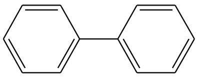
SEMESTER-VH-ORGANIC CHEMISTRY:

Polynuclear hydrocarbons and their derivatives*:*

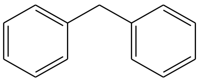
Polycyclic aromatic hydrocarbons (PAHs) are the hydrocarbons containing only carbon and hydrogen. They are composed of multiple benzenoid aromatic rings. They are also known as Polyaromatic hydrocarbons or polynuclaer aromatic hydrocarbons. PAHs are uncharged, nonpolar molecules found in coal and tar deposits. PAHs are also getting immense importance as they are one of the main reason for skin, lung, bladder, liver, and stomach cancer. Polycyclic aromatic hydrocarbons may be classified into two groups

.A) PAHS WITH ISOLATED RING SYSTEMS

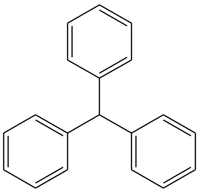
e.g. 1. Biphenyl,



2. Diphenylmethane

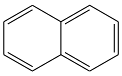


3. Triphenyl methane

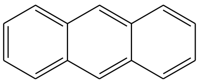


B) PAHS WITH FUSED RING SYSTEMS

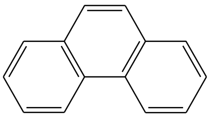
e.g. 1.Napthalene



2. Anthracene



3. Phenanthrene.



In our course, we will discuss only about fused polynuclear systems.

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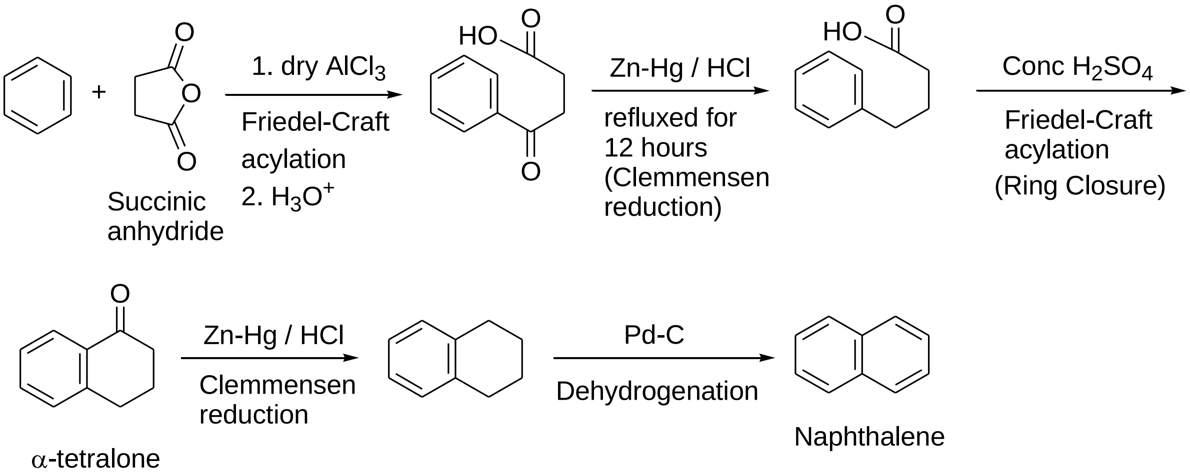
Naphthalene:

Napthalene $C_{10}H_8$ is the largest constituent of coal tar (around 9%) and it is highly volatile (m.p.80°C)

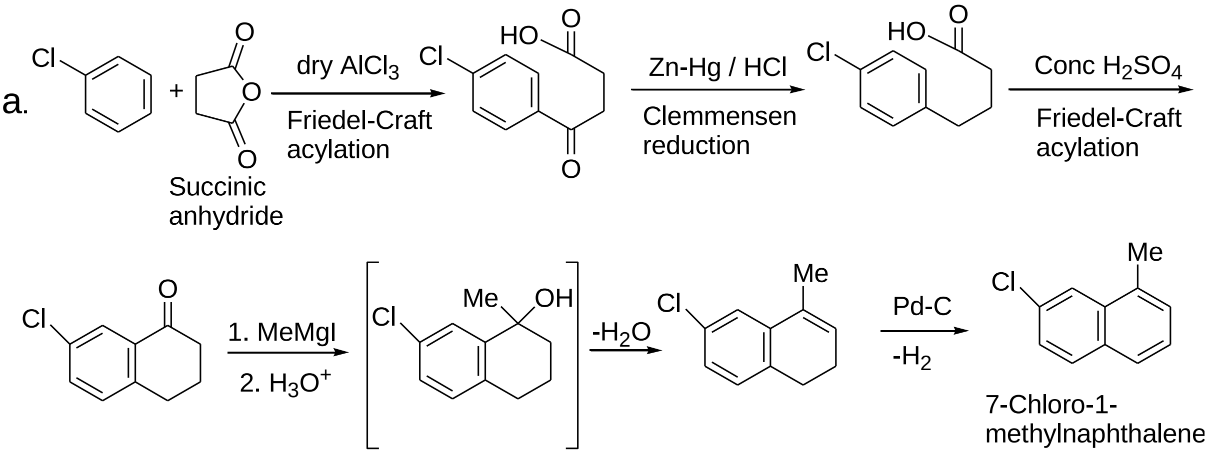
Synthesis of Naphthalene:

1) Haworth method of synthesis of naphthalene is given below.
   The synthesis starts with benzene and succinic anhydride involves the following steps.

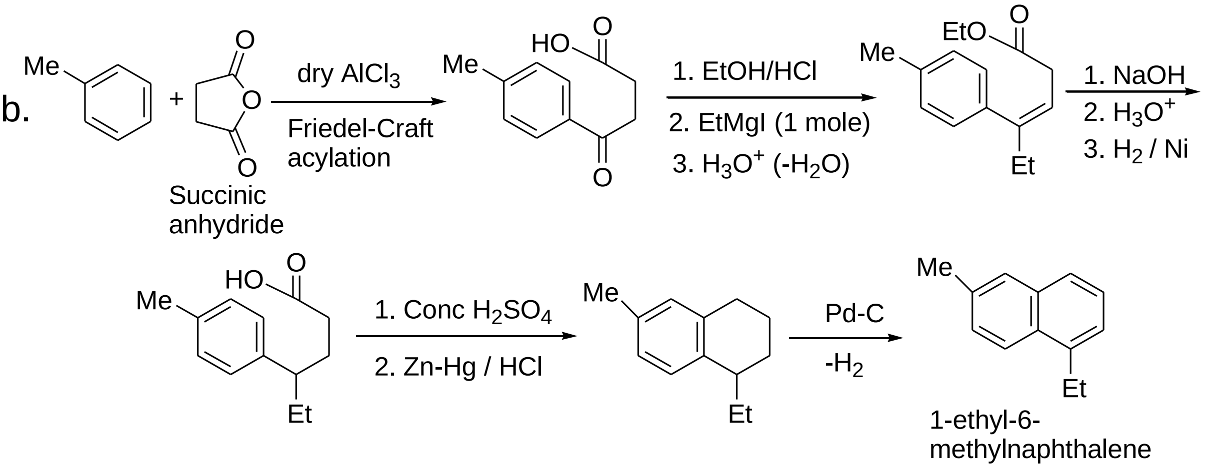


Various substituted naphthalenes are also prepared by Haworth method as shown below.

a.



b.



