Polynuclear Aromatic Compounds

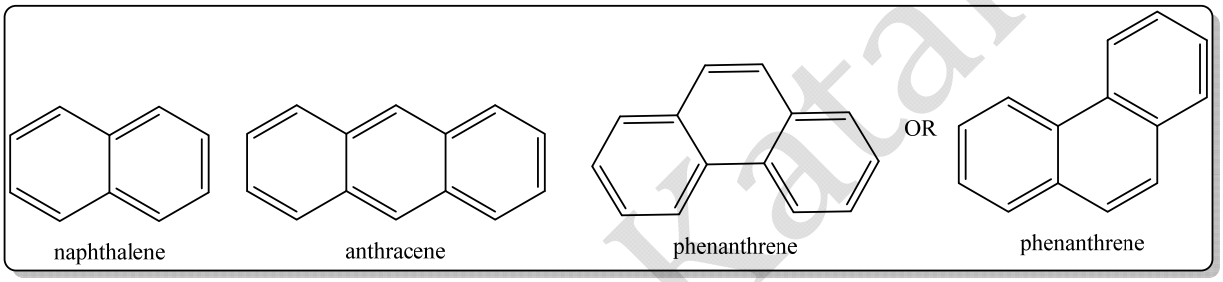
For T. Y. B. Sc. (Sem-VI)

US06CCHE01

By Dr Vipul Kataria

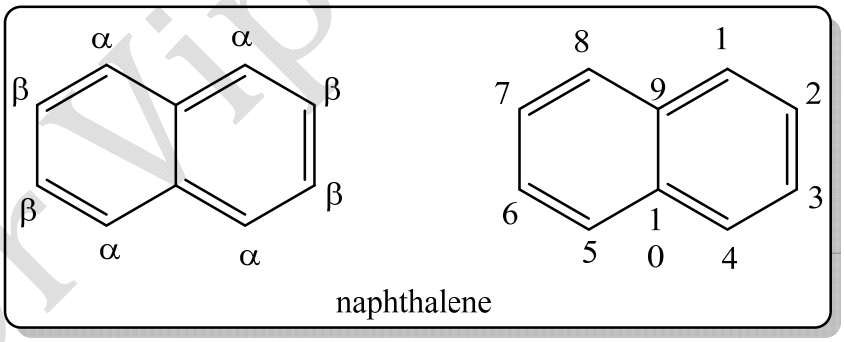
❖ Introduction

Aromatic compounds containing more than one benzene ring are referred as **polynuclear aromatic compounds**. Naphthalene, Anthracene and phenanthrene are the examples of polynuclear aromatic compounds.

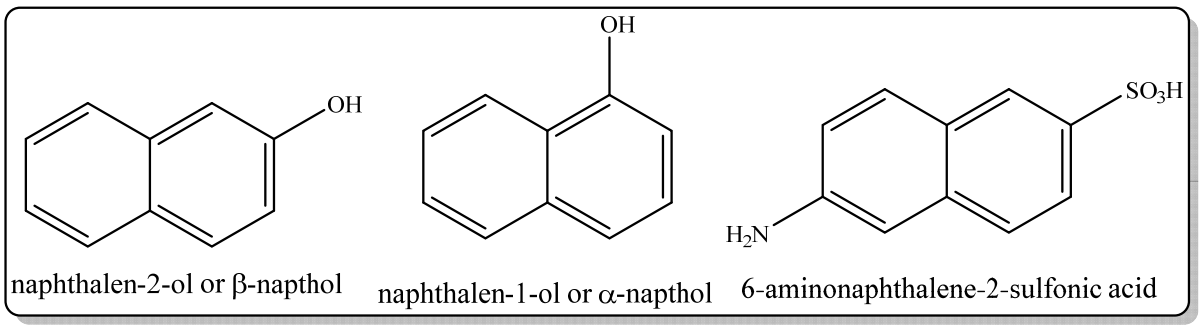


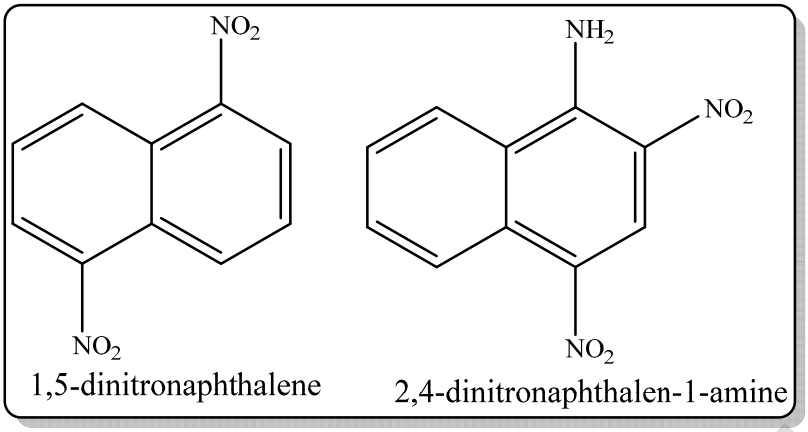
Nomenclature of naphthalene derivatives

A common nomenclature if only one substituent is on the naphthalene ring system involves the use of **alpha and beta**, in more than one substituents **number system** can be used.



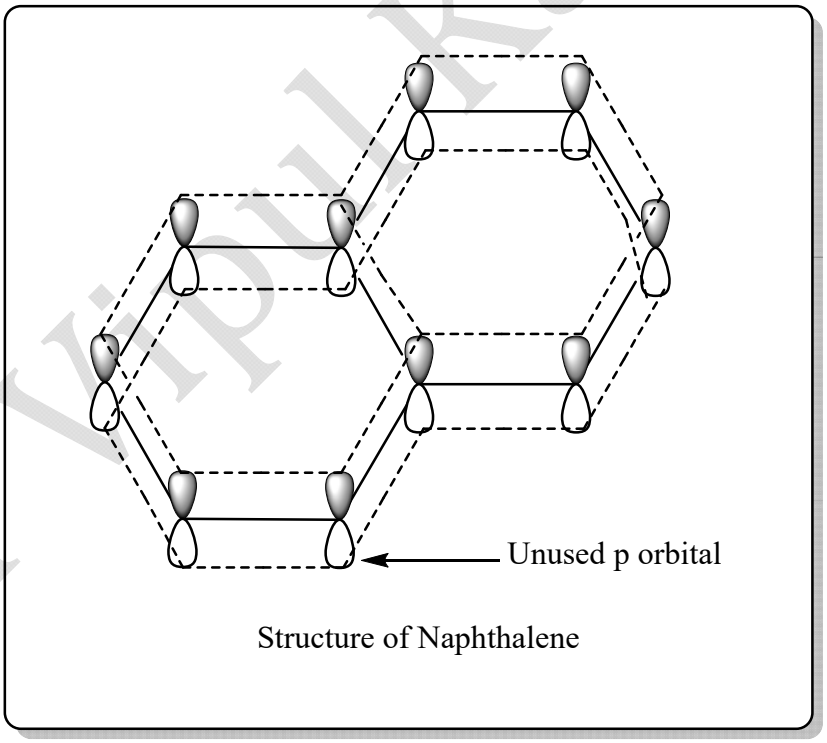
Examples





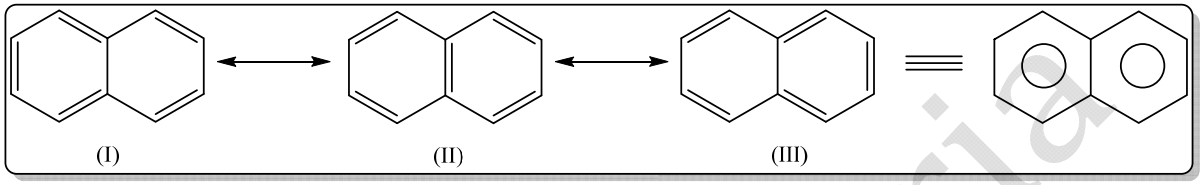
❖ **Structure of Naphthalene**

- Naphthalene is **aromatic** in nature.
- Naphthalene contains **ten carbons** and each carbon has an **unused *p* orbital**.
- *p* orbital of each carbon overlaps with next carbon atom to form **continuous π molecule orbitals**.



