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# [POLYNUCLEAR HYDROCARBONS]

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[ORGANIC CHEMISTRY B.sc – III (HONS)]



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[DR. SHASHI KUMAR]

[ASSOCIATE PROFESSOR G.J COLLEGE RAMBAGH BIHTA (PATNA) OF HOD DEPARTMENT OF CHEMISTRY]

## "POLYNUCLEAR HYDROCARBONS"

### "NAPHTHALENE"

It is polynuclear aromatic hydrocarbon. In this, the two benzene rings are found.

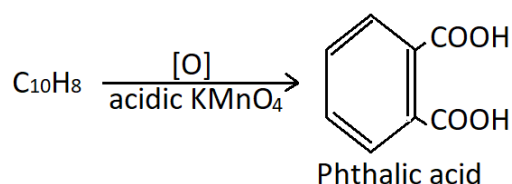
SOLUTION:- It was isolated from the coal tar distillate. The heavy oil and the middle oil fractions of the coal tar distillate cooling deposit naphthalene. This is separated and treated with.

- (i) Dilute  $\text{H}_2\text{SO}_4$  (To remove basic impurities).
- (ii) Water (To remove  $\text{H}_2\text{SO}_4$ ).
- (iii)  $\text{NaOH}$  solution (To remove acidic impurities).
- (iv) Water (To remove  $\text{NaOH}$ ).

Finally, the solid obtained after these treatments is distilled to get pure Naphthalene.

### "STRUCTURE DETERMINATION"

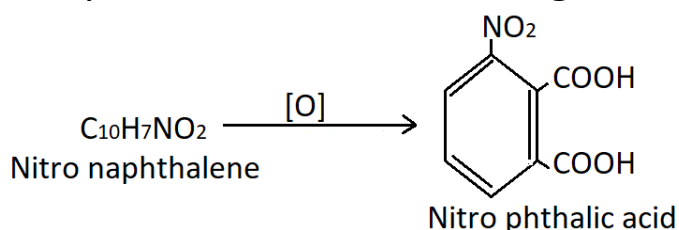
- (1) From analysis and molecular weight determination the molecular formula is found to be  $\text{C}_{10}\text{H}_8$ .
- (2) From its molecular formula it appears to be a highly unsaturated hydrocarbon. But its reaction (like substitution reaction eg. Nitration, Sulphonation, Halogenation etc). indicate it to be similar character with benzene.
- (3) When Naphthalene is oxidised with acidic  $\text{KMnO}_4$ , we get phthalic acid.



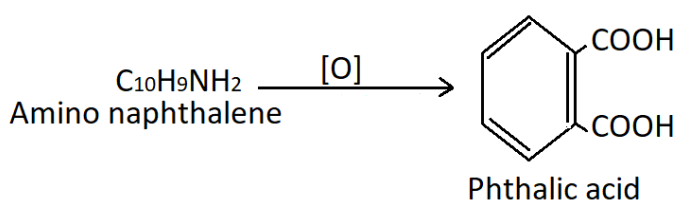
"Formation of phthalic acid indicates presence of at least are benzene ring and some type of side chain" at the two ortho position.

- (4) When Naphthalene is nitrated (with conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ ), we get nitro naphthalene.

(a) Nitro naphthalene on oxidation gives nitro phthalic acid.



(b) When nitrobenzene is reduced amino naphthalene is produced. This on oxidation gives phthalic acid.

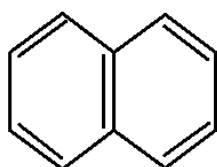


Conclusion:- These observations lead to the conclusion that there are two benzene ring based at the ortho position to one another, when nitrobenzene is oxidised that benzene ring is broken which does not carry  $\text{NO}_2$  group. And when amino benzene ring is broken which carries  $\text{NH}_2$  group.

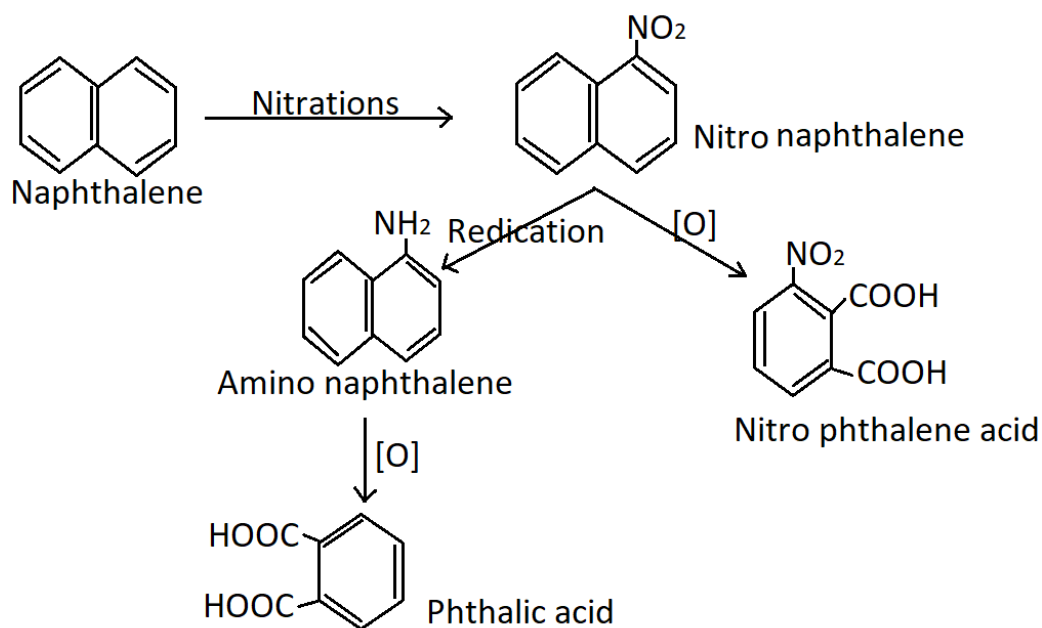
This can be explained as  $\text{NO}_2$  group is electron withdrawing and deactivating group. So, when nitro naphthalene is oxidised the more reactive benzene ring is destroyed.

Amino group is an electron releasing group and so it is an activating group. That is why due to its ( $-\text{NH}_2$ ) presence benzene ring is destroyed which carries the  $\text{NH}_2$  group.

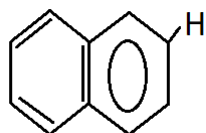
(5) Based on the observation recorded following structures are suggested for naphthalene group.



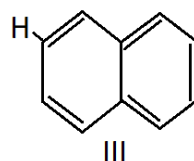
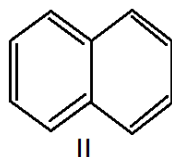
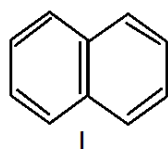
This explains the reaction sequence seen earlier.



(6) It was concluded that in naphthalene there are two benzene rings fused together.



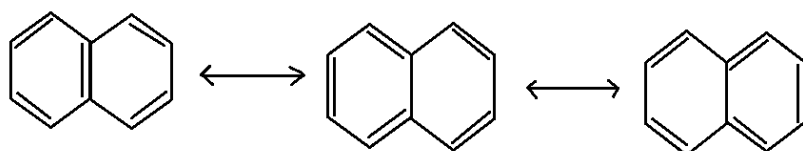
But the explanation of the fourth valency of each carbon – atom was given by placing the double bond at different position. This following, structures are suggested.



Structure II and III have only one benzene ring. But structure I has both rings benzenoid character. According to Fries' rule that structure is most stable which carries maximum number of benzenoid rings.

$\therefore$  Structure I is correct structure.

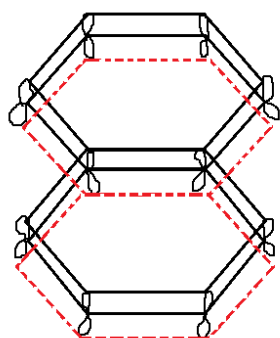
Refinance:- Naphthalene is a resonance hybrid of following resonating structures.



Resonance energy is found to be 63 kcal/mole.

This high degree of resonance energy explains the stable nature of naphthalene structure based on molecular orbital theory:-

All the 10 C – atoms present in naphthalene are  $sp^2$  hybridised. This molecule is planer. The ring is formed due to  $\sigma$  – *bond* between the different C – atoms. H – atoms are also hold by  $\sigma$  – *bond* with the C – atoms. Each of the 10 C – atoms has one unhybridized P – orbitals which remains perpendicular another. So, any two adjacent parallel P – orbital can overlap side wise to give a  $\Pi$  bond. This  $\Pi$  – electrons remain in a state of delocalization.

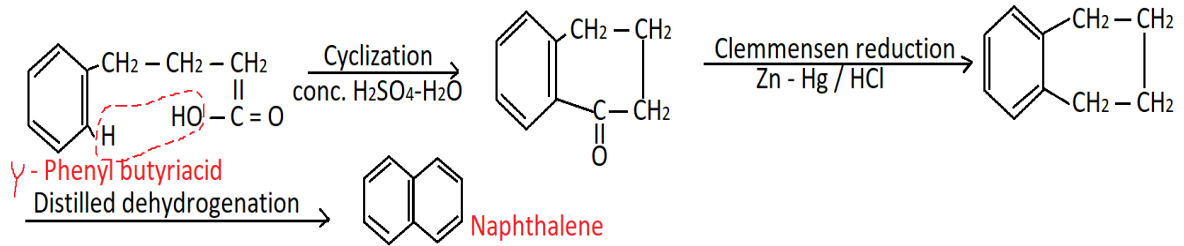
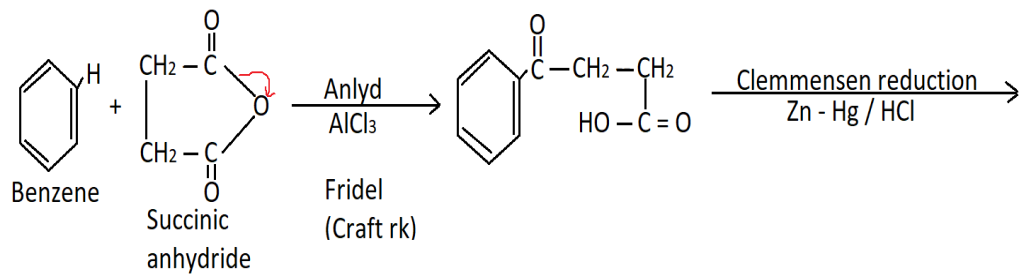


