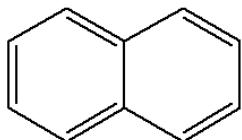


Notes on Polynuclear hydrocarbons

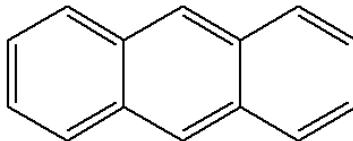


By
Dr. Gangutri Saikia

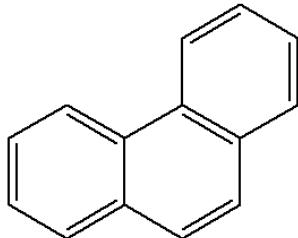
Polycyclic aromatic hydrocarbons are referred to as polynuclear aromatic hydrocarbon, condensed ring aromatics or fused ring aromatics. They are a class of organic compounds consisting of two or more fused aromatic rings. Two aromatic rings that share a pair of carbon atoms are said to be fused.



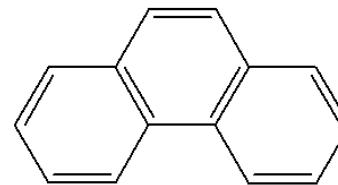
Naphthalene



Anthracene



Or



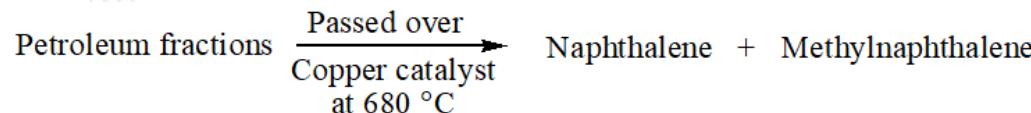
Phenanthrene

All three of these hydrocarbons are obtained from coal tar, naphthalene being the most abundant (5%) of all constituents of coal tar.

Naphthalene

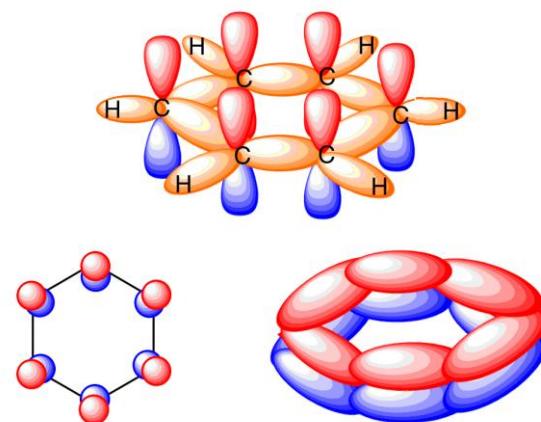
Naphthalene is a bicyclic aromatic hydrocarbon in which two benzene rings are fused together at o-positions. Its molecular formula is $C_{10}H_8$. It is obtained by cooling the middle and heavy oils of coal tar, whereupon naphthalene crystallises out. The oil is pressed free from naphthalene, the crude naphthalene cake melted, treated with concentrated sulphuric acid (to remove basic impurities), washed with water and then treated with aqueous sodium hydroxide (to remove acidic impurities). Finally, naphthalene is distilled to give pure product.

Naphthalene is also now being synthetically made from petroleum. Petroleum fractions are passed over a heated catalyst, e.g., at 680 ° and higher, naphthalene and higher aromatics are obtained.

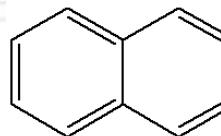


Structure of naphthalene

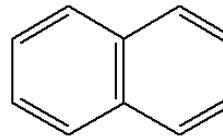
Naphthalene is classified as aromatic on the basis of its properties. Like benzene, naphthalene is unusually stable. From theoretical stand-point also, naphthalene has the structure required for an aromatic compound. It contains flat six-membered rings and the structure can provide pi clouds containing six electrons- the aromatic sextet. Ten carbons lie at the corners of two fused hexagons. Each carbon is attached to three other atoms by sigma bonds, since these sigma bonds result from the overlap of trigonal sp^2 orbitals, all carbons and hydrogen atoms lie in a single plane. Above and below this plane, there is a cloud of pi electrons formed by the overlap of p orbitals.



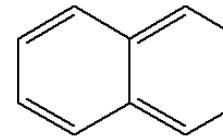
In terms of valence bonds, naphthalene is considered to be a resonance hybrid of the three structures, I, II & III. Its resonance energy , as shown by the heat of combustion is 61 Kcal/mole.



I



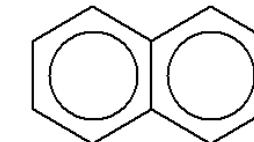
II



III

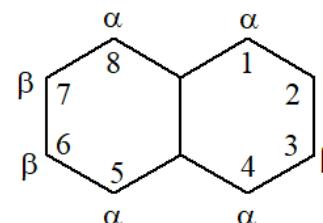
X-ray analysis shows that , in contrast to benzene, all C-C bonds in naphthalene are not the same, in particular, the C1-C2 bond is considerably shorter (1.365 Å) than C2-C3 bond (1.404 Å). Examination of I, II and III structures shows that this difference in bond lengths is to be expected. The C1-C2 bond has double bond characteristics in two structures and single in only one structure, while C2-C3 bond has single bond characters in two structures while double bond character in one structure. Therefore, it is reasonable that C1-C2 bond has more double bond character than C2-C3 bond.

For convenience, naphthalene can be represented as the single structure IV-



IV

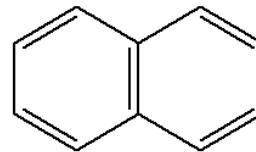
The positions in the naphthalene ring systems are designated as in I.



I

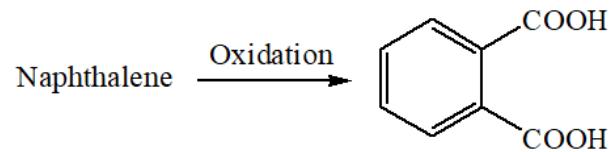
Structure elucidation of naphthalene

1. From the analytical data and molecular weight determination, the molecular formula of naphthalene is found to be $C_{10}H_8$.
2. Naphthalene resembles benzene in its chemical reactions; it can be nitrated, sulphonated, halogenated, chloromethylated like benzene. Its hydroxy derivatives also resemble phenols. Furthermore, it is stable and cannot be oxidised by nitric acid and other mild oxidising agents. All these suggest a ring structure for naphthalene as for benzene. Erlenmeyer in 1866, proposed a fused ring system for naphthalene as shown below-

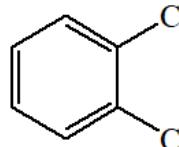


This is supported by the following facts-

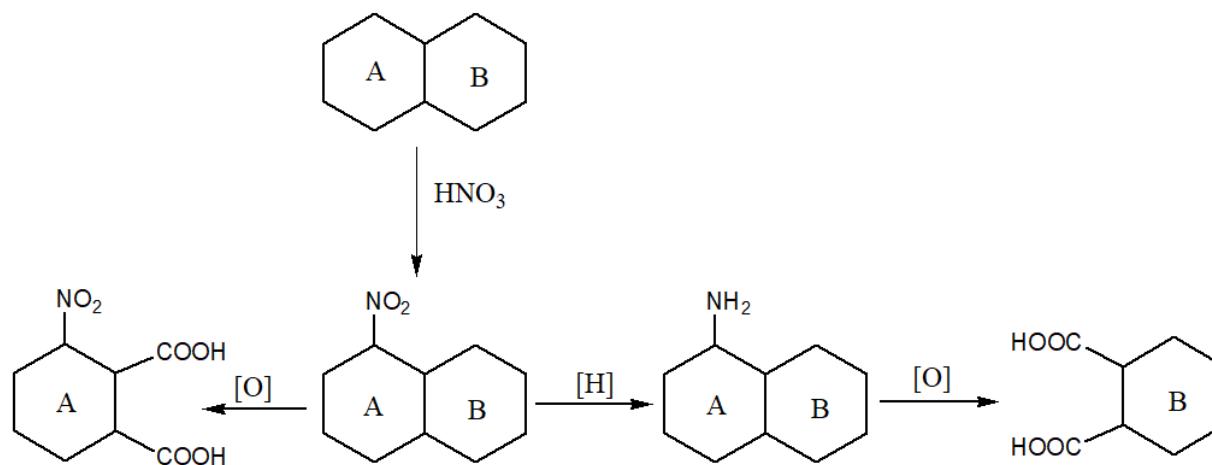
- I. Oxidation of naphthalene yields benzene-1,2-dicarboxylic acid, phthalic acid.



This indicates that naphthalene contains at least a benzene ring with two side-chains or a closed chain at ortho-positions. Thus, naphthalene is-

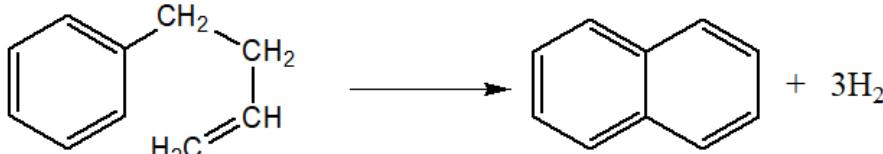


II. On nitration, naphthalene gave nitronaphthalene which on oxidation gave o-nitrophthalic acid. This indicates that the nitro group is in benzene ring and it is the side-chains which are oxidised. When the nitronaphthalene was reduced and the corresponding aminonaphthalene oxidised, phthalic acid was obtained. The presence of amino group attached to the nucleus renders the latter extremely sensitive to oxidation. Hence, the inference is that the benzene ring in phthalic acid obtained by oxidation of aminonaphthalene is not the same ring as that originally containing the nitro group in nitronaphthalene, i.e. Naphthalene contains two benzene rings in its structure. The above facts fit the following scheme-

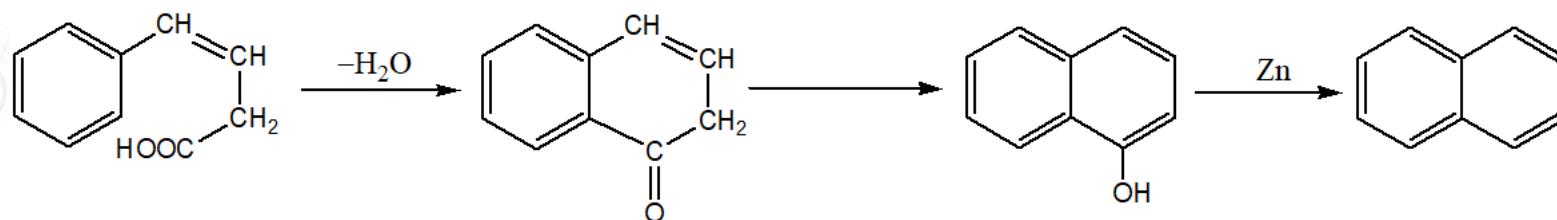


This structure of naphthalene has been confirmed by many syntheses.

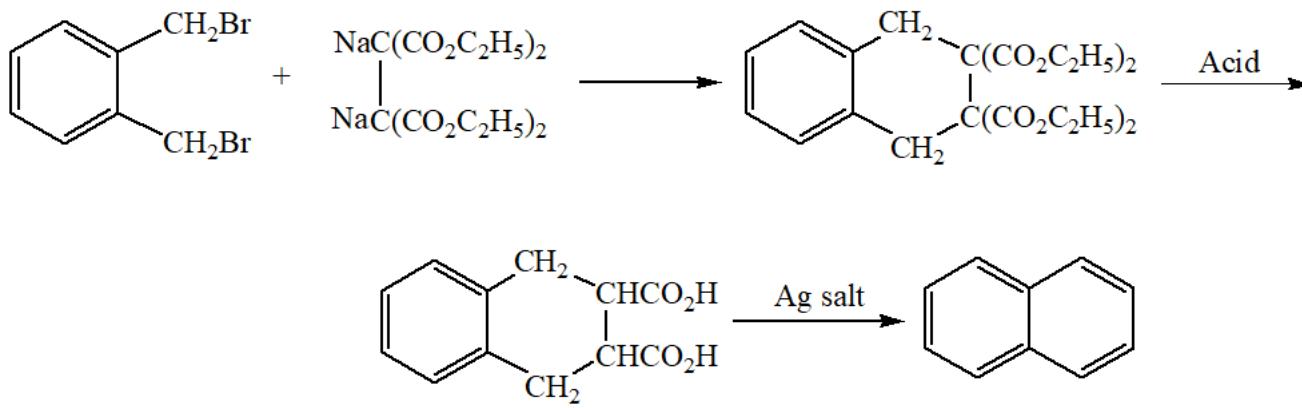
(i) When 4-phenylbut-1-ene is passed over red hot calcium oxide, naphthalene is formed.