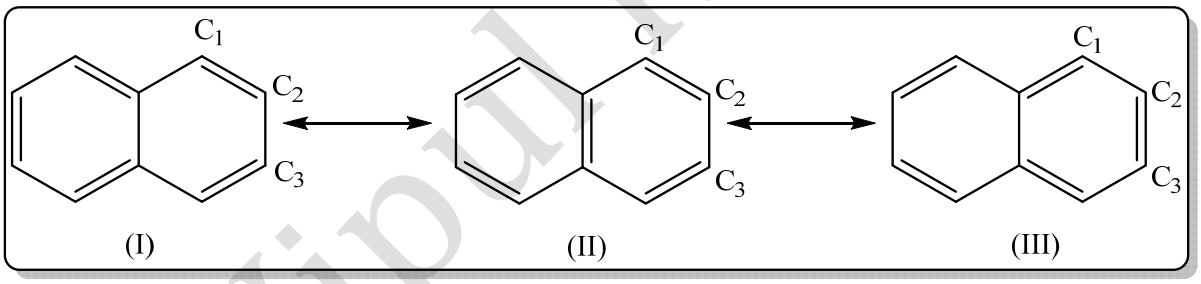
- The π electron cloud contains **ten electrons**.
- Each carbon is attached to **three other atoms** (two carbons and one hydrogen) by **σ bond**.
- This σ bond formed by overlapping of **trigonal sp^2 orbital**.

- Naphthalene contains **10 π electrons** and π cloud above and below of the naphthalene ring.
- The number of π electrons is in agreement with the **huckle rule of aromaticity** so that naphthalene is aromatic in nature.
- Naphthalene cannot be represented with **one structure** however it is represented as **resonance hybrid of three structures**.



❖ **All C-C bonds are not identical in naphthalene**

- In naphthalene, all C-C bonds are **not identical** (as in case of benzene where all C-C bonds are equal).
- In naphthalene, **C_1-C_2 bond is 1.36 Å** whereas **C_2-C_3 bond is 1.40 Å** long.
- This can be explained by following **resonance structures**.

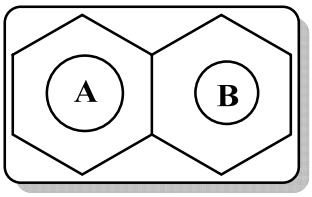


- From above structure, we can see that **structures (I & II)** have **double bond between C_1-C_2**.
- We can also see that **structure III** has not **double bond** between **C_1-C_2**.
- Thus, **two structures (I & II)** having double bond between C_1-C_2 has **shorter bond length** than the structure III.
- Similarly, **structures (I & II)** have **single bond** between **C_2-C_3**, whereas **structure III** has **double bond** between **C_2-C_3**.
- Thus, **structures (I & II)** have **longer bond length** for **C_2-C_3** as compare to structure III.
- It is also been seen that **structures (I & II)** have more **double bond character (66 %)** for **C_1-C_2** and more **single bond character for C_2-C_3**.
- Thus, **C_1-C_2 bond is smaller than C_2-C_3 bond in naphthalene**.

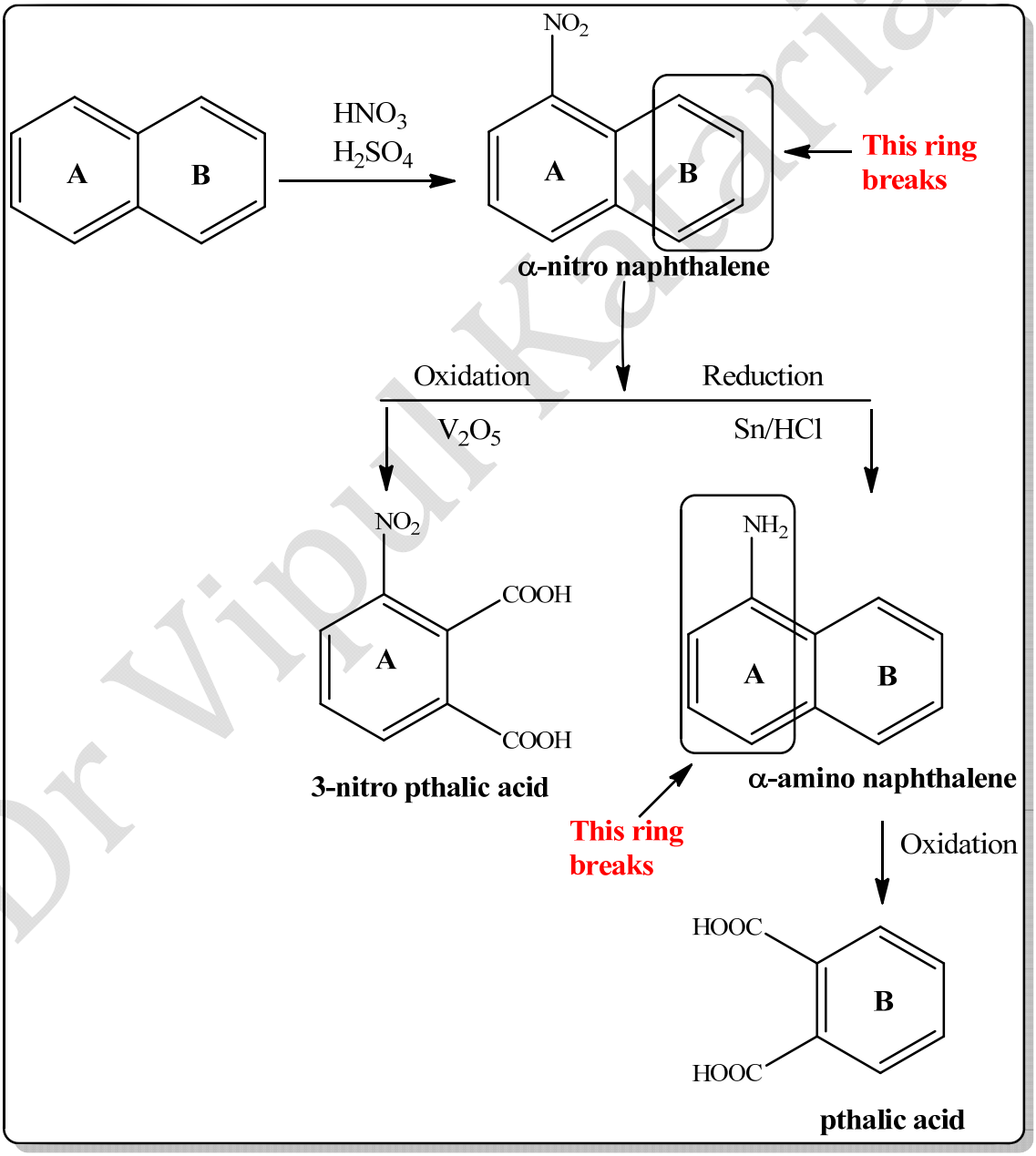
❖ **Prove that naphthalene contains two identical benzene rings**

➢ Naphthalene contains **two benzene rings**.

➢ For the sake of understanding, let us name the rings as A and B



➢ Let us consider nitration of naphthalene.