Naphthalene is an aromatic compound because it satisfies Huckel's rule of aromaticity i,e No. of  $\Pi$  - electron =  $4n+2$   
 Here, No. of  $\Pi$  - electron = 10  
 $\therefore 4n+2=10$   
 $\therefore n = 2$

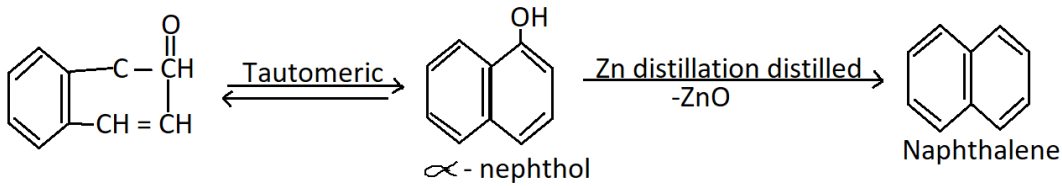
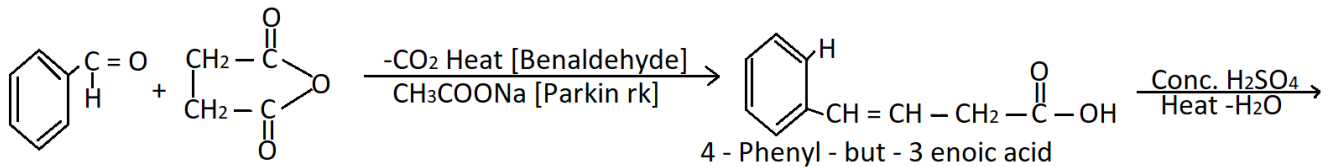
Therefore, Huckel's rule is obeyed.

### Synthesis:-

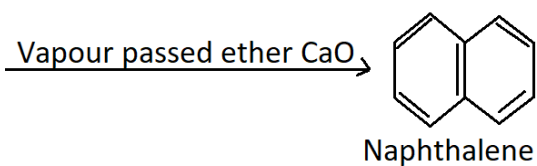
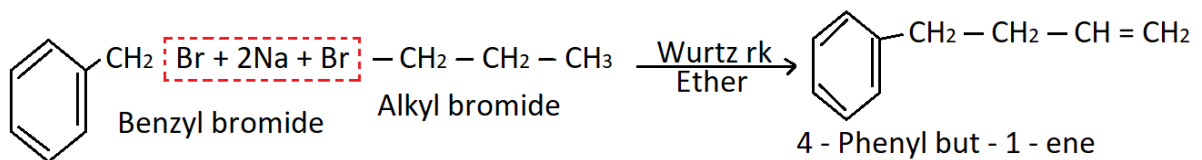
#### (1) How Orth's synthesis:-



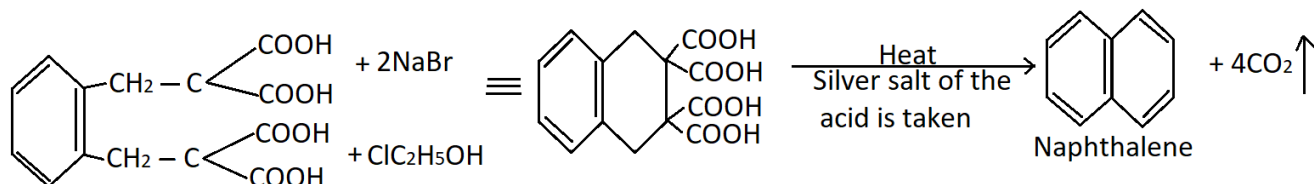
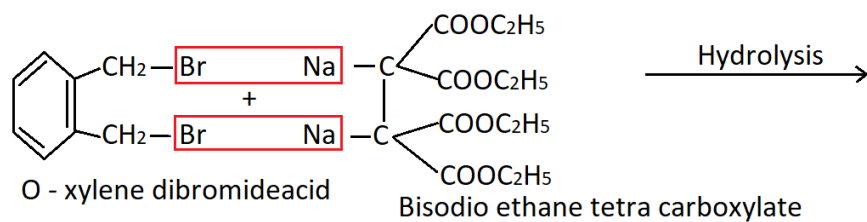
## (2) Fitting synthesis :-



## (3) Wurtz reaction:-

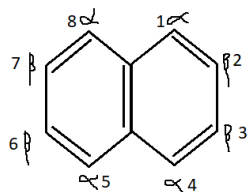


## (4) From O-xylene dibromide:-



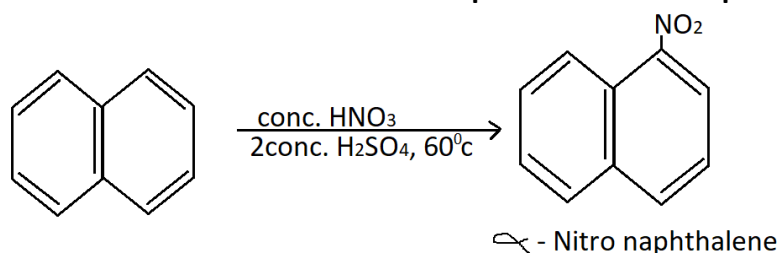
**Physical properties:-** Naphthalene is a colourless crystalline solid, M.P 180<sup>o</sup>c, B.P 218<sup>o</sup>c. It is insoluble in water but soluble in organic solvent such as benzene, ether etc.

**Reactions:-** Naphthalene undergoes electrophilic substitution reaction preferentially at  $\alpha$  - position.



### (1) Nitration:-

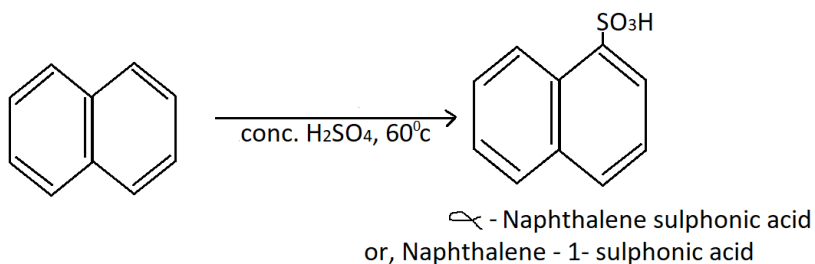
(a) At  $\alpha$  - position when it is reacted with conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub> at 60<sup>o</sup>c  $\alpha$  - nitro naphthalene is produced.



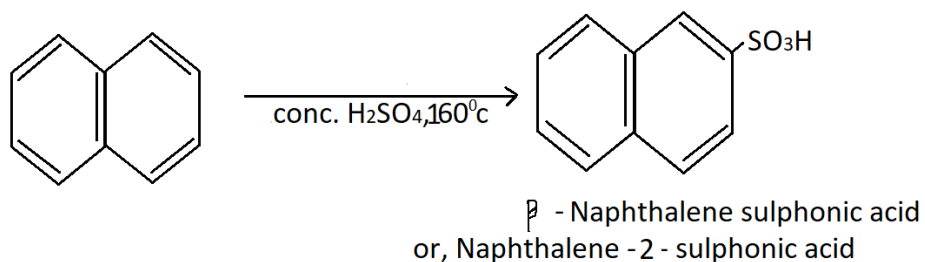
(b) At  $\beta$  - position not possible.

### (2) Sulphonation:-

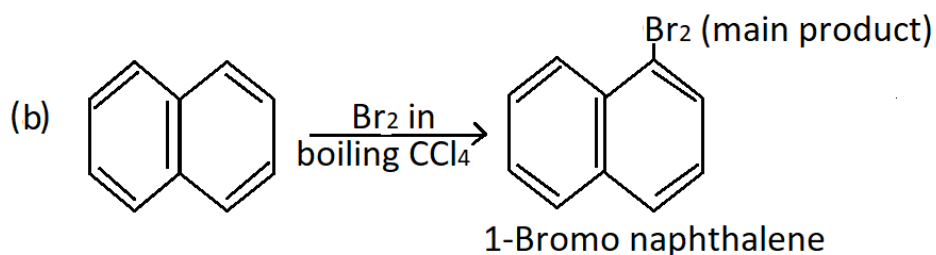
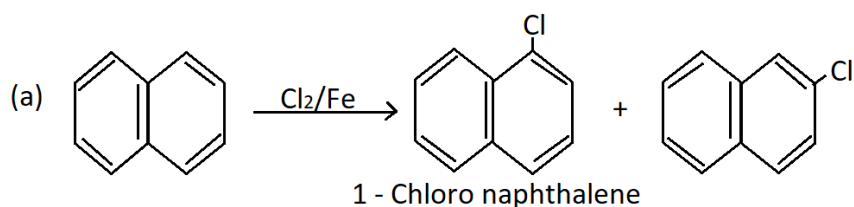
(a) At  $\alpha$  - position:-