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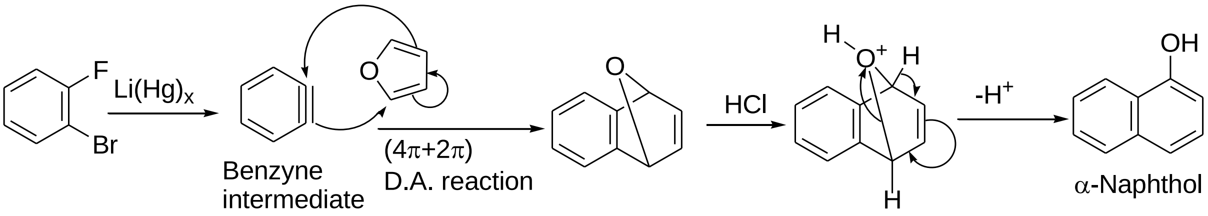
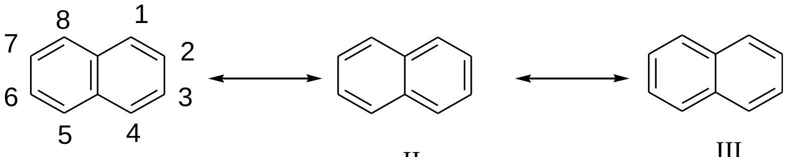
2) Synthesis of α-Naphthol by Diels-Alder reaction:



Here o-bromo fluorobenzene is treated with lithium amalgam in presence of furan. The product 1,4-epoxy-1,4-dihydronaphthalene is treated with aqueous HCl to form α-naphthol. The reaction goes via benzyne intermediate as shown above.

Position of double bonds in naphthalene (Fries rule): Naphthalene is the resonance hybrid of following three resonating structures.



I II III

Out of three canonical forms, in two forms (I and III), C_1-C_2 bond gets double bond character whereas in one structure (II) C_2-C_3 bond gets double bond character. Therefore double bond character of C_1-C_2 bond is higher than that of C_2-C_3 bond. That's why C_1-C_2 bond is shorter than C_2-C_3 bond. This concept is known as concept of '*Partial Bond Fixation*'

The most stable resonating structure of poly nuclear hydrocarbons was excellently formulated by Fries with the following rule;

'*The most stable arrangement of a polynuclear compound is that form which has the maximum number of rings in the benzenoid condition i.e. three double bonds in each individual rings.*'

Thus according to Fries rule, naphthalene tends to behave as structure I (with two benzenoid rings) rather than as structure II and III (with one benzenoid rings and one quinonoid ring). The rule is, of course, in agreement with the concept of *partial bond fixation.*

Polynuclear Hydrocarbons and Their Derivatives

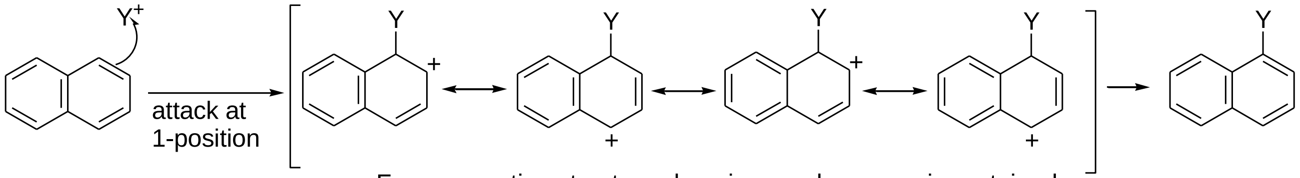
Lecture 2:

Properties of Naphthalene: Resonance energy of benzene is 150.6 kJ/mole. Since Naphthalene contains two benzene ring, it is expected that resonance energy of naphthalene would be close to (150.6 X 2) = 301.2 kJ/mole. But actually the resonance energy of naphthalene is much less (255.2 kJ/mole) due to annelation. That's why naphthalene is less aromatic and hence more reactive than benzene.

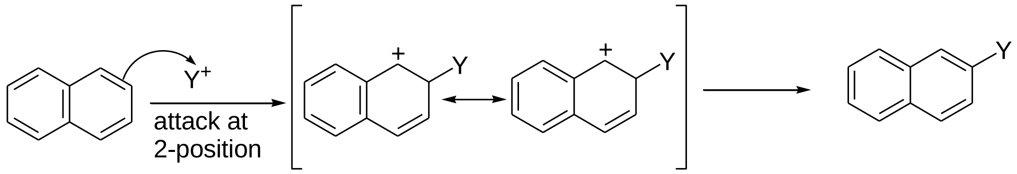
The phenonmenon, whereby some rings in fused systems give up part of their aromaticity to the adjacent rings, is called annelation.

Reactions of Naphthalene:

Substitution products of naphthalene: In general naphthalene gives 1-substituted naphthalene on electrophilic substitution reaction. This is because the intermediate carbocation obtained during substitution at 1 position is more stable than that of 2 position due to larger number of resonating structure as shown below.



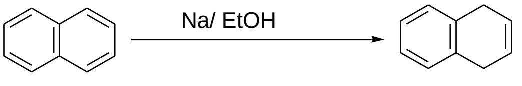
Four resonating structures keeping one benzene ring retained



Two resonating structures keeping one benzene ring retained

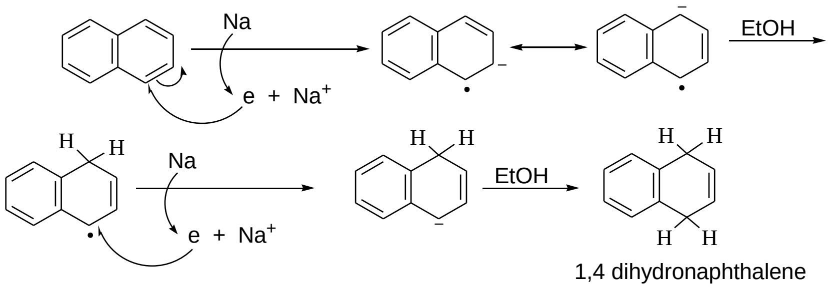
Thus the carbocation intermediate formed during attack at 1-position is more stable than that of 2-position

Reduction: In contrast to benzene, naphthalene is more susceptible to reduction as the loss of resonance energy is less than that of benzene. Naphthalene on reflux with Na/EtOH gives 1, 4 dihydronaphthalene.



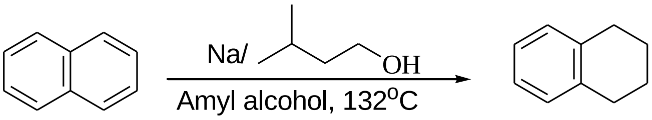
1,4 dihydronaphthalene

Mechanism:



1,4 dihydronaphthalene

Naphthalene can be reduced to 1,2,3,4 tetrahydronaphthalene (tetralin) by carrying the reaction with sodium and alcohol at higher temperature. Amyl alcohol having boiling point 132°C is generally used. The reaction goes via 1,4 dihydronaphthalene intermediate product.