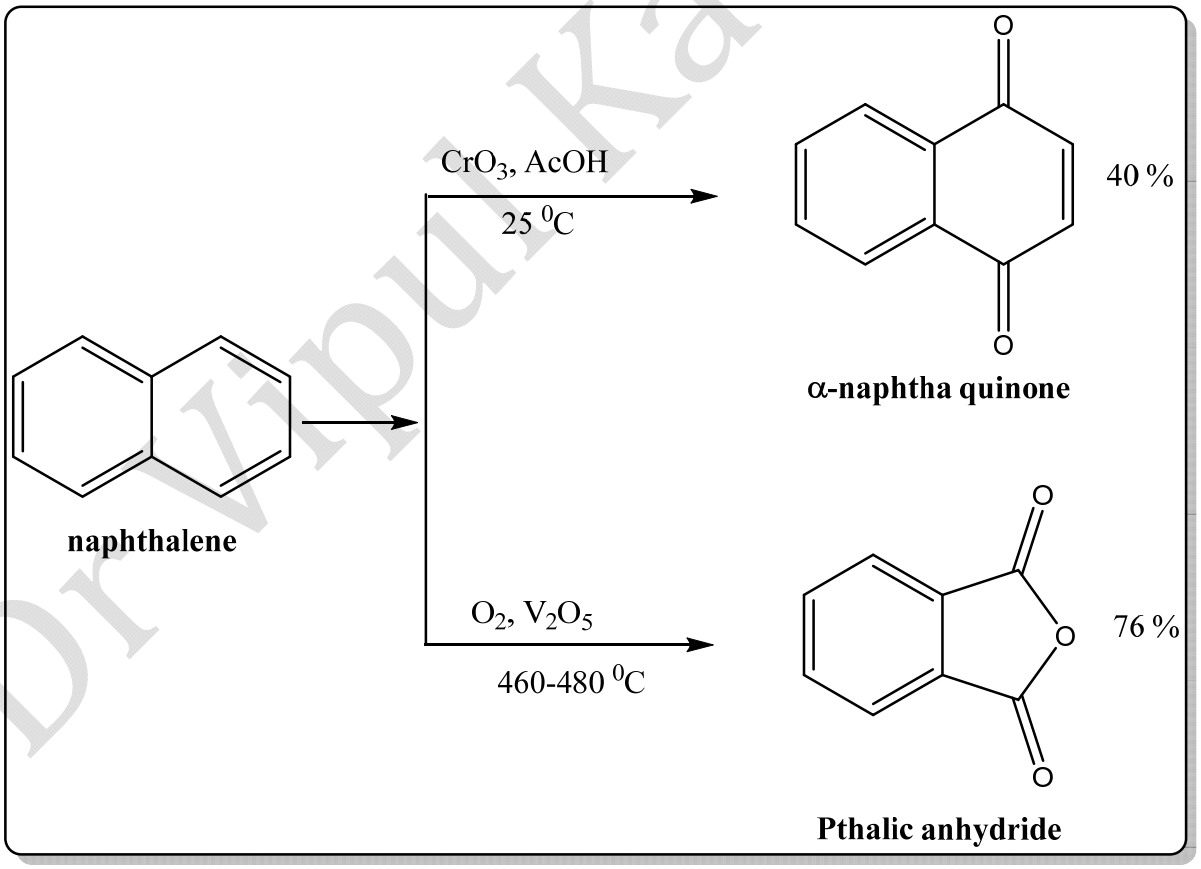


➢ Now, from the above reaction we can see that upon nitration naphthalene gives **α-nitro naphthalene**.

- α-nitro naphthalene upon oxidation gives **3-nitro pthalic acid (in which ring A remain unchanged)**. The ring containing NO_2 group is **resistant to oxidation** due to **electron withdrawing effect** of nitro group making the ring deactivated.
- α-nitro naphthalene upon reduction gives **α-amino naphthalene** which on further oxidation gives **pthalic acid (in which ring B remain unchanged)**. The ring containing NH_2 group completely oxidised to pthalic acid as **electron donating effect of NH_2** group making this ring more activating.
- In both the cases, we get **same product** (3-nitro naphthalene can be converted to pthalic acid indirectly) so we can say that both the rings are equivalent fused together.

❖ **Oxidation of Naphthalene**

- The oxidation reaction can be proposed as below.

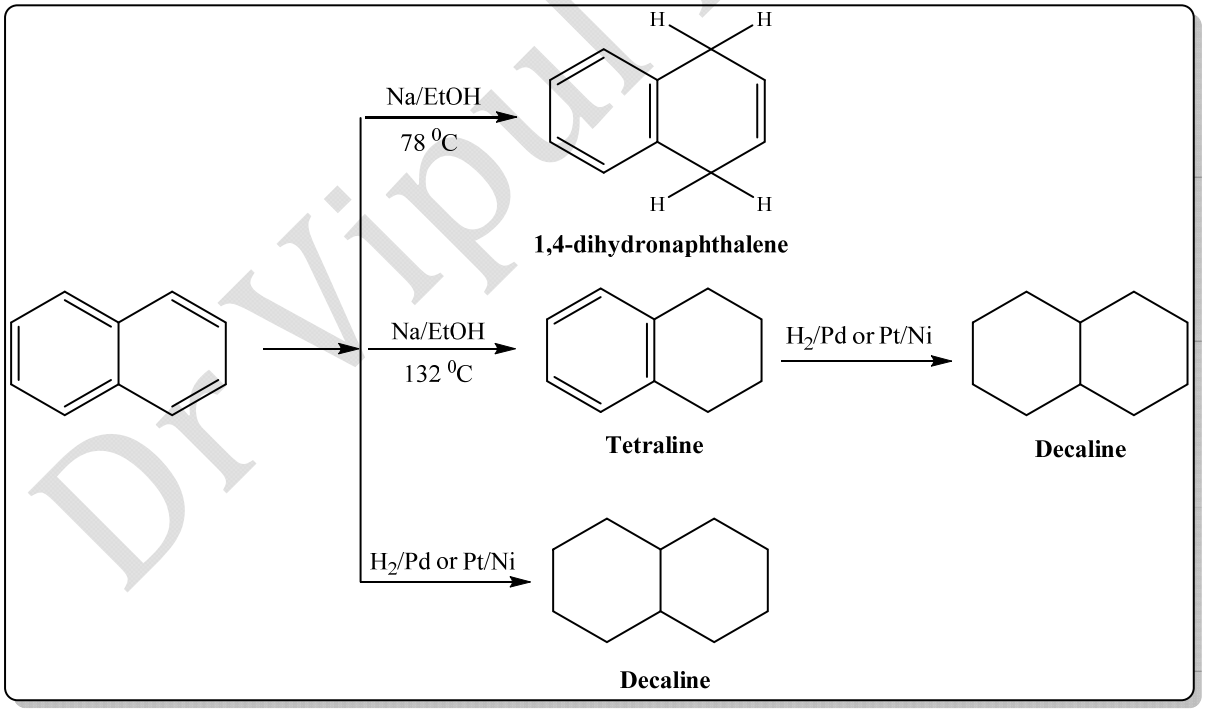


- Upon examination of above reaction we can see that in both the conditions **only one ring oxidised**.

- This is due to **resonance energy**. Upon oxidation the first ring oxidised and sacrificed **25 K Cal/mole** whereas oxidation of second ring requires further **36 K Cal/mole** that cannot be provided.
- Thus total resonance energy for both the rings is **61 K Cal/mole**.
- This indicates that **first substitution is very easy** but second substitution requires vigorous conditions (due to extra 36 K Cal/mole).
- Naphthalene undergoes oxidation or reduction more easily than benzene due to **high resonance energy**. (benzene 36 K Cal/mole; naphthalene 61 K Cal/mole)
- Naphthalene on mild oxidation (CrO_3, AcOH, 25 ˚C) gives **α-neptha quinone**.
- Naphthalene on vigorous oxidation (O_2, V_2O_5, 460 – 480 ˚C) gives **phthalic anhydride**.

❖ **Reduction of Naphthalene**

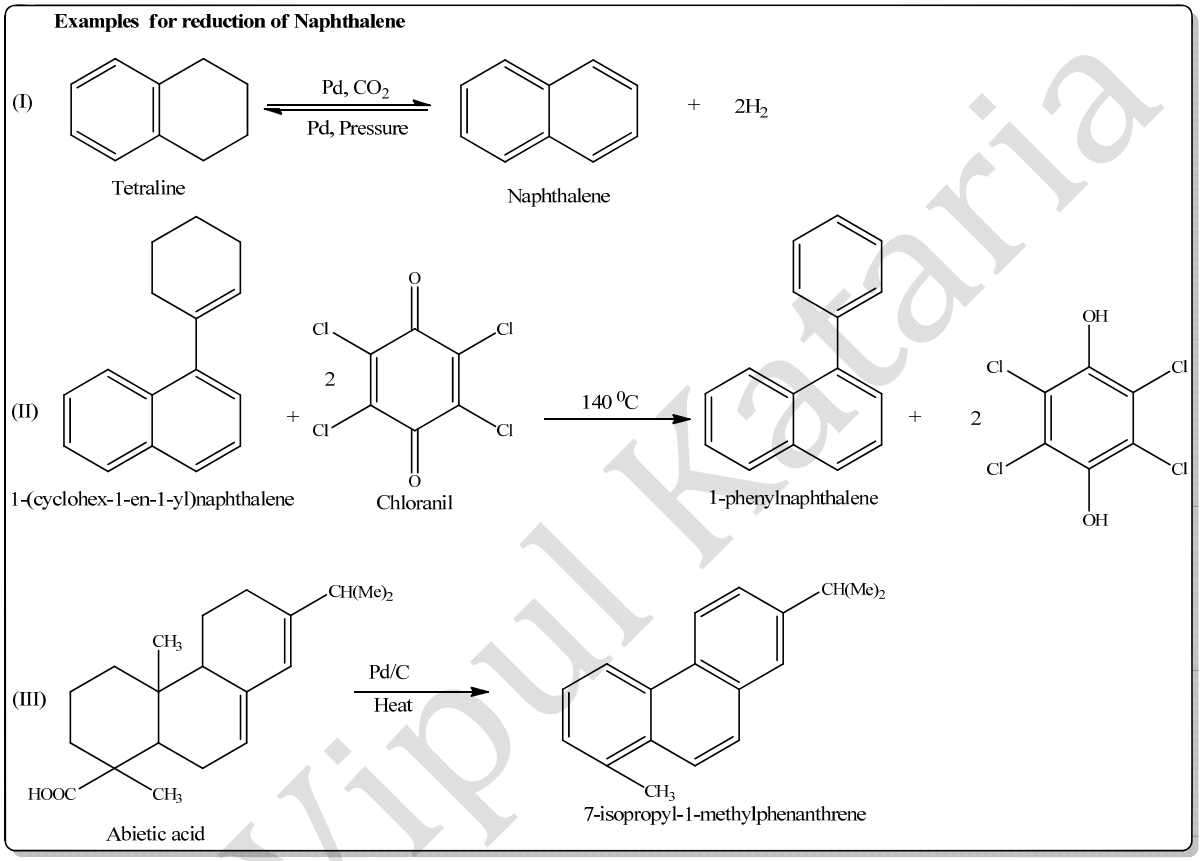
- Naphthalene undergoes **stepwise reduction reaction**.
- It can be reduced by **Na & EtOH at 78 ˚C** to give **1,4 dihydro naphthalene** and at **132 ˚C** to give **1,2,3,4-tetrahydro naphthalene (Tetraline)**.



