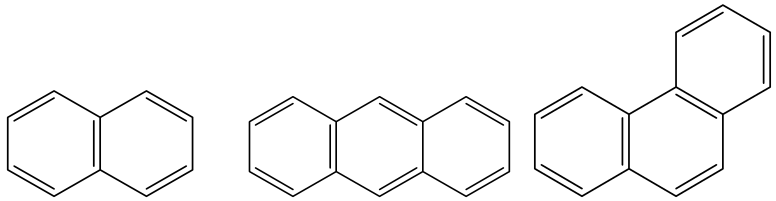
Polynuclear Aromatic Hydrocarbons

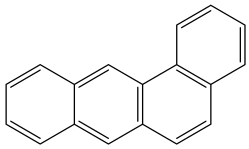
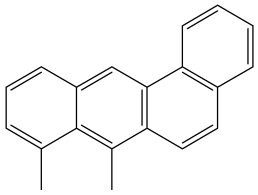
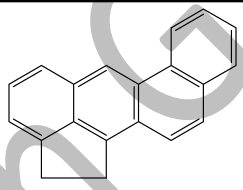
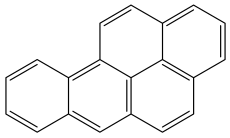
Preparation, Reaction and Structure of Naphthalene, Synthesis and Reactions of Anthracene and Phenanthrene.

Polynuclear hydrocarbons: Two or more benzene rings are joined to each other either directly (fused) or through carbon chains. Eg.:-



naphthalene anthrancene phenanthrene biphenyl

Potent carcinogens (cancer producing) derivatives:

			
1,2-Benzanthrancene	5,6-dimethyl-1,2-Benza nthrancene	Methylcholanthrene	3,4-benzypyrene

Preparation, Reaction and Structure of Naphthalene

Naphthalene, $C_{10}H_8$ (Double Bond Equivalent [DBE] =7; complete hydrogenation gives decalin (decahydronaphthalene implying 5 double bonds)

Mp 80^0 C, volatile solid, forms yellow picrate, insecticide, aromatic (resists addition reaction), undergoes electrophilic substitution reaction

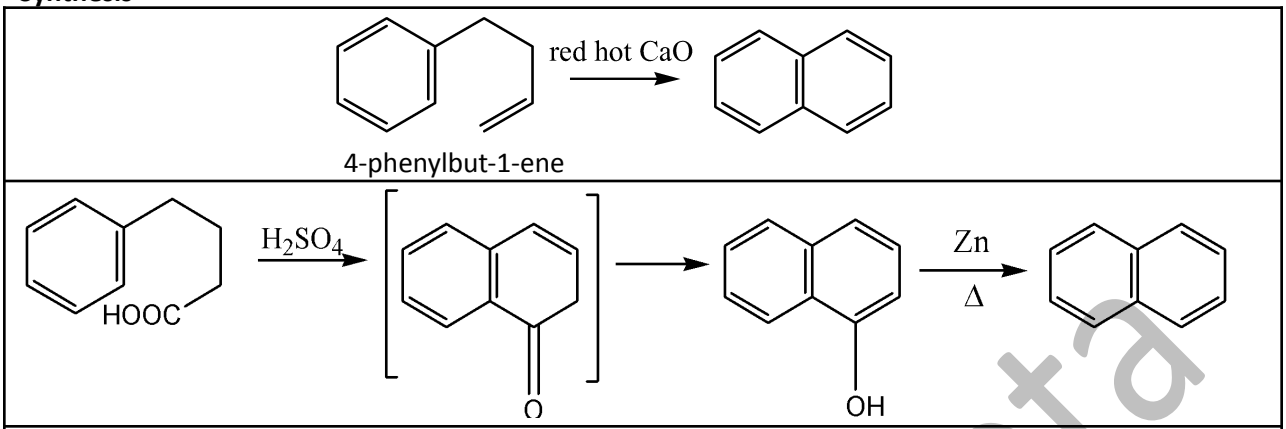
Preparation of Naphthalene

Naphthalene constitutes about 6 % of coal-tar and is obtained from the middle and heavy oils by cooling when it crystallizes out. The crude naphthalene is pressed free of the oil and treated with conc. H_2SO_4 to remove basic impurities and then with alkali to remove acidic impurities. Finally the crude solid is purified by distillation.

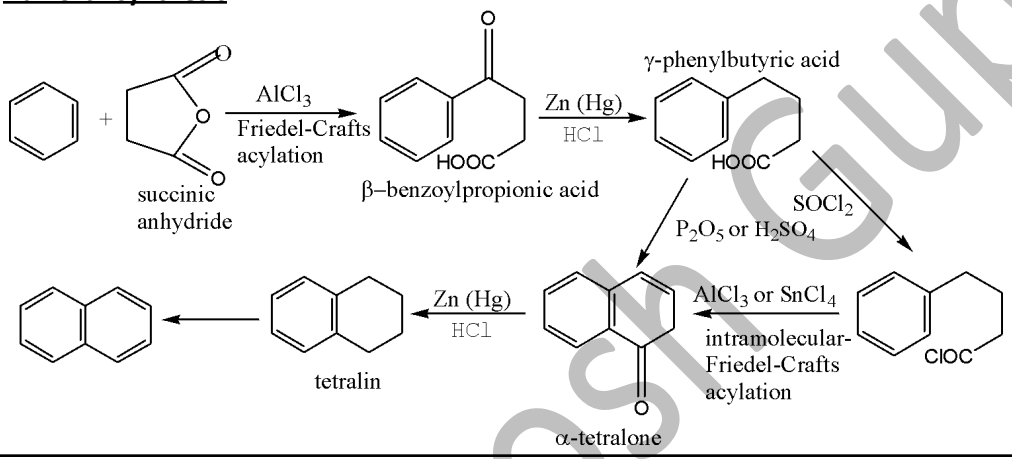
Industrially, it is prepared from suitable petroleum fractions which on passing over a heated copper catalyst at 680^0 C give naphthalene and methylnaphthalenes. Methylnaphthalenes are hydrodealkylated to naphthalene by heating with hydrogen under pressure in the presence of a metal oxide catalyst.