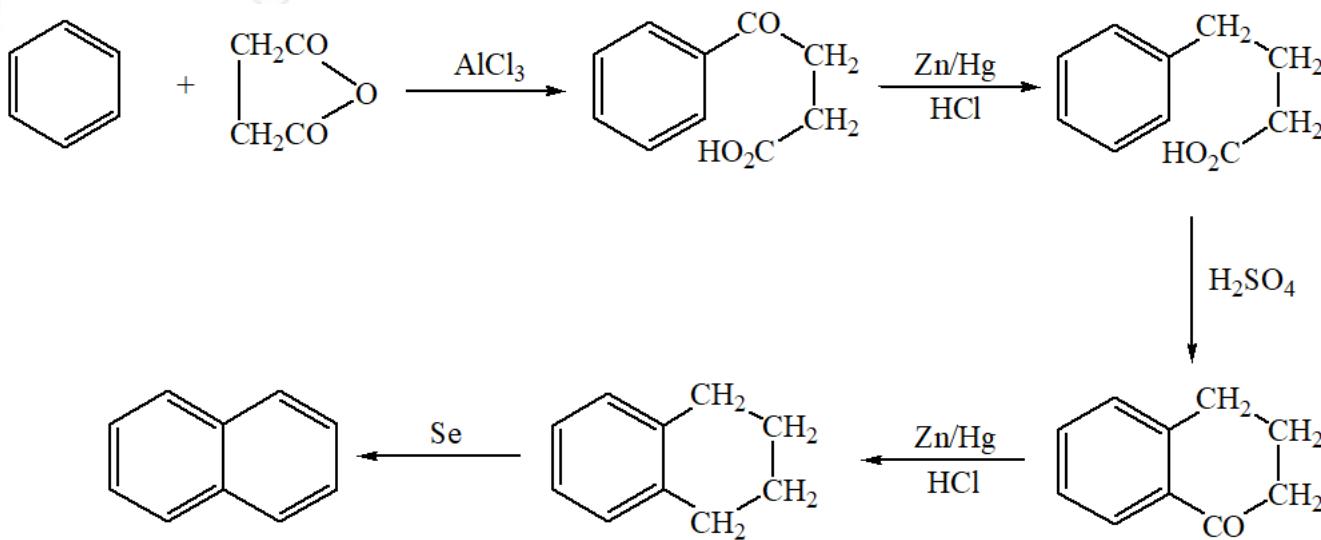
(ii) When 4-phenylbut-3-enoic acid is heated, 1-naphthol is formed and this, on distillation with zinc dust, gives naphthalene.



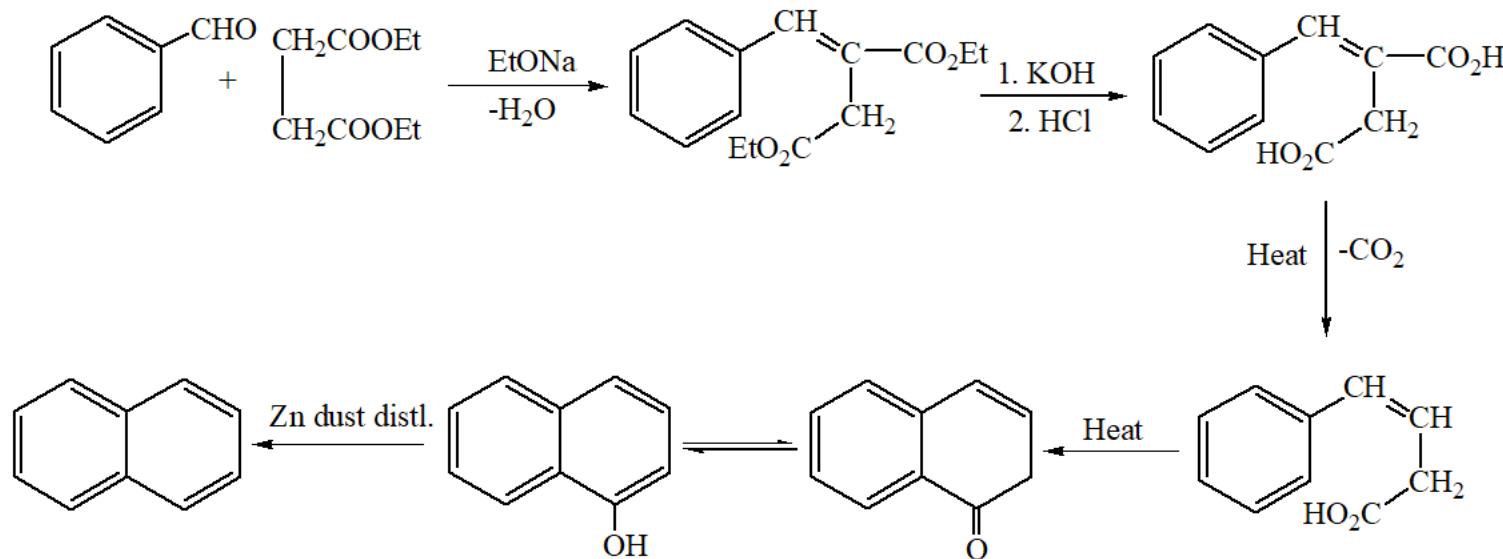
(iii) o-xylene bromide combines with disodioethanetetracarboxylic ester to form tetrahydronaphthalenetetracarboxylic ester and this, when refluxed in acid solution, gives tetrahydronaphthalenedicarboxylic acid. When the silver salt of the acid is heated, naphthalene is formed.



(iv) **Haworth synthesis:** Benzene is treated with succinic anhydride in presence of aluminium chloride, and the ketonic acid produced is reduced by Clemmensen method. The ring is closed by heating with concentrated sulphuric acid and the product α -tetralone reduced to tetrahydronaphthalene by Clemmensen method. This compound is then dehydrogenated to naphthalene by distilling it with selenium.

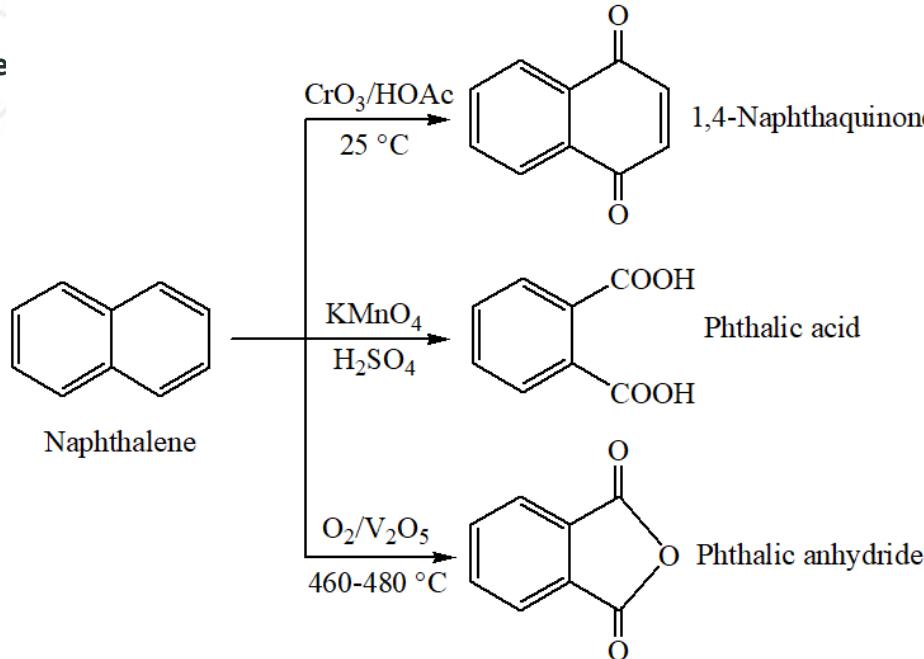


(v) Fitting and Erdmann synthesis:

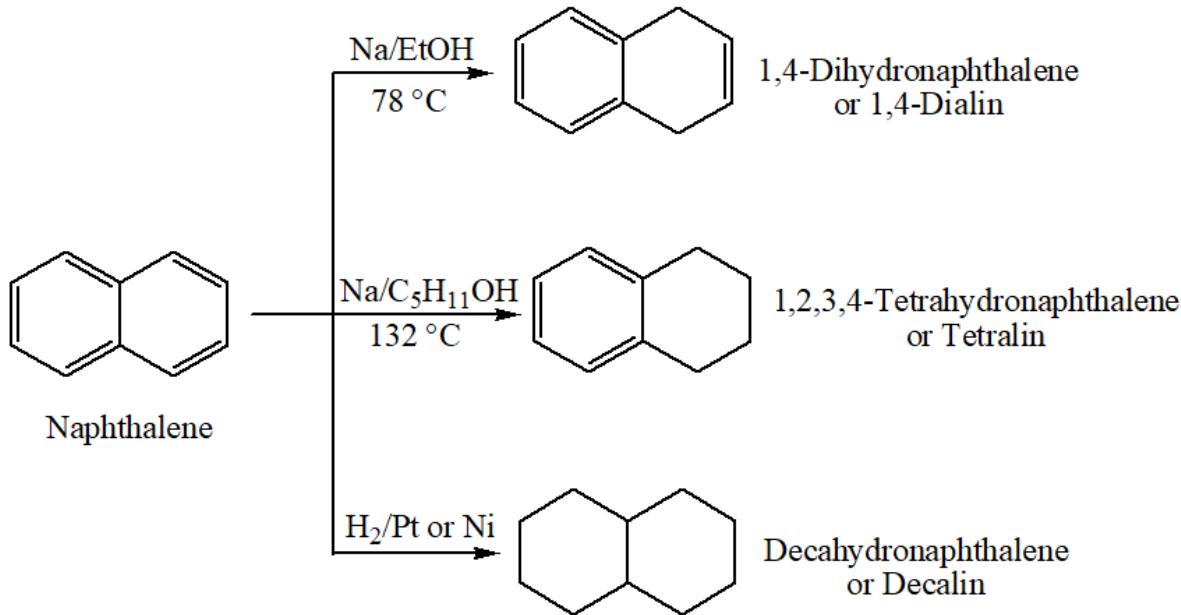


Reactions of naphthalene

(i) Oxidation

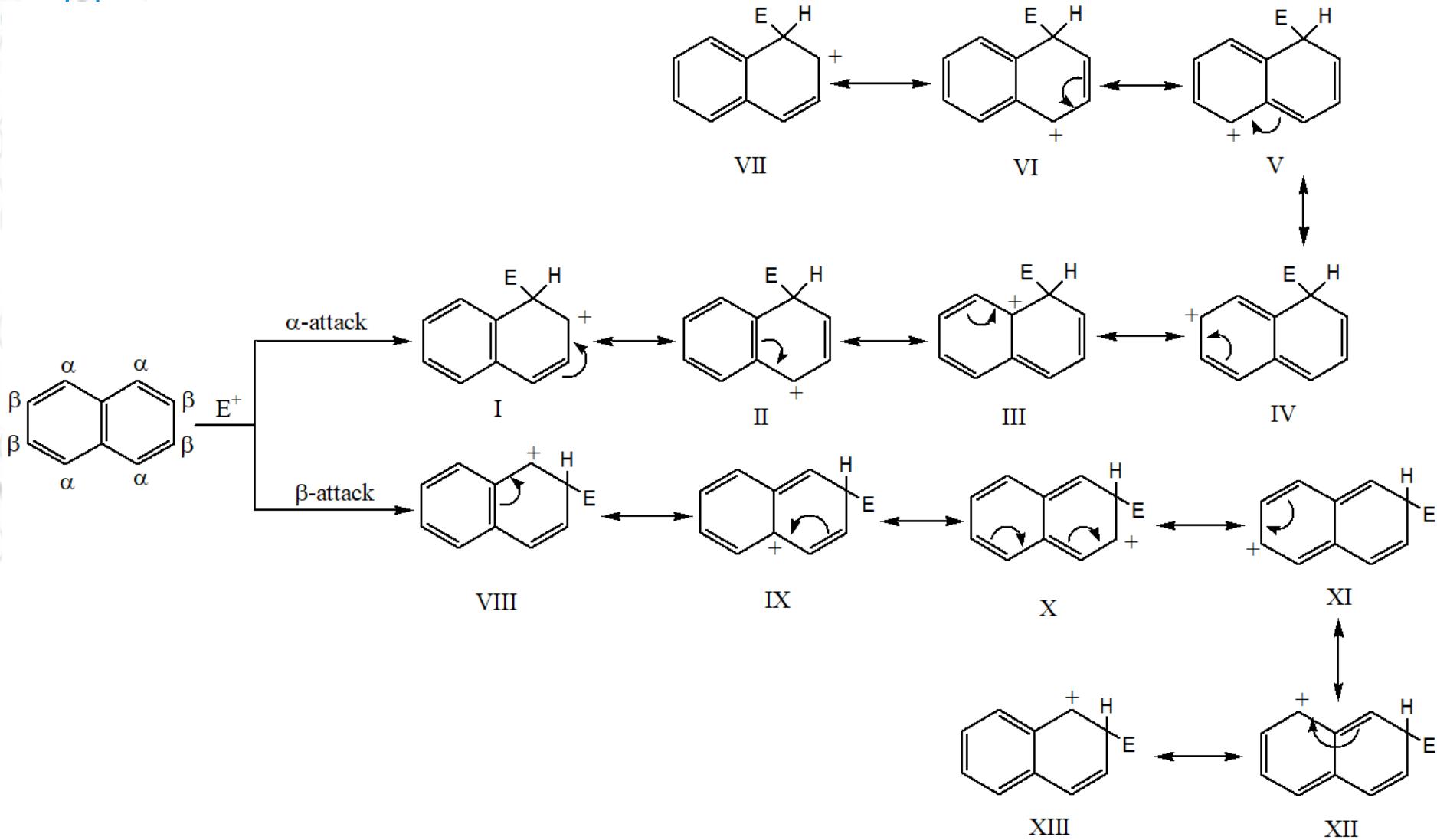


(ii) Reduction



(iii) Electrophilic substitution: Naphthalene is more reactive than benzene towards electrophilic substitution. This is due to the fact that the resonance energy of naphthalene is 255.2 KJ/mole which is much lower than the expected resonance energy of naphthalene (Resonance energy of benzene $\times 2 = 150.6 \times 2 = 301.2$ KJ/mole for the presence of two benzene rings in its structure).

Orientation in naphthalene nucleus is more complicated than benzene nucleus due to the presence of two nucleus.

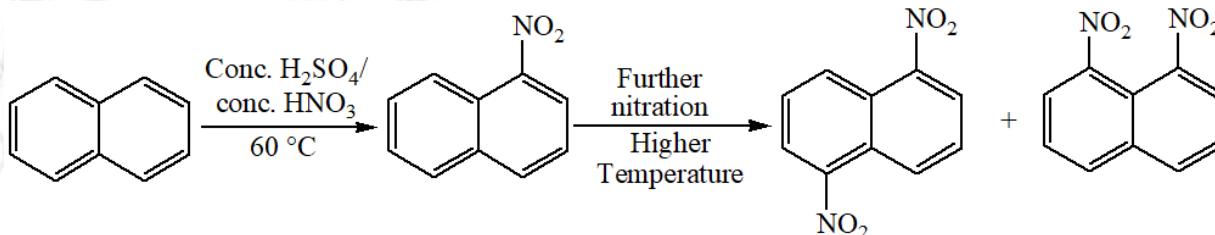


It was observed that the resonance hybrid for α -attack contains 7 resonating structures while that for β -attack contains 6 resonating structures. Furthermore, the former contains 4 structures containing benzene ring whereas the latter contains only two structures with benzene ring. Canonical structures with benzene ring are more stable than those without benzene ring, complex obtained for α -attack is more stable than complex obtained for β -attack. Therefore electrophilic substitution on naphthalene occurs mostly at α -position.

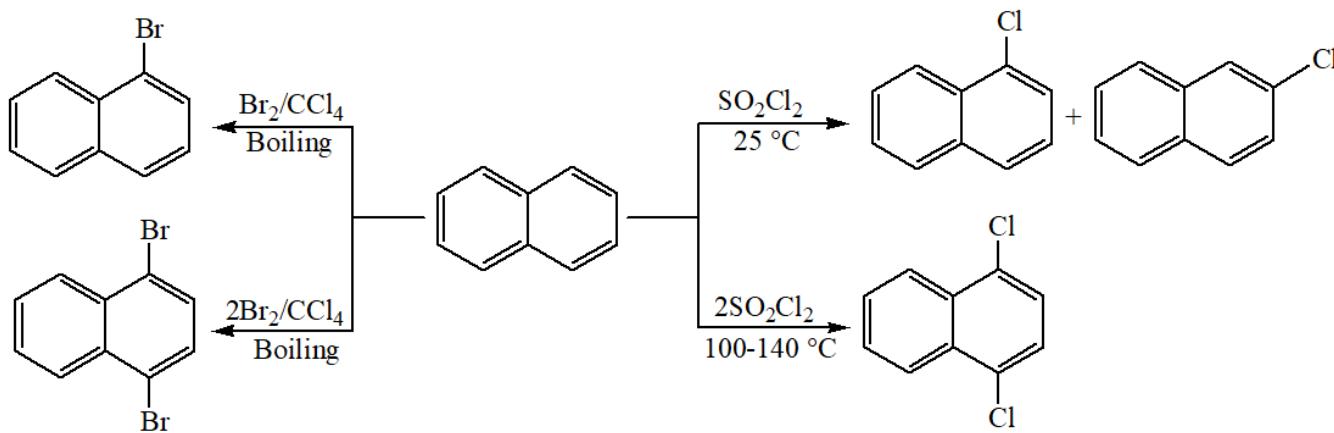
In case of monosubstituted naphthalene, the predominant product for further substitution can be predicted by the following empirical rules:

- (i) An activating group such as Cl, Br, OH, CH_3 , NHR or NHCOCH_3 at 1-position directs an incoming electrophile to 4-position preferentially and to a lesser extent to 2-position.
- (ii) When OH, CH_3 , NHR or NHCOCH_3 group is at position-2, it directs the electrophile to take position-1. Introduction of $-\text{SO}_3\text{H}$ group is an exception, if the first group is at position-2, it normally enters at position-6.
- (iii) A deactivating group such as $-\text{NO}_2$, $-\text{SO}_3\text{H}$ at position 1 or 2 directs the incoming electrophile towards the second ring at position 5 or 8.
- (iv) If halogen or NH_2 is at position-2, then further substitution occurs in the second ring at position 5 or 8.

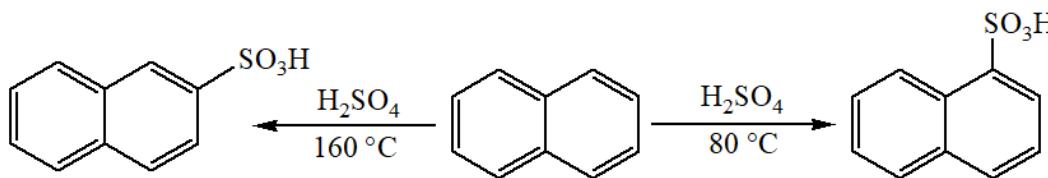
(a) Nitration:



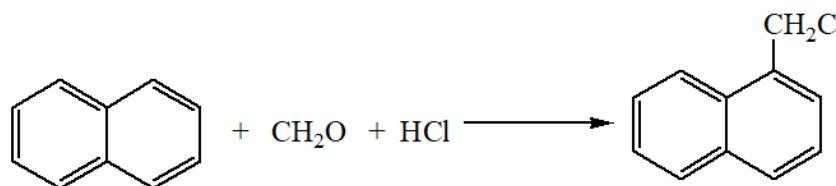
(b) Halogenation:



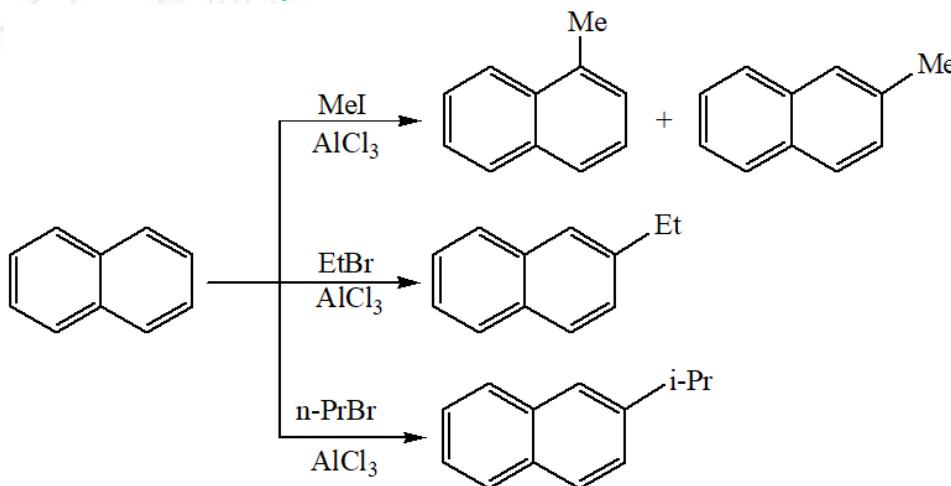
(c) Sulphonation:



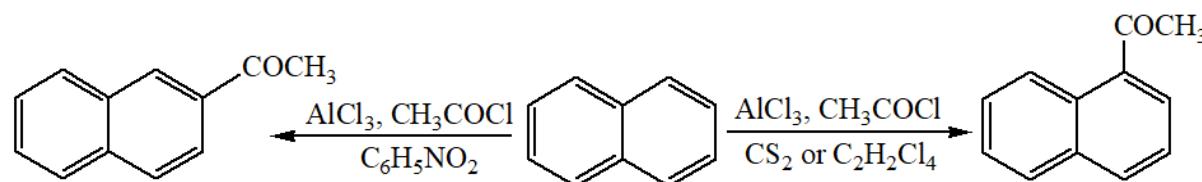
(d) Chloromethylation:



(e) Friedal-Crafts alkylation:

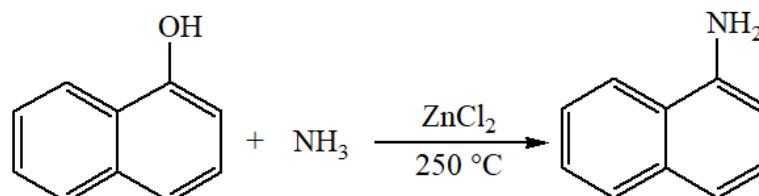
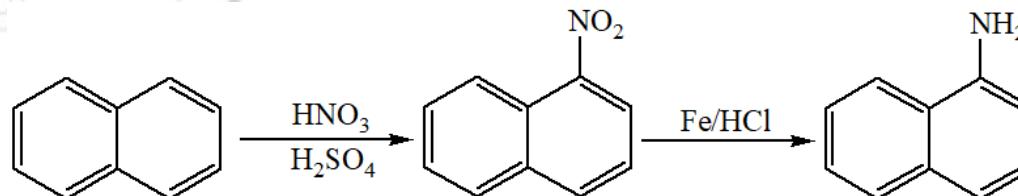