- Tetraline on further reduction with **H_2/Pd or Pt/Ni** gives **decaline**.
- Naphthalene on direct reduction **H_2/Pd or Pt/Ni** gives **decaline**.
- Thus, reduction of naphthalene dependent upon **reducing agent and temperature**.

❖ **Dehydrogenation of hydro aromatic compounds**

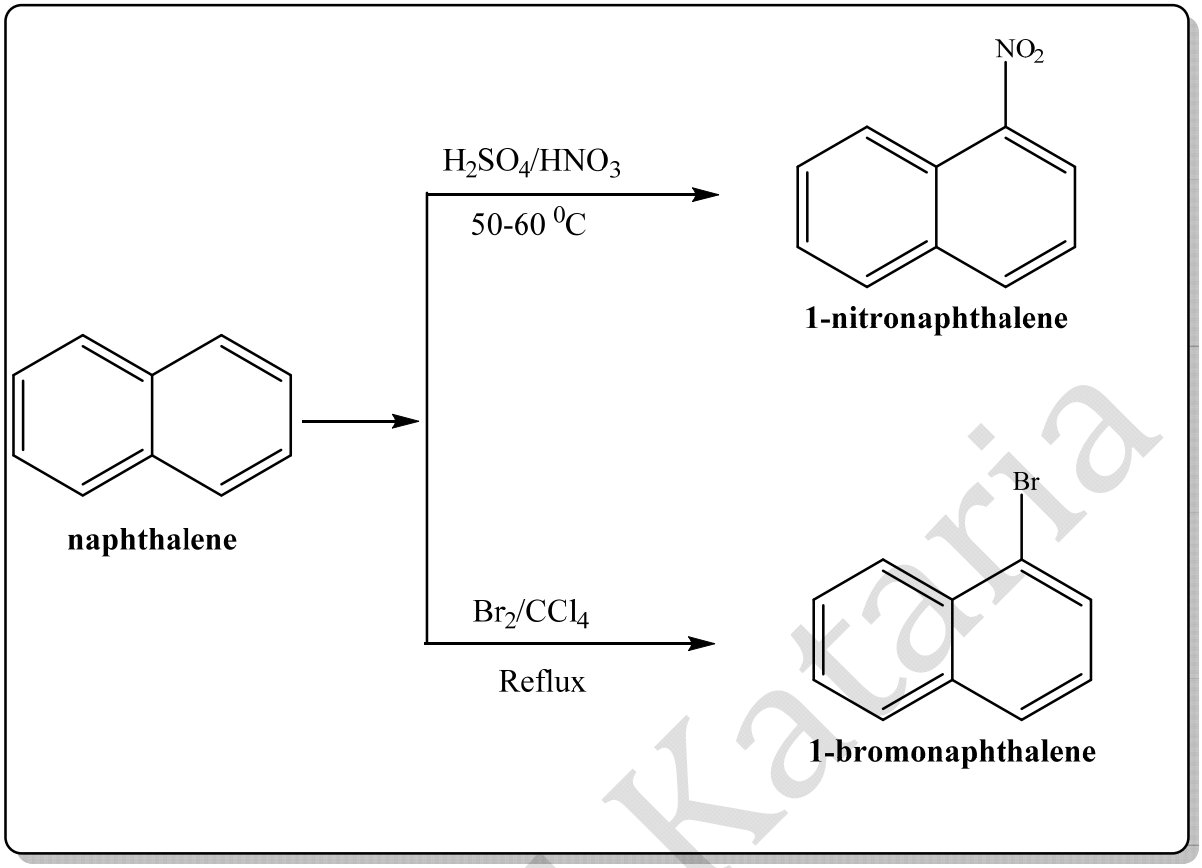
- The compounds containing **carbon skeleton of an aromatic system** but have **large number of hydrogen atom** for aromaticity are called **hydro aromatic compounds**. i.e. tetraline, decaline.
- Hydro aromatic compounds can be converted to aromatic compounds via the process called **aromatization**.

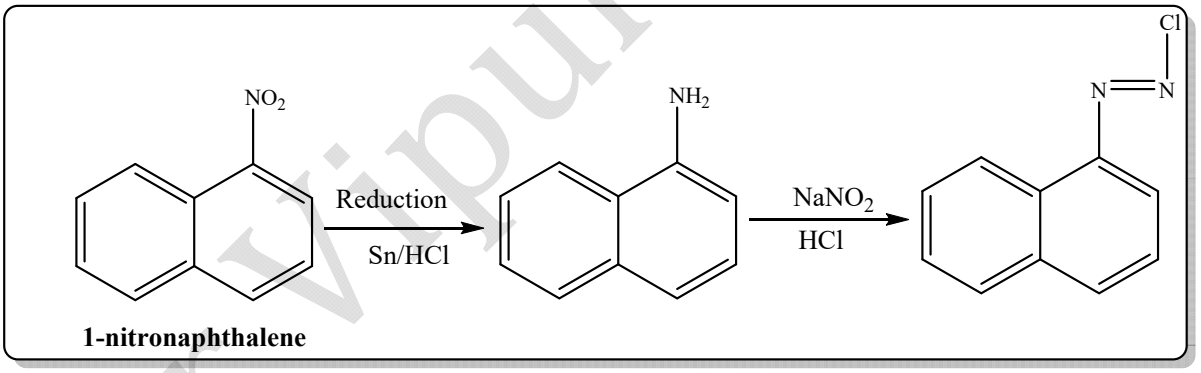


- The best available method for such conversion is use of catalyst metal like Pd, Ni, Pt.

