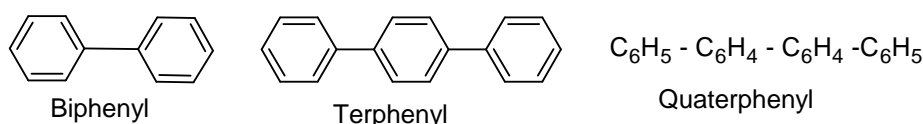


Unit 2: Polynuclear Hydrocarbons

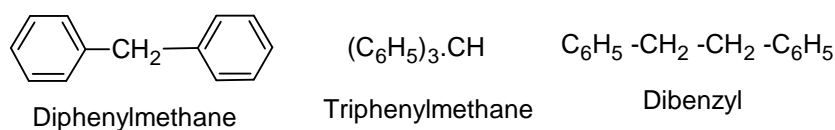
2.1: Introduction

Polynuclear hydrocarbons are a large group of organic compounds with two or more fused aromatic rings. They have a relatively low solubility in water, but are highly lipophilic. When dissolved in water or adsorbed on particulate matter, it can undergo photodecomposition when exposed to ultraviolet light from solar radiation. They may be broadly divided into two ways depending on nature of linkage between rings.

1. Isolated polynuclear hydrocarbons : The compounds in which the rings are isolated i.e., benzene nuclei are either linked directly to each other or through one or more carbon atoms. For example diphenyl, diphenylmethane etc.

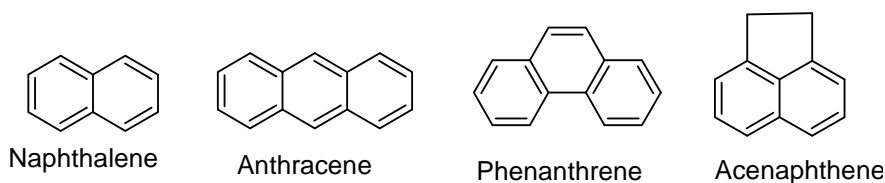


Compounds with benzene nuclei linked directly



Compounds with benzene nuclei linked through one or more carbon

2. Condensed polynuclear hydrocarbons: The compounds in which two or more rings are fused due to the sharing of two or more carbon atoms by two or more rings. They are known as fused or condensed polynuclear hydrocarbons, e.g.,



Condensed polynuclear hydrocarbons

The chemistry of isolated polynuclear compounds is similar to that of simple aromatic hydrocarbons. However, the condensed polynuclear hydrocarbons like naphthalene, anthracene etc., differ considerably in their behavior from simple hydrocarbons. The chemistry of some representative members is being dealt in this chapter.

2.1.1 : Naphthalene ($C_{10}H_8$)

Naphthalene is the simplest example of a polycyclic aromatic hydrocarbon containing the benzene rings fused in ortho positions. It was discovered by Garner.

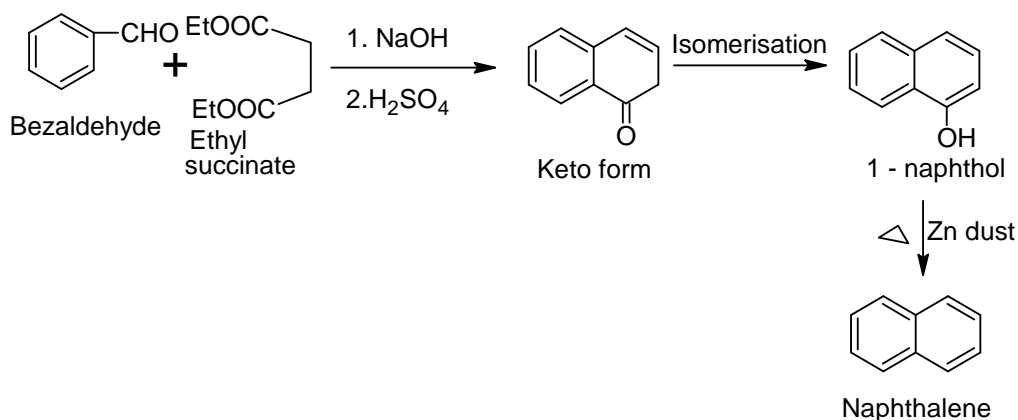


It is made from crude oil or coal tar. It is also produced when things burn, so naphthalene is found in cigarette smoke, car exhaust, and smoke from forest fires. It is used as an insecticide and pest repellent. Naphthalene was first registered as a pesticide in the United States in 1948.

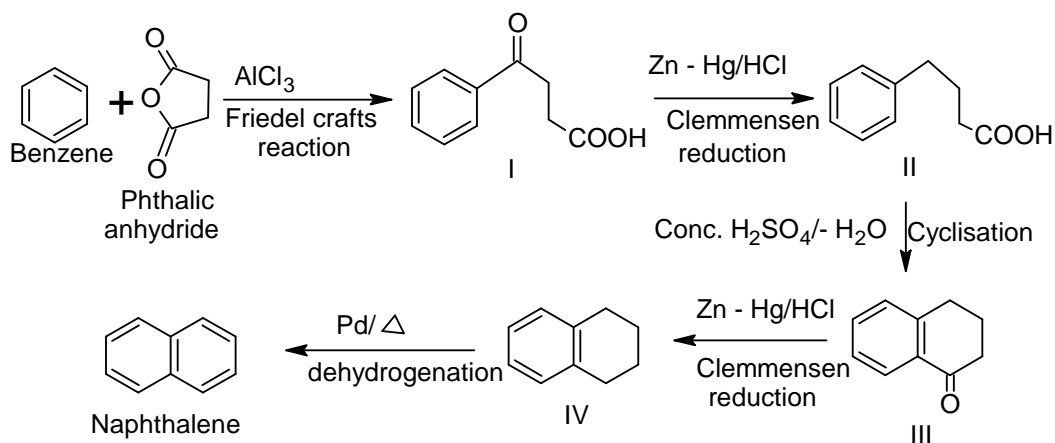
2.1.2: Source and its isolation: It is largest single compound present in coal-tar. It is obtained from 'middle or heavy oil' by chilling these fractions when naphthalene crystallizes out. The crude naphthalene is separated by pressing or centrifuging. The resultant solid mass is washed with hot water and aqueous alkali to remove traces of oils and phenols. It is then washed with dilute sulphuric acid to remove basic impurities. Finally it is purified by sublimation.

2.1.3: Method of preparation : It can be prepared by using following methods-

1. From benzaldehyde and ethyl succinate (Fitting and Erdmann Synthesis): The reaction of benzaldehyde and ethyl succinate in the presence of basic catalyst like sodium hydroxide or potassium tertiary butoxide followed by cyclisation and isomerisation gives α -naphthol which further on reduction with Zn dust afforded naphthalene.



2. Haworth synthesis (1932) : Friedel crafts reaction of succinic anhydride with benzene in presence of AlCl₃ gives a ketonic acid I which is reduced to II. This on cyclisation gives ketone III which on reduction yields tetralin IV. Dehydrogenation of tetralin gives naphthalene.



2.1.5 : Constitution or Structure of Naphthalene:

A] Analytical evidence: The structure of naphthalene was arrived at by following analytical evidence.

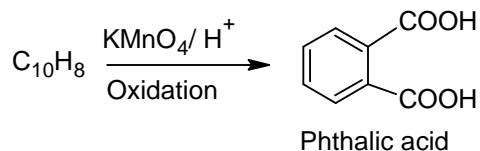
1. On the basis of analytical data its molecular formula is found to be C₁₀H₈ .

2. Like benzene it is resistant to addition reactions though less than benzene.

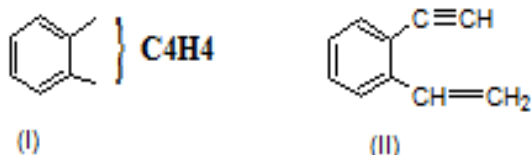
It resembles benzene in other chemical properties also and undergoes electrophilic substitution reactions like halogenation, nitration etc., more readily than benzene.

3. Its nuclear substituted hydroxy derivatives are phenolic in nature and amino derivatives undergo diazotization and coupling reactions. This again shows it to be similar to benzene the structure.

4. Graebe in 1869 obtained phthalic acid (o-benzene dicarboxylic acid) on oxidation of naphthalene with acid permanganate. This showed that at least one benzene ring is present in naphthalene and there may be two side chains in ortho positions to each other.



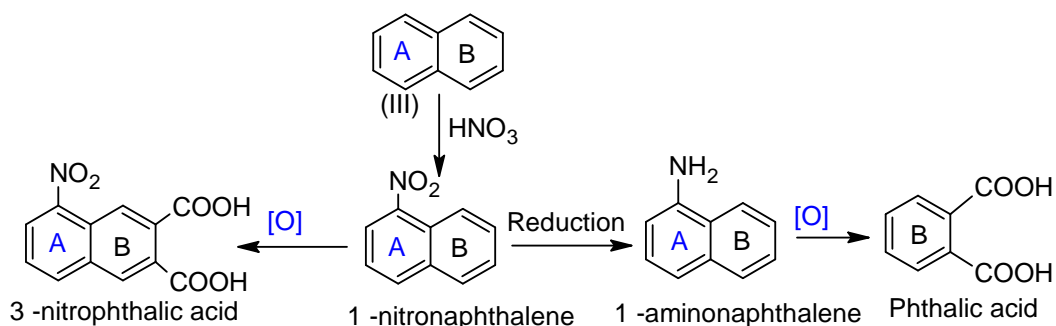
Hence the formula of the naphthalene may be written as (I). The two side chains on the basis of valency requirements must be highly unsaturated and formula (II) may be suggested for it.



However, such structure would be in contrast to known aromatic character of naphthalene. Therefore, structure (II) and related structures for naphthalene are ruled out.