(f) Friedal-Crafts acylation:

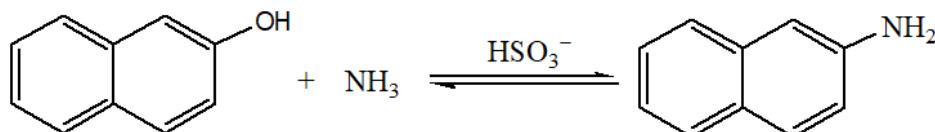


Important derivatives of Naphthalene

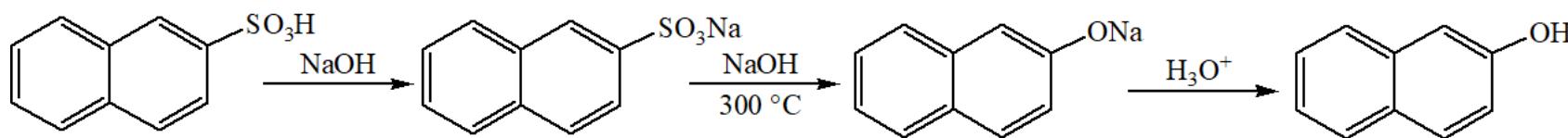
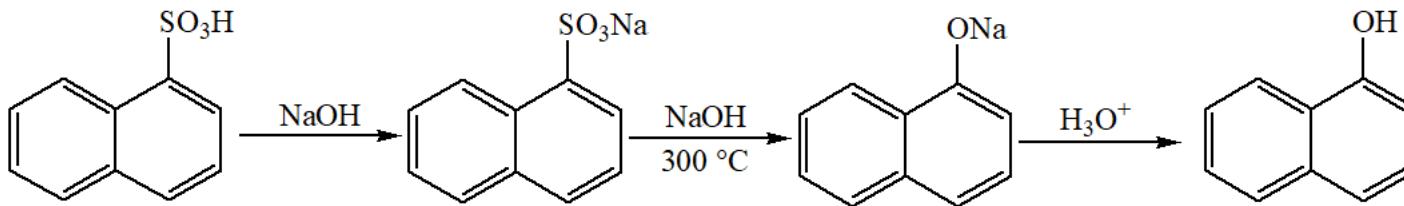
α -Naphthylamine:



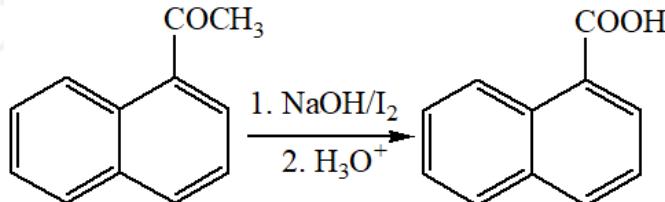
β -Naphthylamine:



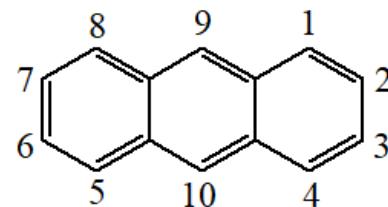
Naphthol:



Naphthoic acid:



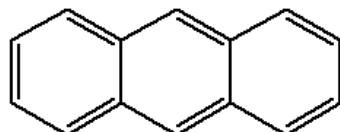
Anthracene



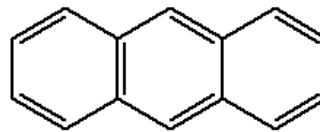
Anthracene is a tricyclic aromatic hydrocarbon in which three benzene rings are fused together in a linear manner. It is obtained from the anthracene oil fraction of coal-tar by cooling the latter and pressing the solid free from liquid. The crude anthracene contains phenanthrene and carbazole. The anthracene cake is powdered and washed with solid naphtha which dissolves the phenanthrene and the remaining solid is then washed with pyridine which dissolves carbazole. The anthracene is purified by sublimation.

Structure of anthracene

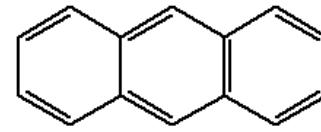
Like naphthalene, anthracene is also classified as aromatic on the basis of its properties. It is also a flat structure with partially overlapping π clouds lying above and below the plane of the molecule. In terms of valence bonds, anthracene is considered to be a hybrid of structures I-IV. Anthracene has a resonance energy of 84 Kcal/mole.



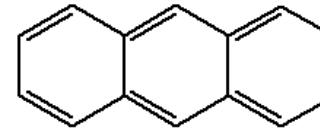
I



II



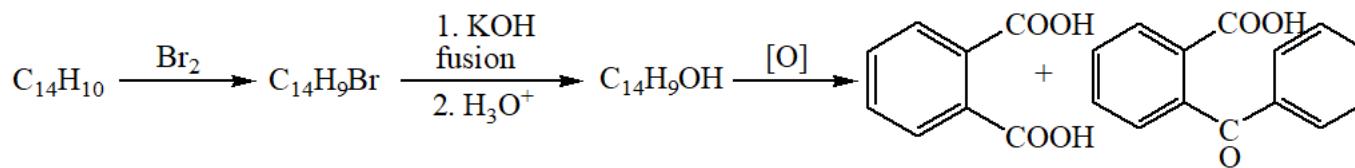
III



IV

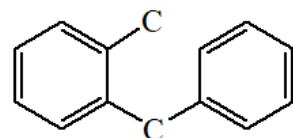
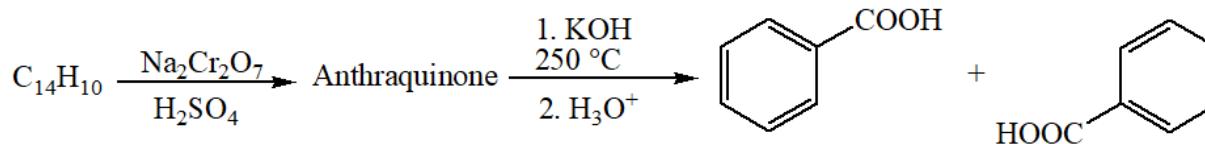
Structure elucidation of anthracene

1. Analysis and molecular weight determination of anthracene show that the molecular formula of anthracene is $C_{14}H_{10}$.
2. Bromination of anthracene gives bromoanthracene, $C_{14}H_9Br$ which on fusion with potassium hydroxide forms hydroxyanthracene, $C_{14}H_9OH$ and this on vigorous oxidation gives phthalic acid and a small amount of o-benzoylbenzoic acid.

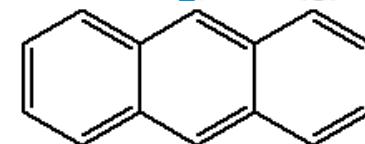


This suggests that anthracene contains at least two benzene rings and that its skeleton is as shown.

3. The presence of two benzene rings is confirmed by the fact that on fusion with potassium hydroxide at 250°C , anthraquinone (which may be obtained by direct oxidation of anthracene) gives two molecules of benzoic acid

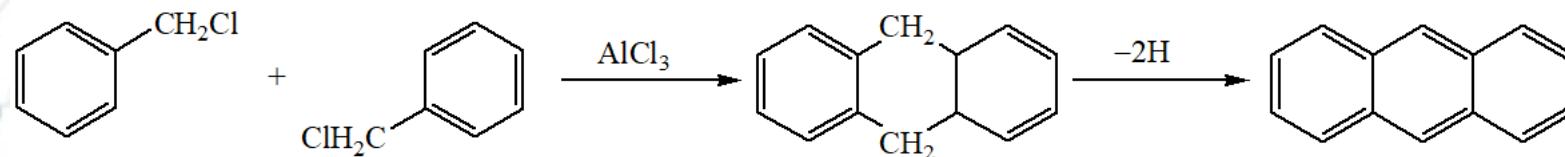


The above skeleton contains 14C atoms and to fit in 10 hydrogen atoms and retain the quadrivalence of carbon, the middle ring must be closed i.e. a structure of anthracene which is consistent with the foregoing reactions is three benzene rings fused together in a linear manner.

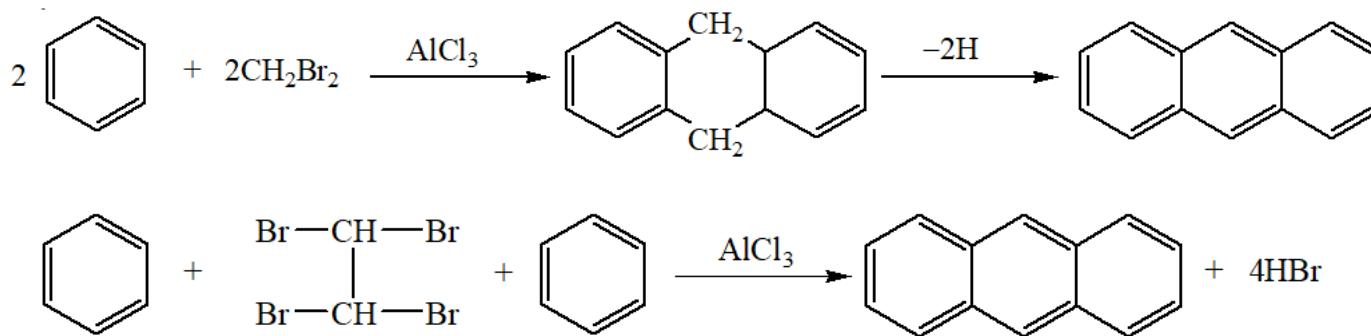


This structure of anthracene has also been established by many synthesis.

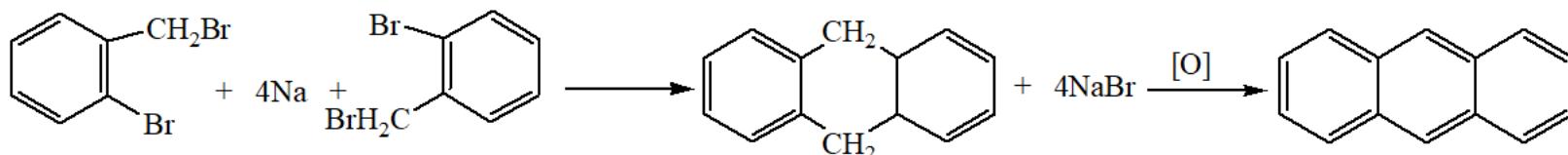
(i) By a Friedal-Crafts reaction using benzyl chloride, 9,10-dihydroanthracene is formed which readily eliminates two hydrogen atoms to form anthracene.