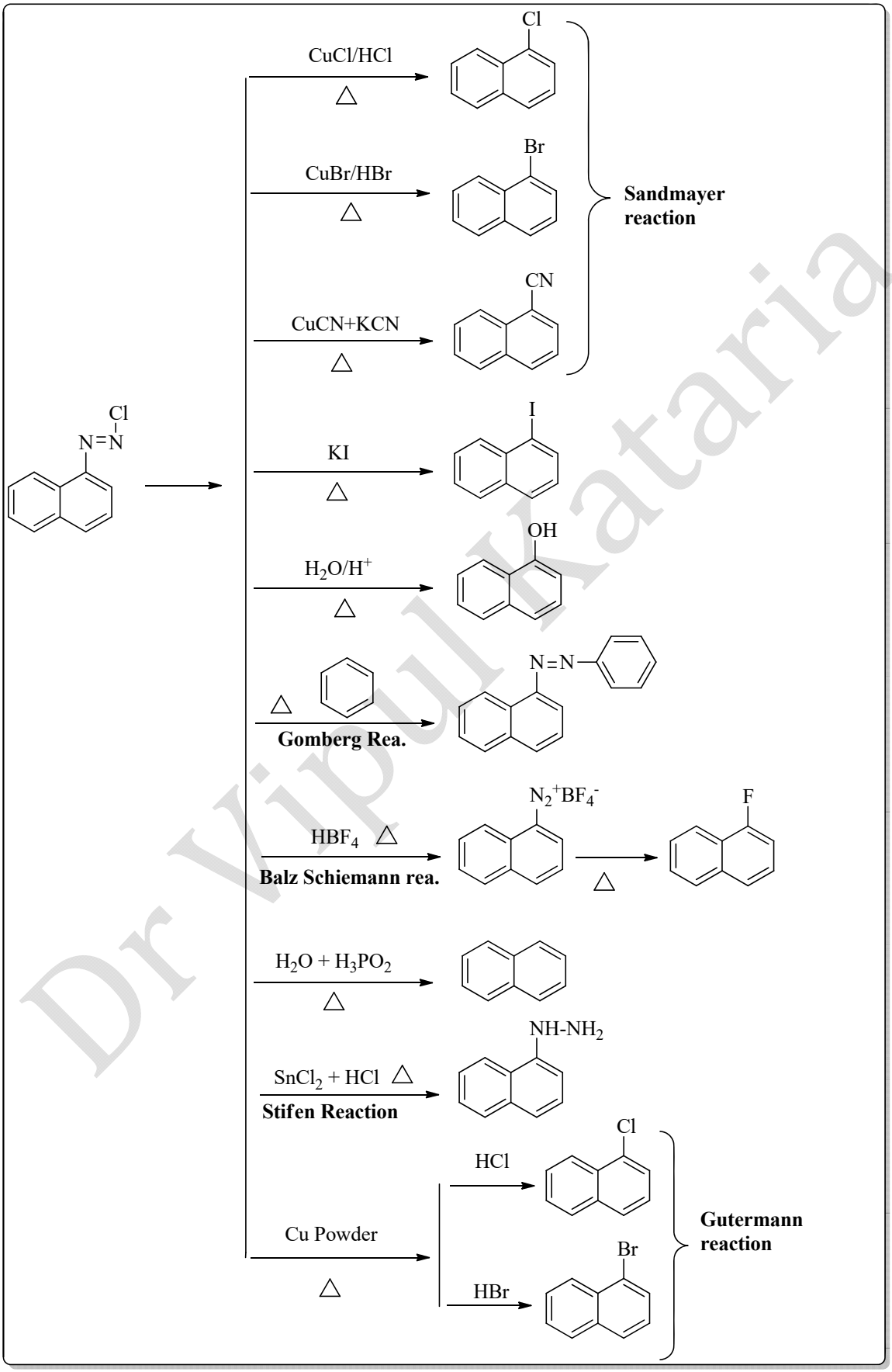
❖ **Electrophilic substitution reaction of naphthalene**

- Naphthalene easily undergoes **electrophilic substitution reaction** at **α position**.
- Naphthalene with **Br_2/CCl_4** in reflux condition gives **α-bromo naphthalene**.
- Naphthalene upon nitration with **HNO_3/H_2SO_4** gives **α-nitro naphthalene**.
- **α-nitro naphthalene** upon reduction with **Sn/HCl** gives **α-amino naphthalene** which on further reaction with **$NaNO_2$** gives **diazonium salt**.
- Diazonium salt of naphthalene upon reaction with different reagent gives different **α substituted derivatives of naphthalene**.
- Electrophilic substitution reaction is very useful method to prepare α substituted derivative of naphthalene.



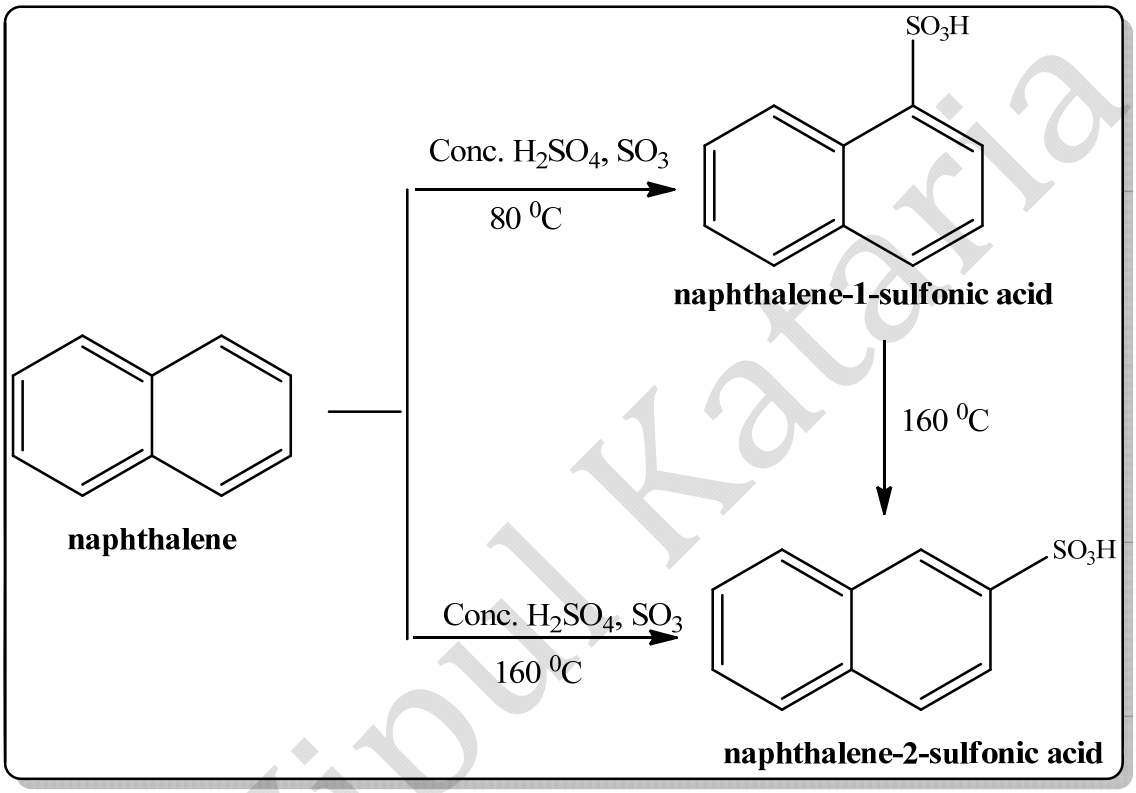


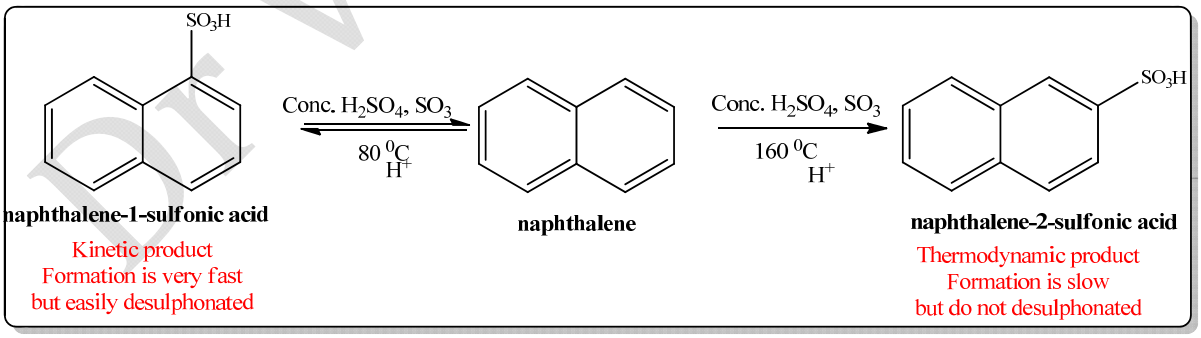
Electrophilic reactions **જે નાખો તે મળે**



❖ **Sulphonation of Naphthalene**

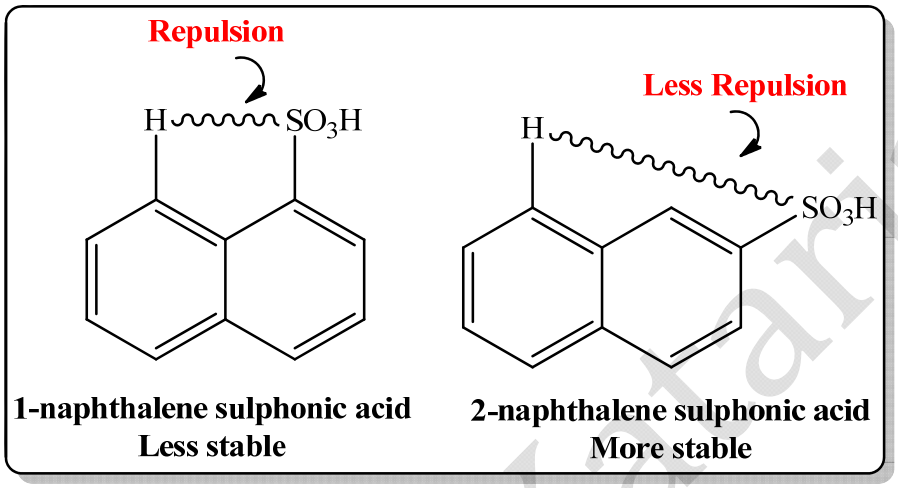
- Sulphonation of naphthalene is **temperature and equilibrium controlled reaction**.
- It has been observed that naphthalene with **conc. H_2SO_4 at 80 ˚C gives naphthalene-1-sulphonic acid** whereas at **160 ˚C naphthalene-2-sulphonic acid**.
- The formation of **naphthalene-1-sulphonic acid** is **very fast reaction** as compare to formation of **naphthalene-2-sulphonic acid**.