5. Graebe further proved that naphthalene consists of two benzene rings fused in o-positions. This was based on following experimental proof:

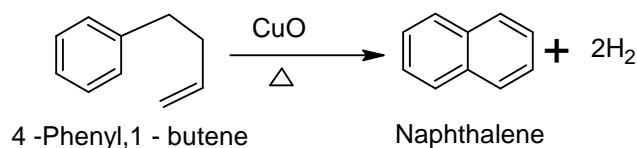
Naphthalene gave phthalic acid on oxidation. When naphthalene was nitrated it yielded nitronaphthalene which oxidation gave 3-nitro phthalic acid. This showed that nitro group was present in the benzene ring and side chains were oxidized. But when nitro group of nitro naphthalene was reduced to amino group and the resulting aminonaphthalene oxidized, phthalic acid and not amino phthalic acid was obtained. An amino group attached to benzene ring is known to render the ring highly susceptible to oxidative degradation. The logical conclusion therefore could be that during the oxidation of aminonaphthalene – it was the benzene ring containing an amino group which was destroyed and the benzene ring present in oxidation product phthalic acid is other than that which had the nitro group. It was therefore concluded that two benzene rings were fused in ortho-position i.e. naphthalene contained two benzene rings. In oxidation of nitronaphthalene, nitro phthalic acid was obtained because nitro group attached to benzene ring made the ring resistant to oxidation.



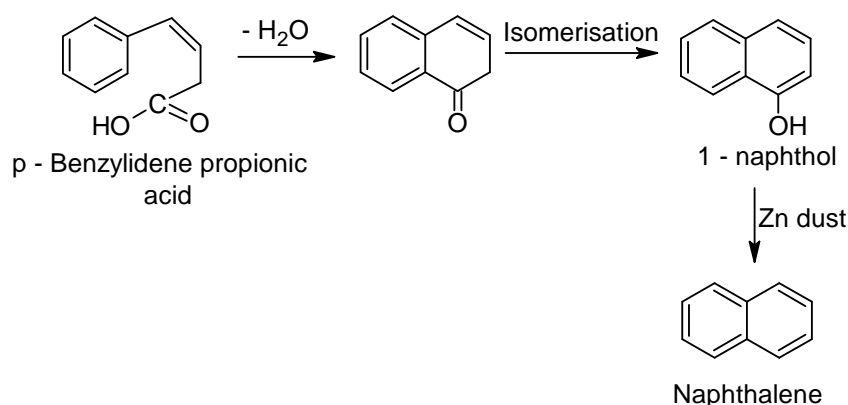
The above scheme clearly demonstrates the presence of two benzene rings fused in o-positions. The structure (III) was intuitively suggested by Erlenmeyer in 1866 and is known as Erlenmeyer's structure of naphthalene.

B] Synthetic evidence: Synthetic evidence which support the Erlenmeyer's formula for naphthalene, some are given below:

a) If 4-phenylbutene-1 is passed over red hot calcium oxide, naphthalene is obtained.

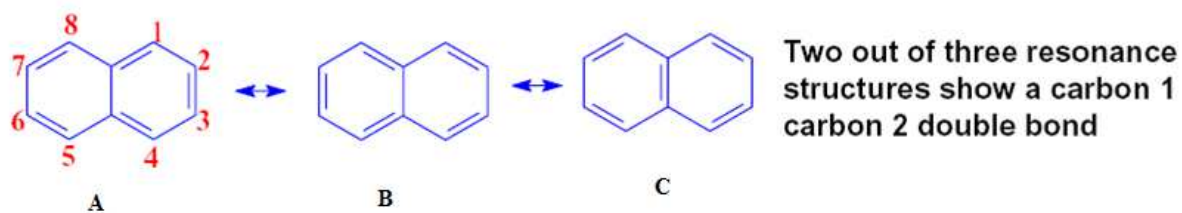


b) **Fittig's synthesis:** Cyclisation of p-benzylidene propionic acid gives α -naphthol which on distillation with zinc dust yields naphthalene.

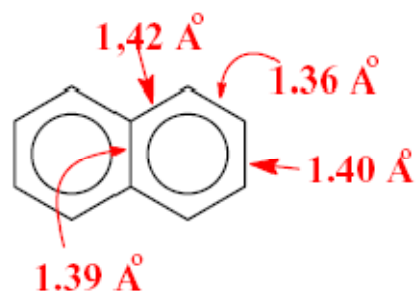


2.1.6 : Modern views about structure of Naphthalene: Like benzene, the structure of naphthalene can be explained on the basis of following concepts.

i) **Resonance concept:** Naphthalene is considered to be the resonance hybrid of various contributing structures of which following three are important.

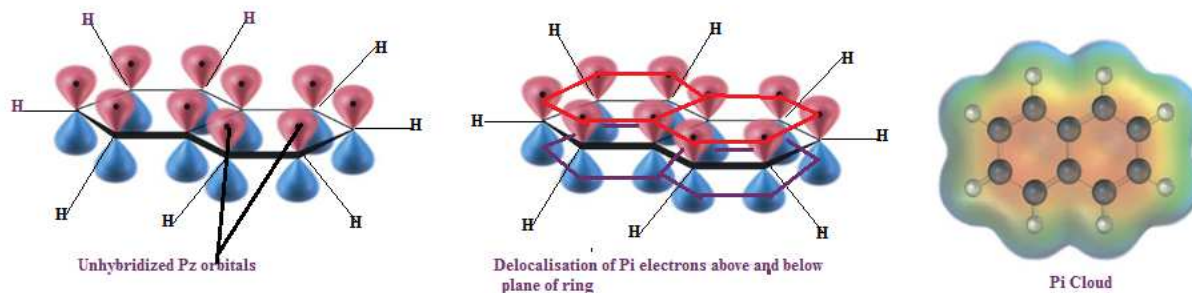


Naphthalene is planar molecule. X-ray studies have indicated that all carbon-carbon bonds in naphthalene are not equivalent. The C_1-C_2 bond is having relatively greater double bond character and is 1.36\AA as compare to C_2-C_3 bond having greater single bond character length 1.40\AA . This is obvious, if we see the contributing structures in which C_1-C_2 bond are double bond in structures B and C and single bond character in the structure A. Thus it has a two-third double bond character. On the other hand C_2-C_3 bond is a single bond in structures B and C and double bond in structure A. Thus it has two-third single bond character.



The resonance energy of naphthalene is 61 Kcals. Since the resonance energy of benzene is 36 Kcals, the additional energy due to second benzene ring is only 25 Kcals. This decreased resonance energy is in accordance with relatively greater reactivity of naphthalene.

II) Molecular orbital concept: All carbon atoms in naphthalene are in sp^2 hybridization state and lie at the corners of two fused hexagons. Each one of the carbon atom is attached to two other carbon atoms and one hydrogen by σ -bonds formed by the overlapping of trigonal sp^2 hybrid orbitals. The unhybridized p orbital at each carbon overlaps with the p orbitals on its side forming a π electron cloud above and below the plane of the ring containing all the carbon and hydrogen atoms. The π electron cloud has a shape of 8 and consists of two partially overlapping sextets-thus imparting aromatic character to naphthalene. However, since a pair of π electrons is common to both the rings, it has less aromatic character than benzene. It must be noted that it contains 10π electrons, a number for exhibiting aromatic character according to Huckel's rule.



M.O. Picture of Naphthalene

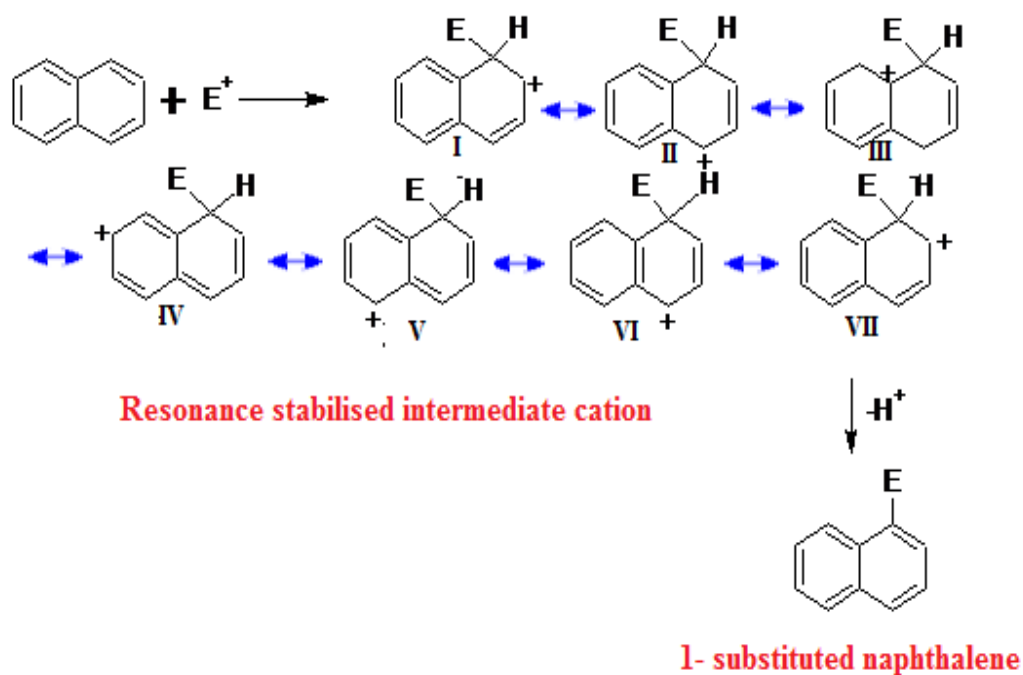
The M.O. picture of naphthalene also explains the nature of substitution reactions. Since it has a π electron cloud on either side of the plane of the ring, it acts as a source of electrons and its important reactions are electrophilic substitution reactions.

2.1.7 : Physical properties: Naphthalene exist as a colourless lustrous plates, m.p. 353K, insoluble in water but soluble in alcohol, ether and benzene. It has strong characteristic odour. It is volatile and sublimates on heating.