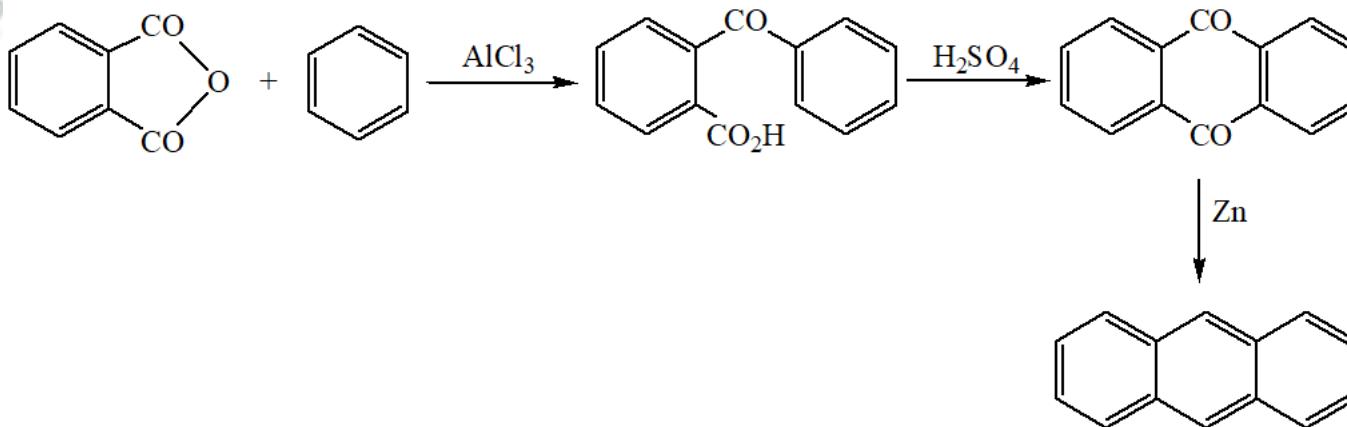
(ii) Anthracene is also formed by Friedal-Crafts condensation benzene and methylene bromide or between benzene and acetylene tetra bromide.



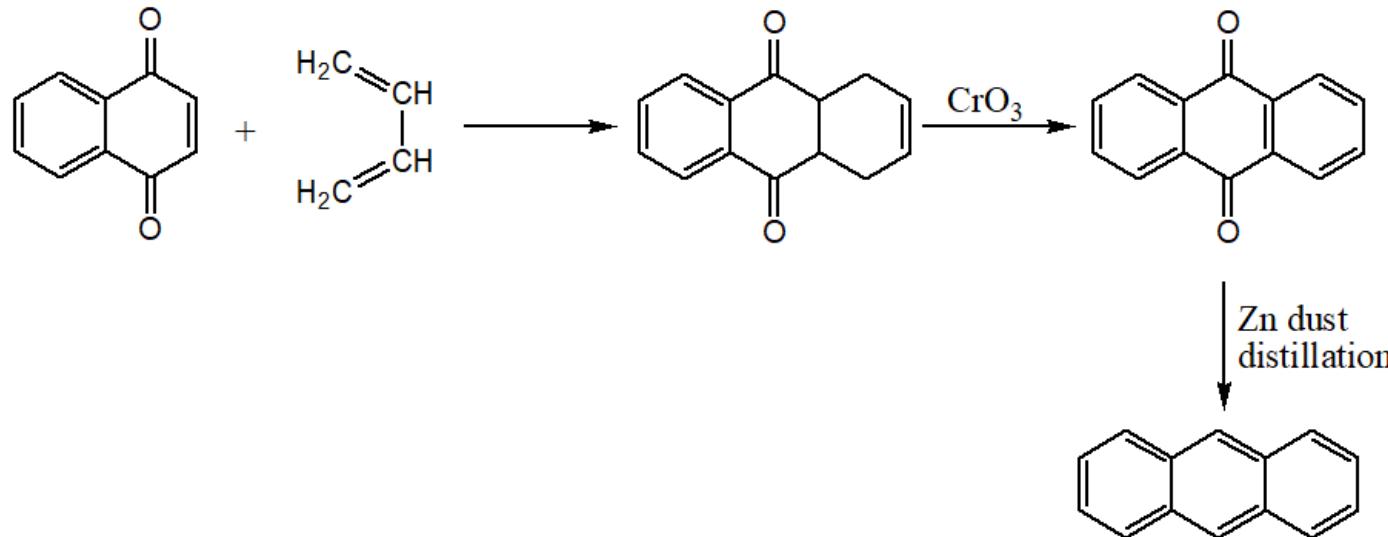
(iii) By heating o-bromobenzylbromide with sodium, the product dihydroanthracene is converted into anthracene by mild oxidation.



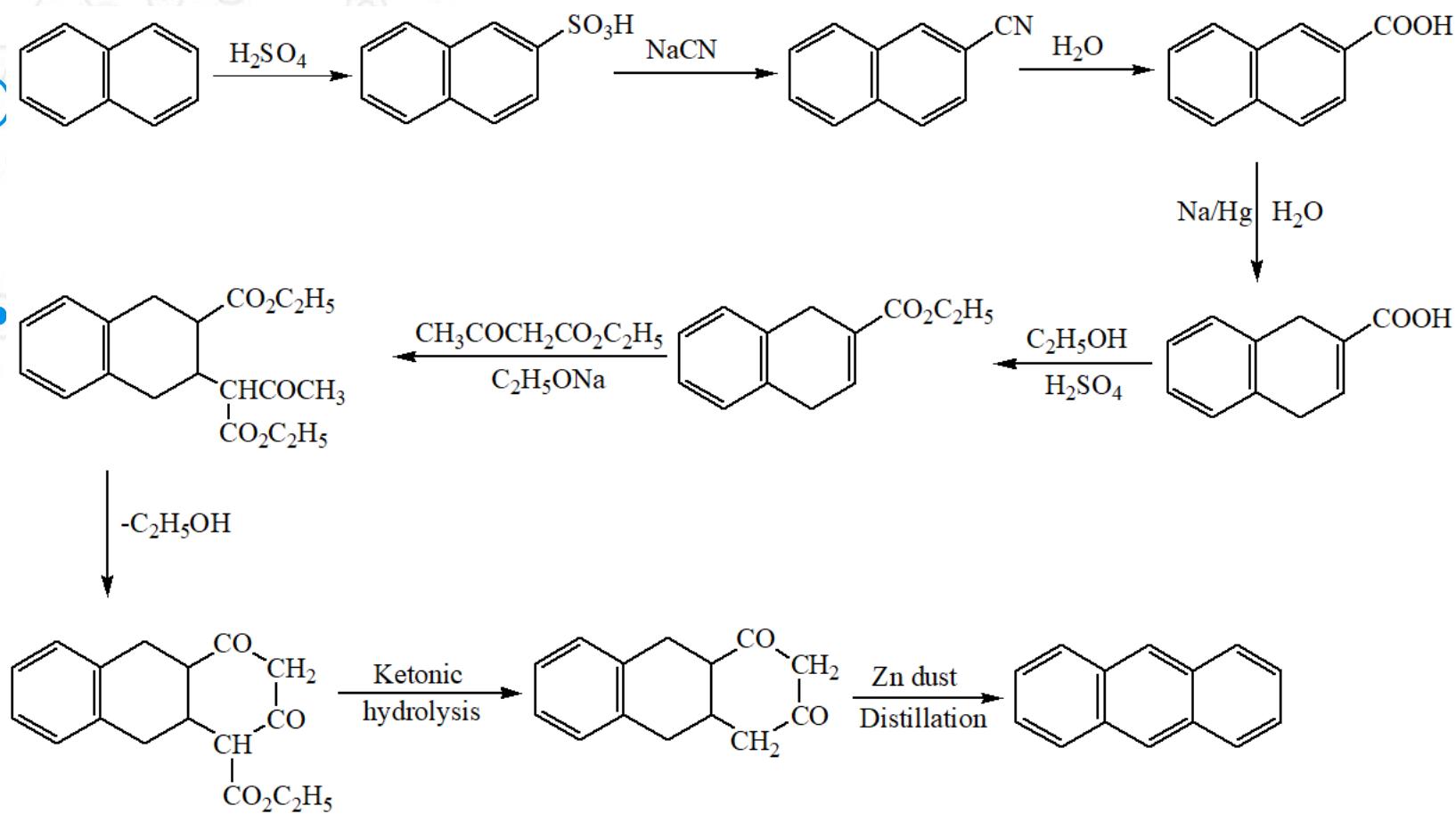
(iv) When phthalic anhydride in benzene solution is treated with aluminium chloride, o-benzoylbenzoic acid is formed. This on heating with concentrated sulphuric acid at 100 °C forms anthraquinone, which on distillation with Zn dust gives anthracene.



(v) 1,4-napthaquinone undergoes Diels-Alder reaction with butadiene to form 1,4-dihydroanthraquinone which on oxidation with chromium trioxide in glacial acetic acid gives anthraquinone. Anthraquinone on zinc dust distillation produces anthracene.

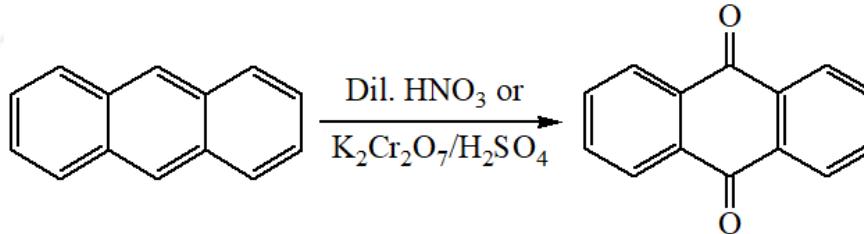


(vi) In this method, naphthalene is converted into 1,4-naphthalene-2-carboxylic ester, and this is then made to undergo the Michael condensation with acetoacetic ester etc.

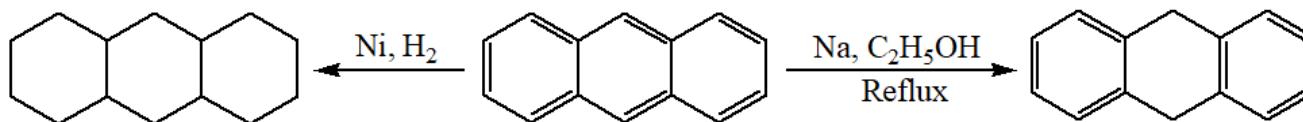


Reactions of anthracene

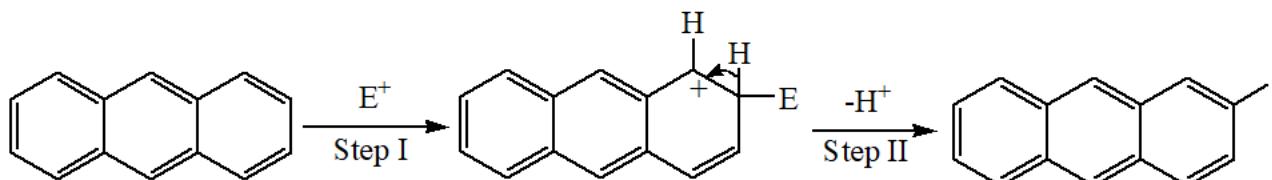
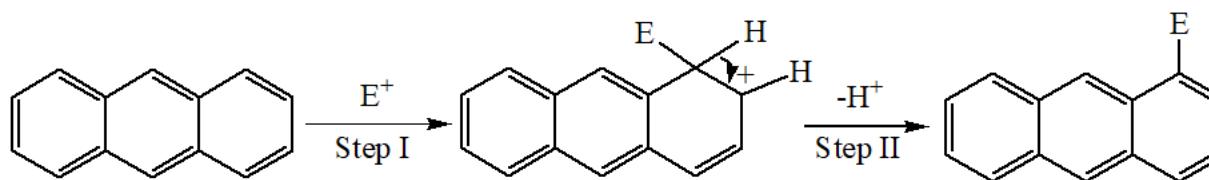
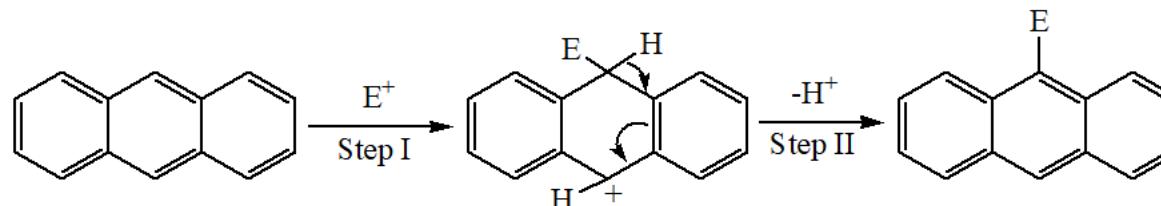
(i) Oxidation