- Naphthalene with **conc. H_2SO_4 at 80 ˚C** gives **naphthalene-1-sulphonic acid** which is **kinetic product** as it forms **very fast** but it can easily **desulphonated back to naphthalene**.

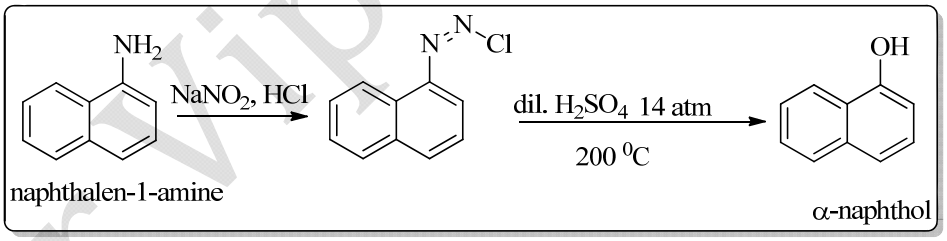
- Naphthalene with **conc. H_2SO_4 at 160 ˚C gives naphalene-2-sulphonic acid** which is **thermodynamic product** as it forms due to high temperature (**slow process**) but it is **resistant to desulphonation due to energy barrier**.
- Sulphonation of naphthalene is a versatile reaction that gives access to formation of β-isomer.



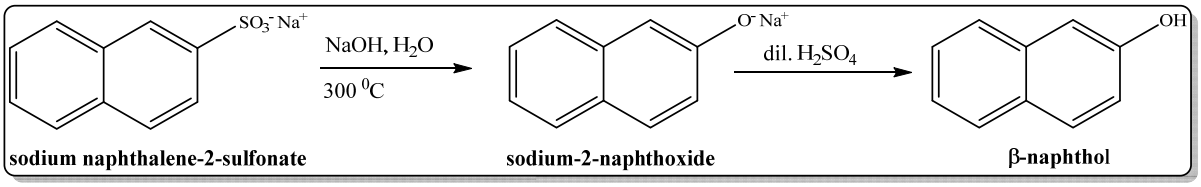
Just for the understanding of the stability of both the isomers.

❖ **Synthesis of Naphthols**

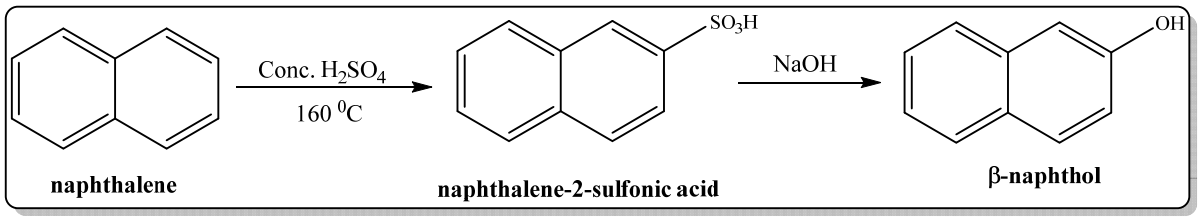
- Presence of **–OH group** on **α or β positions** of naphthalene is referred as **α-naphthol or β-naphthol**.



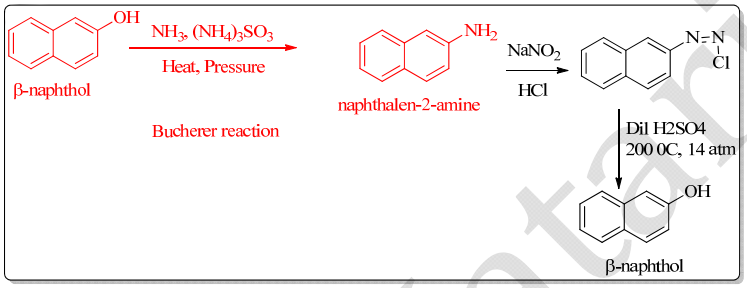
- **Naphthols** can be synthesized from the **naphthyl amines** by **acid at very high temperature** and pressure.



- **Sodium salt of naphthalene-2-sulphonic acid** upon reaction with **NaOH at 300 ˚C** gives **sodium-2-napthoxide** that on further **acidic hydrolysis** gives **β-naphthol**.



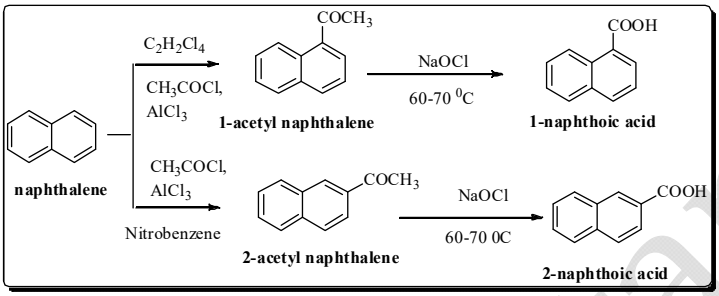
- **Naphthalene** upon **Sulphonation at 160 ˚C** gives **naphthalene-2-sulphonic acid** which on further **alkaline hydrolysis** gives **β-naphthol**.



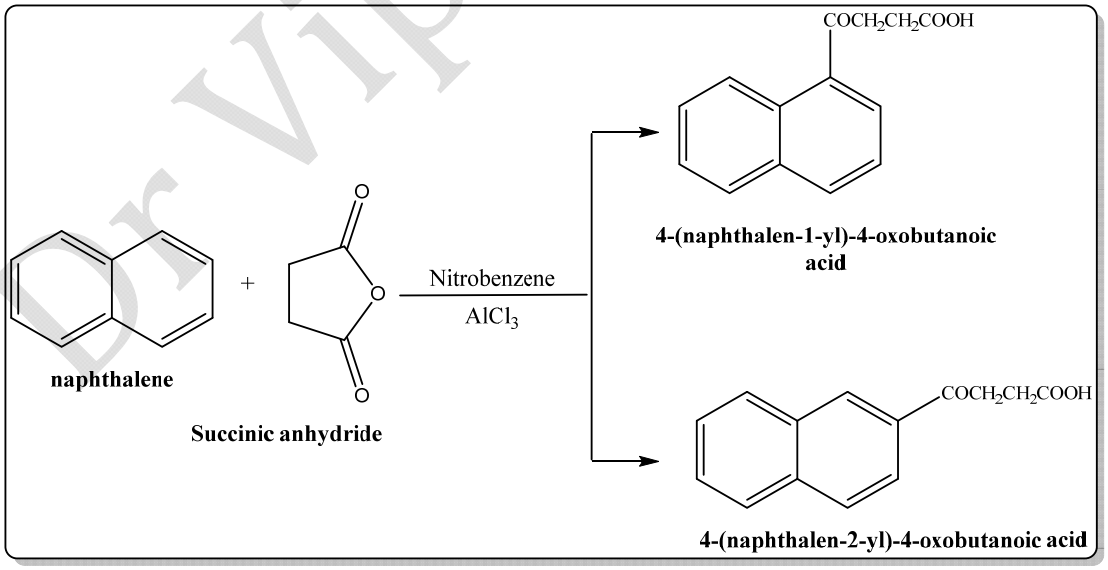
- **β-naphthol** on reaction with **$NaNO_2$/HCl** gives **diazonium salt** which can be **hydrolysed back** to β-naphthol .
- **β-naphthol** on reaction with **ammonia and ammonium sulphite** at certain pressure and temperature gives **naphthalene-2-amine (β-naphthylamine)** (that is referred as **Bucherer** reaction) that can also be further **hydrolysed to β-naphthol**.