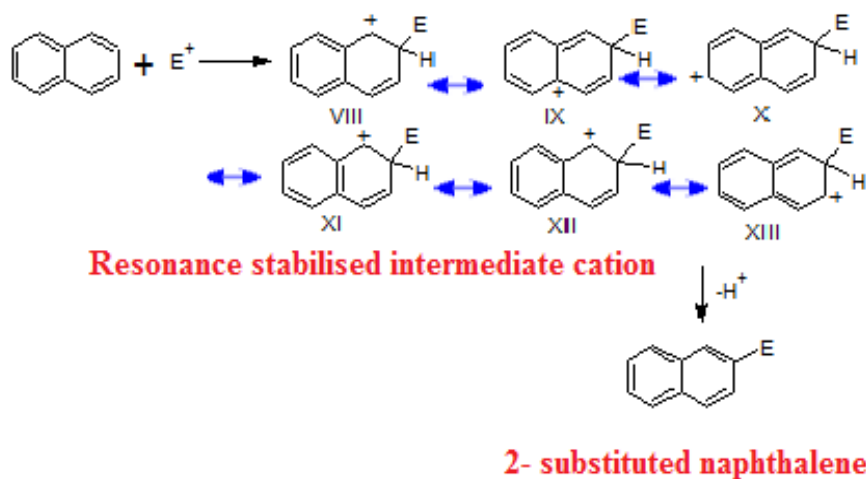
Chemical properties : It resembles benzene in its reactions. However, it is more reactive than benzene and forms the addition and substitution products much more readily. It is also more susceptible to oxidation and reduction. Like benzene, it undergoes electrophilic substitution reactions and normally occurs more readily at α -position than β -position. Because, the carbonium ion intermediate formed by attack on β -position is less stabilized by resonance as the benzenoid structure of both rings is distributed in contributory structures.

Electrophilic substitution reaction: When electrophilic attack takes place at 1- or α -position and 2- or β -position.

For substitution at α - or 1- position:



For substitution at β - or 2-position:

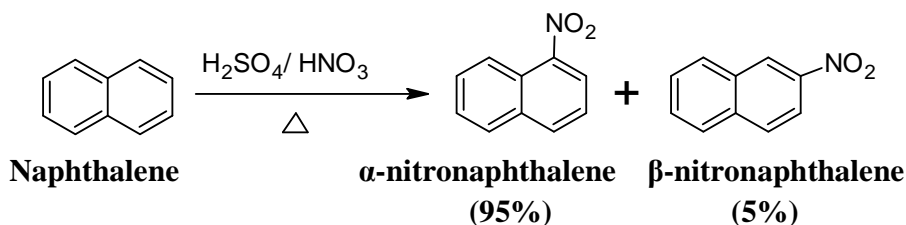


E^+ represents an electrophile and may be Cl^+ , Br^+ , I^+ in halogenation, NO_2^+ in nitration SO_3 in sulphonation, R^+ or RCO^+ in friedel –crafts reaction.

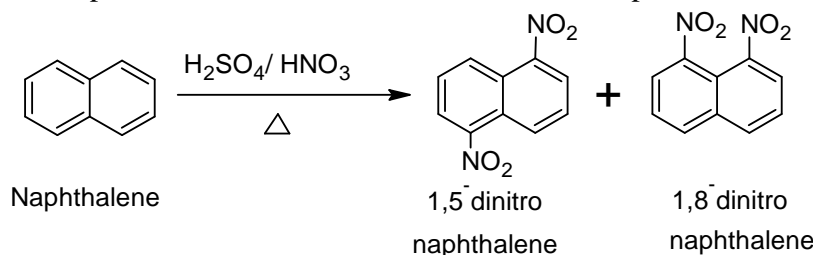
From a comparative study of resonance stabilized intermediate carbocation of 1- and 2- substitution, it is obvious that structures I,II,VI,VII, VIII and XII are more stable because they contain at least one benzene ring intact (because benzene has a large resonance energy).

Out of these four i.e. I,II,VI and VII are involved during α -substitution while only two i.e. VIII and XII are involved during β -substitution. Consequently, the carbocation formed during the α -substitution and transition state leading to that ion is much more stable than the carbocation and the corresponding transition state formed during the β -substitution. Hence the α -substitution is the preferred orientation of substitution in naphthalene.

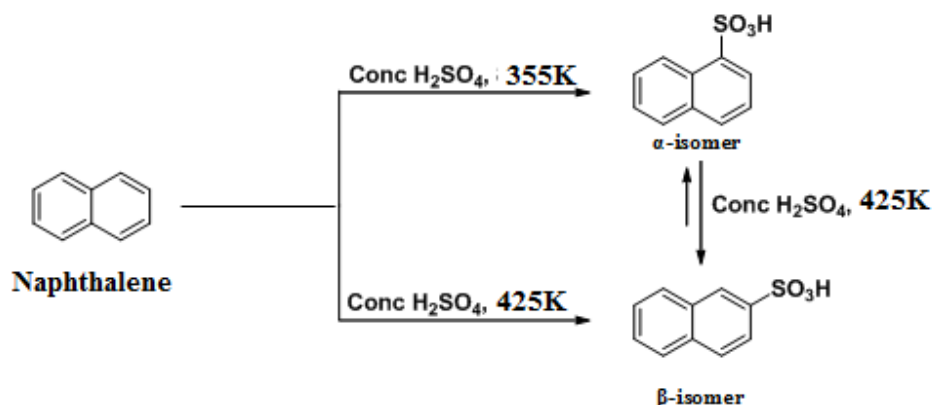
1. Nitration: Nitration of naphthalene with mixture of concentrated nitric acid and sulphuric acid yields predominantly the α -nitronaphthalene (95%) with minor amounts (5%) of β -nitronaphthalene.



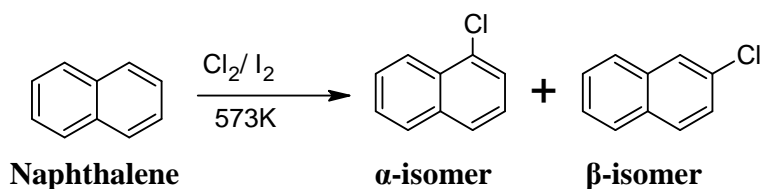
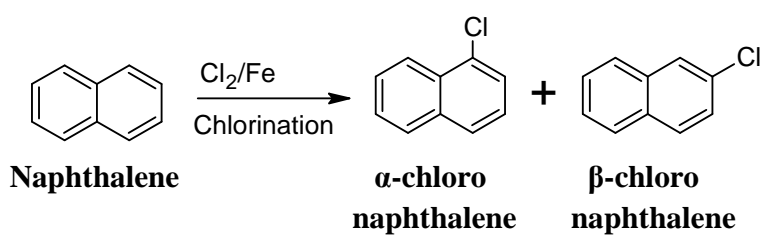
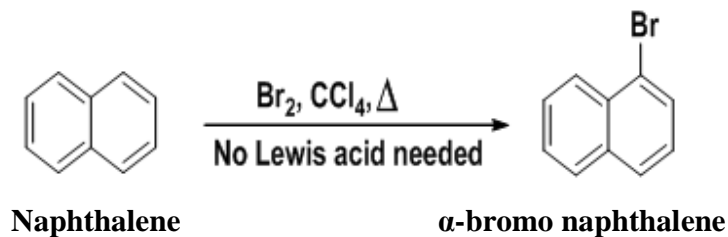
However at higher temperature a mixture of 1,5- and 1,8-dinitro naphthalene are formed.



2. Sulphonation : Naphthalene can be sulphonated at 355K to yield mainly i-naphthalene sulphonic acid whereas if the reaction is carried out at 425K, 2-naphthalene sulphonic acid is the main product. This is reversible. It has been shown that when 1-naphthalene sulphonic acid is heated, it is highly converted in to the 2-isomer.

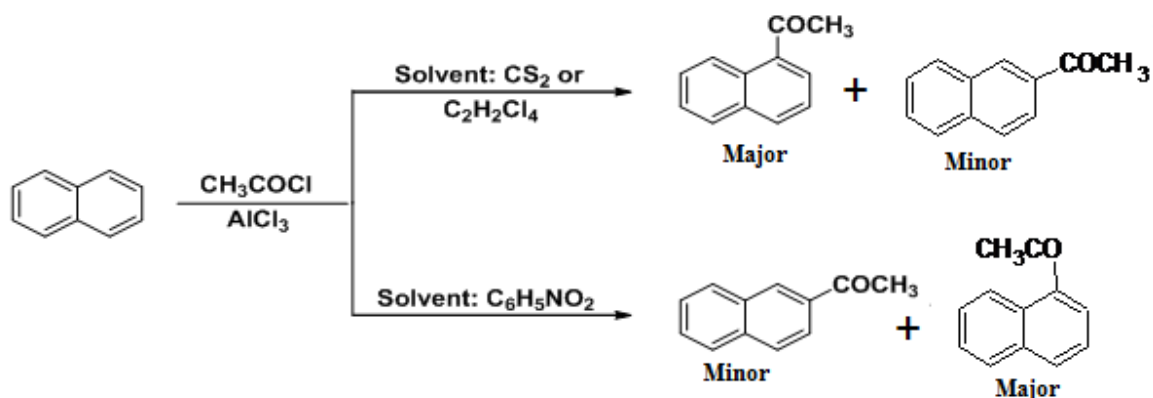


3. Halogenation: Halogenation of naphthalene takes place very readily and no catalyst is needed for the purpose. The reaction takes place almost exclusively at 1- positions. When brominated in boiling carbon tetrachloride solution, naphthalene gives 1-bromo derivative in good yield. 1-Chloronaphthalene can be obtained either by reacting naphthalene with sulphuryl chloride (SO_2Cl_2) in presence of aluminium chloride at 298K or by chlorination in the presence of ferric chloride.