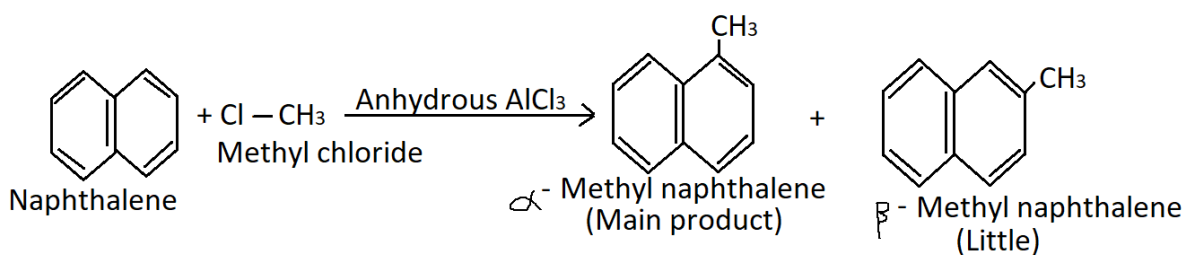
(b) At  $\beta$  - position:-



(3) Halogenation:-



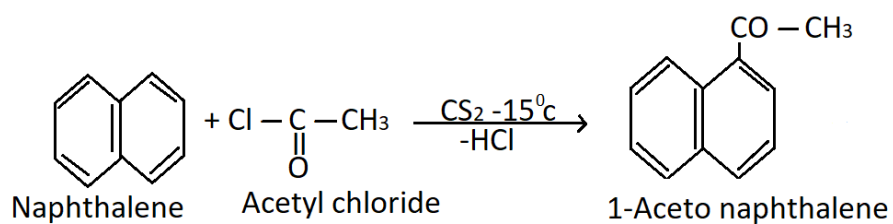
(4) Friedel craft alkylation:-



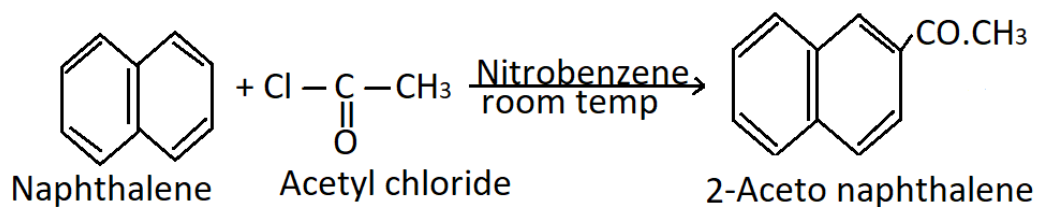
(5) Friedel craft acylation:-

(a) At  $\alpha$  - position:-

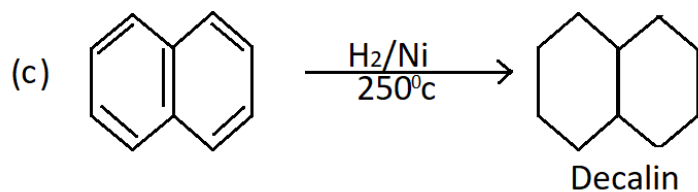
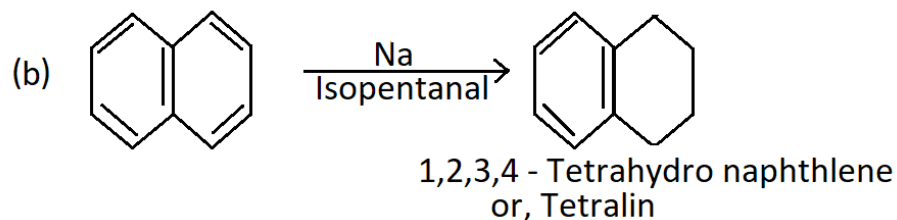
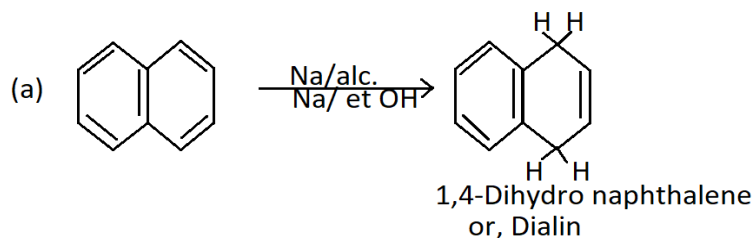




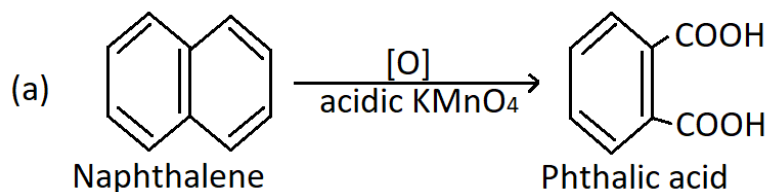
(b) At  $\beta$  – position:-

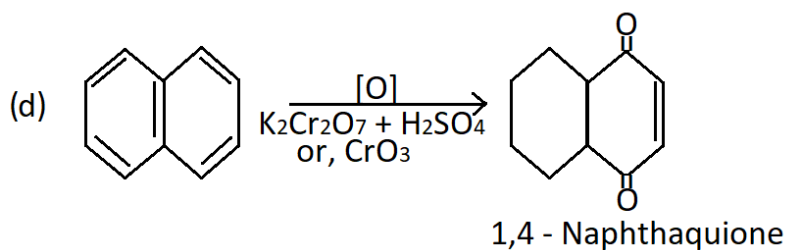
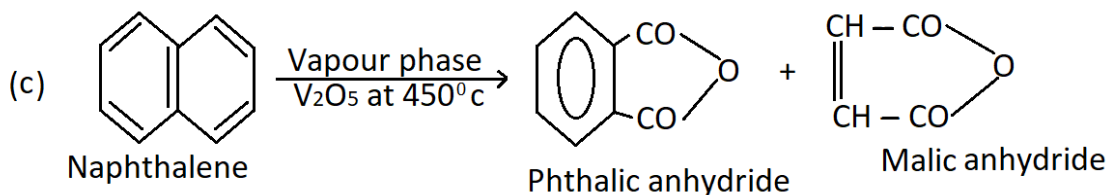
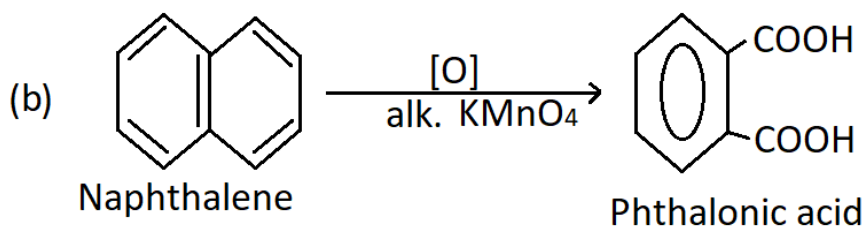


(6) Reduction:-

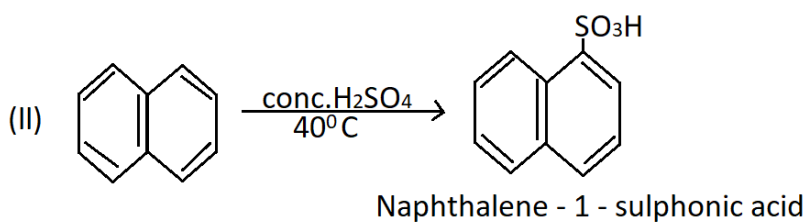
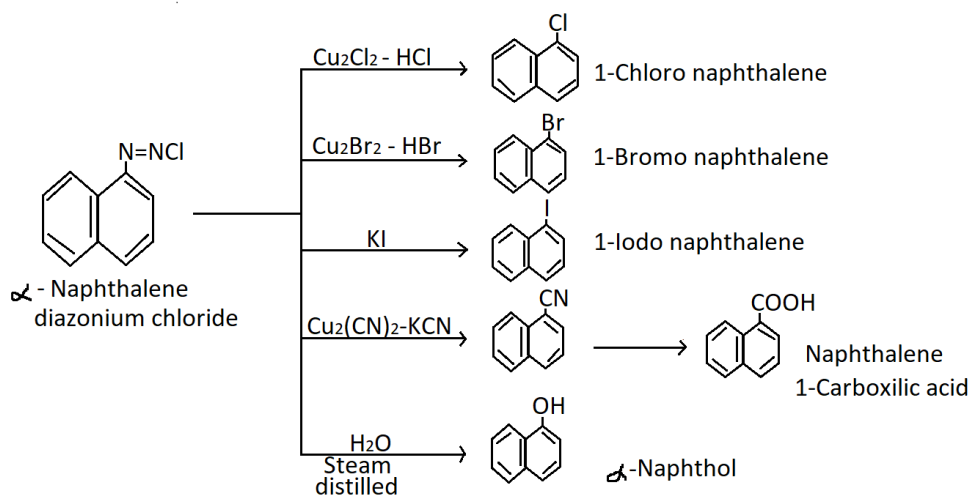
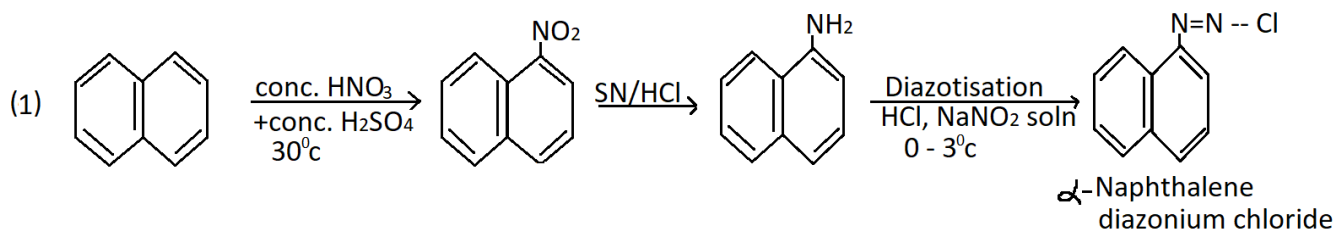