❖ **Friedel Craft acylation of Naphthalene**

- Naphthalene undergoes **Friedel craft acylation** easily to form **acetyl naphthalene derivative**.
- The product (**α or β isomer**) is dependent upon **solvent used**.
- The reagents used for acylation are **$AlCl_3$** and **CH_3COCl**.



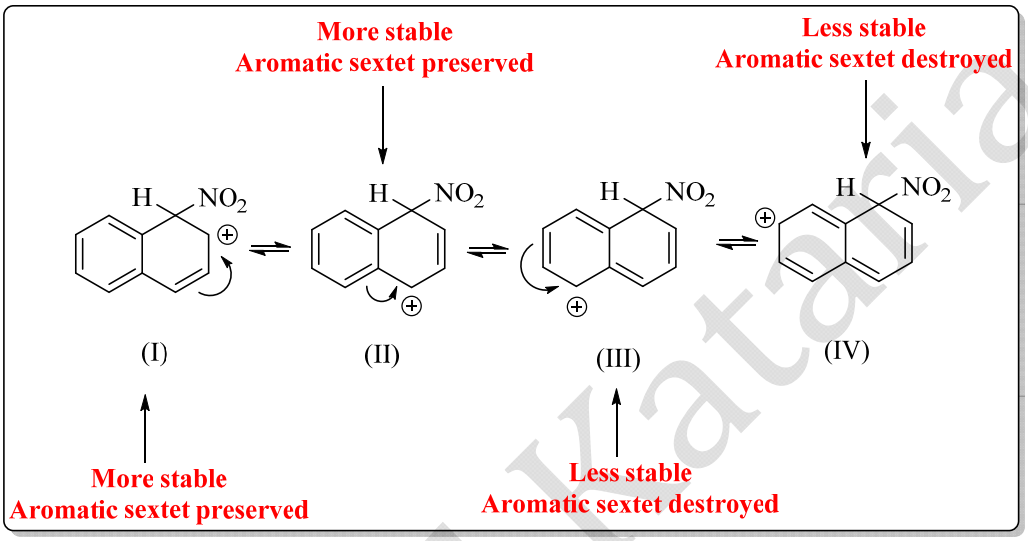
- Naphthalene upon reaction with **$AlCl_3$ and CH_3COCl** using solvent **$C_2H_4Cl_4$ (tetra chloro ethane)** gives **1-acetyl naphthalene (α-position)**.
- Naphthalene upon reaction with **$AlCl_3$ and CH_3COCl using solvent nitrobenzene** gives **2-acetyl naphthalene (β-position)**. This reaction gives **β-isomer** as **nitrobenzene** forms a **complex** with $AlCl_3$ that cannot be joined at α-position due to steric hindrance.
- **Acetyl naphthalene** upon reaction with **sodium hypochloride** gives corresponding **naphthoic acid**.



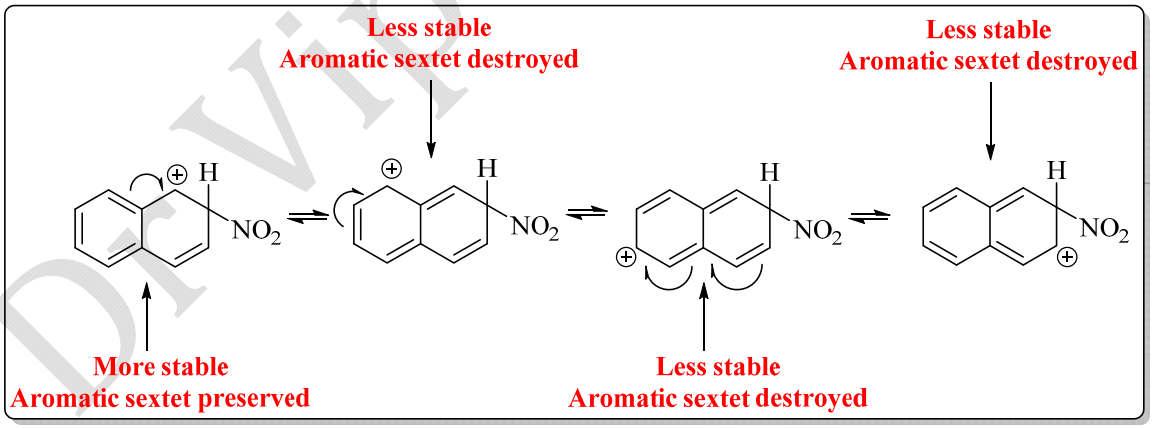
- Acylation of **naphthalene with succinic anhydride** gives a mixture of α and β isomers due to **high reactivity** of naphthalene.

❖ **Orientation of electrophilic substitution in naphthalene**

- The **α-position** in naphthalene is **more reactive** than **β**.
- The **electrophilic reactions** like nitration, halogenation, acylation etc. take place exclusively on **α-position**.
- This can be explained by **reactive stability** of **intermediate carbocation**.



- Upon examination of above resonance structure we can see that among **four structures, two structures** shows stable form with **preserved aromatic sextet**.

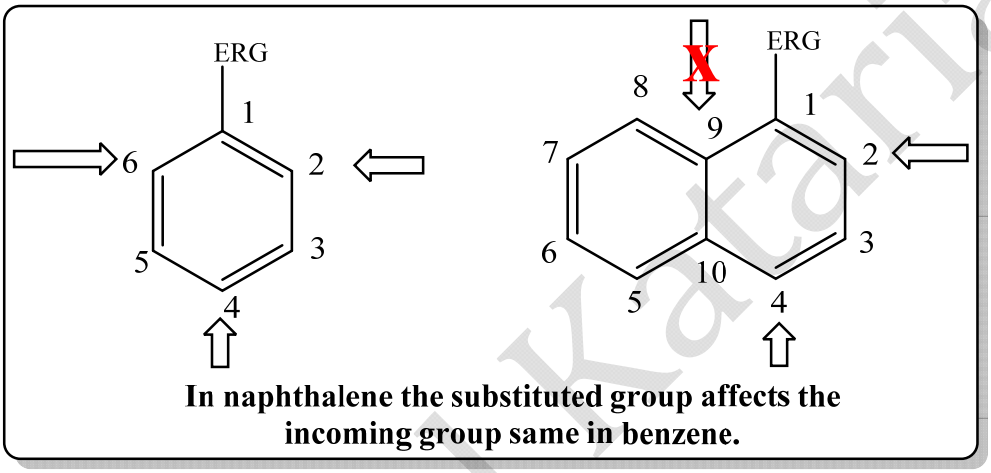


- Upon examination of above structures, we can see that among **four structures, only one structure** shows stable form with **preserved aromatic sextet**.
- When the **aromatic sextet is preserved**, the electrons are delocalized to form **stable carbocation**.
- So, we can say that when incoming group attacks **α position**, it generates **more stable carbocation** than β-position.

- Thus, α-position is more favourable than β-position for electrophilic attack in naphthalene.

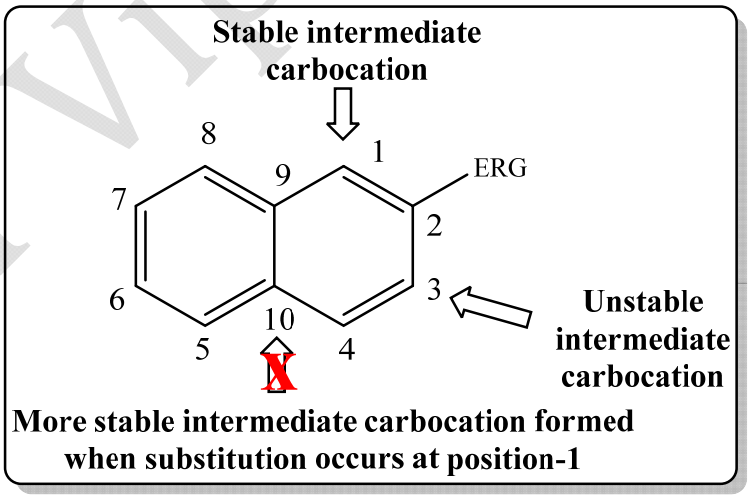
❖ **Orientation of electrophilic substitution in mono substituted naphthalene**

- Like the benzene, **substituted group decides** the **position of incoming group** in naphthalene also.
- The position of incoming group is decided by the **position and nature** (o, p-director or m-director) of the substituted group.