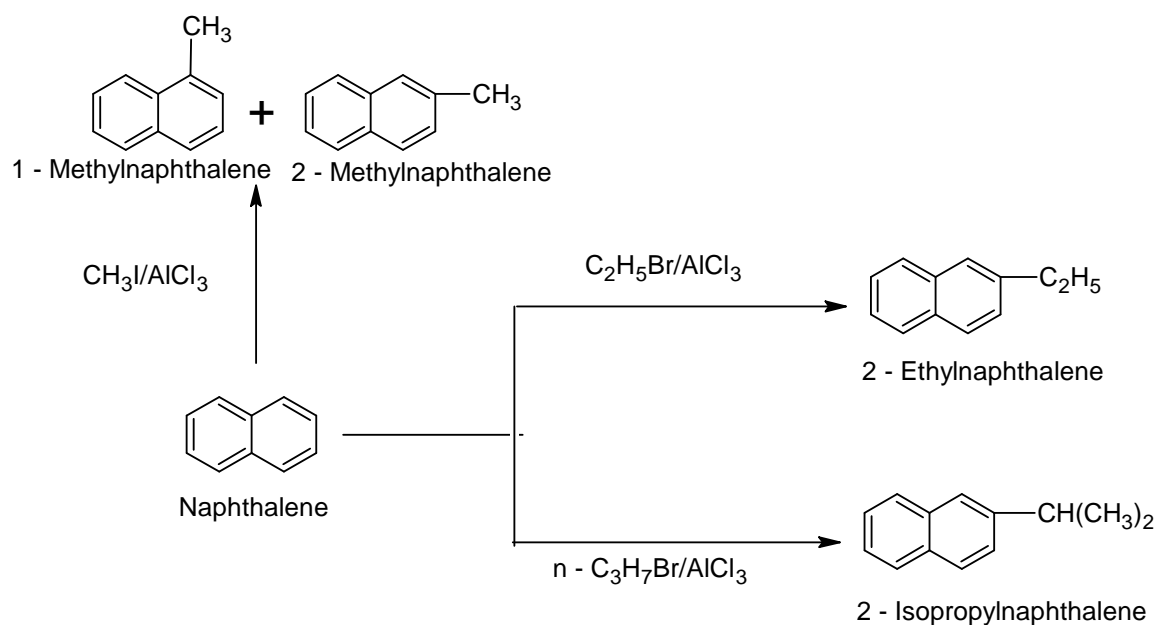


4. Friedel crafts Reaction: Naphthalene undergoes Friedel-Crafts acylation and alkylation to give acylated and alkylated products.

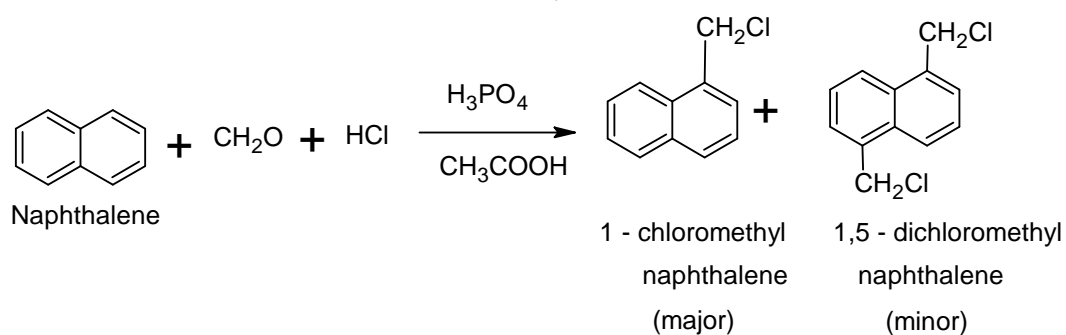
a) Friedel-Crafts acylation: Acylation of naphthalene gives 1- and 2- acyl naphthalene as products but their proportion depends on the solvent used. For instance, acyl chloride in the presence of anhydrous aluminium chloride in carbon disulphide gives 1- and 2-acyl naphthalene in the ratio 3:1 whereas in nitrobenzene as the solvent the ratio is 1:9.



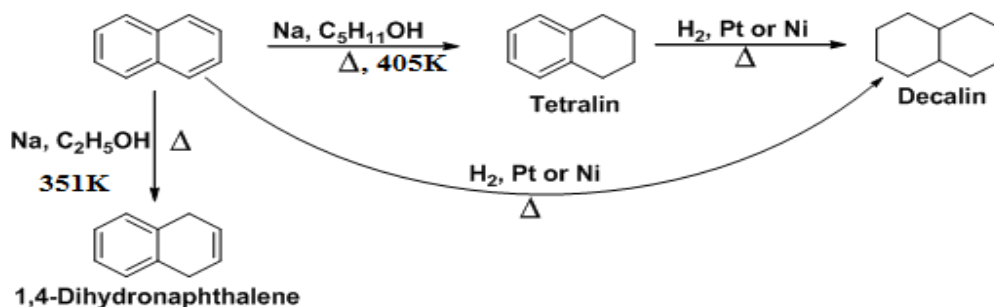
b) Friedel-Craft alkylation: Alkylation of naphthalene gives a mixture of α - and β -isomers, their relative proportions depending on the reaction conditions and the size of the alkyl group to be introduced. Thus, with CH_3I a mixture of α - and β -methyl naphthalenes is formed, while $\text{C}_2\text{H}_5\text{Br}$ gives mainly β -ethylnaphthalene and $n\text{-C}_3\text{H}_7\text{Br}$ forms only β -isopropyl naphthalene, with alcohols usually polyalkylated products are formed.



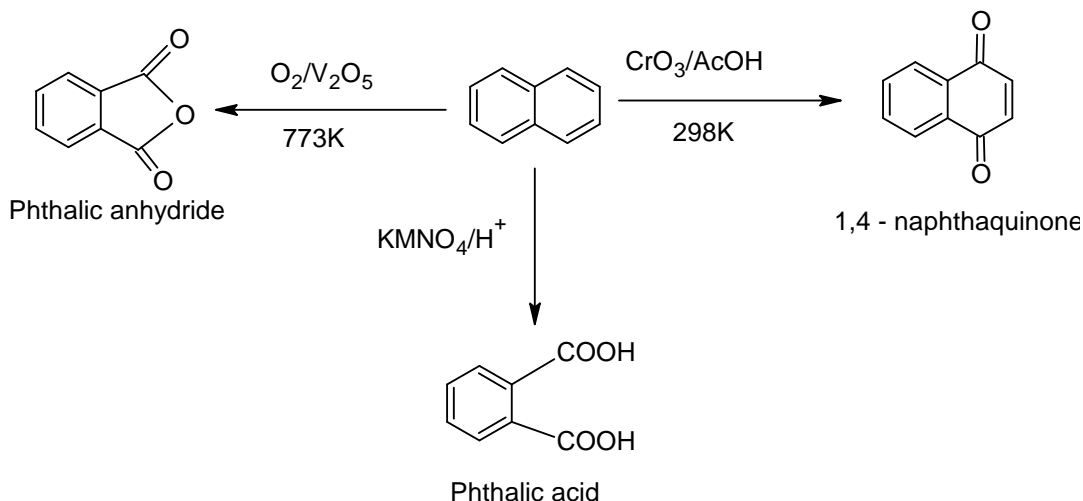
5. Chloromethylation: Naphthalene on reaction with paraformaldehyde, hydrochloric acid, glacial acetic acid and phosphoric acid gives α -chloromethyl naphthalene as the main product (56%) together with 1,5-dichloromethylnaphthalene.



6. Reduction: Unlike benzene, naphthalene on reduction forms number of products which depends on reducing agents used. Naphthalene on reduction with Na in $\text{C}_2\text{H}_5\text{OH}$ (Birch reduction) gives 1,4-dihydronaphthalene, with sodium in amyl alcohol at 405K gives tetralin and with Pt/Ni gives decalin. Tetralin and decalin are widely used as solvents for vernishes, lacquers etc.

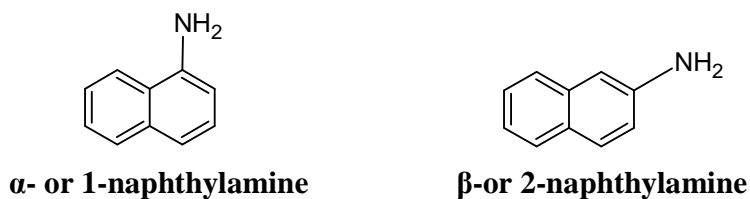


7. Oxidation: Naphthalene on oxidation with oxygen or air in the presence of vanadium pentoxide catalyst forms phthalic anhydride. In place of vanadium pentoxide, Conc. Sulphuric acid with mercuric sulphate can be used and in presence of potassium permanganate in acid it gives phthalic acid while with chromic acid in acetic acid gives 1,4-naphthaquinone

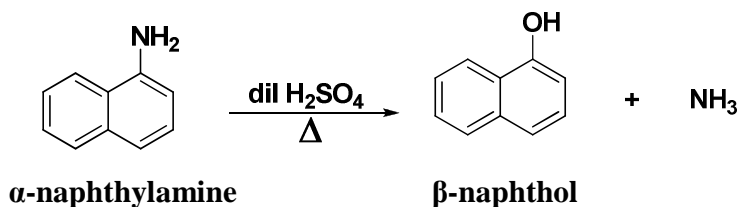


2.1.8: Derivatives of Naphthalene: The chemistry of derivatives of naphthalene is comparable to the corresponding compounds in benzene series. Like benzene, it forms a number of derivatives. We will study here naphthols and naphthylamines which is widely used in dye industry..

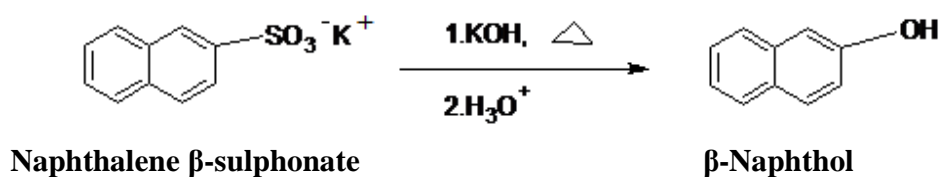
1. **α -naphthylamine:** It is amino derivatives of naphthalene. It has two isomeric forms .i.e. α -naphthylamine and β -naphthylamine. It can be represented as,



They can also be prepared by heating corresponding naphthylamines with dilute sulphuric acid under pressure at 573K. This method is of special importance in the preparation of pure α -naphthol.



β -naphthols : It is prepared by alkali fusion of naphthalene β -sulphonate.



2.2 Anthracene , C₁₄H₁₀ :

Anthracene occurs in the coal tar distillation fraction known as anthracene oil (Greek: *anthrax* meaning coal) or as green oil because of its dark green fluorescence. This fraction collected between 543-633K contains phenanthrene and carbazole besides 1 per cent anthracene.