Tetralin

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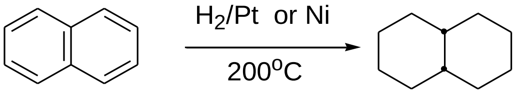
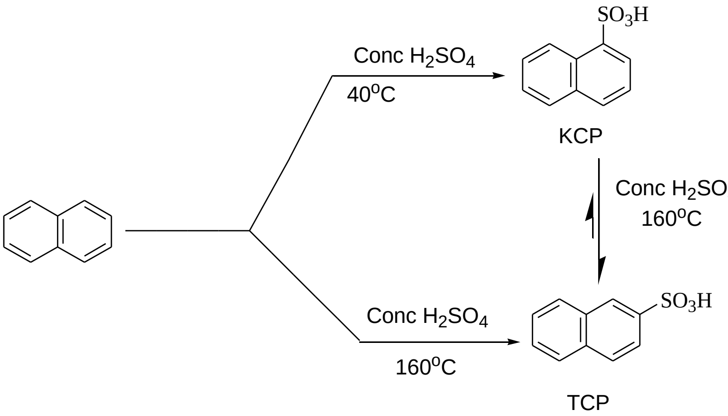
Naphthalene can also be reduced to Decalin by changing the reagent.



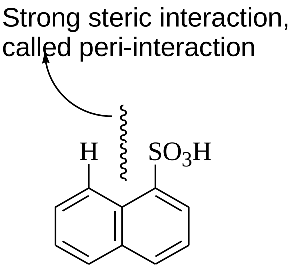
Decalin

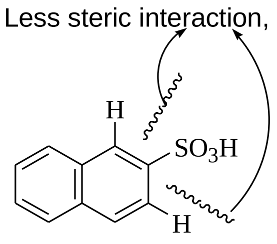
Reactions of Naphthalene:

1. **Sulphonation of naphthalene:** Sulphonation of naphthalene is very important in chemistry. Napthols are prepared from napthyl sulphonic acid. During sulphonation of naphthalene we have following two observations.



- Sulphonation is reversible.
- According to stability of intermediate, attack at 1 or α position is more favourable than position 2 / β attack. So α-napthyl sulphonic acid is KCP.
- 1-napthyl acid is sterically more hindered or congested and therefore less stable than 2 / β napthyl sulphonic acid, as the bulky SO_3H group is within the van-der-Waals radius of C8 Hydrogen. So, β -napthyl sulphonic acid is TCP. (The concept of KCP and TCP was discussed in 3rd SEM)





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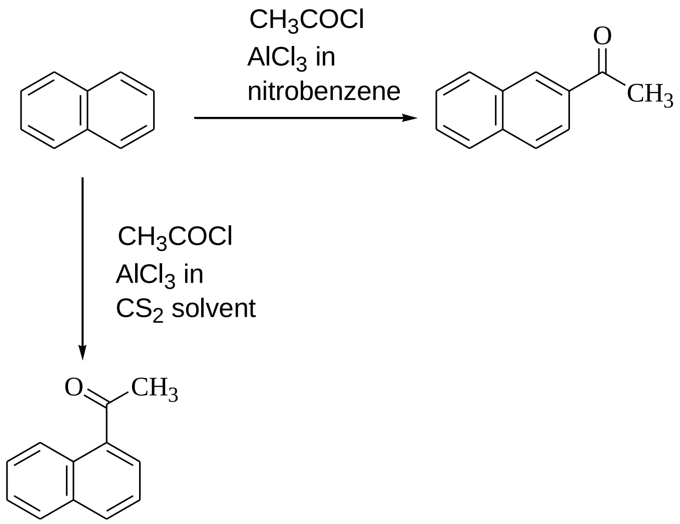
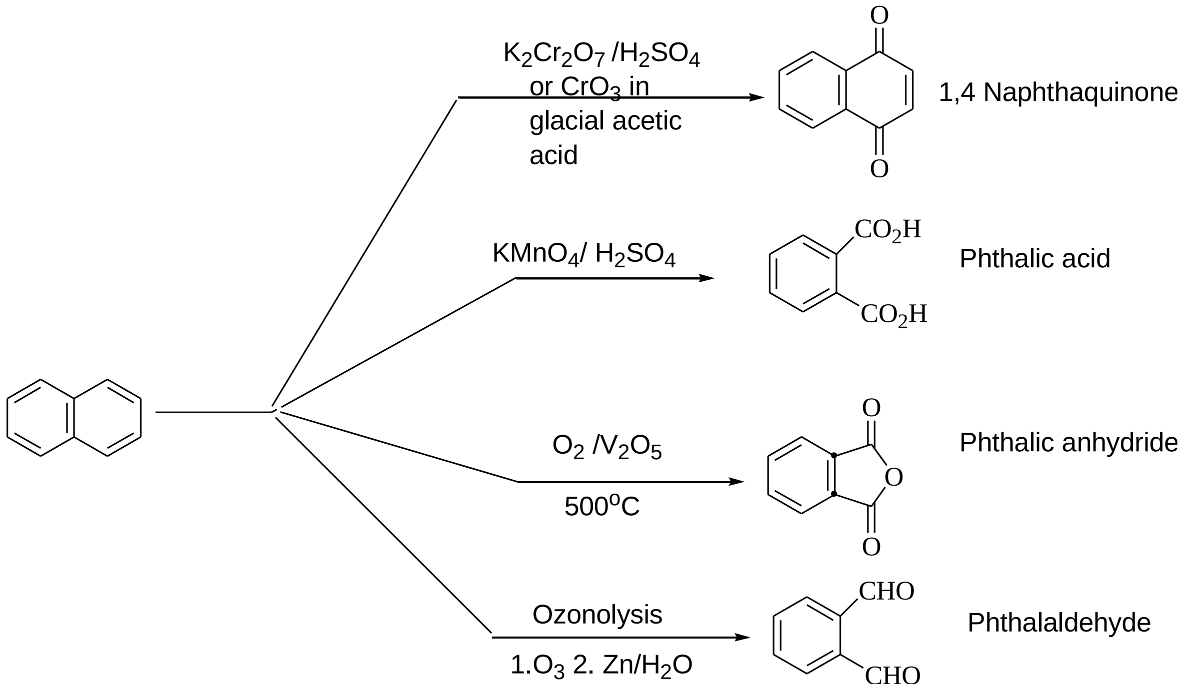
Polynuclear Hydrocarbons and Their Derivatives

Lecture 3: Reactions of Naphthalene:

2. Acetylation of naphthalene: In case of acetylation of naphthalene solvent effect is very crucial. The reaction is believed to proceed mainly via formation of acetylium ion which is stabilized by sovent. Nitrobenzene is more polar than CS_2. Stabilization through Acetylium ion-solvent complex formation is difficult in α position due to steric effect. So β-product is formed in more polar and bulky solvent nitrobenzene whereas α-product is formed in nonpolar CS_2 solvent.