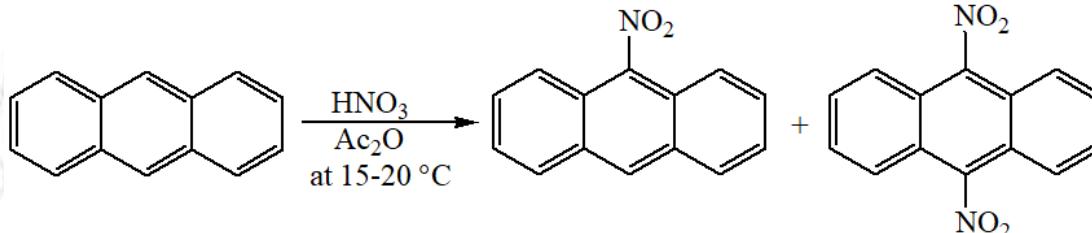
(ii) Reduction



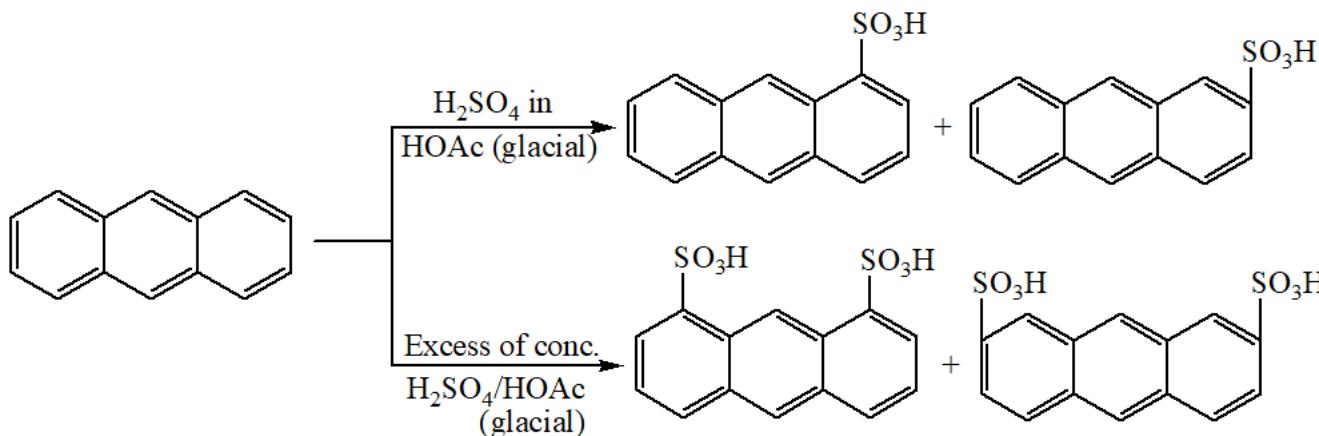
(iii) Electrophilic substitution: In case of both anthracene and phenanthrene, electrophilic substitution most preferably takes place at 9 or 10 position. This is because the σ complexes for attack at 9-position contains 2 benzene rings whereas an attack at any position (1 or 2) forms a σ complex containing a naphthalene moiety. The resonance energy of a naphthalene moiety being less than the resonance energy of two benzene rings, the σ complex for 9-attack is more stable than the σ complex for 1- or 2-attack.



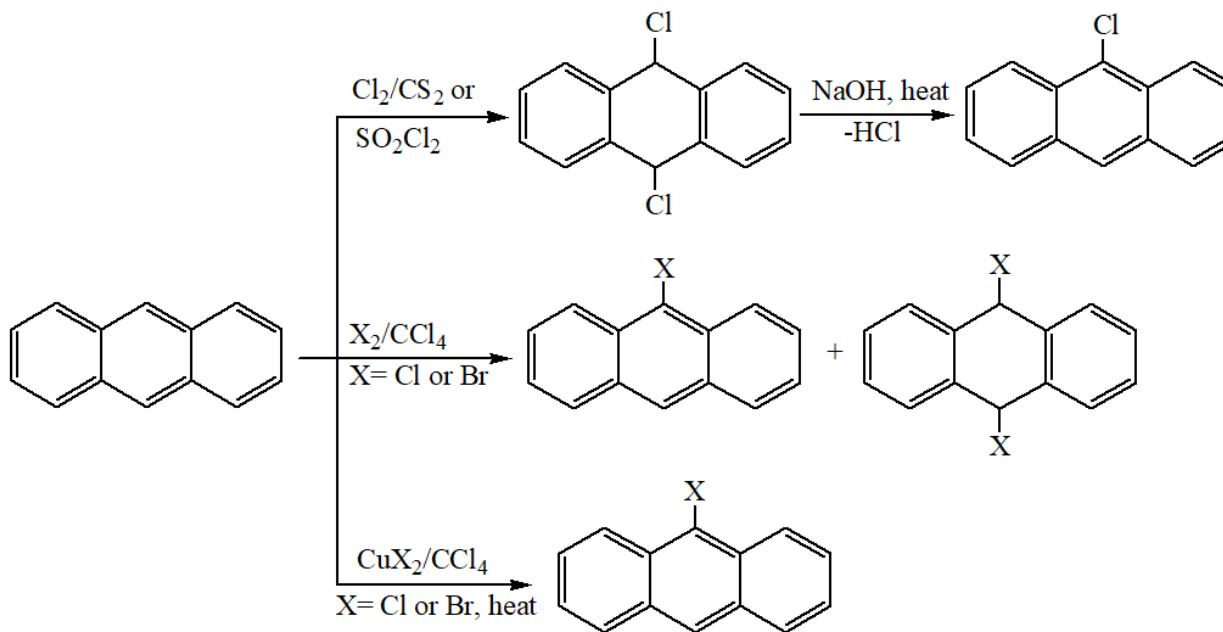
(a) Nitration:



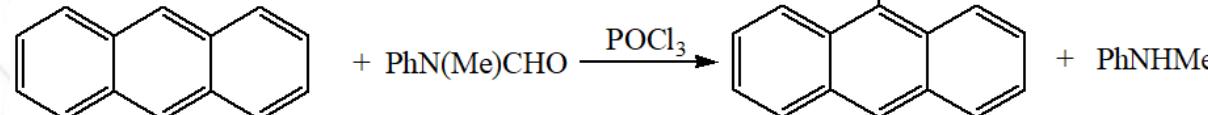
(b) Sulphonation:



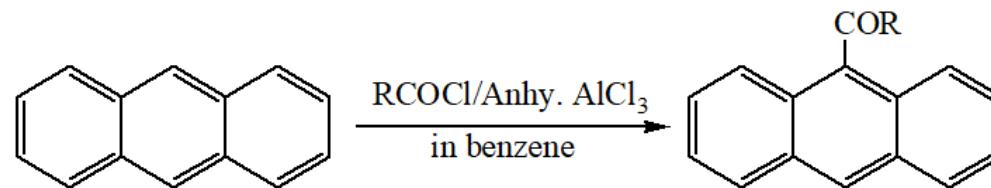
(c) Halogenation:



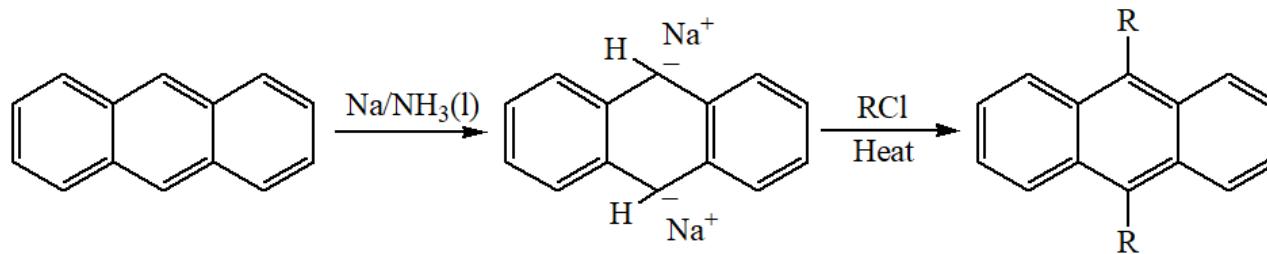
(d) Formylation:



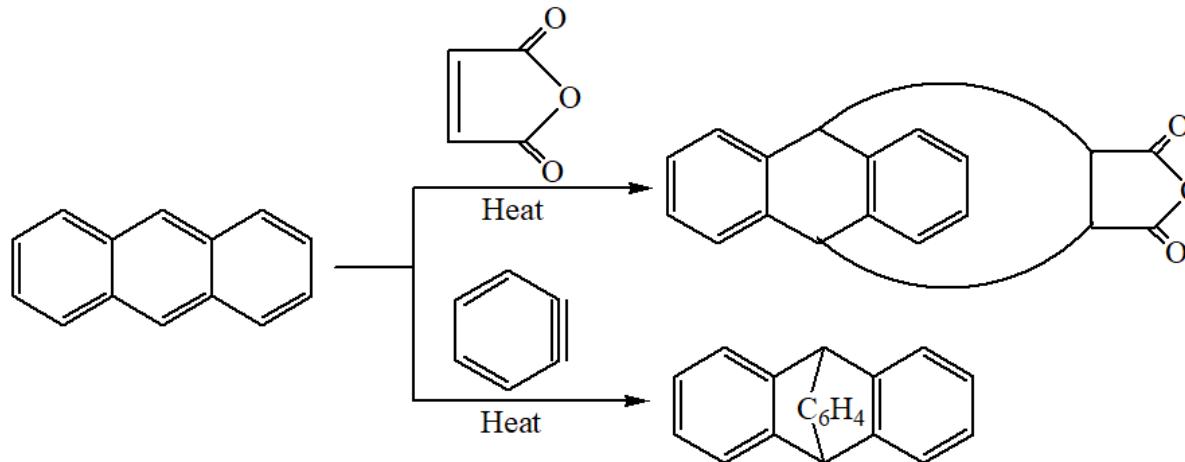
(e) Friedal-Crafts acylation:



(iv) 9,10-alkylation:

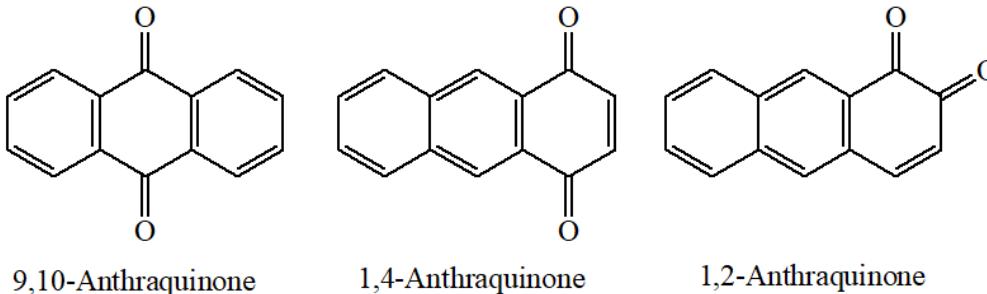


(v) Diels-Alder reaction:

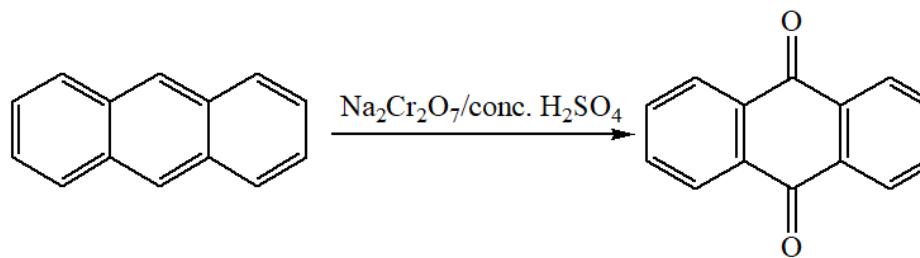
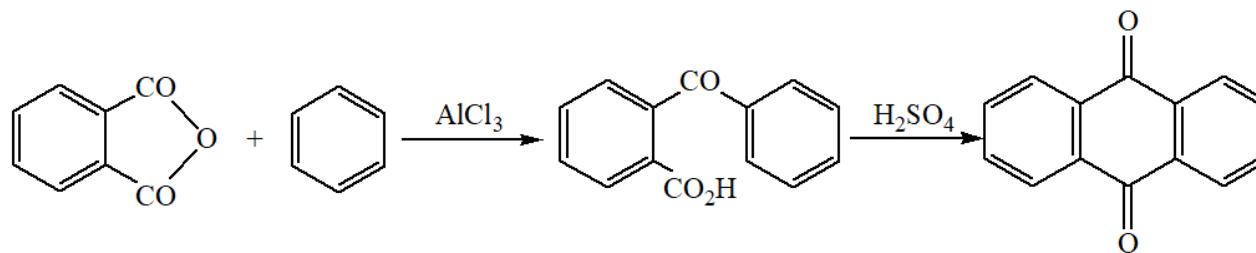


Derivative of Anthracene- Anthraquinone

There are nine possible isomeric quinones of anthracene, but only three are known- 1,2-, 1,4-, and 9,10-anthraquinone. The most important one is 9,10-compound and this is simply referred as 9,10-anthraquinone.