Source and extraction: The anthracene oil is cooled and allowed to crystallize over a period of one week . It is then filtered and the solid known as ‘anthracene cake’ is pressed free from liquid. The cake is powdered and first washed with solvent naphtha to dissolve phenanthrene and then with pyridine to remove carbazole by dissolving it. The remaining solid is crude anthracene and is purified by sublimation.

An earlier method is based on fusing anthracene cake with potassium hydroxide, after removal of phenanthrene, when potassiccarbazole is formed and unreacted anthracene is recovered by sublimation.

Alternatively, after removal of phenanthrene the remaining mixture is oxidized catalytically by air in the presence of V₂O₅ at 573-773K. Under these conditions carbazole is completely oxidized to CO₂ etc. and the anthracene to anthraquinone. The anthraquinone is an important anthracene derivative used in dye industry.

Nomenclature and isomerism of anthracene derivatives: The positions of different carbon atoms in anthracene are indicated by numbers or Greek letters as shown below:

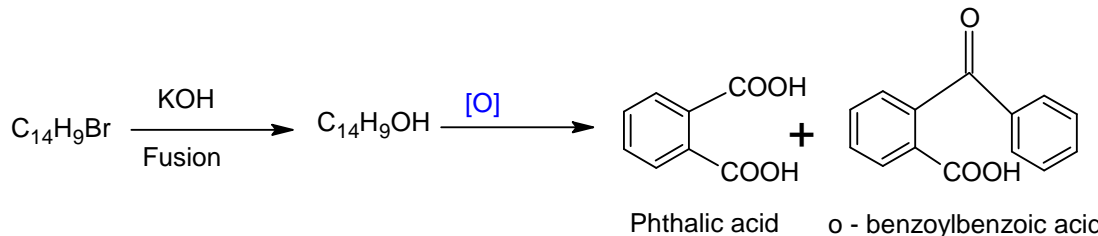


It is clear from these formulae that in anthracene three different positions are available for a substituent and therefore it gives three isomeric monosubstitution products viz α - or 1; β - or 2- and γ - or 9- (or meso) . There are 15 possible disubstituted isomers if the two substituents are identical, if not, the number of isomers is still larger.

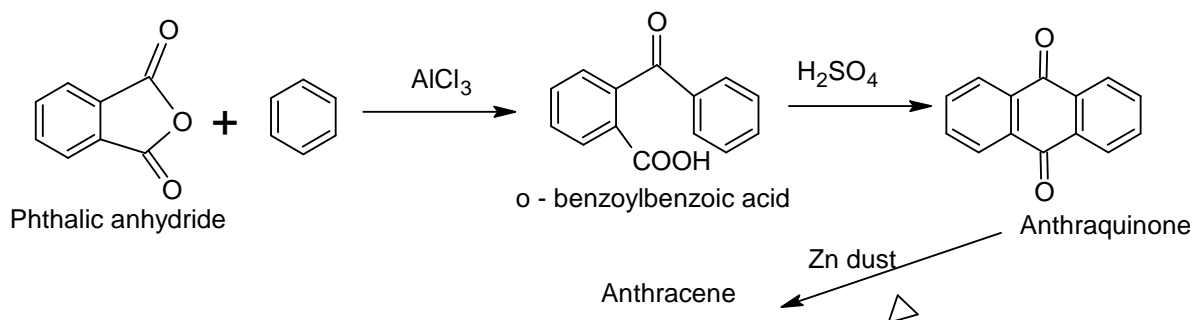
2.2.1: Structure of Anthracene:

A] Analytical evidence:

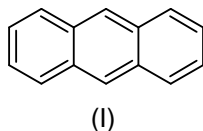
1. From analytical data and determination of molecular weight, the molecular formula of anthracene has been found to be $C_{14}H_{10}$.
2. It readily undergoes electrophilic substitution reactions like other aromatic compounds. Thus it is a typical aromatic compound like benzene and naphthalene in structure.
3. Bromination of anthracene gives bromoanthracene, $C_{14}H_9Br$, which on fusion with KOH forms hydroxyanthracene, $C_{14}H_9OH$ which on vigorous oxidation gives phthalic acid and o-benzoylbenzoic acid, showing presence of at least two benzene ring.



4. On oxidation with chromic acid, it gives anthraquinone whose structure has been established by its synthesis involving Friedel-Crafts acylation of benzene with phthalic anhydride to o-benzoylbenzoic acid which undergoes acid-catalyzed cyclization to anthraquinone. Anthraquinone on distillation with zinc dust gives back anthracene.

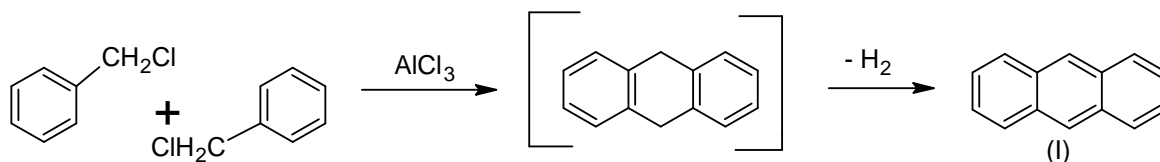


All the above facts lead to the structure (I) for anthracene, a system of three benzene rings fused together in a linear fashion.

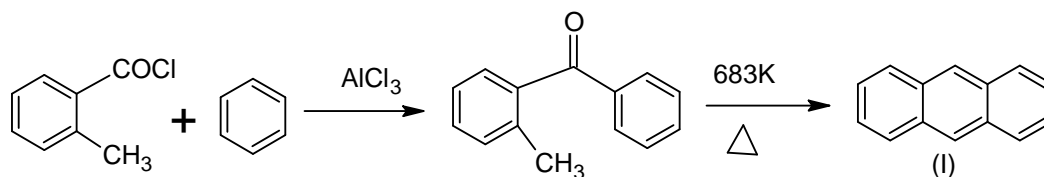


B] Synthetic evidence: The structure (I) for anthracene has finally been confirmed by its synthesis.

1. Friedel crafts alkylation between two molecules of benzyl chloride gives 9,10-dihydroanthracene which is oxidized readily under the reaction conditions yielding anthracene.



2. This method is based on Elbs reaction in which a polynuclear aromatic hydrocarbon having an anthracene moiety is formed by pyrolysis of a diaryl ketone containing a methyl or methylene group ortho to the carbonyl group.



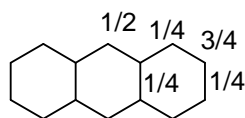
C] Modern view:

1. Resonance concept: X-ray studies indicate that all carbon and hydrogen in anthracene lie in the same plane. Like benzene and naphthalene, anthracene is believed to be the resonance hybrid of the following contributing structures.

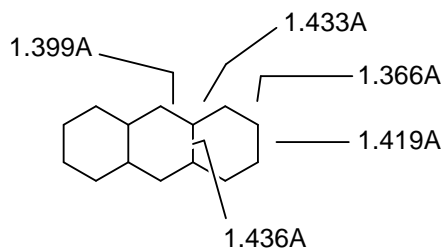


The resonance energy of anthracene is 84 Kcal. This is only 12 Kcal more the resonance energy of two benzene rings (36 Kcal of each) and hence anthracene is highly reactive. The greater reactivity of 9,10 positions forming a product with two benzene ring intact is also explained on the basis of reaction at any other position will have a naphthalene system with lesser (61Kcal) resonance energy.

The above contributing structures also account for the fact C1-C2 bond distance have 3/4 double bond character while C₂-C₃ bond distance have 1/4 double bond character.

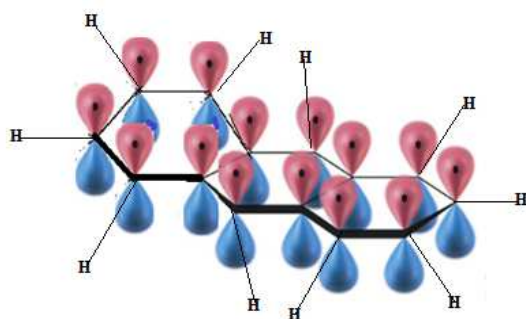


Bond character

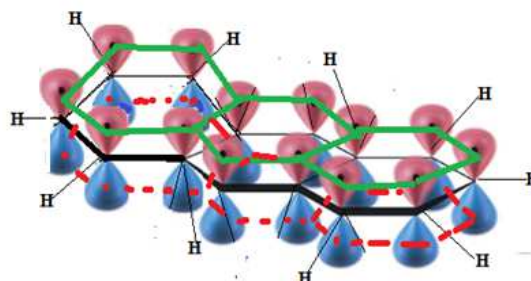


Bond length

2. Molecular orbital concept: Each of the ten carbon atoms at the corners of the two fused hexagons is linked to three other atoms through its trigonal sp^2 -hybridised atomic orbitals. Thus all the ten carbon atoms and the attached hydrogens must lie in one plane as in the case of benzene. Then there are ten singly occupied 2p orbitals—one on each carbon at right angles to the above plane. These orbitals form a π -electron cloud above and below the plane of the ring. This π -electron cloud has the shape of numeral 8 and is formed by the two partially overlapping sextets having 2π electrons in common number of total π -electron in anthracene is 14 which is in accordance with Huckel's rule. Hence anthracene exhibits aromatic character. The M.O. concept explains the planarity of all the 'C' and 'H', its unusual stability and also the fact that it acts as a source of electrons in electrophilic substitution reactions.