$$C_{10}H_7CH_3 \xrightarrow[\text{metal oxide}]{H_2} C_{10}H_8 + CH_4$$

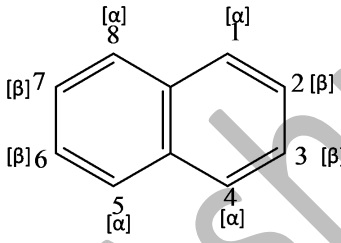
Synthesis



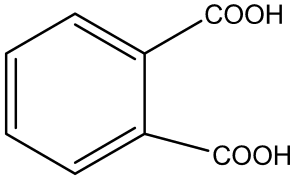
Haworth synthesis



Structure of Naphthalene

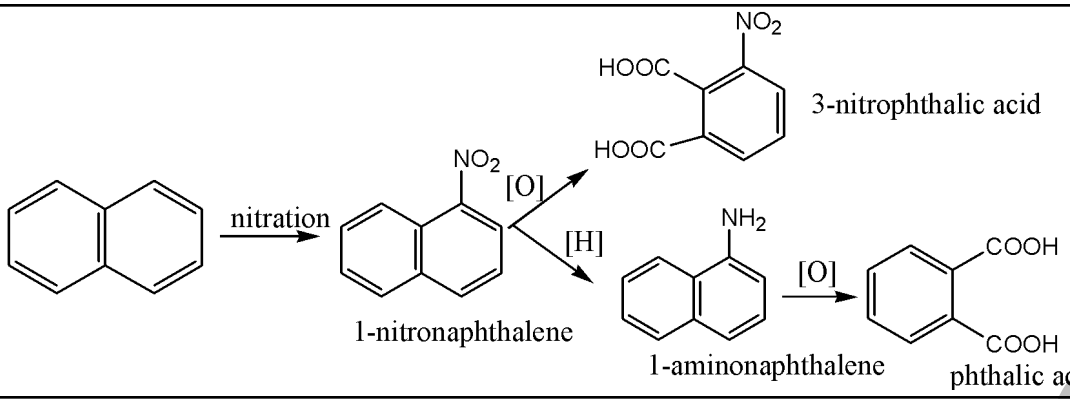


On vigorous oxidation yields phthalic acid



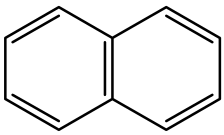
Implying at least one benzene ring with two side chains in ortho position

Erlenmeyer proposed the above structure

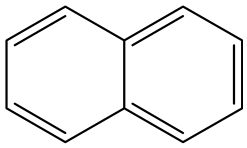


These reactions prove benzenoid character of both the rings

Resonance structure and bond fixation in naphthalene. It is considered as a hybrid of the following three contributing forms:



I



II

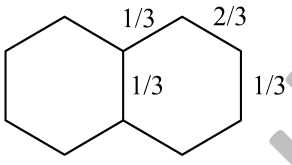
III

Symmetrical structure; both rings benzenoid (benzene like)	II and III unsymmetrical structures in which one ring is o-quinonoid (quinone-like)

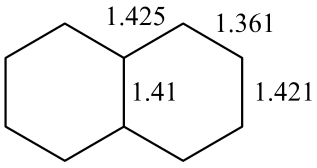
Quinones are more reactive than benzene;

Fries rule: Most stable form of a polynuclear hydrocarbon is that in which maximum number of rings are in the benzenoid form.

I major contribution in stability



IV



V

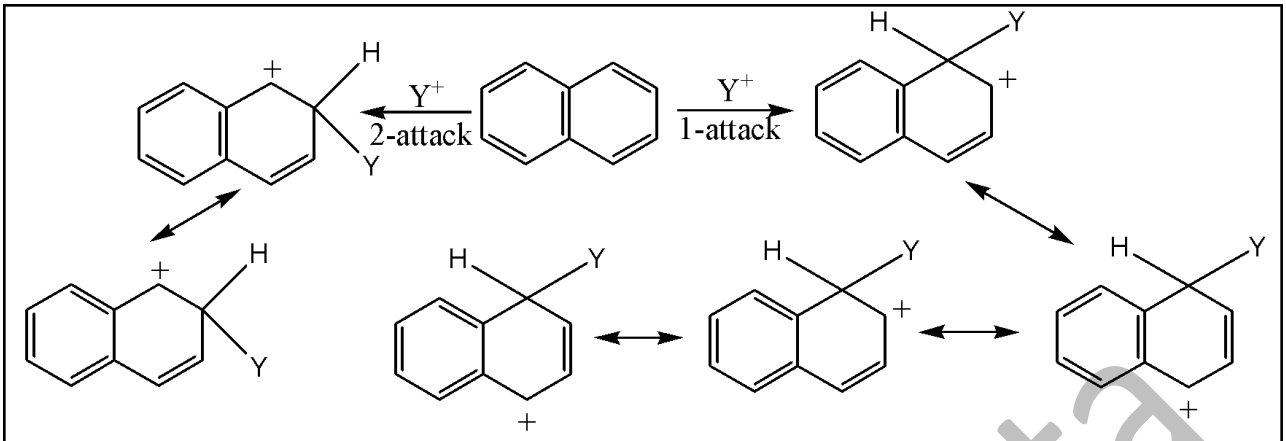
Relative double bond character of various bonds calculated assuming equal contribution of I, II, III;	This has been proved to be true by X-ray and electron-diffraction that 1,2-bond is appreciably shorter than the 2,3-bond

A number of chemical reactions of naphthalene derivatives, particularly diazo-coupling reaction of the various substituted naphthols, also support the fact that the 1,2-bond has more double bond character as compared to 2,3-bond.

Naphthalene is aromatic compound and its resonance energy is 61 kcal/mol, i.e. 30.5 kcal/mol per benzene ring on the average. It is more reactive than benzene.

Reaction of Naphthalene

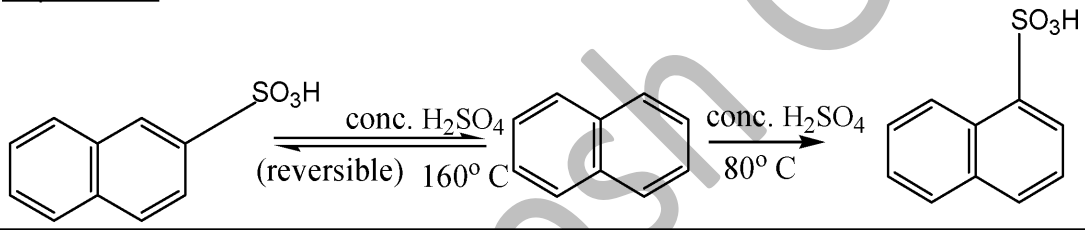
It undergoes electrophilic substitution at 1-position

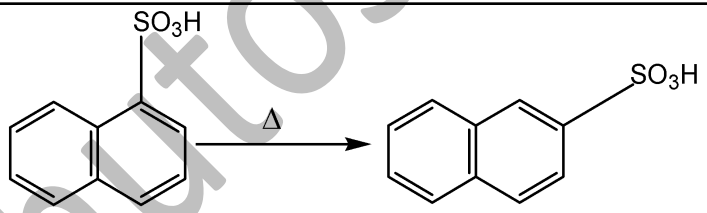


Intermediate formed by the attack at 1-position can have four resonance forms whereas the intermediate corresponding to the attack at 2-position can have only two such resonance forms. Thus, former is preferred.

However, there are several exceptions to the preference for 1-substitution (sulphonation and Friedel-Crafts reaction).
Temperature and solvents decide kind of substitution.

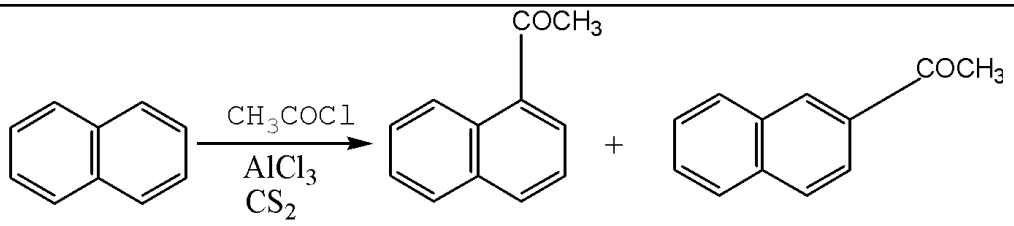
<u>Sulphonation</u>



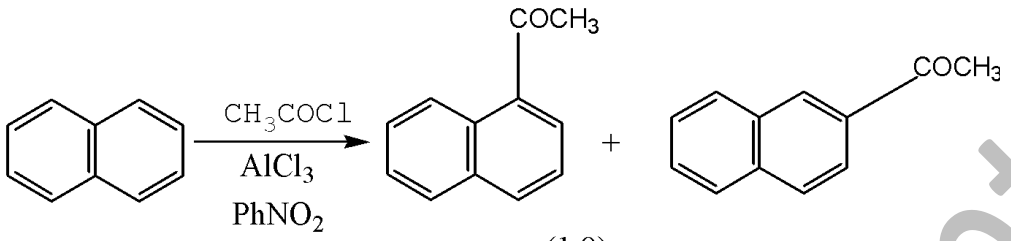


Relative instability of 1-isomer is due to large steric interaction between bulky SO_3H group at 1-position and the *peri*-hydrogen (at 8-position).
1-isomer is kinetically controlled; 2-isomer is thermodynamically controlled.