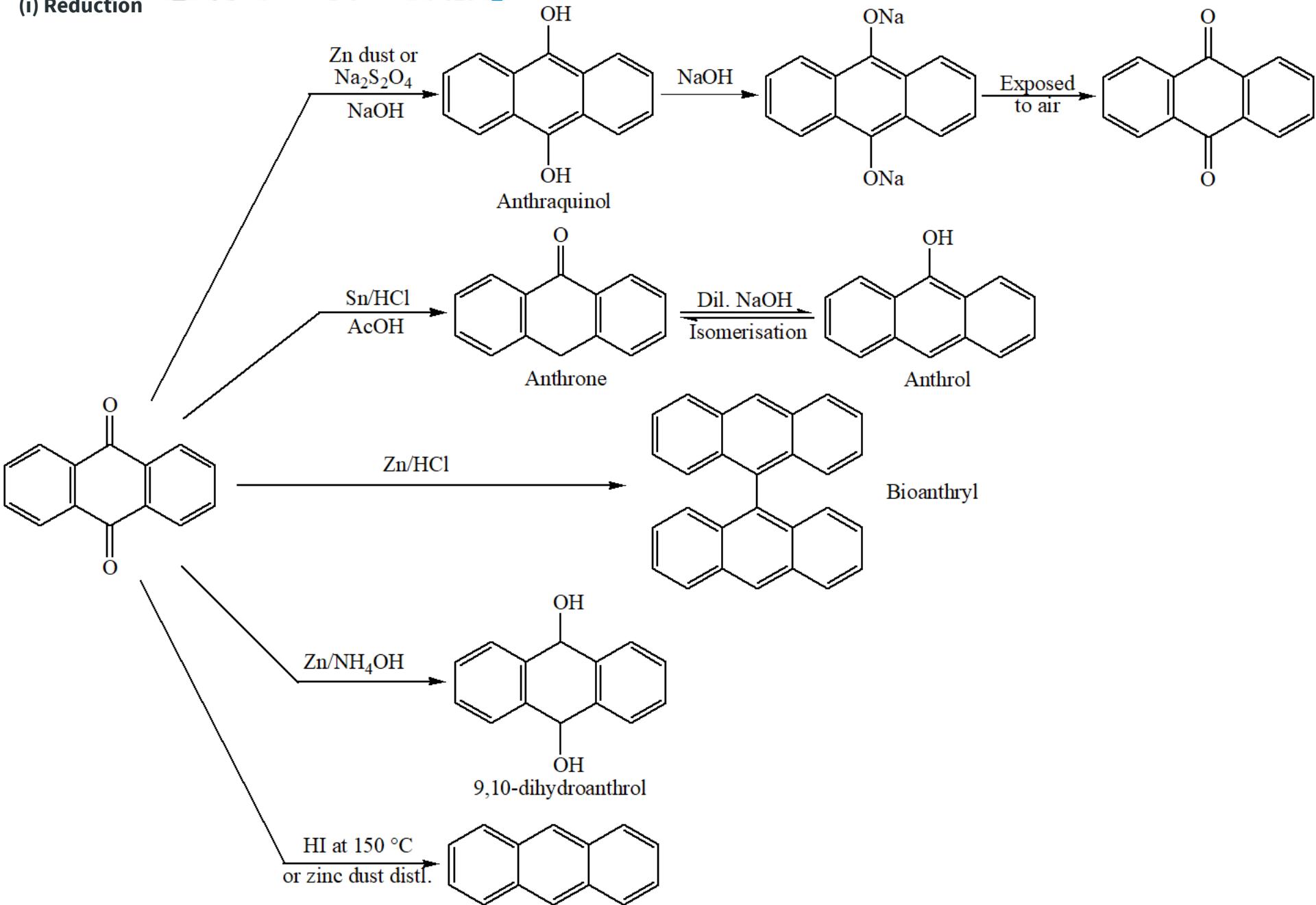


Synthesis of anthraquinone

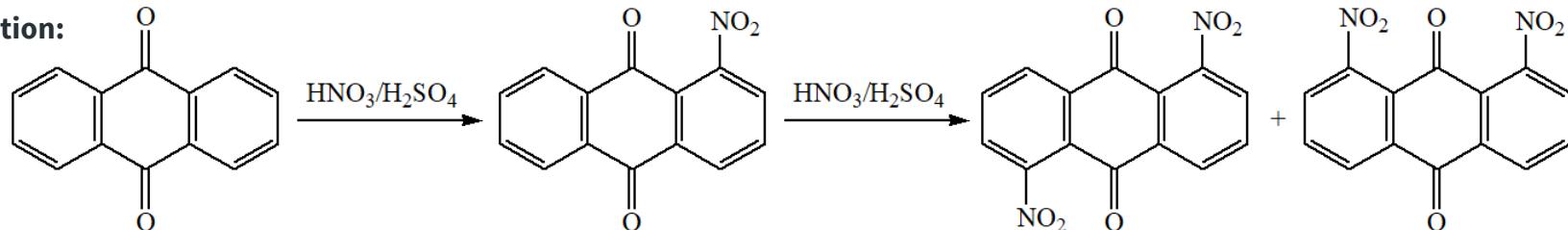


Reactions of anthraquinone

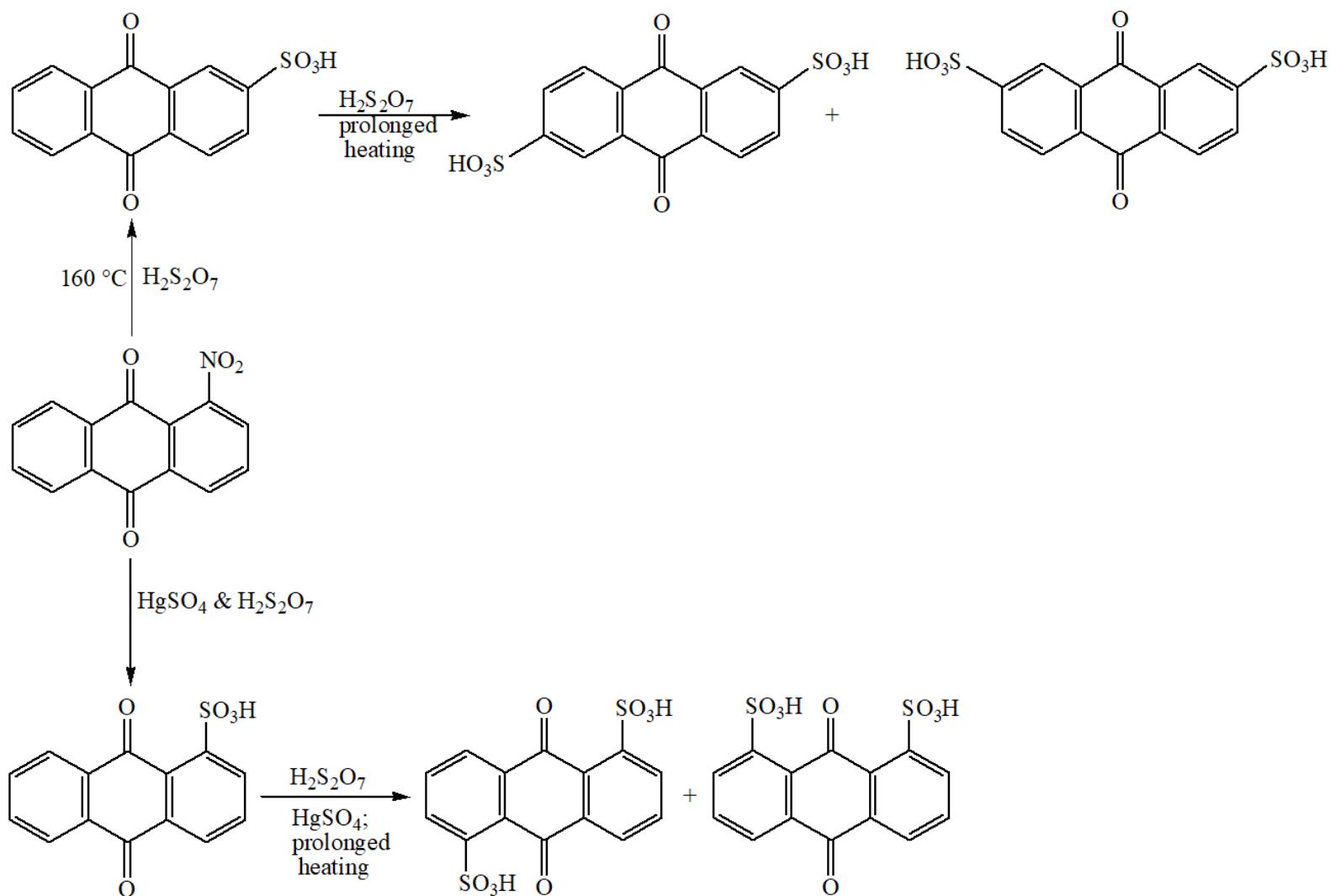
(i) Reduction



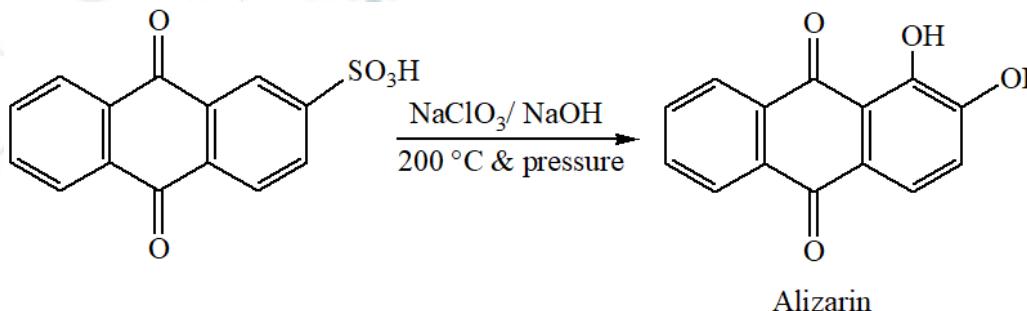
(ii) Nitration:



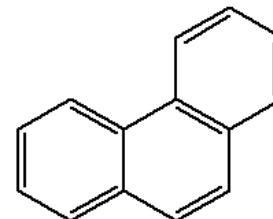
(iii) Sulphonation:



(iv) Dye formation:



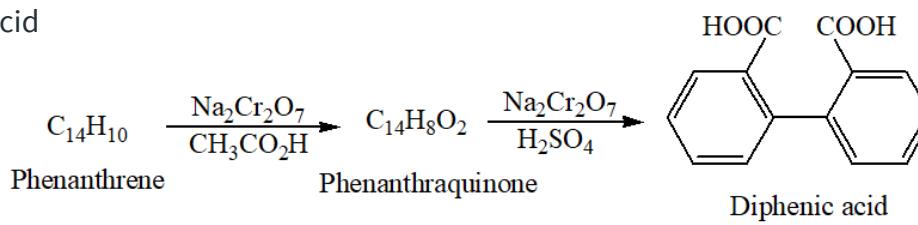
Phenanthrene



Phenanthrene is a tricyclic non-linear fused ring system and an isomer of anthracene, $\text{C}_{14}\text{H}_{10}$. It occurs in the anthracene oil fraction of coal-tar, and is separated from anthracene by means of solution in solvent naphtha.