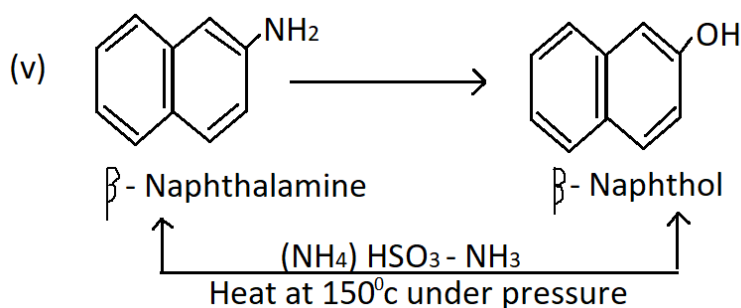
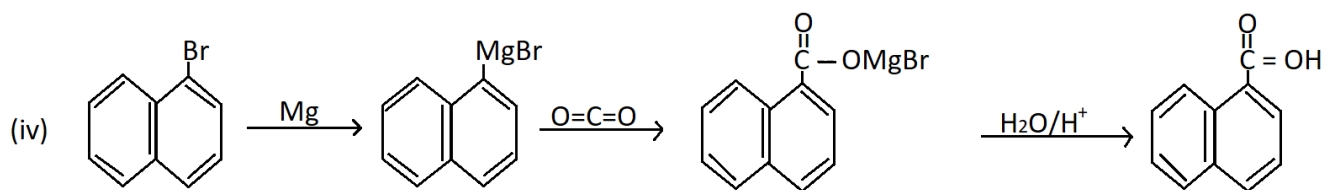
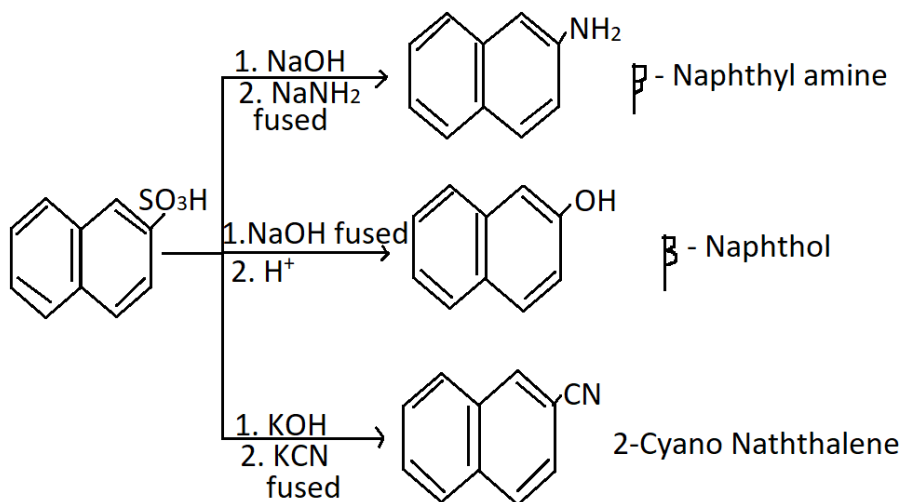
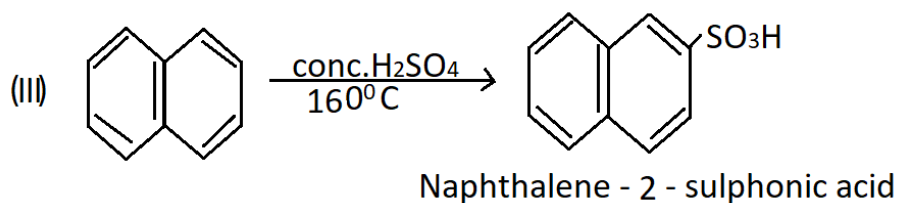
(7) Oxidation:-





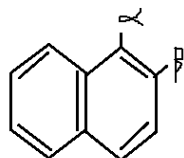
### Conversions:-





**(Q)  $\alpha$  – position in naphthalene is most reactive explain.**

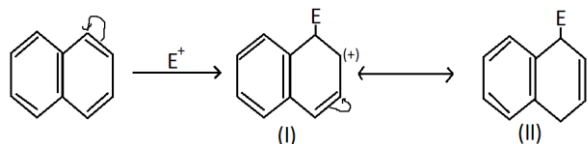
**Ans:-** Electrophilic substitution may occur at  $\alpha$  or  $\beta$  position.



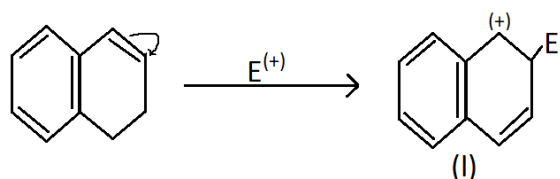
$\alpha$  – position is more reactive. This is solution because the intermediate carbonium ion obtained when substitution is taking place at  $\alpha$  – position is more stabilized (due to greater number of

resonating structures) than the intermediate obtained in case of substitution at  $\beta$  – position.

Reaction at  $\alpha$  – position.

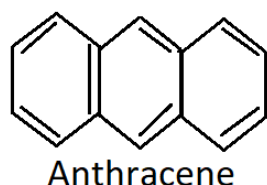


Reaction at  $\beta$  – position.



No other resonating structure possible without the involvement of the other ring.

### “ANTHRACENE ( $C_{14}H_{10}$ )”



It consists of three benzene rings fused in linear manner. It was first isolated in 1832 by Dumas and co – workers from the green oil fraction of coal tar distillate (Greek anthem means) which is still the only commercial source. Anthracene is industrially important for conversion in to anthraquinone, the porin of anthraquinone dies.

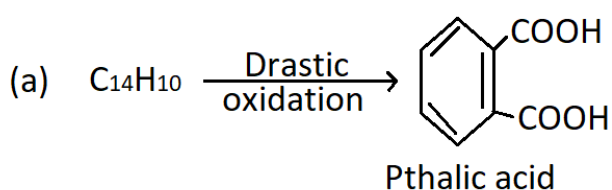
#### Properties:-

Anthracene crystallises in glossy make colourless plates (M.P =  $216^{\circ}c$ ). Which beautiful the florescence in the UV – light if it is quite pure. Traces of impure change the colour to yellowish green or make it colourless. Anthracene is insoluble in water and slightly solution in common organic solvents in the closing ruby – red, needles of anthracene – picric acid complaint (iii) appear on mixing saturated

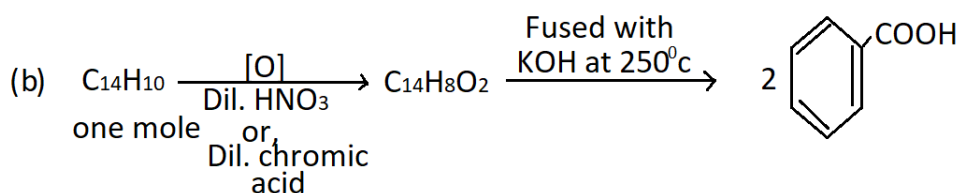
solution of anthracene and picric acid in acetone. The complaint (M.P.=216<sup>0</sup>c) is useful for its identification.

**Constitution:-** The constitution of anthracene has been established on the basis following evidences.

- (1) Anthracene has the molecular formula C<sub>14</sub>H<sub>10</sub> which suggests that it is highly unsaturated.
- (2) It gives usual additions although in certain case it behaves like aliphatic unsaturated compound (it readily forms additions products with one mole of hydrogen or Cl<sub>2</sub> and two atoms of Na). This suggests, that it vulnerable benzene and naphthalene.
- (3) Following sequence of rks. Point to words its suitable carbon skeleton.

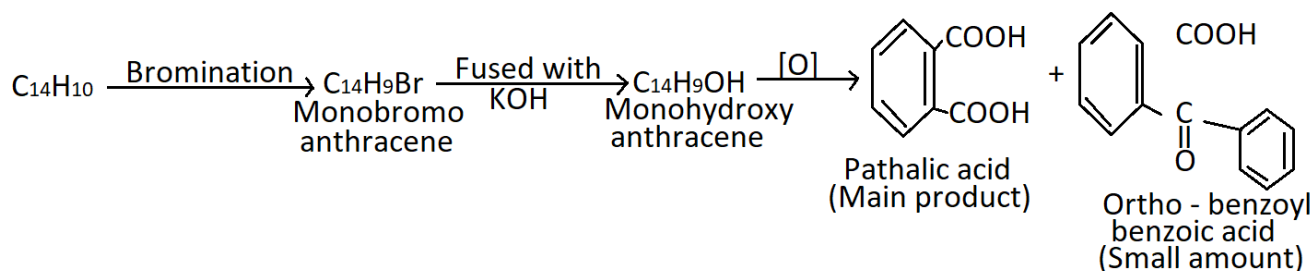


This suggests that it should contain at least one benzene ring.

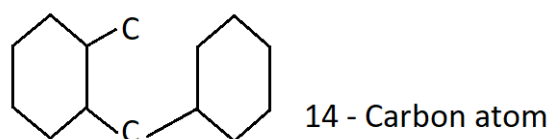


Two molecules of benzoic acid. This suggests that is should contain two benzene rings.

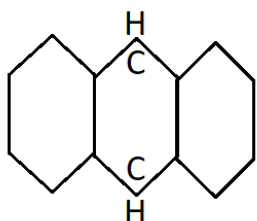
- (c) This is supported by the following reaction carried on anthracene.



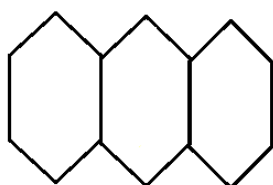
This suggests that anthracene contain at least two benzene rings, and that its skeleton is.



The above skeleton contains 14 – carbon atoms and to fit in 10 – H – atoms and retain the quadri valency of carbon. The middle ring must be closed.

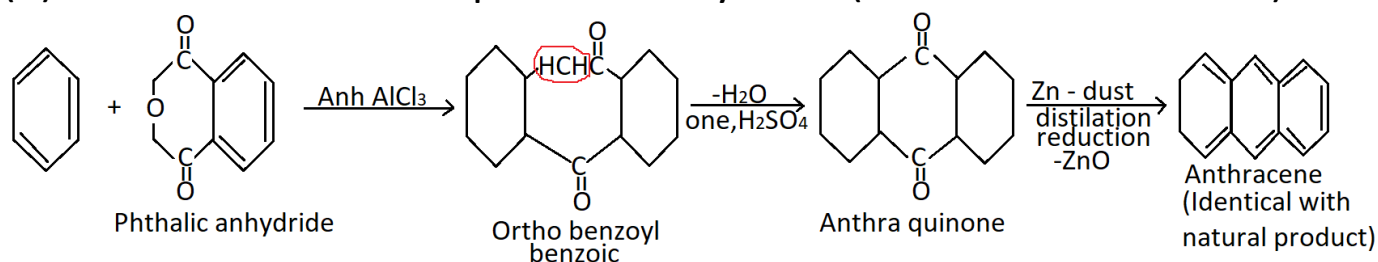


This is a structure of anthracene which is consistent with the forging reaction and this is nothing but three benzene rings fused in a linear fashion or manner.