<u>Friedel-Crafts acylation</u>



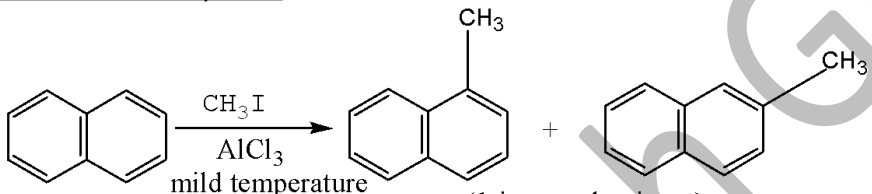
(3:1)



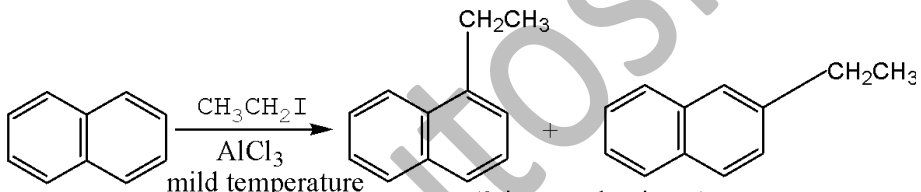
(1:9)

Formation of complex between nitrobenzene, CH_3CO^+ and $AlCl_4^-$. This bulky reagent prefers attack at 2-position.

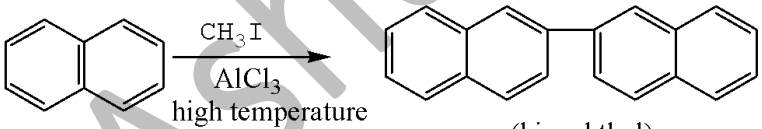
Friedel-Crafts alkylation



(1-isomer dominant)

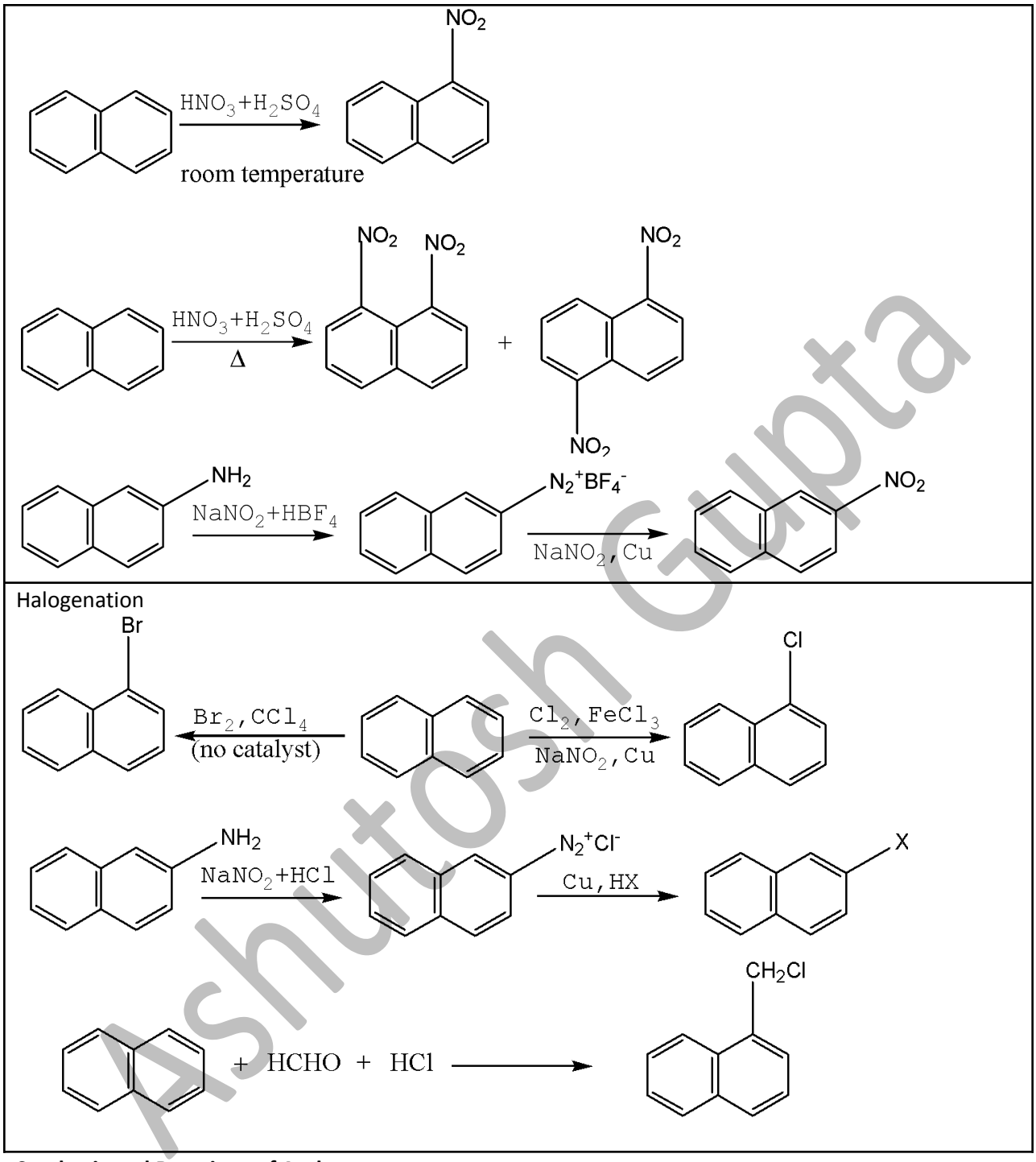


(2-isomer dominant)



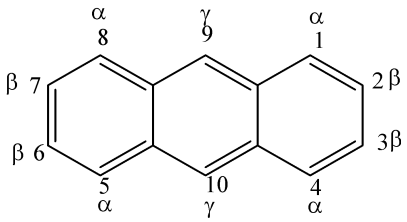
(binaphthyl)