Unhybridised p_z orbitals contain unpaired electron



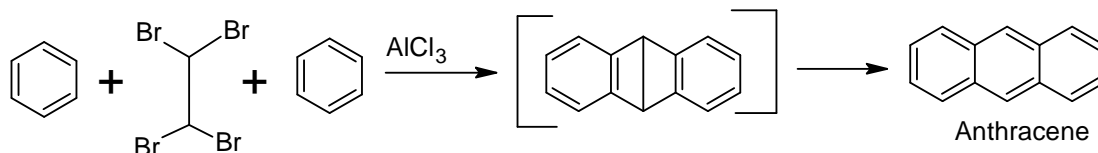
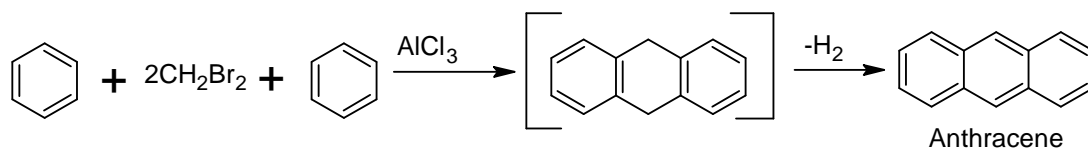
Delocalisation of π electrons above and below plane of the ring

Molecular Orbital Structure of Anthracene

Synthetic methods: The synthesis of anthracene can be carried out by following methods

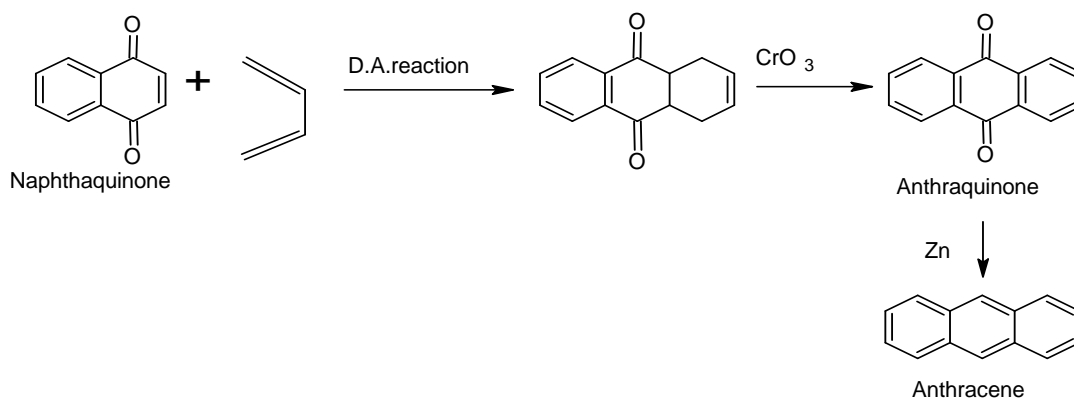
(a) From benzene and methylene dibromide and acetylene tetrabromide:

This method involving Friedel crafts alkylation of benzene with either methylene dibromide or with acetylene tetrabromide.



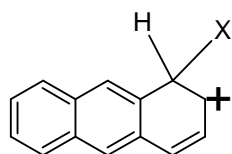
(b) From naphthaquinone and 1,3-butadiene :

This synthesis consists in Diels-Alder reaction between naphthaquinone and butadiene followed by oxidation of the intermediate with chromic acid in glacial acetic acid to give anthraquinone which on distillation with zinc dust yields anthracene.

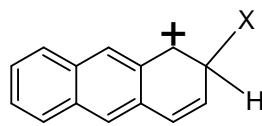


2.2.2: Physical properties: It is a colourless solid, m.p.489K, with a green-yellow or blue fluorescence. It is insoluble in water and sparingly soluble in organic solvents.

Chemical reaction: It resembles benzene and naphthalene in many of its chemical reactions. It is very reactive at positions 9- and 10. Electrophilic substitution, such as halogenations or nitration, preferably gives 9- or 9-,10-disubstituted products. The greater reactivity of the 9,10-positions is readily understandable if we consider the relative stabilities of the σ -complexes formed as a result of electrophile attack 1-,2- and 9-positions. The attack at 1- or 2- position forms a carbocation having a naphthalene moiety whereas the σ -complex formed by attack at 9-position has two benzene rings. The resonance stabilization in the latter will be more since the total resonance energy of two benzene rings is greater than that of a naphthalene ring.

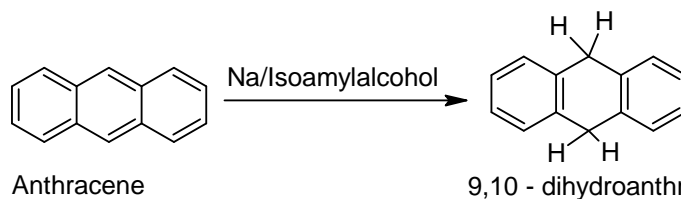


α -complex for 1- and 2- substitution
(a naphthalene ring intact)



α -complex for 9,10-substitution
(two benzene rings intact)

1. Reduction: When reduced with sodium and isoamyl alcohol it forms 9,10-dihydroanthracene which on heating or on reaction with conc. H_2SO_4 reforms anthracene.

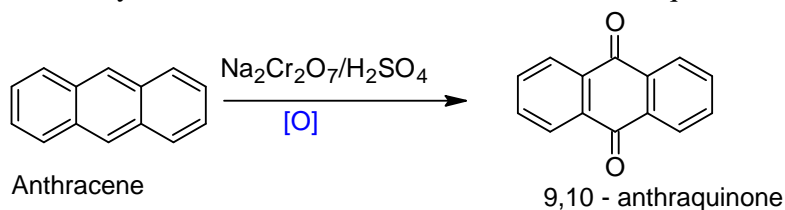


Anthracene

9,10 - dihydroanthracene

Catalytic reduction (H_2/Ni at 473-523K) gives tetra-, octa- and finally perhydroanthracene ($\text{C}_{14}\text{H}_{24}$).

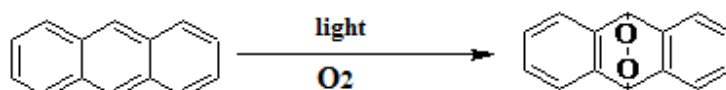
2. Oxidation: It is readily oxidized with chromic acid to 9,10-anthraquinone.



Anthracene

9,10 - anthraquinone

It adds one molecule of oxygen in the presence of light to form a colourless peroxide.

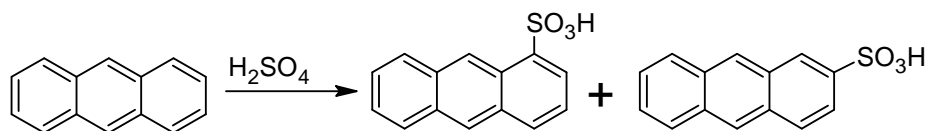


Anthracene

Anthracene peroxide

3. Electrophilic substitution reactions: It undergoes electrophilic substitution reactions like sulphonation, nitration, halogenations etc.

I] Sulphonation: It reacts with H_2SO_4 to form a mixture of 1- and 2- sulphonic acids



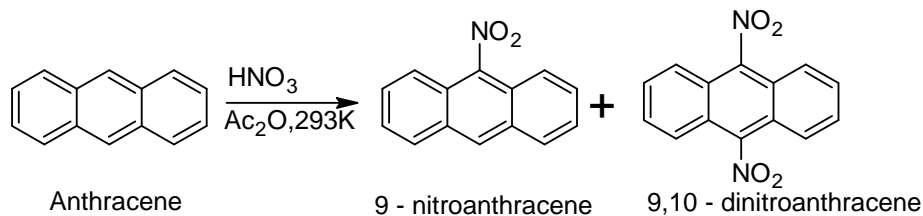
Anthracene

Anthracene 1 -sulphonic acid

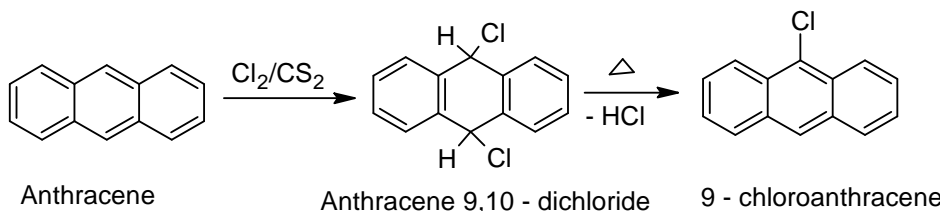
Anthracene 2 -sulphonic acid

At higher temperatures the 2- sulphonic acid is the main product. However, unlike naphthalene, the 1-sulphonic acid of anthracene does not rearrange to 2- sulphonic acid. Sulphonation with conc. H_2SO_4 gives 1,5- and 1,8- anthracene disulphonic acids.

II] Nitration: Anthracene on nitration with concentrated nitric acid in the presence of acetic anhydride gives a mixture of 9-nitro anthracene and 9,10-dinitro anthracene.



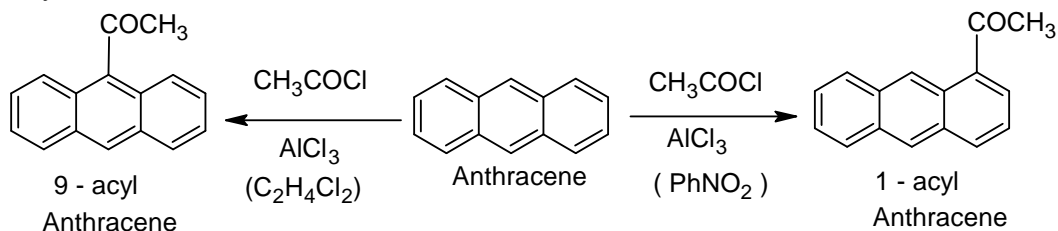
III] Halogenation: Chlorination with chlorine in carbon disulphide solvent in cold gives anthracene dichloride which on heating or treatment with alkali yields 9-chloroanthracene.



9-chloroanthracene may also be obtained by heating anthracene with cuprous chloride in carbon tetrachloride solution. Reaction of sulphuryl chloride with anthracene gives 9,10-dichloro,9,10-dihydro-anthracene. Both 9-chloroanthracene and anthracene dichloride on oxidation form anthraquinone.

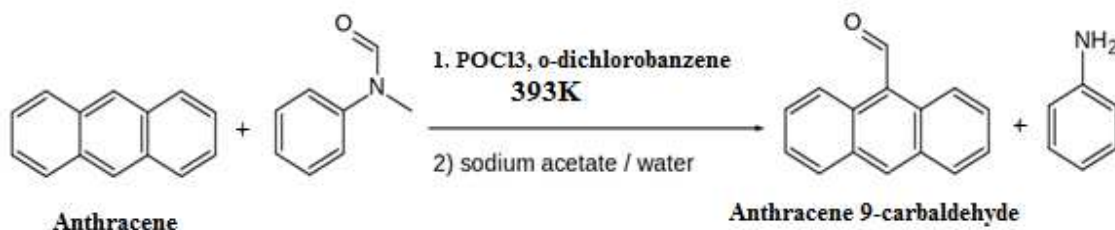
Bromination in carbon tetrachloride follows the same course first forming anthracene dibromide (9,10-dibromo-9,10- dihydro anthracene which on heating yields 9-bromo anthracene.