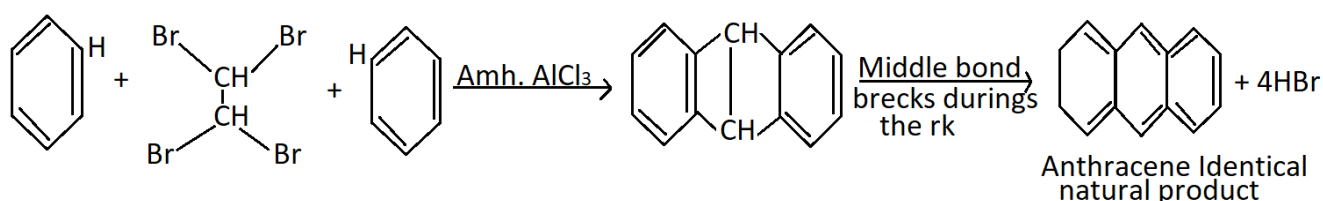


### Conformation by synthesis:-

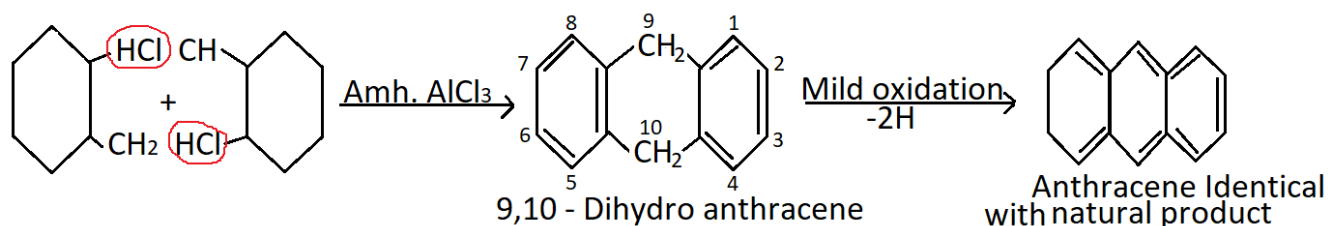
(1) From benzene and phthalic anhydride (Friedel craft reaction):-



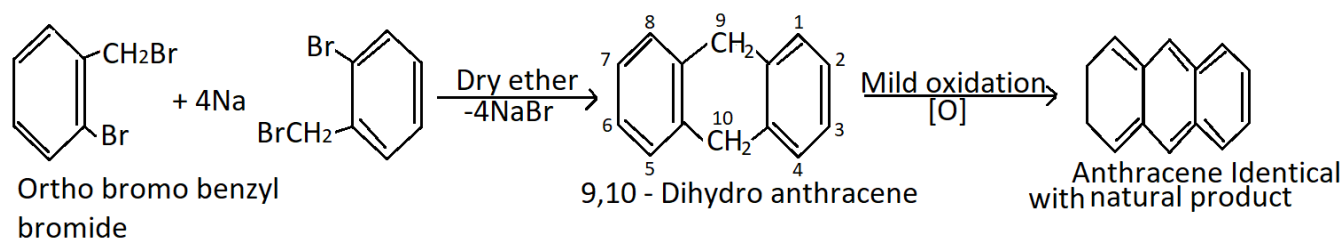
(2) Benzene and tetra bromo ethane also yield anthracene by Friedel craft reaction.



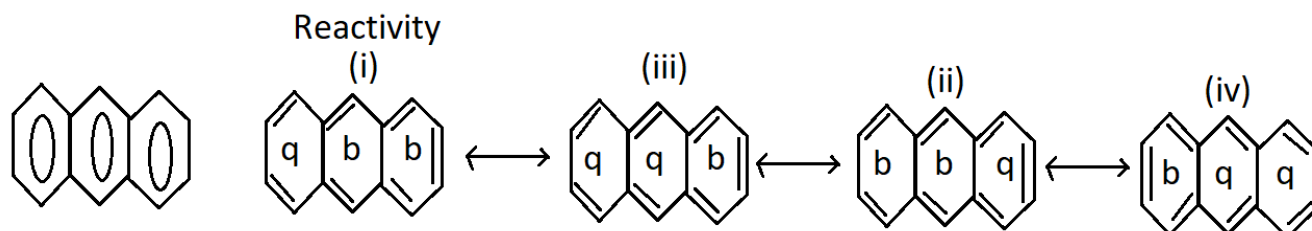
(3) By Friedel craft reaction using two molecules of benzyl chloride.



(4) Wurtz – fitting synthesis:- Ortho benzyl bromide in pressure of metallic sodium gives anthracene.



(5)  $\alpha$  – Naphtha quinone and 1,3 – butadiene when heated to about  $100^{\circ}\text{C}$  in a solvent form tetra hydro anthraquinone by Diels Alder reaction chromic acid oxidises a latter to anthraquinone which on distillation yields anthracene.



Summit position or  $\alpha$  – position  $\longrightarrow$  1,4,5,8

Side position or  $\beta$  – position  $\longrightarrow$  2,3,6,7

Middle position or  $\gamma$  – position  $\longrightarrow$  9,10

Or meso position.

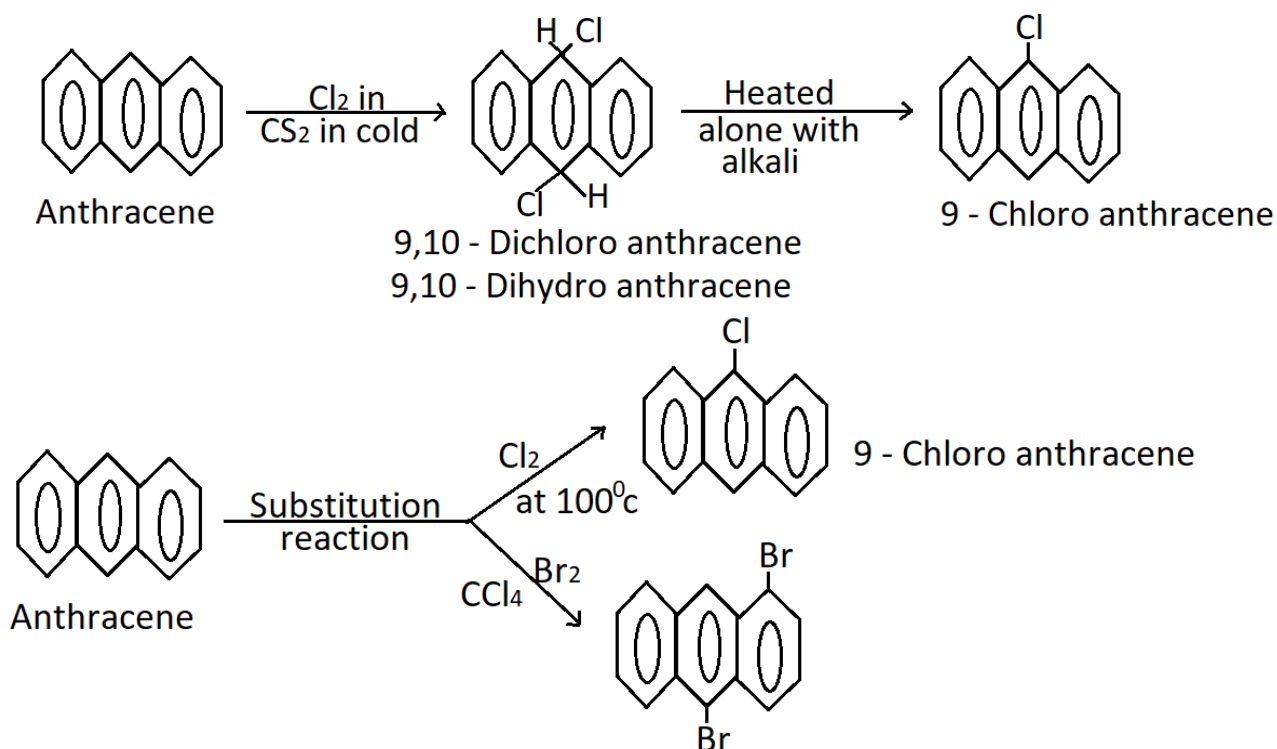
Of the four structure two have two benzenoid and one quinoid rings and the other two have two quinonoid and one benzenoid rings. Resonance energy of anthracene from heat of combustion data is 84k.cals/mole. Which is consistent with this fact. It has  $3 \times 36 - 86$  I.e 24k.cals/mole less than what is required for three benzenoid rings. So, anthracene is less resistant to oxidation or reduction

than naphthalene which has a resonance energy of 61k.cal/mole for one benzenoid and one quinoid rings. The 9,10 – positions of anthracene are most reactive additions of reagents to these positions results in a system that has two fully aromatic benzenoid rings with a resonance energy of  $2 \times 36$  I,e 72k.cals/mole. This means a loss of only 12k.cal/mole (84 – 72) of resonance energy. Such a structure is more stable than any of the four resonating structures and hence addition invariable takes place in these, position 9,10 – dihydro anthracene and 9,10 – anthraquinone are very stable. The former resist further reduction and latter from oxidation. The higher reactivity of anthracene compound with naphthene is also effect, in its low ionization potential (the potential necessary to remove an electron from the neutral molecule) is 7.6 ev compared with 9.6 ev for benzene and 8.3 ev for naphthalene. Judging from the resonance structures, the 1,2 – bond of anthracene have  $\frac{3}{4}$  double bond character ion. If all the four forms contribute equally to hybrid structures. So, it is expected to be shorter in length than the 2,3 – bond which has only  $\frac{1}{4}$  double bond character. This is fact is the case that the 1,2 – bond length is  $1.37\text{\AA}$  and 2,3 – bond length is  $1.42\text{\AA}$ .

In anthracene  $14\pi$  – *electrons* are distributed over 16 C – C bonds. Whereas, 10 such electrons are distributed over 11 C – C bonds in naphthalene and  $6\pi$  – *electrons* over 6 C – C bonds in benzene. So, the aromatic character of anthracene is less pronoulaced than that of naphthalene or benzene.