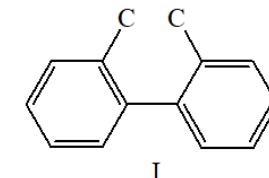
Structure elucidation of Phenanthrene

1. As an isomer of anthracene, the molecular formula of phenanthrene is $\text{C}_{14}\text{H}_{10}$.
2. On oxidation with sodium dichromate and acetic acid, phenanthrene forms phenanthraquinone which on further oxidation with dichromate and sulphuric acid, gives diphenic acid

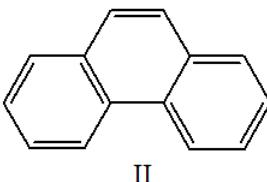


3. This on distillation with soda lime gives diphenyl.

4. The structure of last two compounds are known, therefore phenanthrene contains the skeleton I.

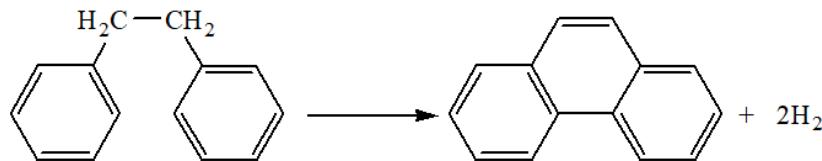


5. The structure I is equivalent to $C_{14}H_8$. Thus two hydrogen atoms are missing, these may be fitted in by closing the middle ring, i.e., a possible structure for phenanthrene is II.

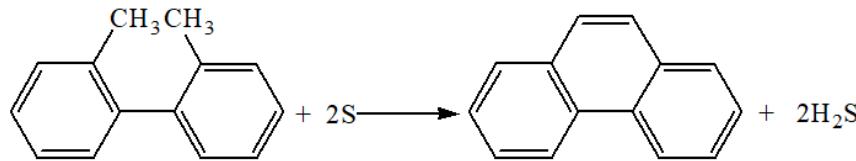


This structure has been amply confirmed by many synthesis.

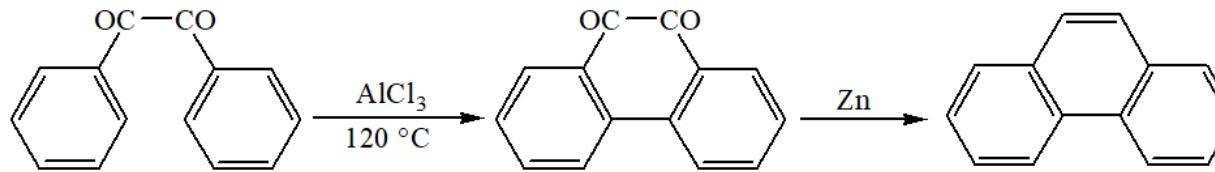
(i) By passing 2,2'-dimethyldiphenyl, dibenzyl or stilbene through a red hot tube.



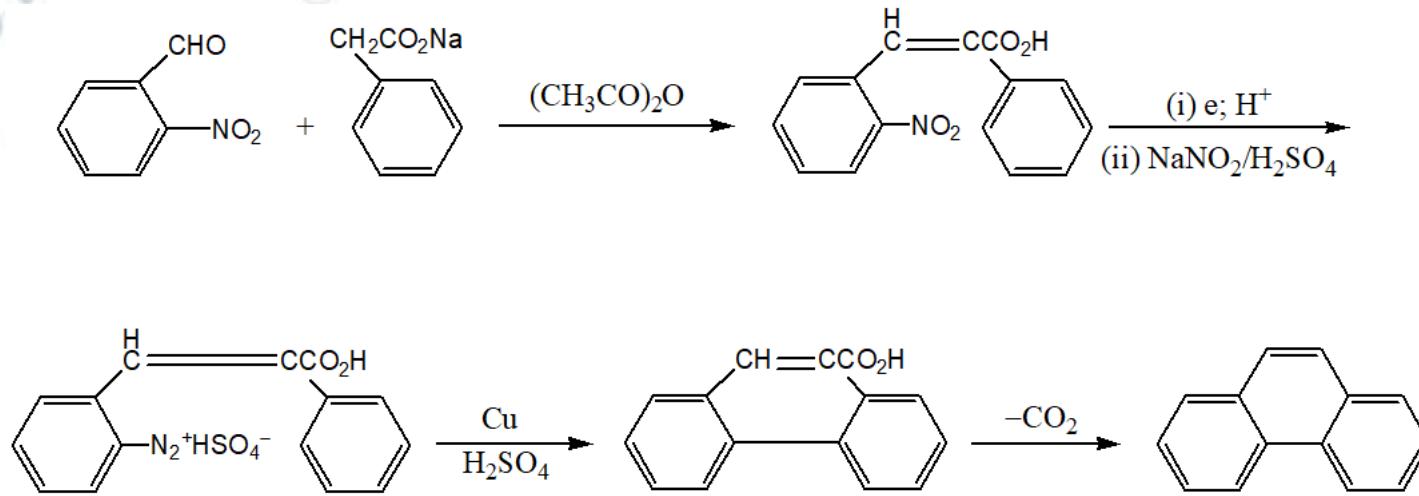
(ii) By cyclodehydrogenation of 2,2'-dimethyldiphenyl by means of sulfur.



(iii) By treating benzil with aluminium chloride at 120°C and then heating the product, phenanthraquinone with zinc dust-

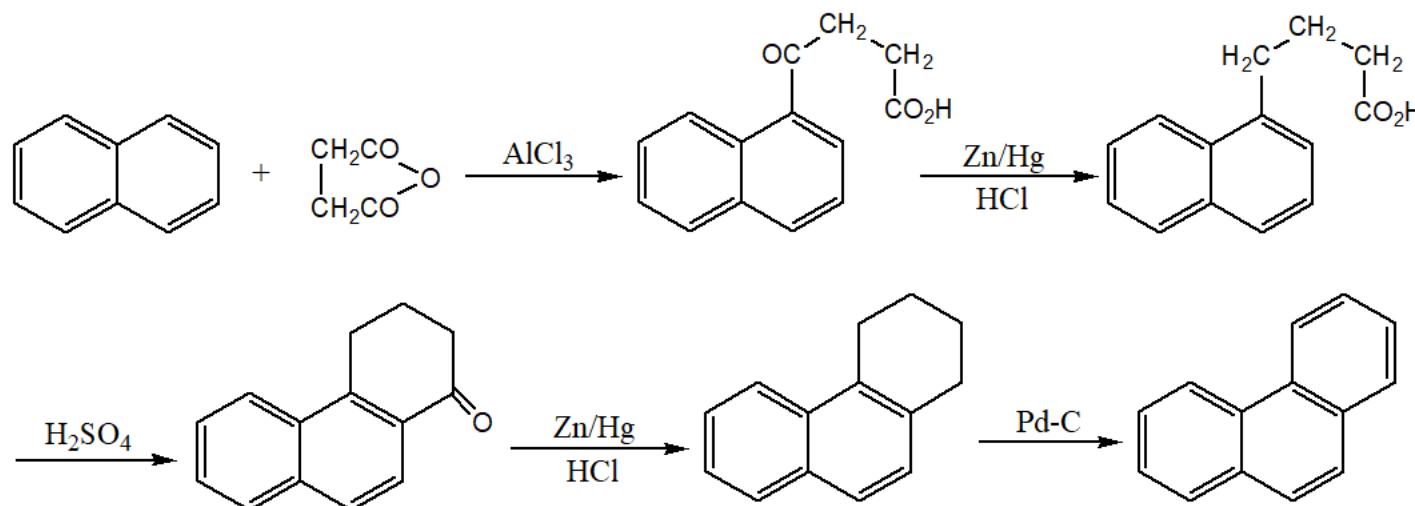


(iv) **Pschorr synthesis:** This is carried out by heating o-nitrobenzaldehyde with sodium β -phenylacetate in the presence of acetic anhydride (Perkin's condensation), reducing and diazotising the product, α -phenyl-o-nitrocinnamic acid, and treating the diazonium salt with sulphuric acid and copper powder. Phenanthrene-9-carboxylic acid is produced, and this on strong heating forms phenanthrene.

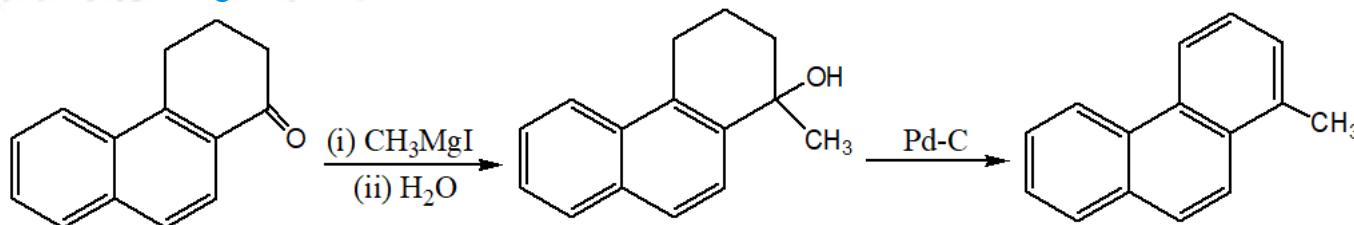


The synthesis provides a means of substituted phenanthrene with the substituents in known positions.

(v) **Haworth synthesis:**

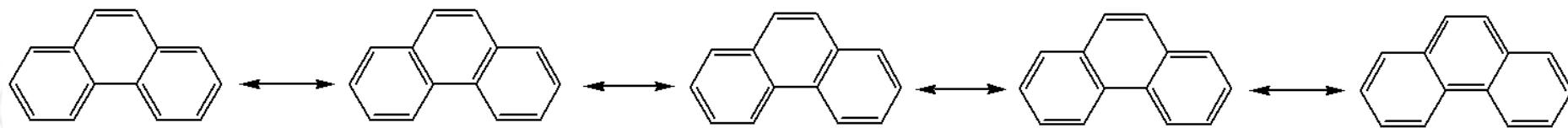


The Haworth synthesis is very useful for preparing alkylphenanthrenes with the alkyl groups in known positions, e.g., after ring closure of the 1-derivative, 1-methylphenanthrene may be obtained by the action of methyl magnesium iodide on the ketone.

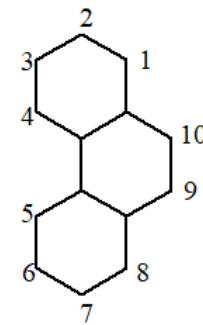
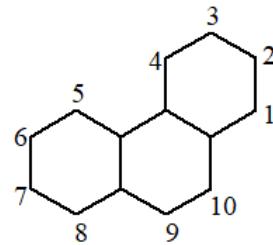
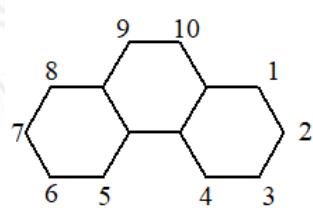


Positions of double bonds in Phenanthrene

Phenanthrene is best represented as a resonance hybrid of 5 resonating structures



Isomerism of Phenanthrene derivative



Reactions of Phenanthrene

Phenanthrene is very reactive in the 9,10-positions.