3. Oxidation of Napthalene: Depending on reaction condition different oxidation products can be obtained.



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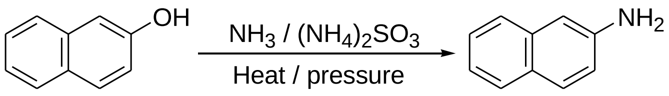
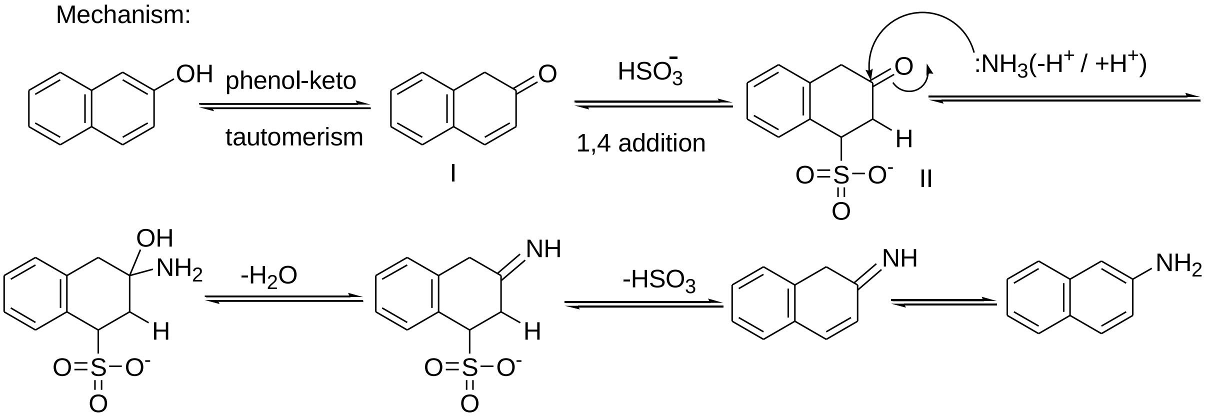
4. Bucherer reaction: When *β*-naphthol is treated with NH_3 and $NaHSO_3/(NH_4)_2SO_3$ under pressure, we get *β*-naphthylamine.

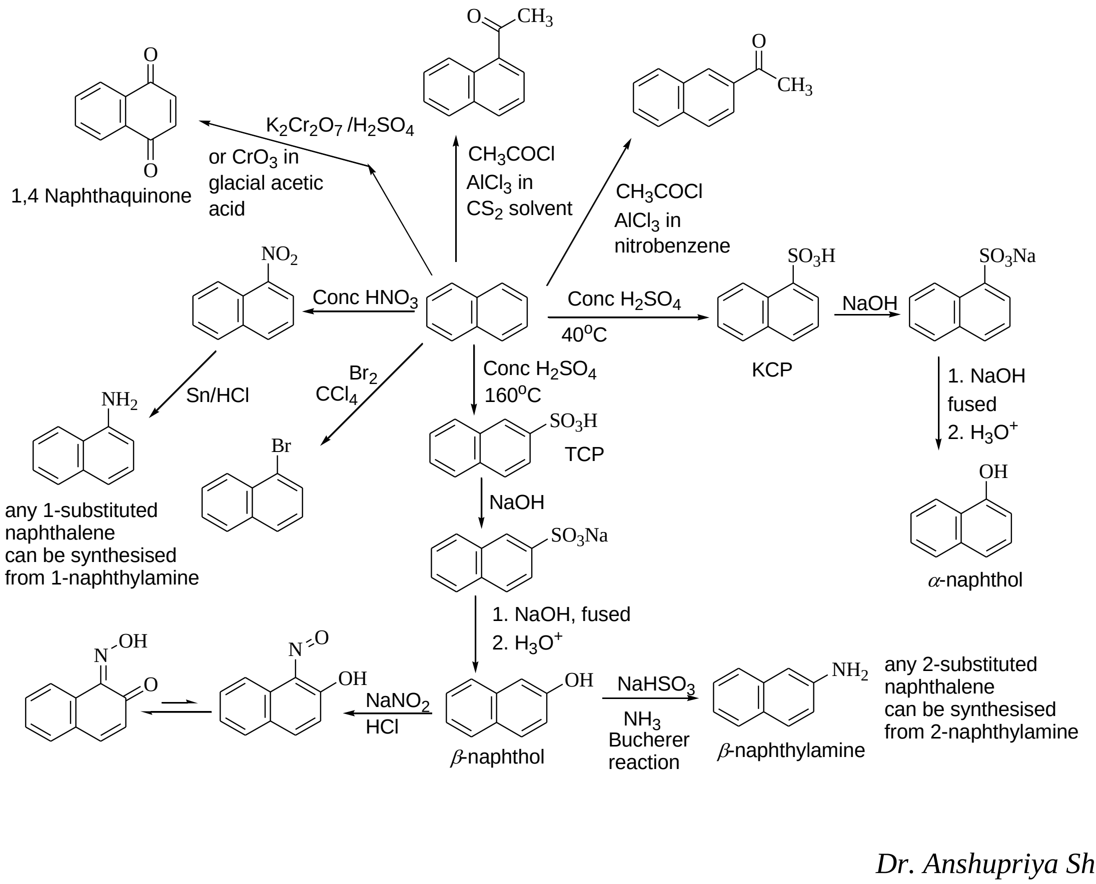


Mechanism:



phenol-keto tautomerism takes place as the resonance energy of naphthalene is less than benzene. After tautomerism, the reactant becomes an αβ unsaturated carbonyl compound (I) which undergoes 1,4 addition reaction with HSO_3^-. This reaction effectively gives 3,4, addition pdoruct (II)

Reactions and conversion of Naphthalene:



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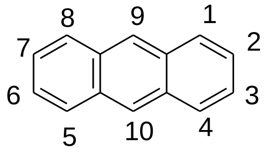
Polynuclear Hydrocarbons and Their Derivatives

Lecture 4:

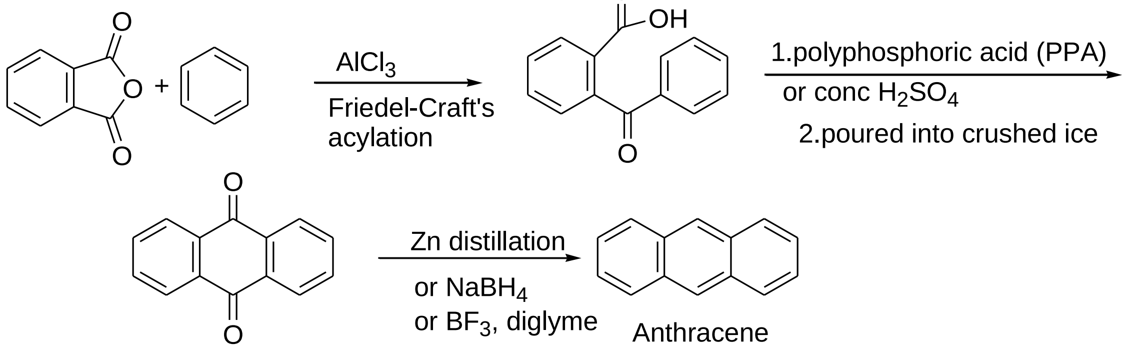
Anthracene



Anthrecene with position numbering

Synthesis of Anthracene:

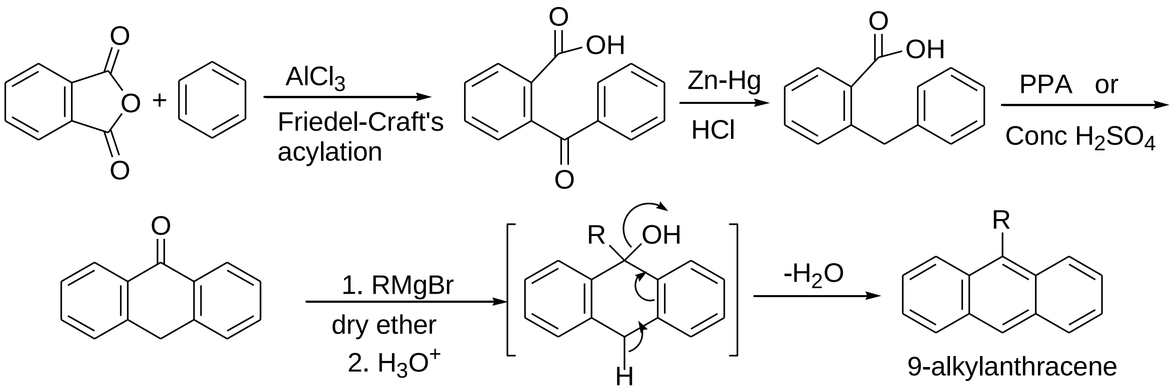
1. Haworth synthesis (Using Friedel- Crafts Acylation):



9,10 anthraquinone

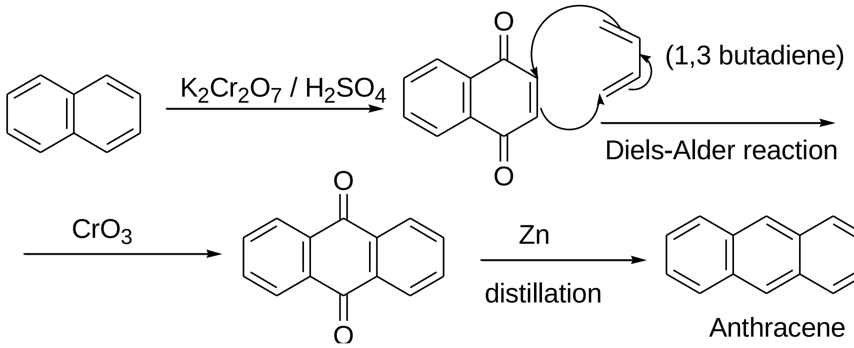
Anthracene

2. Synthesis of 9-alkylanthracene

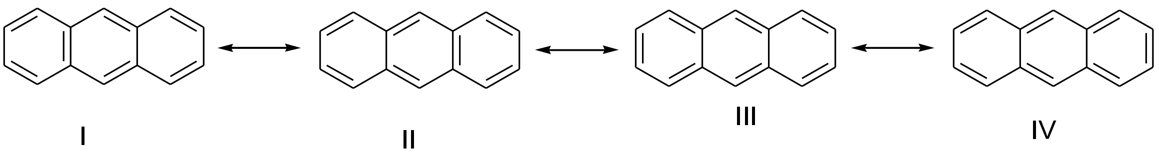


9-alkylanthracene

3. Anthracene from naphthalene via Diels-Alder reaction



Resonating structure of anthracene:

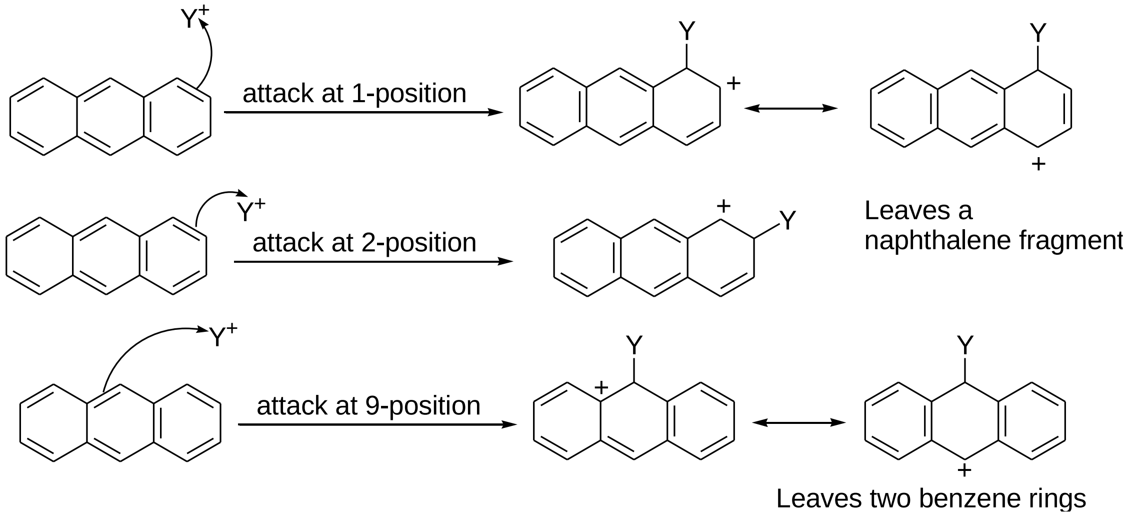


Resonance energy is 351.5 kJ / mole

According to Fries rule the most stable structures are I and II since both of the structure has two benzenoid rings. Structure III and IV has one benzenoid ring each. Again, out of four structures in three structures C_1-C_2 bond gets double bond character whereas C_2-C_3 bond gets double bond character in only one structure. Thus C_1-C_2 bond has more double bond character than C_2-C_3 bond and hence C_1-C_2 bond is shorter than C_2-C_3 bond.

Reactions of anthracene:

Anthracene is very reactive in the 9, 10 position. Electrophilic reaction to form a σ complex at 1 or 2 position leave a naphthalene fragment with the loss of resonance energy (351.5-255.2)=96.3 kJ / mole whereas σ complex formed from the attack at 9 position leaves two benzene rings intact, and so the loss of resonance energy is (351.5-150.6X2) = 50.3 kJ / mole. Thus the loss of resonance energy is less during the attack at 9 position than that of 1 or 2 position. That's why anthracene is very reactive at 9, 10 position.