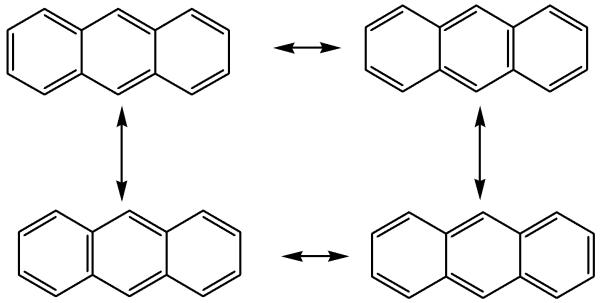
Nitration

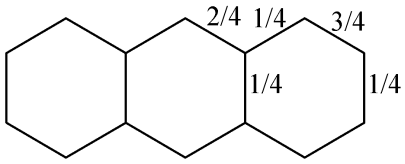


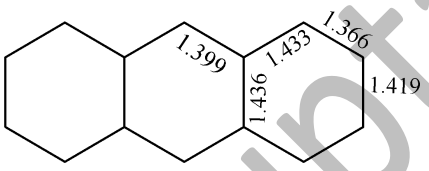
Synthesis and Reactions of Anthracene

Synthesis of Anthracene (m.p. 216^0 C), sublime, fluorescence, forms picrate









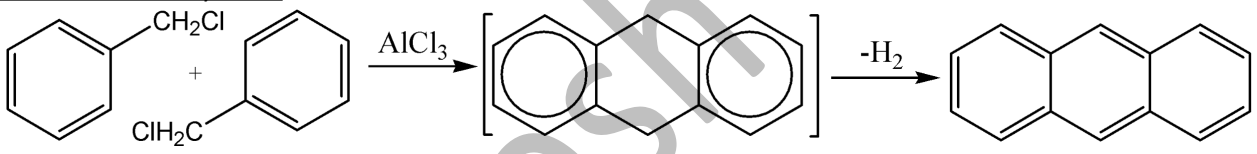
Double bond character

Resonance energy (RE) of anthracene is 84 kcal/mol, i.e., 28 kcal/mol per ring.

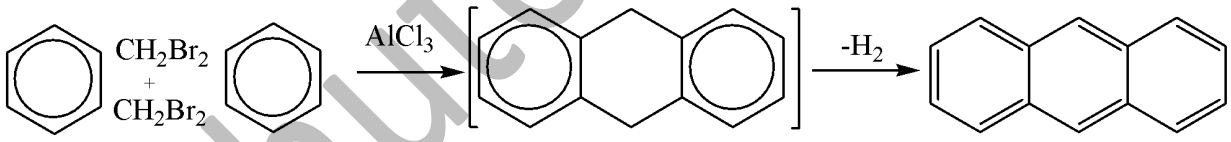
Anthracene is more reactive than benzene and naphthalene.

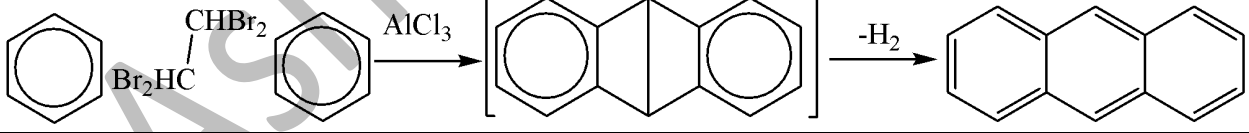
Synthetic Methods

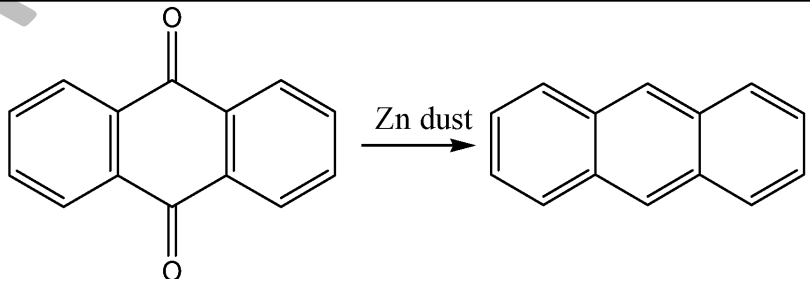
Friedel-Crafts alkylation



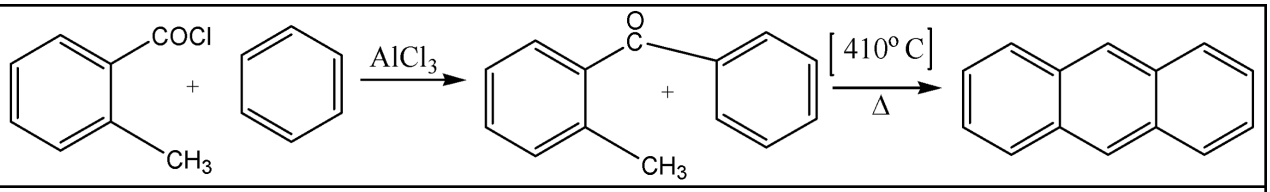
Benzyl chloride 9,10-dihydroanthracene anthracene



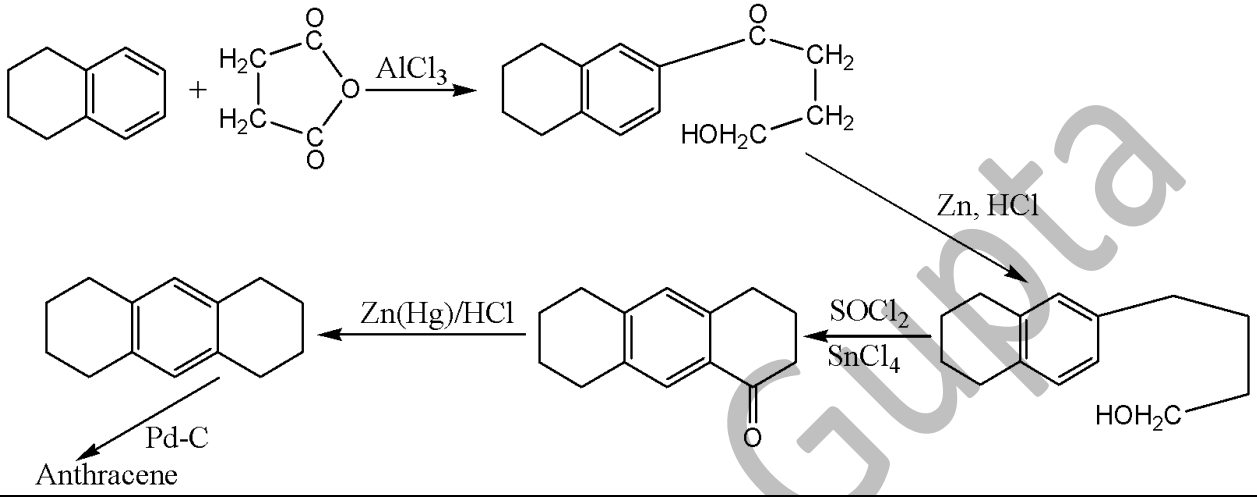




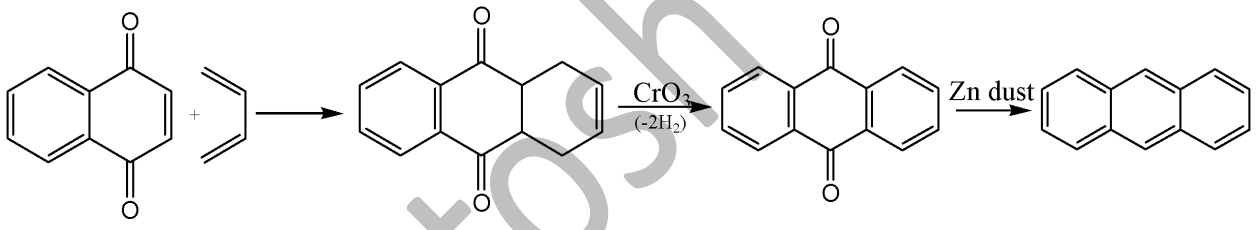
Elbs reaction



Friedel-Crafts acylation of tetralin with succinic anhydride by Clemmensen reduction, cyclization, again Clemmensen reduction, and dehydrogenation.