IV] Friedel craft acylation: Friedel crafts acylation of anthracene with acetyl chloride in benzene or nitrobenzene gives a complex mixture. However, the main product in nitrobenzene as solvent is the 1-acetyl derivative whereas in ethylene dichloride it is the 9-acetyl derivative.

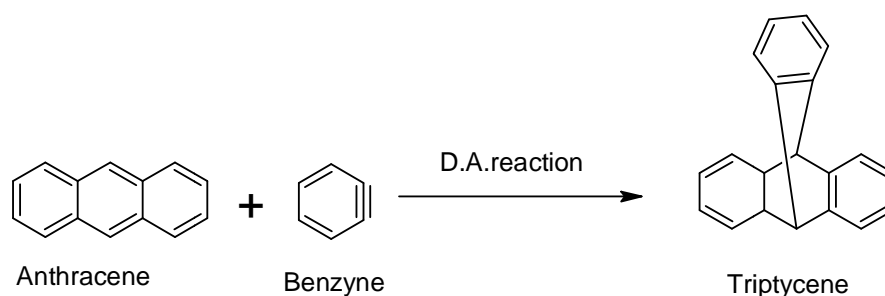
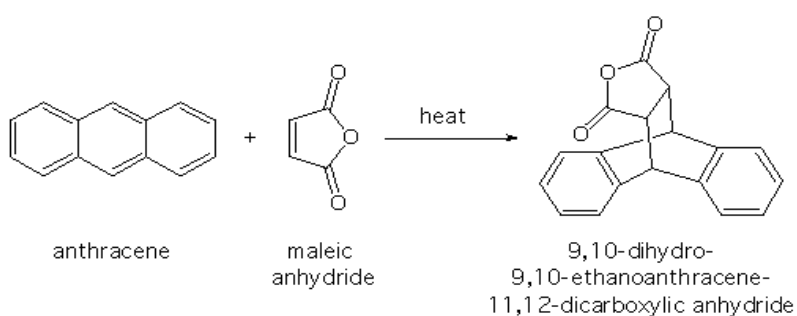


4. Formylation by Vilsmeier – Haack method: Anthracene can be formylated exclusively at the 9-position. The reaction of anthracene with *N*-methylformanilide, also using

phosphorus oxychloride gives Anthracene 9-carbaldehyde (9-Anthraldehyde) is shown below:

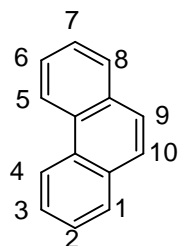


5. Diels-Alder reaction: Anthracene undergoes facile Diels-Alder reaction with maleic anhydride and benzyne to give 1,4-addition products.



2.3 : Phenanthrene – Phenanthrene is a polycyclic aromatic hydrocarbon composed of three fused benzene rings. The name phenanthrene is a composite of phenyl and anthracene. It provides the framework for the steroids. In its pure form, it is found in cigarette smoke and is a known irritant, photosensitising skin to light. It appears as a white powder. It is insoluble in water but soluble in most organic solvents such as toluene, carbon tetrachloride, ether, chloroform, acetic acid and benzene.

Nomenclature and Isomerism: To indicate their positions, the ring carbon atoms are numbered as shown below.

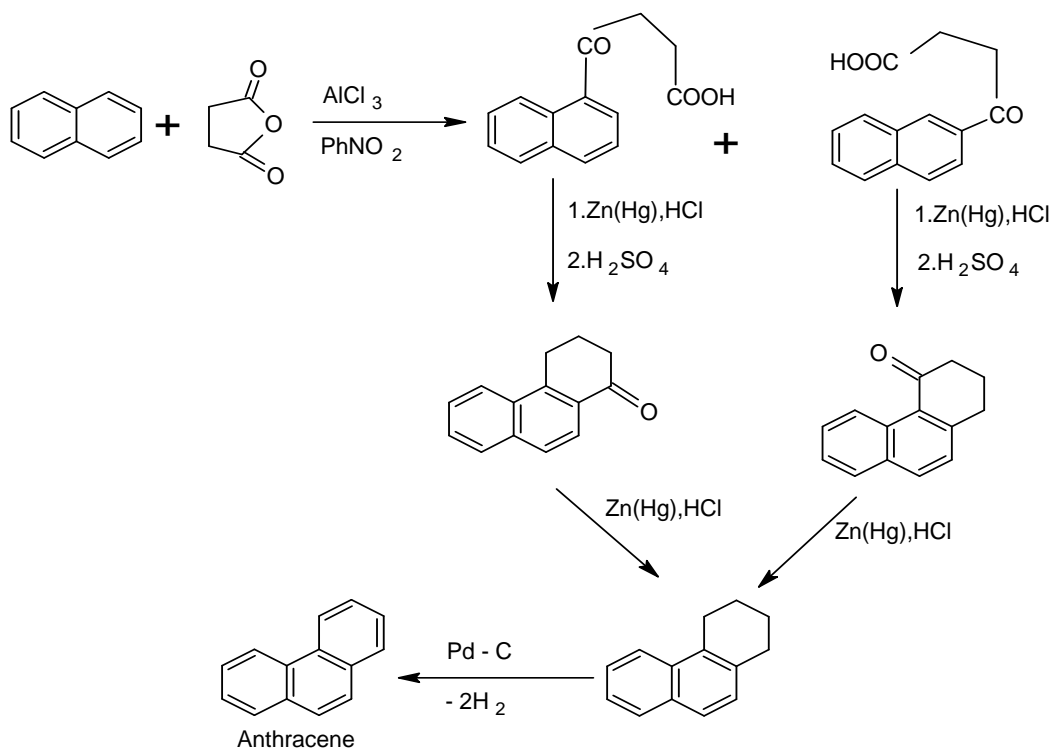


Phenanthrene

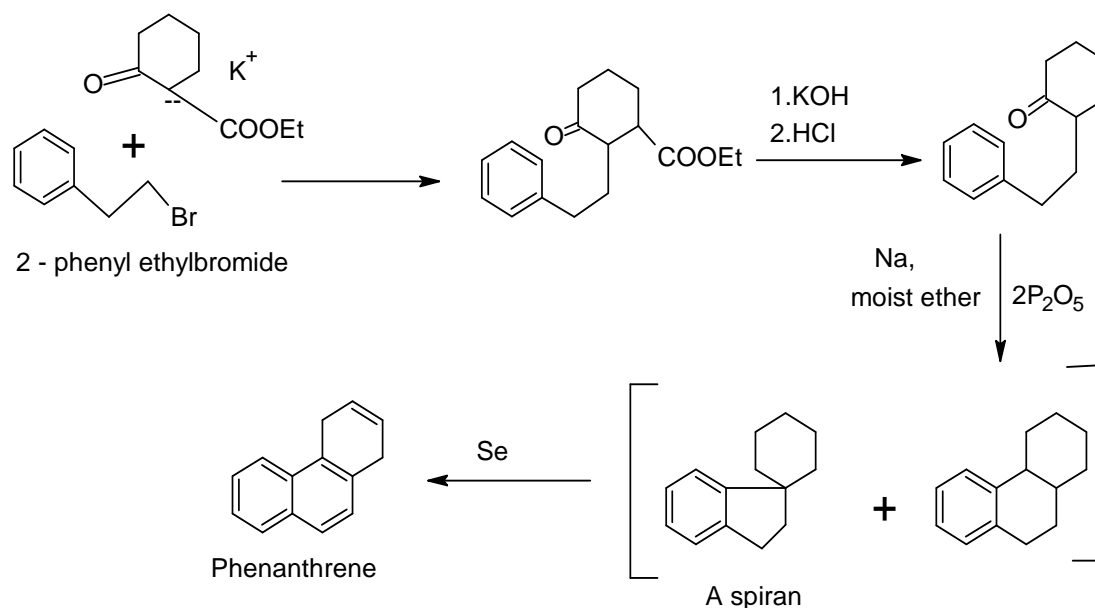
It forms five isomeric monosubstituted derivatives, viz., 1,2,3,4 and 9-substituted phenanthrene. On disubstitution, if the two substituents are same, 25 isomers are possible.

2.3.1: Synthesis of Phenanthrene : Synthesis of phenanthrene can be carried out by following methods.

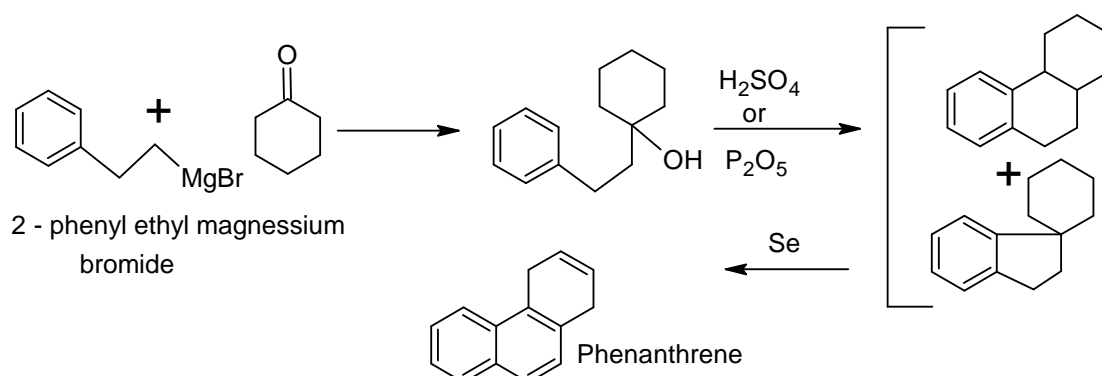
1) Haworth synthesis: Succinylation of naphthalene produces two isomeric keto acids: β -(1-naphthoyl) propionic acid and β -(2-naphthoyl) propionic acid. These two isomers can be readily separated. Clemmensen reduction affords γ -(1-naphthyl) butyric acid and γ -(2-naphthyl)-butyric acid respectively. Acid catalysed cyclisation gives 1-keto-1,2,3,4-tetrahydro- and 4-keto-1,2,3,4-tetrahydrophenanthrene. Clemmensen reduction of either isomer followed by aromatization.