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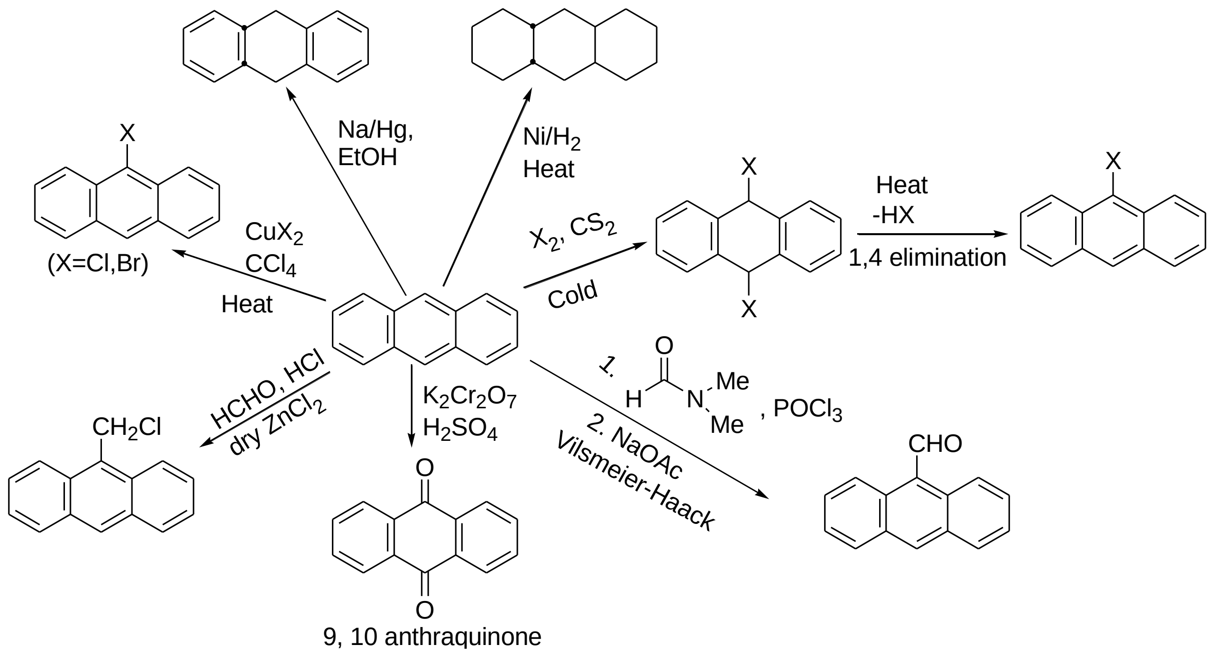
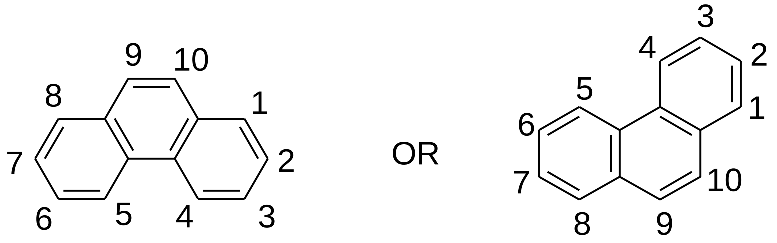
Some reactions are given below.



During halogenations under cold condition, anthracene adds to halogen to give 9, 10 adduct (1,4 addition mechanism) which on warming eliminates HX (1,4 elimination mechanism) to give 9 substituted product. Direct halogenations takes place at 9 position when anthracene is heated with cupric halide in CCl_4 solvent.

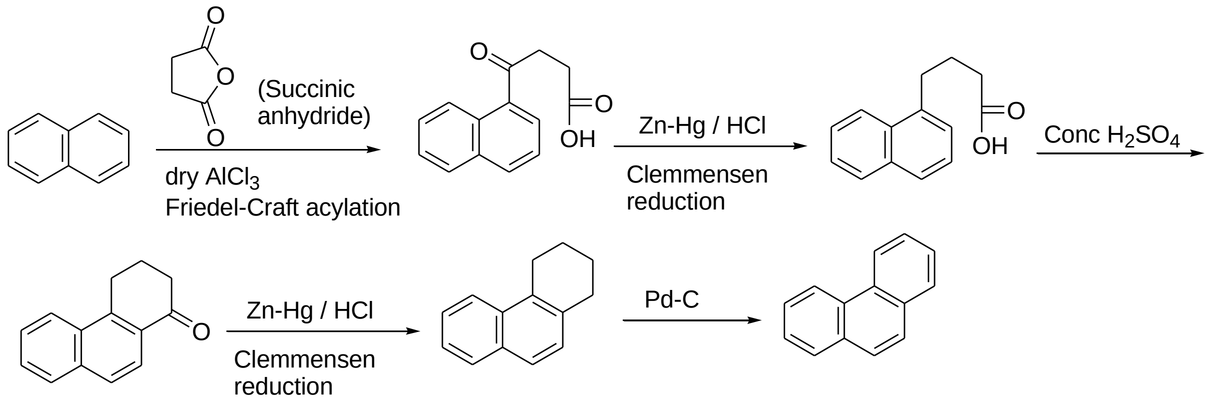
Phenanthrene



Structure with numbering the positions

Synthesis:

1. **Haworth synthesis**



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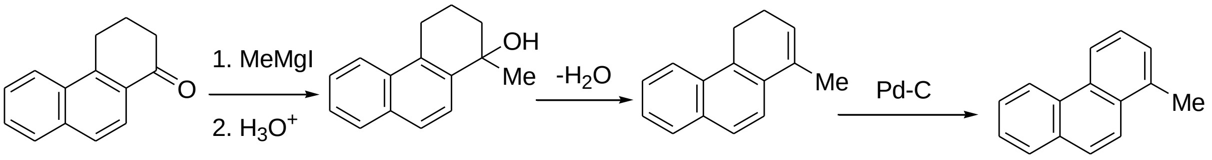
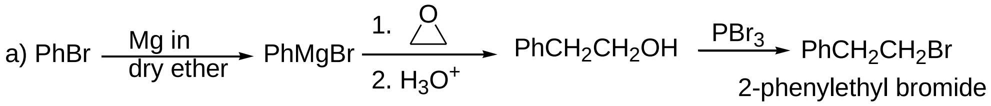
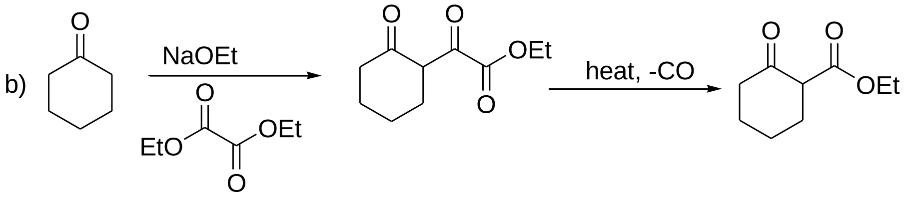
1) 1-alkyl phenanthrene can be synthesised following the same reaction pathway as shown below.