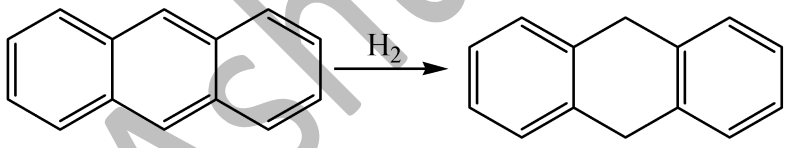
Diels-Alder reaction



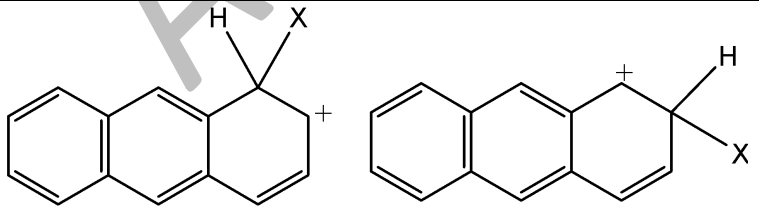
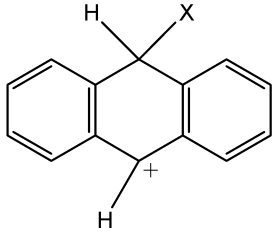
Naphthaquinone butadiene anthraquinone

Reactions of Anthracene

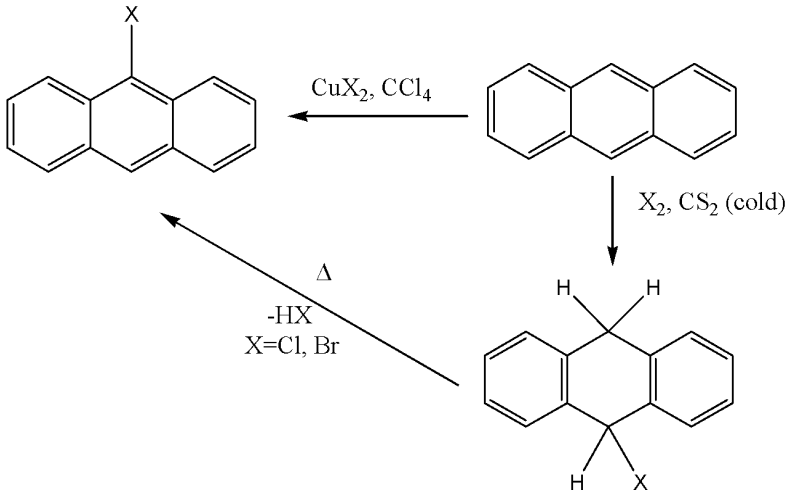
The 9,10-positions of anthracene are very reactive. Catalytic or chemical reduction gives 9,10-dihydroanthracene as the first product.

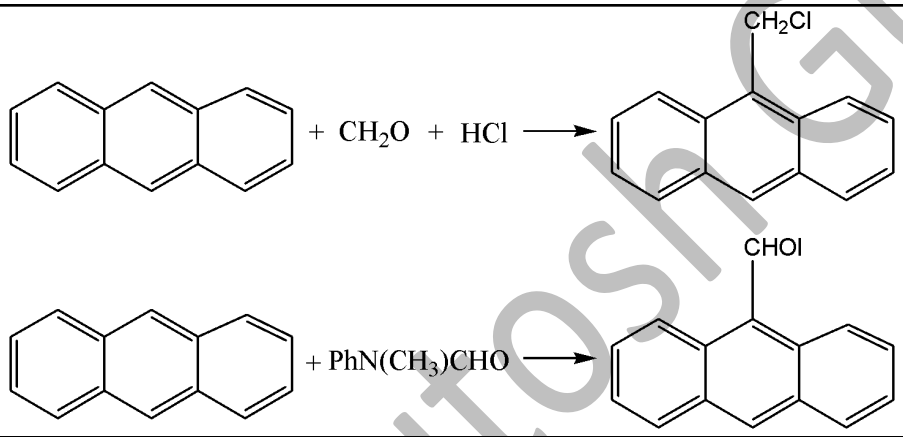


Electrophilic substitution gives 9,10-disubstituted products.

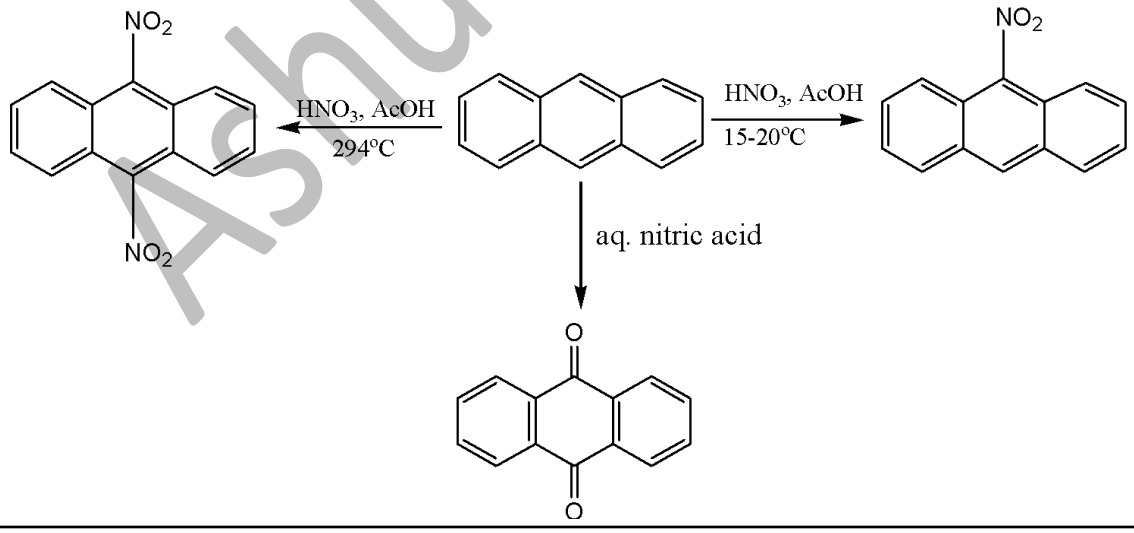
	
σ-complex for 1- and 2-substitution (one naphthalene ring intact)	σ-complex for 9,10-substitution (two benzene rings intact)

Halogenation:

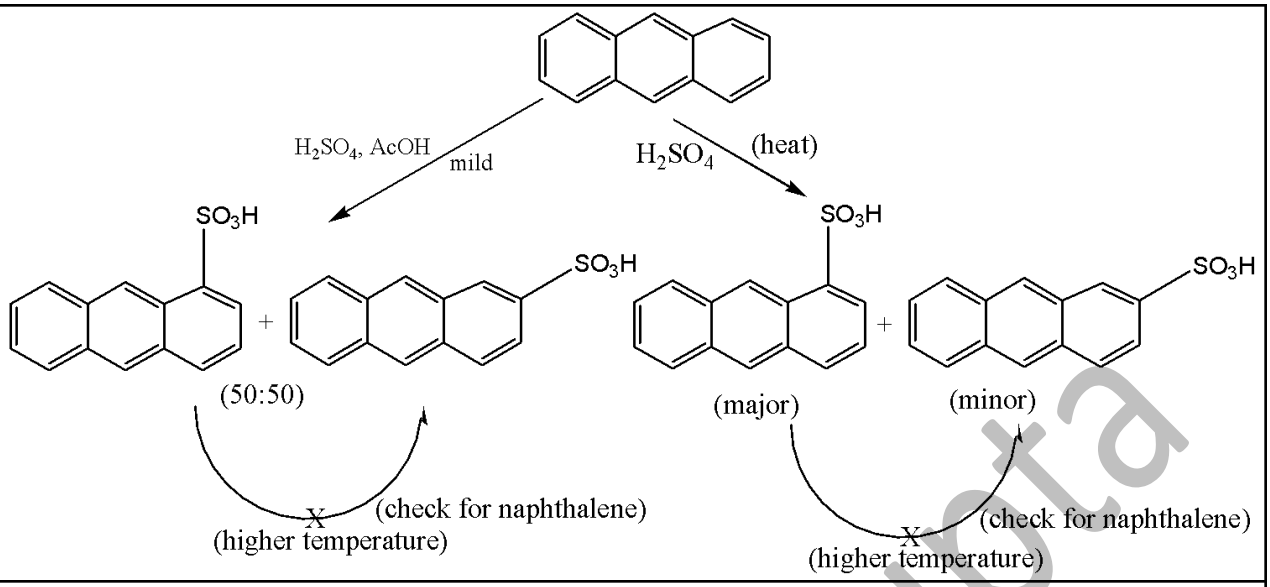




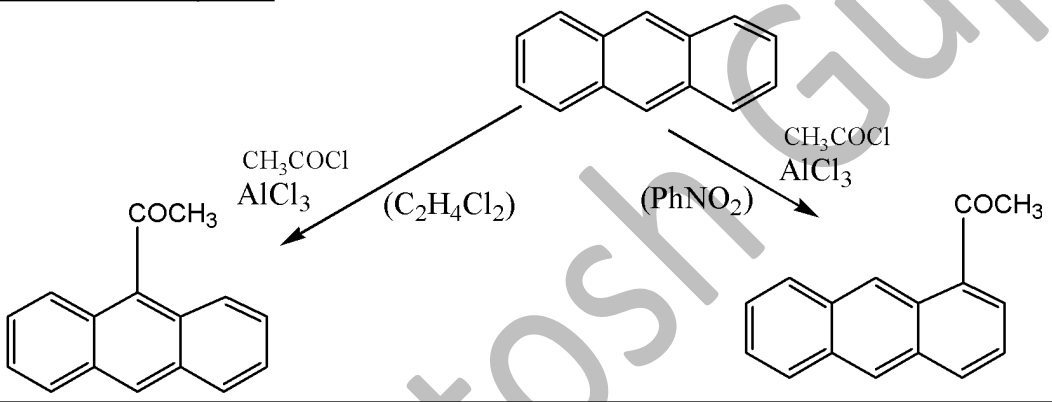
Nitration



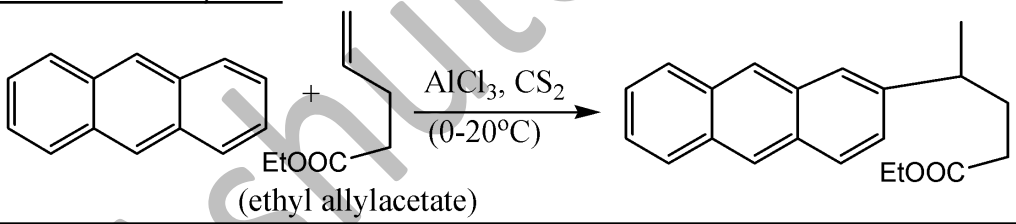
Sulphonation



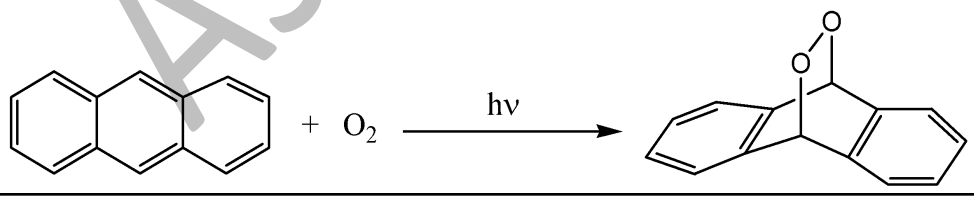
Friedel-Crafts acylation



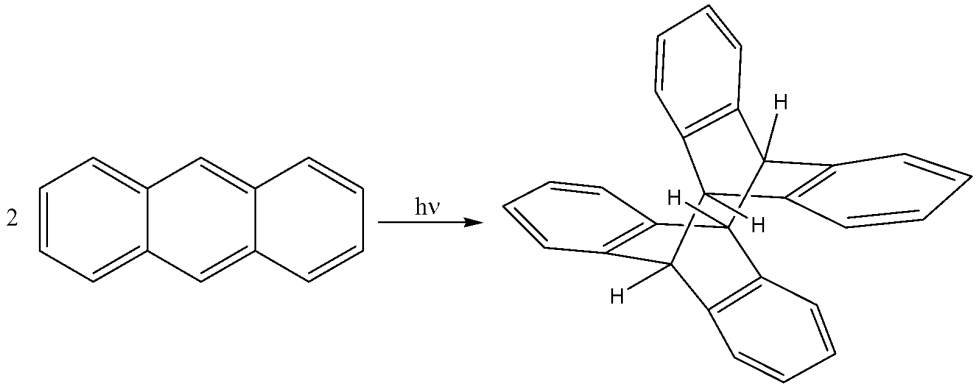
Friedel-Crafts alkylation



Peroxidation

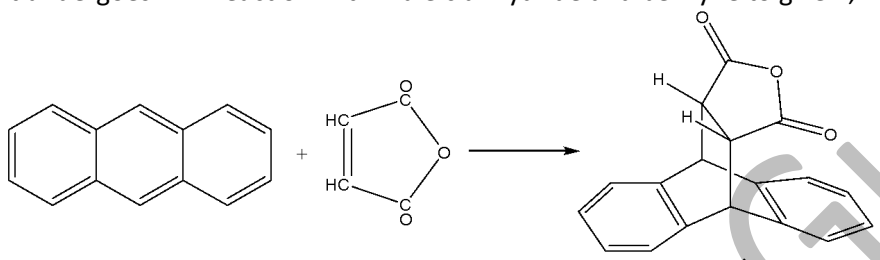


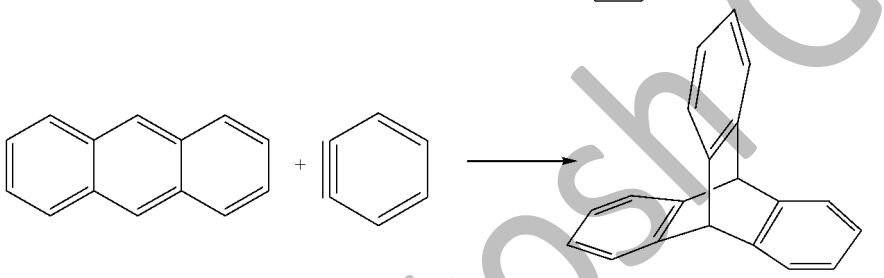
Dimerization occurs on exposing it to light in solution of xylene.