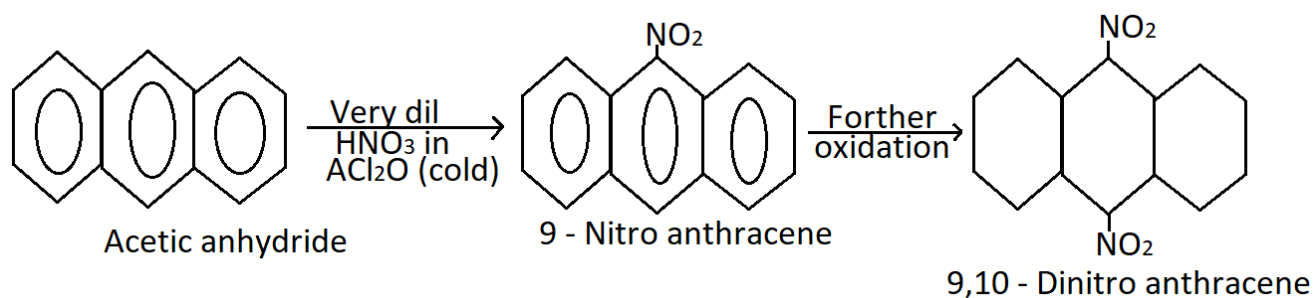
(1) Halogenation:-



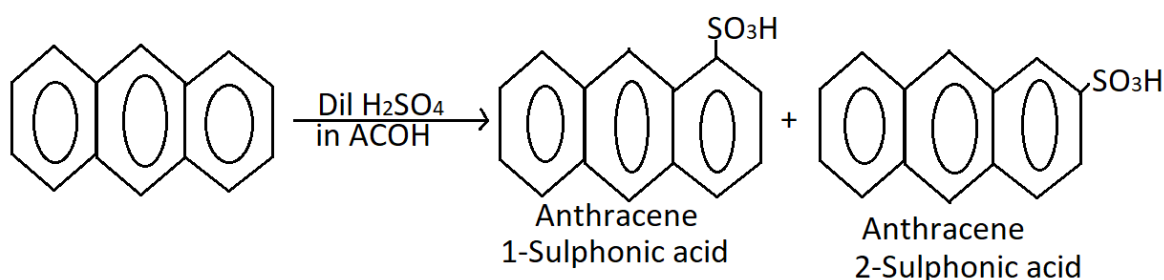


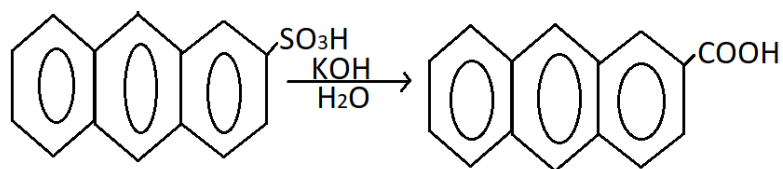
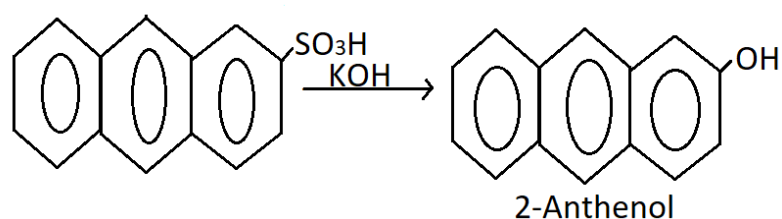
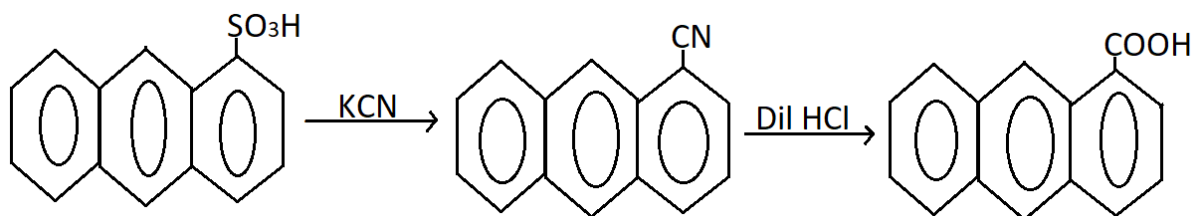
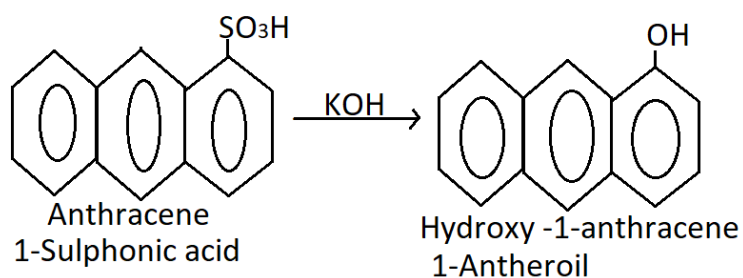
In anthracene aromatic character is reduced and this is very clear by the fact here addition takes place whereas in case of benzene substitution takes place.

(2) **Nitration:-** Normal nitrating reagent give oxidised product 9,10 – anthraquinone.

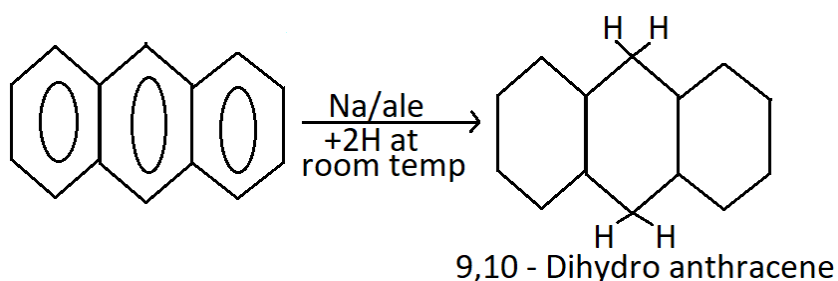


(3) **Sulphonation:-** Due steric hindrance of bigger  $\text{HSO}_3$  group the more reactive 9,10 – position are not effected.

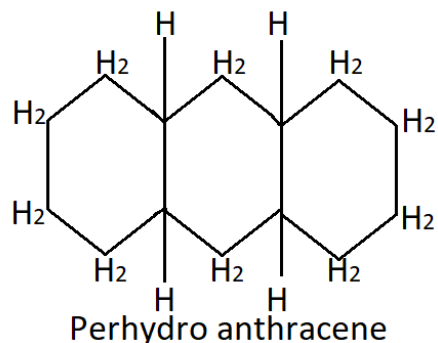




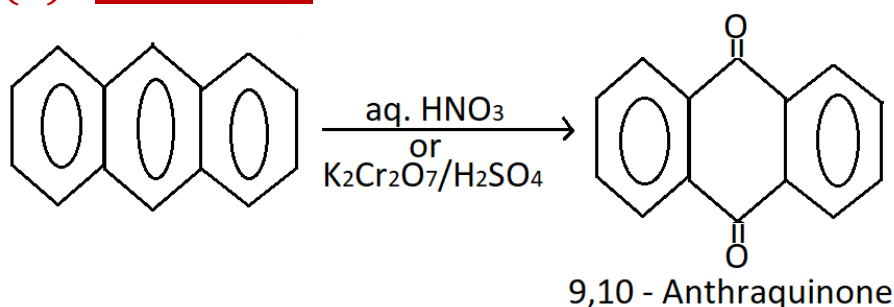
#### (4) Reduction:-



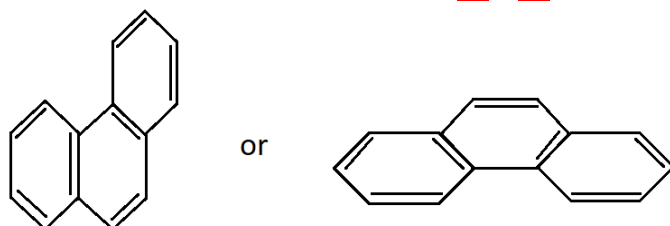
Tetra, Hexa, Octa, Hydro anthracene from depending upon the amount of hydrogen used. More groups hydrogenation at high temperature and pressure gives the completely reduced molecule  $\text{C}_{14}\text{H}_{22}$ .



(5) Oxidation:-

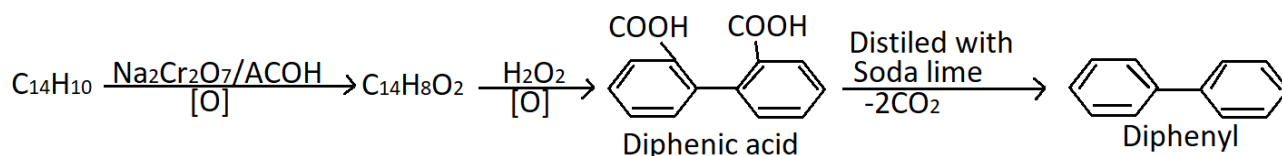


“PHENANTHRENE (C<sub>14</sub>H<sub>10</sub>)”

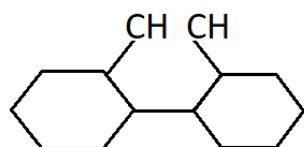


Phenanthrene is isomeric with anthracene. It is an example of an angular polynuclear hydrocarbon. It occurs in the anthracene oil fraction of coal tar and is separated from anthracene by means of solution in solvent naphtha.

Structure:- When oxidised with sodium dichromate and acetic acid, phenanthrene forms phenanthrene quinone which on further oxidation with hydrogen peroxide gives diphenic acid. The latter forms diphenyl, when distilled with soda lime.

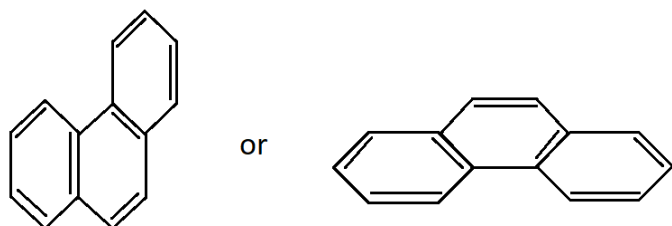


The skeleton structure of phenanthrene therefore is written as.



