives of diphenyl methane:

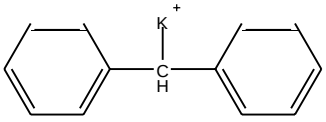


Benzhydrol Benzophenone

Medicinal uses of diphenylmethane:

1.Diphenylmethane is widely used in the synthesis of luminogens for aggregation induced emission.

2.Diphenylmethyl potassium used in the preparation of polymerization.

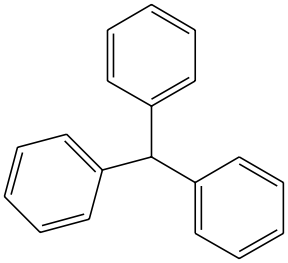


Diphenylmethyl potassium

Triphenylmethane

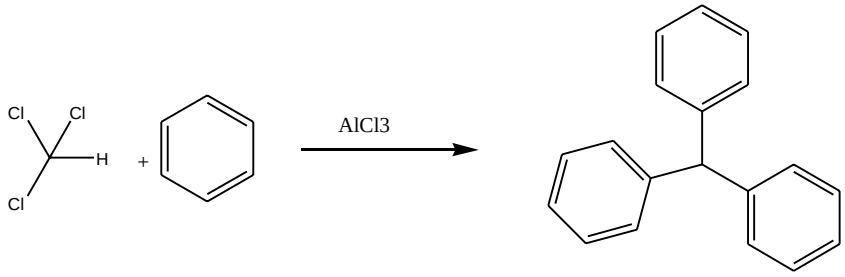
Triphenylmethane $(C_6H_6)_3CH$ is the chromogen of a large number of dyes.The common chromophore is the p-quinoid structure and the auxochromes are OH,NH_2 and NR_2.

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 pastncess to light is not so important.



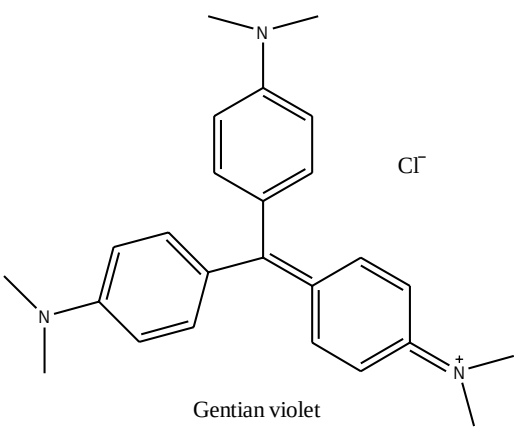
Triphenylmethane

Preparation of triphenylmethane :

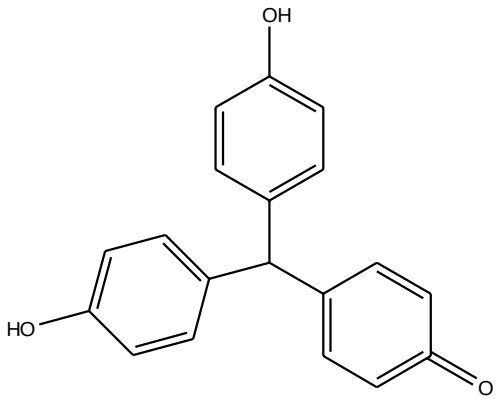


Triphenylmethane

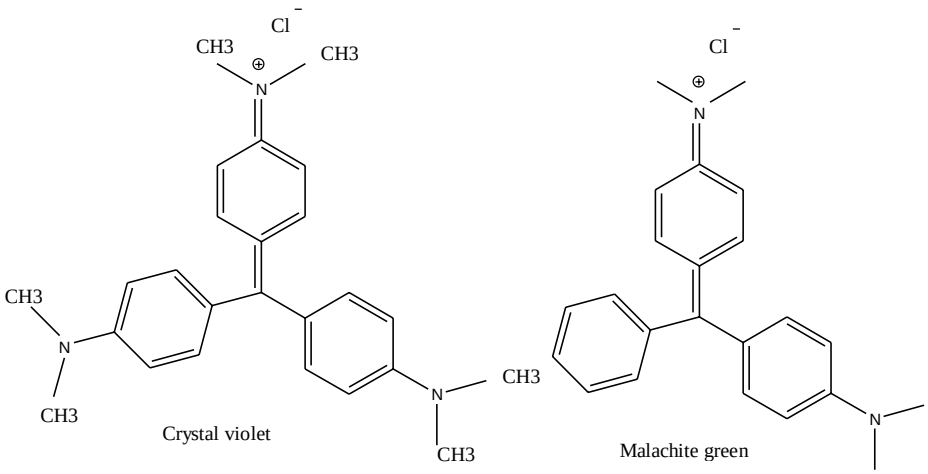
Derivatives of triphenylmethane:



Gentian violet

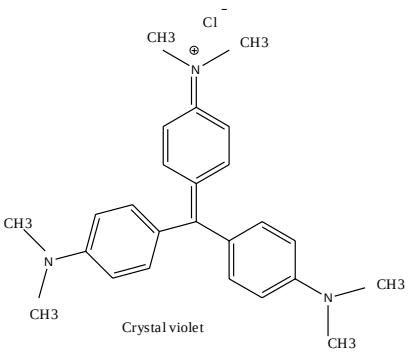


Aurin

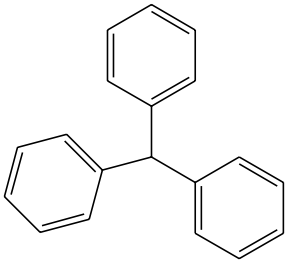


Medicinal uses of triphenylmethane:

Crystal violet used as preparation of detergents , fertilizers, textile dye.



Triphenymethane is used in copying papers, in hectograph and printing inks.



Triphenylmethane