Diels-Alder reaction

It undergoes D.A. reaction with maleic anhydride and benzyne to give 1,4-addition products.

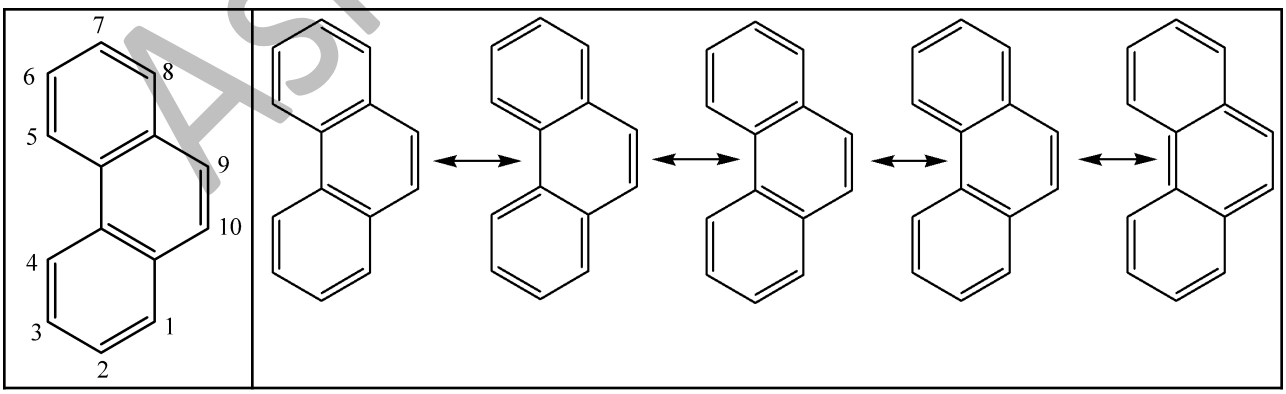




Triptycene

Synthesis and Reactions of Phenanthrene.

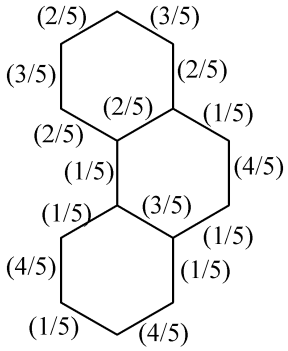
Phenanthrene (m.p. 99^0 C), found in morphine, sterols, bile acids, sex hormones; gives blue fluorescence, forms picrate.



Resonance energy of phenanthrene is 92.5 kcal/mol.

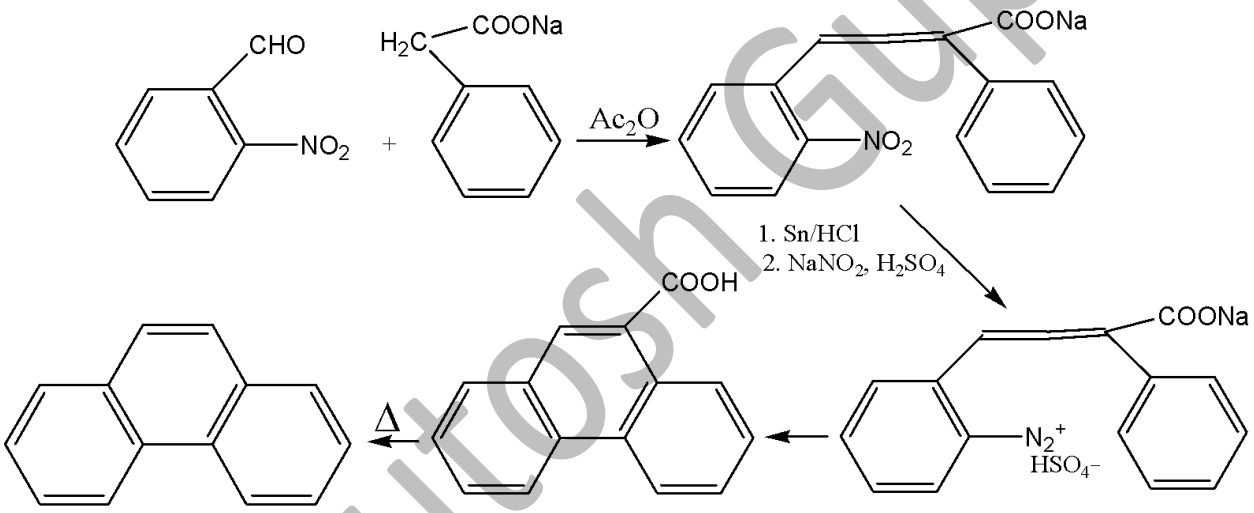
(Resonance energy (RE) of anthracene is 84 kcal/mol, i.e., 28 kcal/mol per ring)

Partial double bond character:



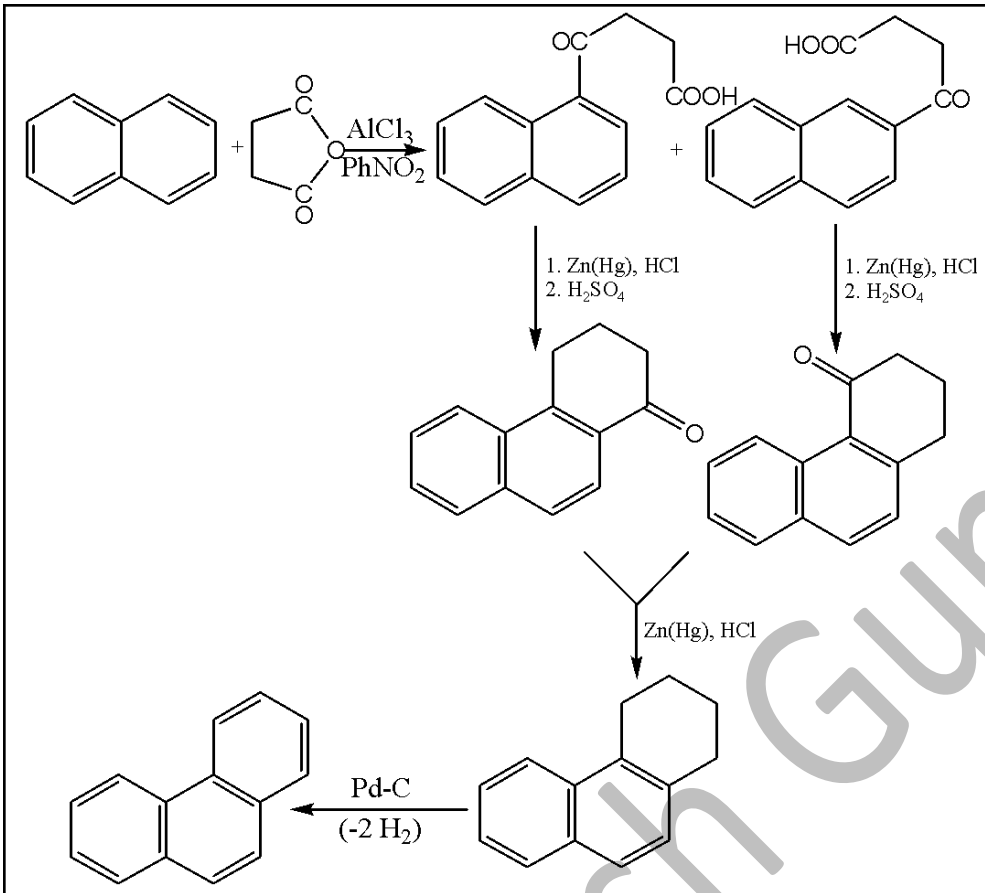
Synthesis

Pschorr's method



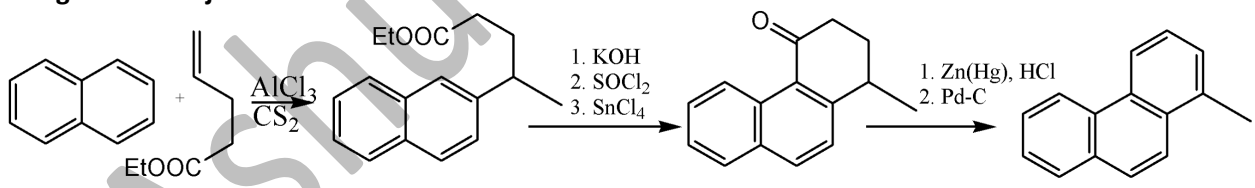
o-nitrobenzaldehyde + sodium phenylacetate [Perkin reaction] gives α-phenyl-o-nitrocinammic acid. Its reduction gives corresponding amino acid which is further diazotized. Resulting diazonium salt with Cu powder undergoes intramolecular phenylation (Gomberg's reaction) most probably via free radical intermediate to produce phenanthrene-9-carboxylic acid which on heating strongly loses carbon dioxide to give phenanthrene.

Haworth's method



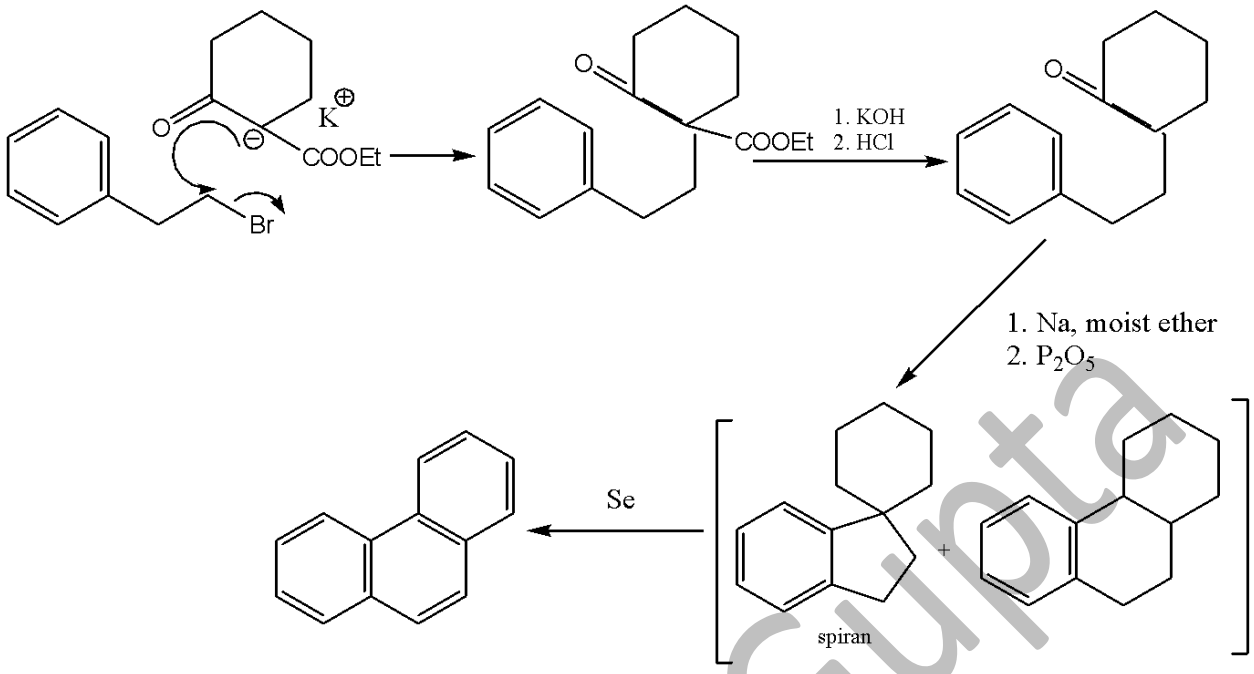
Succinoylation of naphthalene produces two isomeric keto acids: β-(1-naphthoyl) propionic acid and β-(2-naphthoyl) propionic acid. These two isomers can be readily prepared. Clemmensen reduction affords ϒ-(1-naphthyl) butyric acid and ϒ-(2-naphthyl) butyric acid, respectively. Acid-catalyzed cyclization gives 1-keto-1,2,3,4-tetrahydro- and 4-keto-1,2,3,4-tetrahydrophenanthrene. Clemmensen reduction of either isomer followed by aromatization gives phenanthrene.

Cologne-Mukherji method



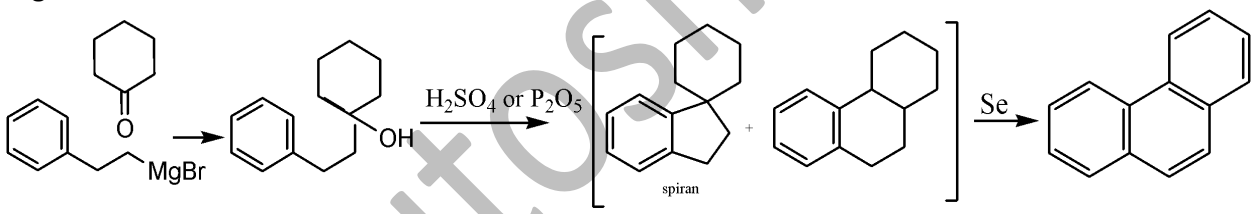
Alkylation of naphthalene with ethyl allylacetate in presence of $AlCl_3$ to give 1-methyl-phenanthrene

Bardhan-Sengupta method



Potassium salt of cyclohexanone-2-carboxylic ester (β-keto ester) treated with 2-phenylethyl bromide followed by hydrolysis and decarboxylation. The resulting ketone on reduction forms corresponding alcohol which undergoes acid-catalyzed cyclization to a mixture of octahydrophenanthrene and the corresponding spiran. This mixture is then aromatized to phenanthrene with selenium.

Bogart-Cook method



Treatment of 2-phenylethylmagnesium bromide with cyclohexanone and tertiary alcohol so produced is cyclized with H_2SO_4 (or P_2O_5) followed by aromatization.

Reactions of Phenanthrene

Like anthracene, 9,10-positions of phenanthrene are very active. The first product of catalytic or chemical reduction is 9,10-dihydro derivative. Preparation of monosubstituted phenanthrene derivatives by direct substitution is very difficult as a large number of isomers are possible.