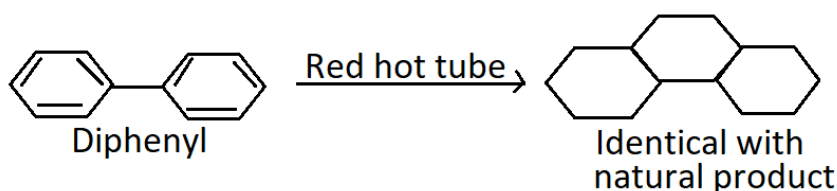
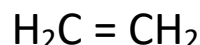
In which two CH may be linked by a double bond so, as to form a third benzene ring.

Thus, phenanthrene has the following three condensed benzene rings.

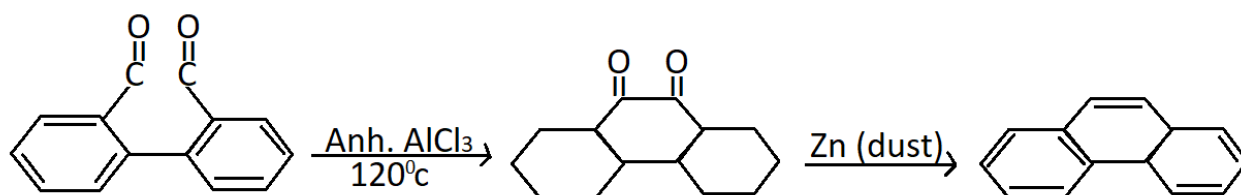


### Conformation by synthesis:-

- (1) This was confirmed by Barber in 1876 who prepared phenanthrene by passing ethylene and diphenyl vapours through a red hot tube.

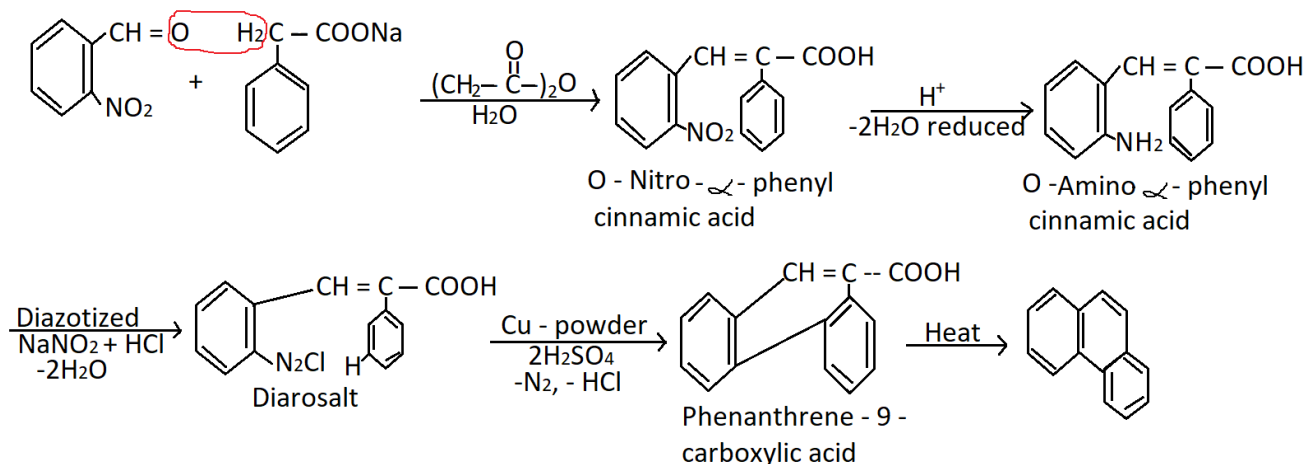


- (2) If Benzil is baked with  $\text{AlCl}_3$  at  $120^\circ\text{C}$ , phenanthrene quinone result, the latter yields phenanthrene on distillation with zinc dust.



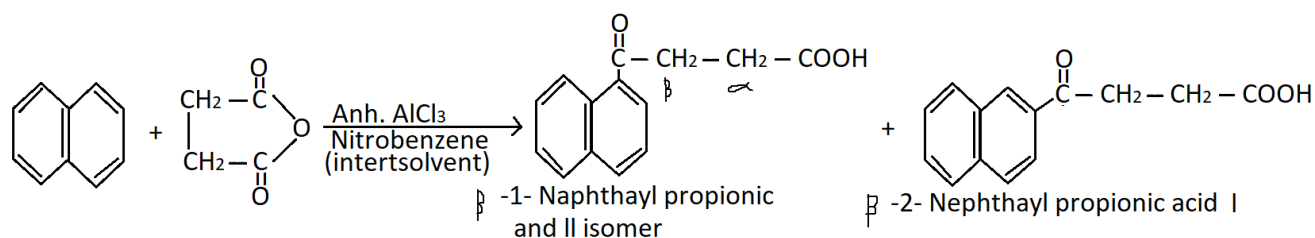
- (3) Pschorr synthesis:- Ortho nitro benzaldehyde is condensed with sodium phenyl acetate in the presence of acetic anhydride (perkin's reaction) to form ortho nitro  $\alpha$ -phenyl cinnamic acid. The latter is reduced to aminoderivative, diazotised and diazo salt

shaker with Cu powder and H<sub>2</sub>SO<sub>4</sub>. Phenanthrene – 9 – carboxylic acid, thus obtained loses CO<sub>2</sub> on heating strongly and yields phenanthrene.

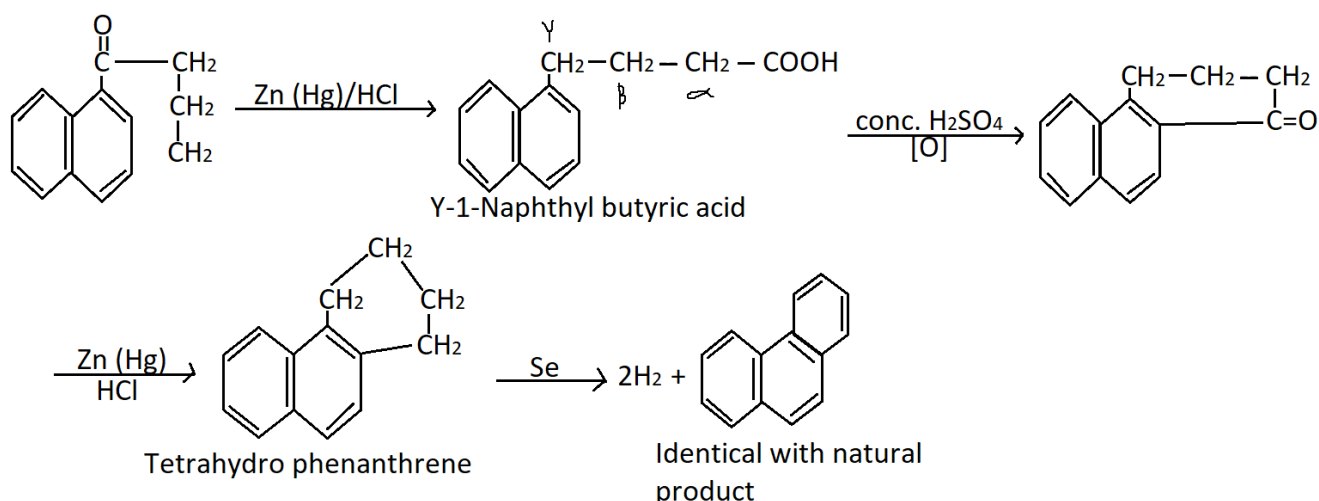


### Haworth synthesis:- (1932)

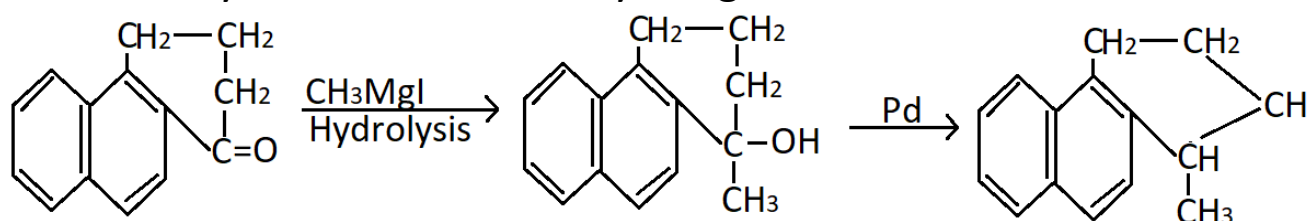
This involves cyclisation followed by aromatization, a new benzene ring is thus introduced. Naphthene and succinic anhydride are condensed in presence of AlCl<sub>3</sub> (Friedel craft rxn) to a mixture of  $\beta - 1$  and  $\beta - 2$  naphthyl propionic acids. The one isomer is separated and reduced with amalgamated Zn and HCl (Clemmensen reduced) to  $\gamma - 1 - naphthyl$  butyric acid. The latter by ring closure in presence of conc. H<sub>2</sub>SO<sub>4</sub>, forms tetrahydro phenanthrene which on reduction by Clemmensen method, gives tetrahydro phenanthrene. The latter is finally dehydrogenated by heating with selenium to phenanthrene.



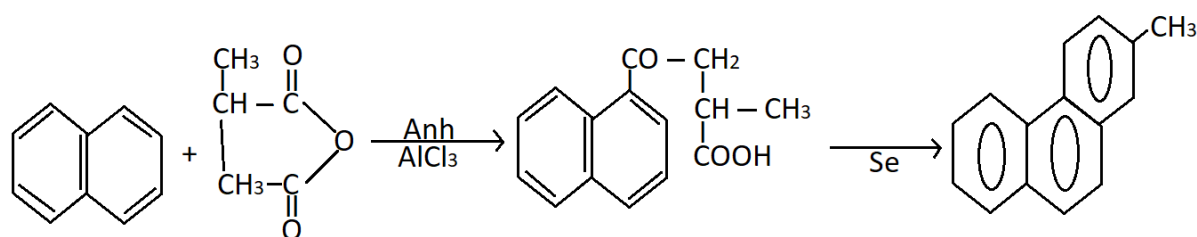
These can be separated easily for preparing phenanthrene is taken as starting material.