2) Bardhan – Sengupta synthesis : It consists in treating potassium salts of cyclohexanone 2-carboxylic ester (a β -keto ester) with 2-phenylethyl bromide (S_N2) followed by hydrolysis and decarboxylation. The resulting ketone on reduction forms the corresponding alcohol which undergoes acid catalyzed cyclisation to a mixture of octahydrophenanthrene and the corresponding spiran. This mixture then aromatized to phenanthrene with selenium.

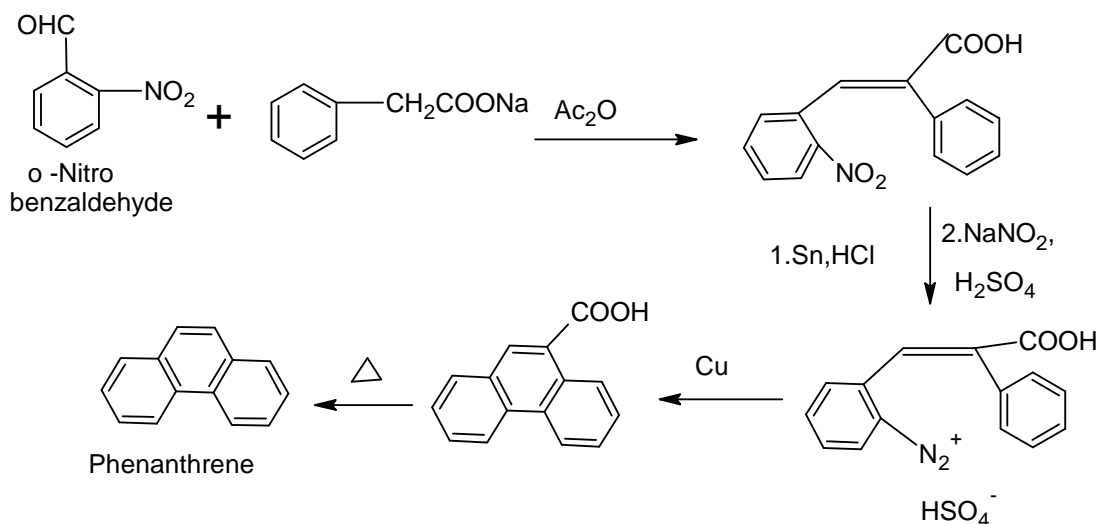


3) Bogert – cook synthesis : This method involves treatment of 2-phenylethyl magnesium bromide with cyclohexanone and the tertiary alcohol so produced is cyclized with H_2SO_4 (or P_2O_5) followed by aromatization.



4) pschorr synthesis: o-Nitrobenzaldehyde is subjected to Perkin reaction with sodium phenylacetate to produce α -phenyl-o-nitrocinnamic acid. Reduction of this acid gives the corresponding amino acid which is diazotized. The resulting diazonium salt on treatment with

copper powder undergoes intramolecular phenylation most probably via free radical intermediate to produce phenanthrene-9-carboxylic acid which on heating strongly loses carbon dioxide to give phenanthrene.



Exercises

[A] OBJECTIVE TYPE QUESTIONS

I] Select the most correct alternative from among those given below.

- is not a condensed polynuclear compound ?
 a) Anthracene b) Naphthalene c) Biphenyl d) Phenanthrene
- Sulphonation of naphthalene with H_2SO_4 at 425 K yields mainly.....
 a) α -naphthalene sulphonic acid b) β -naphthalene sulphonic acid c) γ -naphthalene sulphonic acid d) A mixture of all of these
- The largest single compound present in 'middle oil' fraction of coal tar is.....
 a) benzene b) diphenyl c) Naphthalene d) β -naphthol
- Oxidation of naphthalene with O_2 in presence of V_2O_5 at 773K forms.....
 a) benzoic acid b) phthalic acid c) naphthaquinone d) phthalic anhydride
- Bucherer reaction is used to prepare.....
 a) β -naphthol b) α -naphthol c) α -naphthylamine d) β -naphthylamine
- Which of the following exhibits Diels-Alder reaction?

- a) naphthalene b) anthracene c) phenanthrene d) acenaphthene
7. Monohalogenation of anthracene gives.....
- a) 1-haloanthracene b) 2-haloanthracene c) 3-haloanthracene d) 9-haloanthracene
8. Anthraquinone when distilled with zinc dust forms.....
- a) anthracene b) dihydroanthracene c) phenanthrene d) anthraquinol
9. Phenanthrene is a..... hydrocarbon.
- a) polynuclear b) aliphatic c) alicyclic d) mononuclear
10.π-electrons present in anthracene.
- a) 14 b) 8 c) 10 d) 12
11. Electrophilic substitution in naphthalene occurs more readily at.....position.
- a) α- b) β- c) 5th d) 8th
12. Naphthalene is prepared from benzene and.....
- a) pyridine b) phthalic acid c) succinic anhydride d) maleic acid
13. α-naphthylamine when treated with dilute sulphuric acid at 573K gives
- a) α-naphthol b) β-naphthol c) 2-naphthol d) phenol
14. Alkali fusion of naphthalene with β-sulphonate gives.....
- a) α-naphthol b) β-naphthol c) 2-naphthol d) phenol
15. Cyclisation of o-benzoylbenzoic acid in presence of sulphuric acid gives.....
- a) anthracene b) α-naphthol c) anthraquinone d) β-naphthol
16. Resonance energy of anthracene is
- a) 84 KCals b) 61 KCals c) 36 KCals d) 48 KCals
17. Oxidation of naphthalene in presence of KMnO₄ gives.....
- a) 1,4-naphthaquinone b) phthalic anhydride c) phthalic acid d) anthraquinone
18. Catalytic reduction of naphthalene with Ni gives.....
- a) decalin b) tetralin c) 1,4-dihydronaphthalene d) perhydronaphthalene
19. Bromination of naphthalene in presence of CCl₄ gives.....
- a) 1-bromonaphthalene b) 2-bromonaphthalene c) β-bromonaphthalene
d) α-and β-dibromonaphthalene
20. Resonance energy of naphthalene is.....
- a) 84 KCals b) 61 KCals c) 36 KCals d) 48 KCals
21. 4-phenyl,1-butene is passed over red hot CuO gives.....

- a) naphthalene b) anthracene c) phenanthrene d) 1-naphthol
22. Fittig and Erdmann synthesis is used in preparation of.....
- a) anthracene b) phenanthrene c) naphthalene d) 2-naphthol

Answer:

1. c) Biphenyl 2. b) β -naphthalene sulphonic acid 3. c) Naphthalene 4.d) phthalic anhydride
5. a) β -naphthol 6. b) anthracene 7. d) 9-haloanthracene 8. a) anthracene 9. a) polynuclear
10. a) 14 11 a) α - 12. c) succinic anhydride 13, a) α -naphthol 14. b) β -naphthol
15. c) anthraquinone 16. a) 84 KCals 17. c) phthalic acid 18. a) decalin
19. a) 1-bromonaphthalene 20. b) 61 KCals 21. a) naphthalene 22. c) naphthalene

[B] SHORT AND LONG ANSWER TYPE QUESTIONS:

1. What are polynuclear compounds ? How they are classified ? Give examples of each group.
2. Discuss the constitution of naphthalene.
3. What is modern view regarding the structure of naphthalene ?
4. How will you show that naphthalene has two benzene rings fused in o-position ?
5. Write note on:
 - i) Orientation in naphthalene ring system.
 - ii) Electrophilic substitution reactions of naphthalene.
 - iii) Bucherer reaction
 - iv) Aromatic nature of naphthalene
 - v) Sulphonation of naphthalene
 - vi) Electrophilic substitution reactions of anthracene
6. How can α - and β - naphthols and naphthylamines be obtained ?
7. In what respect anthracene and phenanthrene resemble benzene? Explain why position 9,10 are reactive in them.
8. Give one synthesis for each one of the following:
 - i) Anthracene
 - ii) Naphthalene
 - c) Phenanthrene
9. Explain why α - position of naphthalene is more reactive than β -position ?
10. What product(s) are formed when naphthalene is reacted with :

a) Cl_2/Fe b) CrO_3/AcOH at 298K c) $\text{Conc. H}_2\text{SO}_4$ at 355K d) $\text{HNO}_3/\text{Conc. H}_2\text{SO}_4$

11. Describe the isolation of anthracene from coal tar.
12. How will be establish the structure of anthracene on the basis of analytical evidence ?
13. Write the resonating structures of anthracene and naphthalene
14. How will you synthesize α - and β -naphthols?
15. Explain in Haworth synthesis, the clemmensen reduction of the keto acid is essential before cyclisation.
16. What are the methods used for synthesis of phenanthrene?
17. Explain anthracene is more reactive than naphthalene.
18. Why the 9,10-position of anthracene are very reactive ?
19. Illustrate the following:
 - i) Elbs reaction for the synthesis of anthracene
 - ii) Bardhan-Sengupta synthesis of phenanthrene
20. Comment on the modern views about the naphthalene structure.
21. What are naphthyl amines? How are they prepared ? Give their chemical reactions.
22. Why naphthalene is less aromatic than benzene
23. Give the oxidation and reduction reactions of naphthalene.
24. How will you prepared naphthalene from benzaldehyde and benzene ?
25. How will you synthesize naphthalene ? Give its chemical reactions with respect to sulphonation, chloromethylation and friedel crafts alkylation.
26. What happens when anthracene reacts with:

i] $\text{HNO}_3, \text{Ac}_2\text{O}$ at 293K

ii] $\text{CH}_3\text{COCl}, \text{AlCl}_3, \text{C}_2\text{H}_4\text{Cl}_2$

iii] Cl_2/CS_2

iv] $\text{CH}_3\text{COCl}, \text{AlCl}_3, \text{PhNO}_2$

27. How will you prepare phenanthrene by Haworth process ?

28. Write note on :

i) Vilsmeier-Haack method

ii) Diels Alder reaction in Anthracene.