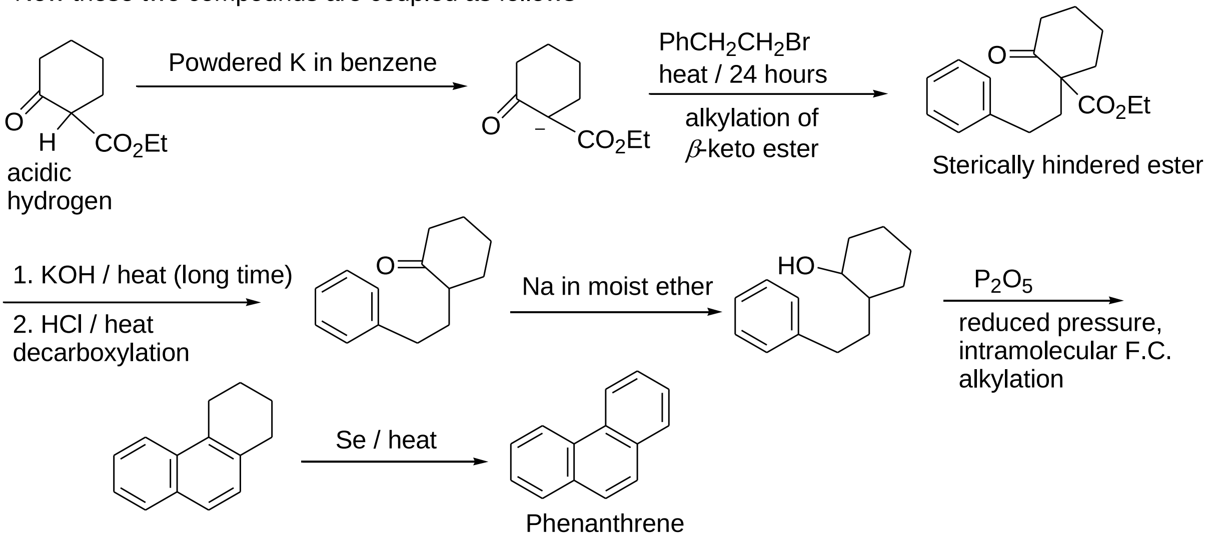


2) **Bardhan-Sengupta Synthesis**:





Now these two compounds are coupled as follows



Limitations:

1. In the above process the hydrolysis of the intermediate β-ketoester was found to be too slow with low yields of the product β-ketoacid. To avoid this hydrolysis the reaction was modified as shown below.

2 In Bardhan-Sengupta synthesis there is a regioselectivity problem. During cyclisation via acid catalysed intramolecular alkylation it gives the following by-product

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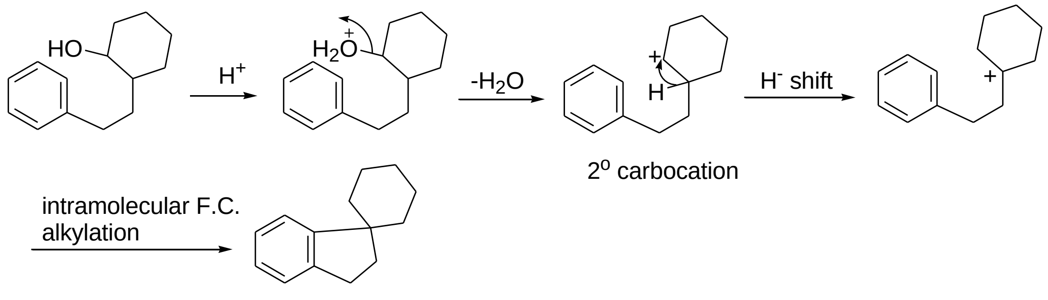
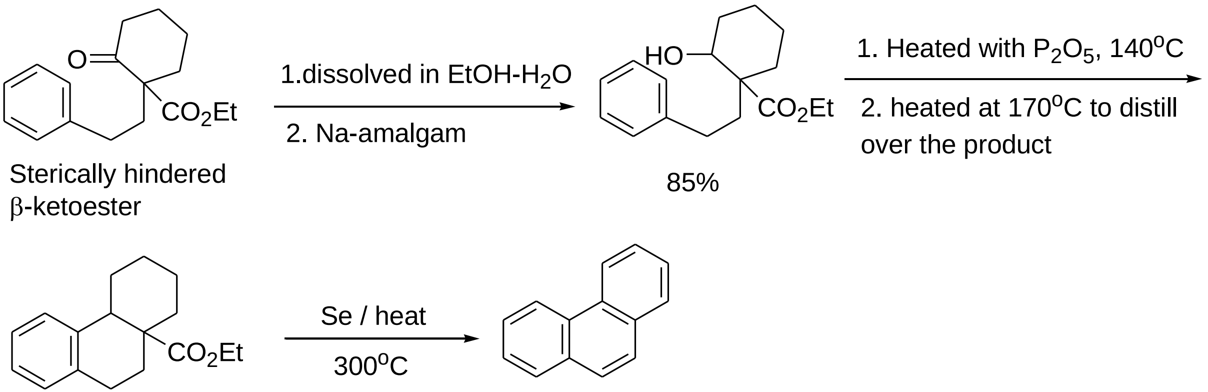


2° carbocation

Spiro compound

Modifications:

To avoid this rearrangement, by-product and low yield we have to follow the modified route of the synthesis.

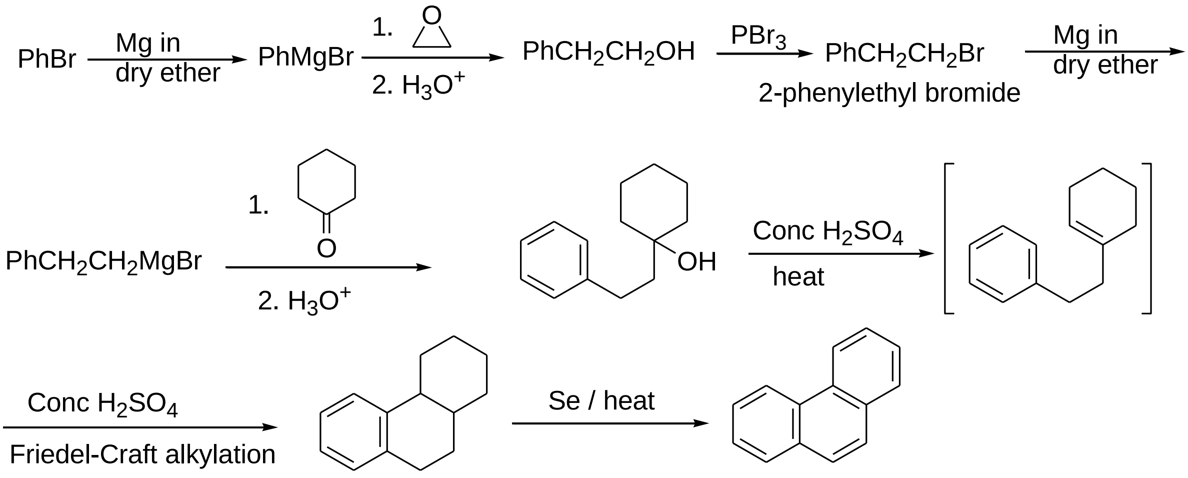


Sterically hindered
β-ketoester

85%

Phenanthrene

3) **Bogert-Cook Synthesis**:



2-phenylethyl bromide

Phenanthrene

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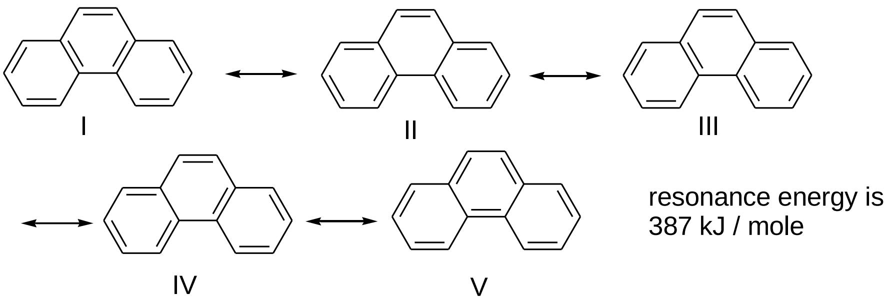
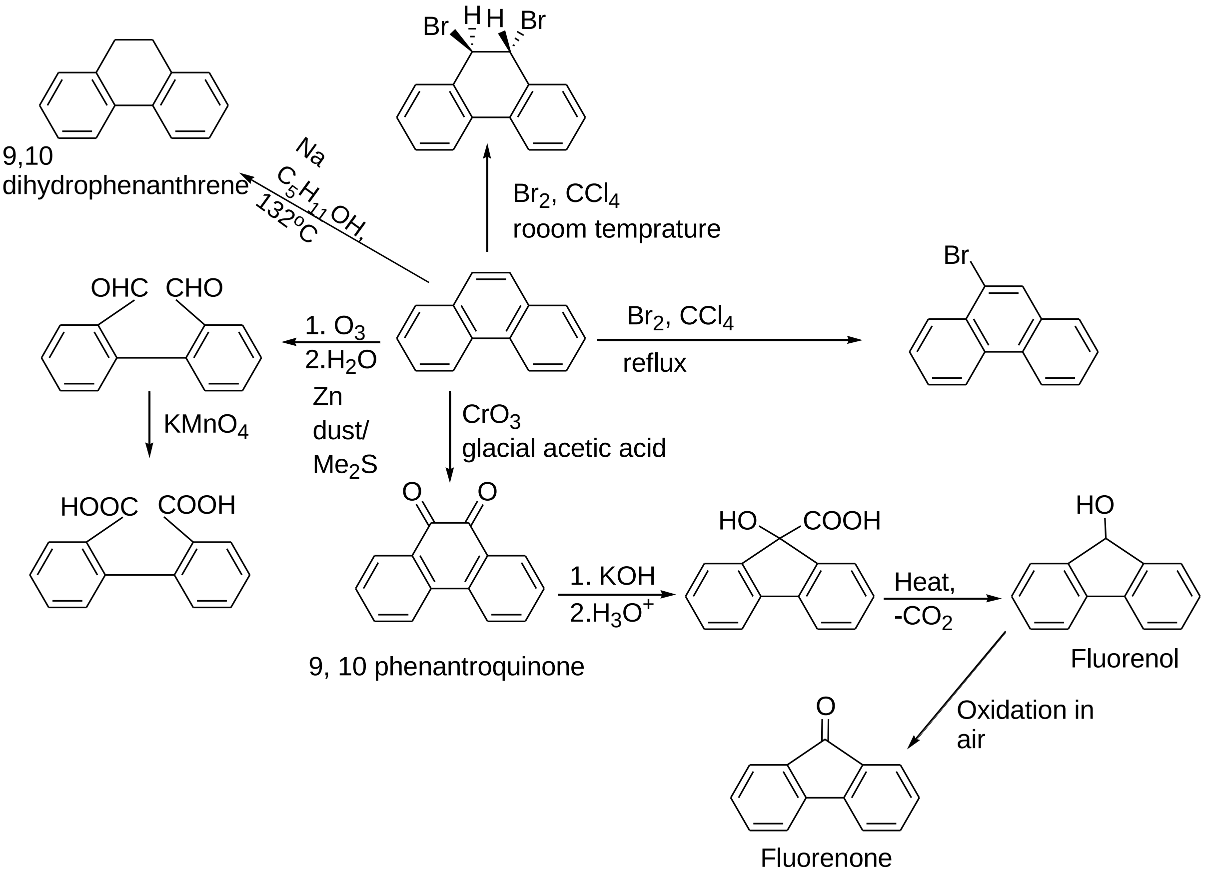
Resonating structures:



Since structure (I) has all the three rings benzenoid, structure (I) is most stable structure. Again, C_9-C_{10} has the highest double bond character and hence shortest among the all the bonds.

Reactions of phenanthrene: Like anthracene, phenanthrene is also reactive at 9, 10 position. Electrophilic reaction to form a σ complex at 1 or 2 position leave a naphthalene fragment with the loss of resonance energy (387-255.2)=131.8 kJ / mole whereas σ complex formed from the attack at 9 or 10 position leaves two benzene rings intact, and so the loss of resonance energy is (387-150.6X2) = 85.8 kJ / mole. Thus the loss of resonance energy is less during the attack at 9 or 10 positions than that of 1 or 2 positions. That's why phenanthrene is reactive at 9, 10 position.



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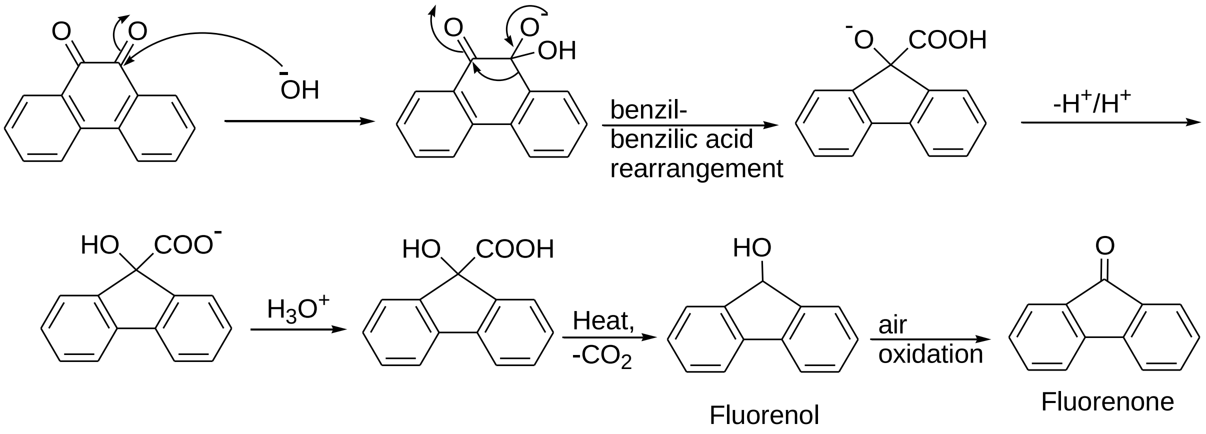
Synthesis of fluorenone: When 9,10 phenanthraquinone is heated with ethanolic KOH, it undergoes benzilic acid rearrangement to form 9-hydroxyfluorene-9-carboxylic acid which on heating in air, eliminates CO_2 followed by oxidation to form flluorenone.



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