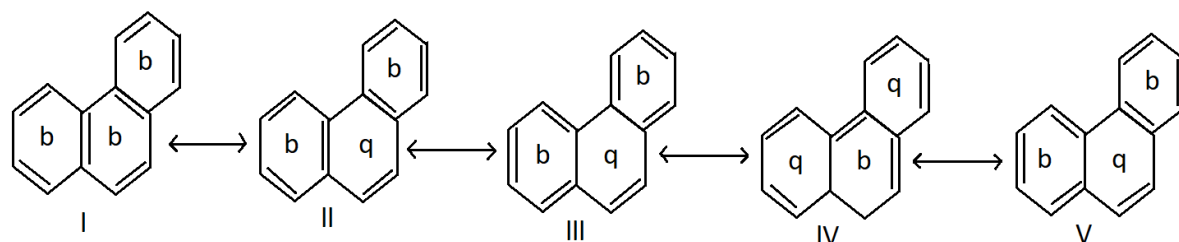
Similar I also gives phenanthrene. No, anthracene is formed since the ring close is only at the 1 – position of naphthalene and not in 3 – position takes. The haworth synthesis is very useful for preparing alkyls phenanthrene with the alkyl groups is known positions. The after ring closer, 1 – methyl phenanthrene may be obtained by the action of methyl magnesium iodide on the ketone.



By using methyl succinic anhydride in stead succinic anhydride, a methyl group can be introduced in 2 – position.

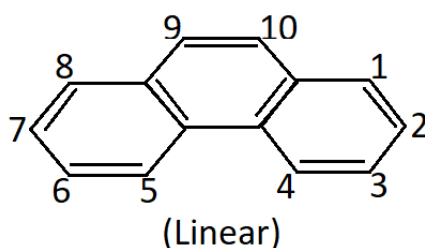
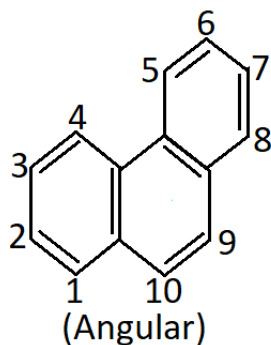


**Structure:-** Phenanthrene is a resonance hybrid of five forms.



Only in I, all the three rings are benzenoid out of five (frieza rule).

The structure of phenanthrene is written in different manner. Two more commonly used are show with the positions indicated by numbers.



The 9, 10 bond of the middle ring is a double bond in four out of five resonating structures. So, it has 4/5 double bond character resembling an ethylenic double bond closely. Naturally, therefore the 9, 10 – position are most reactive in phenanthrene.

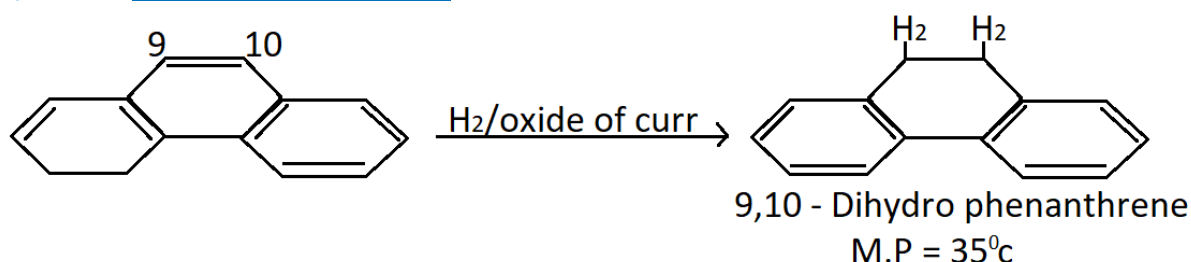
#### Properties of phenanthrene:-

It is a white solid M.P = 99<sup>o</sup>c. It's solution in benzene shows a blue Florence. It is very reactive in the 9, 10 – position.

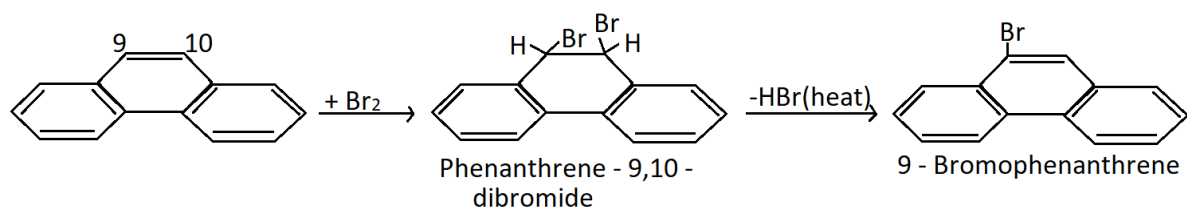
#### Addition reaction:-

With 9, 10 – position of phenanthrene addition reaction occurs almost as easily as with a pure ethylenic bond.

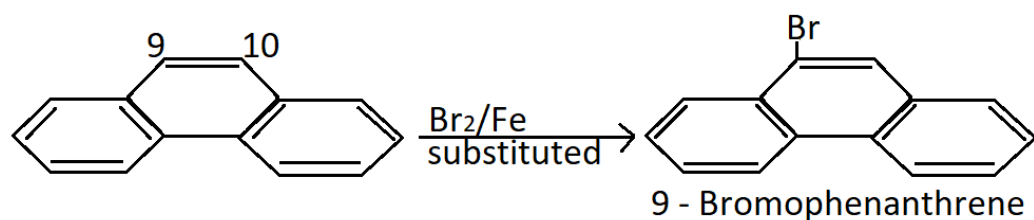
#### (i) Hydrogenation:-



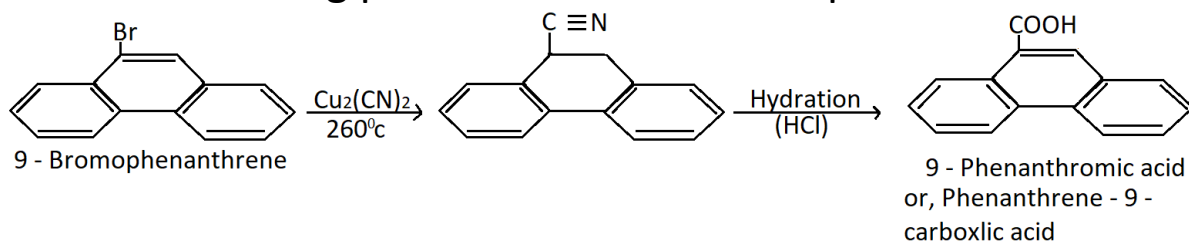
(ii) Bromination:- It readily get with to form a dibromide. Which splits out hydrogen bromide (HBr) on heating and give 9 – bromo phenanthrene.



The 9-bromo phenanthrene is also formed when phenanthrene is treated with  $\text{Br}_2$  in the presence of iron as halogen carrier.



This is the starting point of 9-substituted phenanthrene.



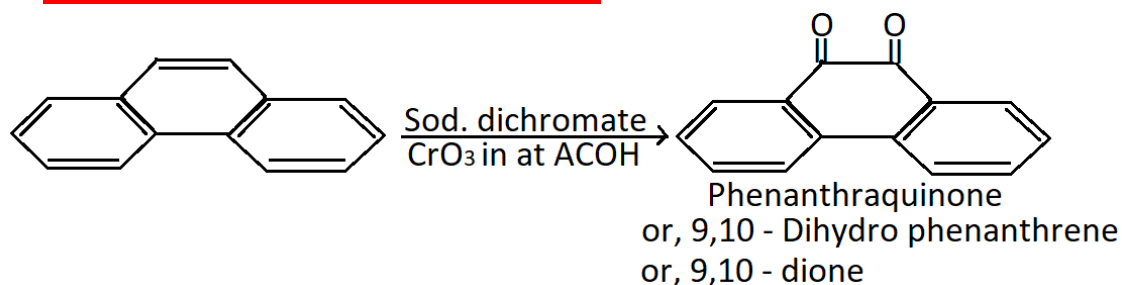
Most substitution reactions proceed poorly with phenanthrene.

### Isomerism of phenanthrene derivatives:-

There are five substitution products possible 1,2,3,4,9.

If the two substituents are identical then 25 di-substitution products are possible. Due to the great number of isomers, derivatives of phenanthrene are usually prepared synthetically and not by direct substitution in the phenanthrene molecules.

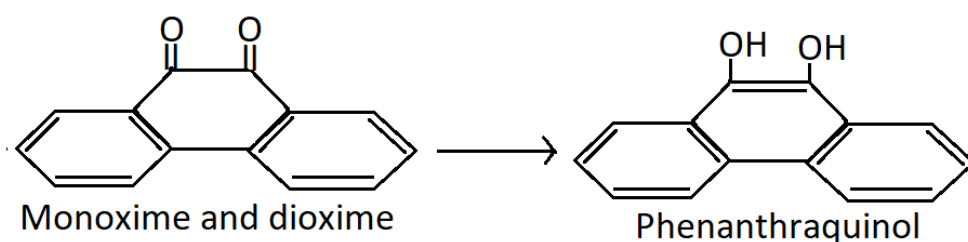
### Oxidation of phenanthrene:-



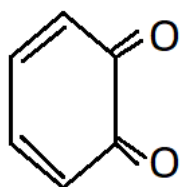
### Phenanthraquinone:-



Phenanthrene is an orange solid, M.P = 208<sup>0</sup>c. which is colourless and not steam volatile. It combines with one or two molecules of hydroxyl amine to form phenanthraquinone mono oxime and di oxime respectively and it is reduced by sulphurous acid to phenanthrene – 9,10 – diol (phenanthraquinol).



In all these phenanthraquinone resemble O – benzoquinone.



Phenanthraquinone readily reacts with O – phenylene diamines to form phenazines. Which are very useful for characterizing O – phenylene diamines.