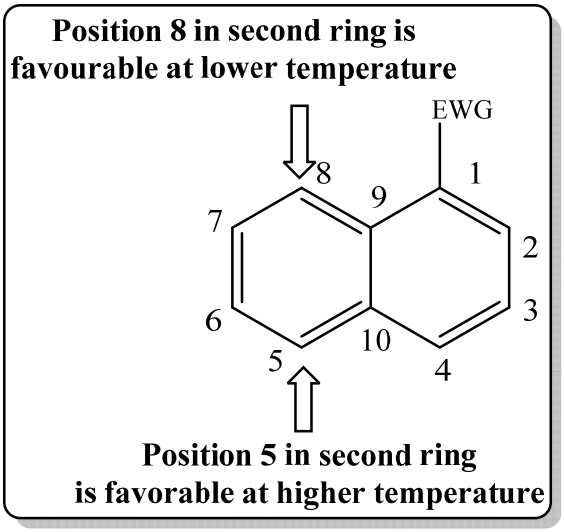
In naphthalene the substituted group affects the incoming group same in benzene.

- If an **electron releasing group (activating)** is present at **α-position (position 1)** in naphthalene then incoming group will join at **2 or 4 position** in the same ring. The incoming group mostly occurs at **position 4**.

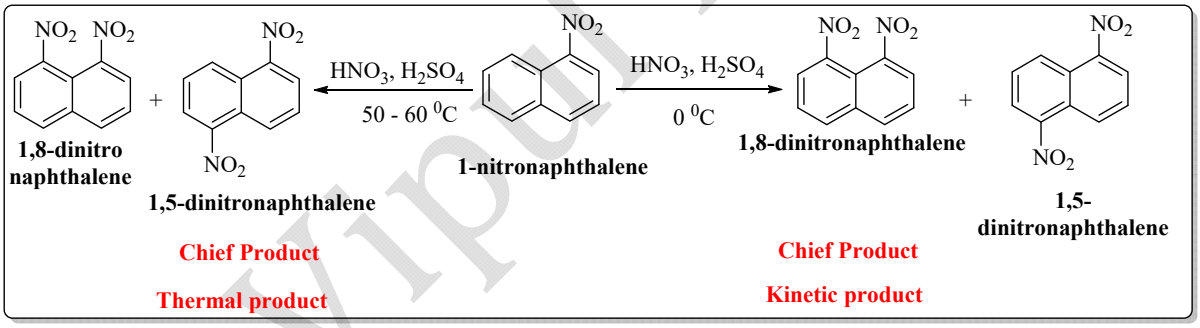


More stable intermediate carbocation formed when substitution occurs at position-1

- If **electron releasing group (activating)** is present at **β-position (position 2)** in naphthalene then incoming group will join at **1 or 3 position**. As intermediate carbocation for position-3 is unstable, the incoming group prefers **position 1**.

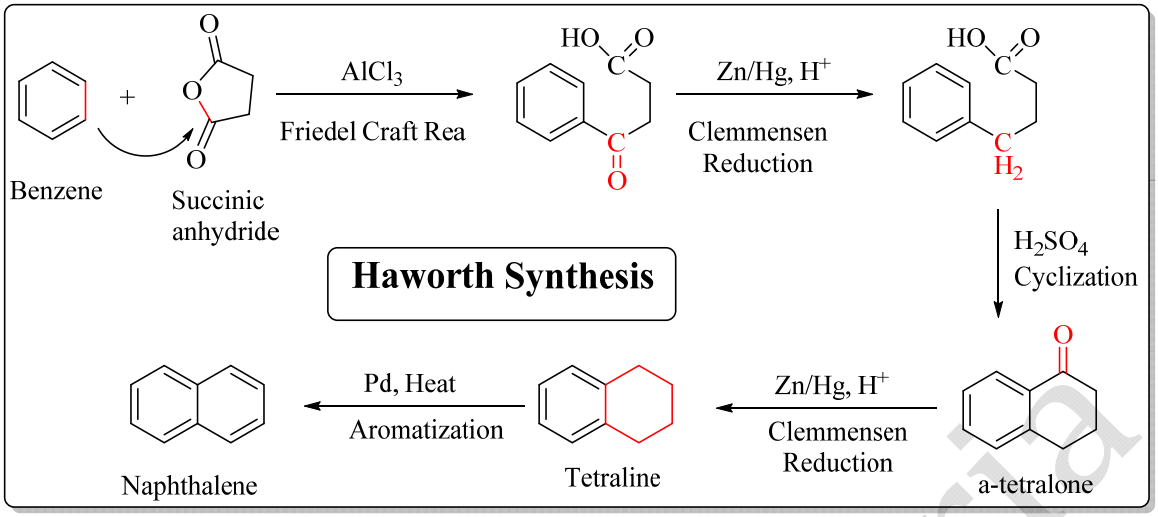


- If **electron withdrawing group (deactivating)** is present at **α-position (position 1)** in the naphthalene then incoming group will join on the other ring at **position 5 or 8**.
- There are two possibilities for incoming group in second ring (position 5 and position 8) however it will prefer **position 8 (kinetic product)**.
- If it is thermodynamically controlled product than the incoming NO_2 group will join at **position 5 (thermal product)**.

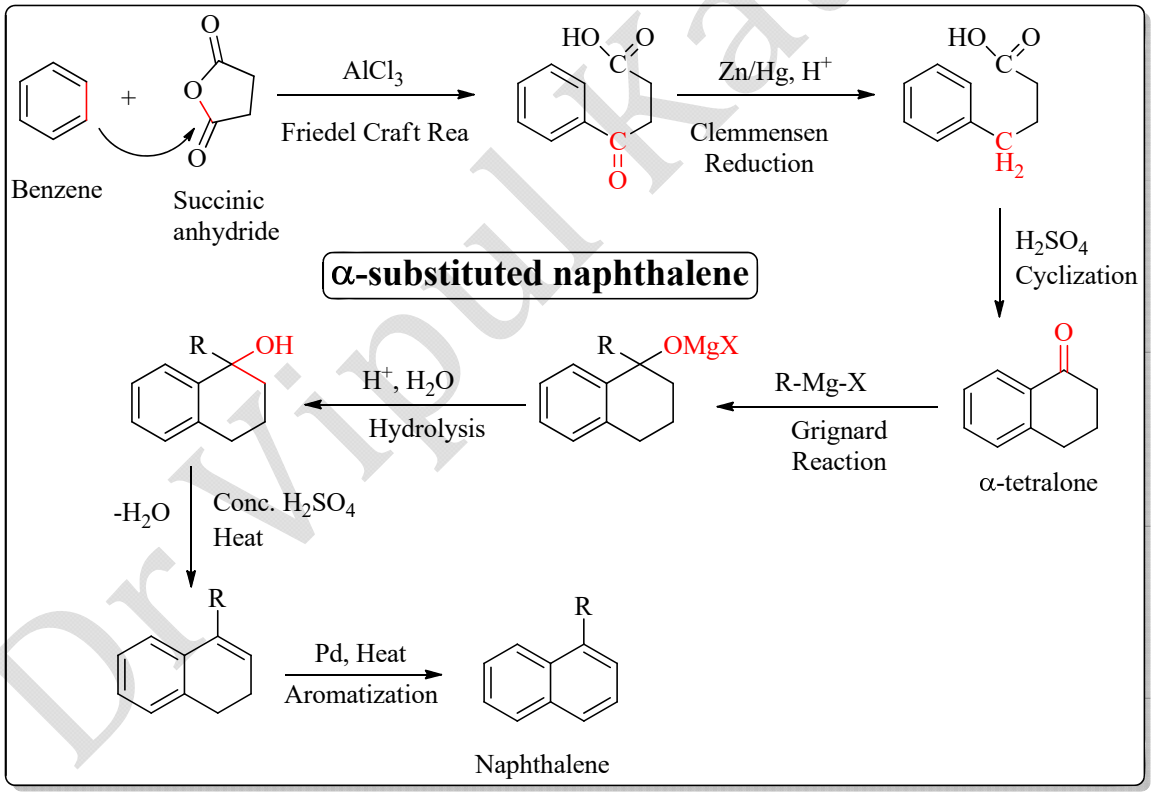


❖ Haworth synthesis

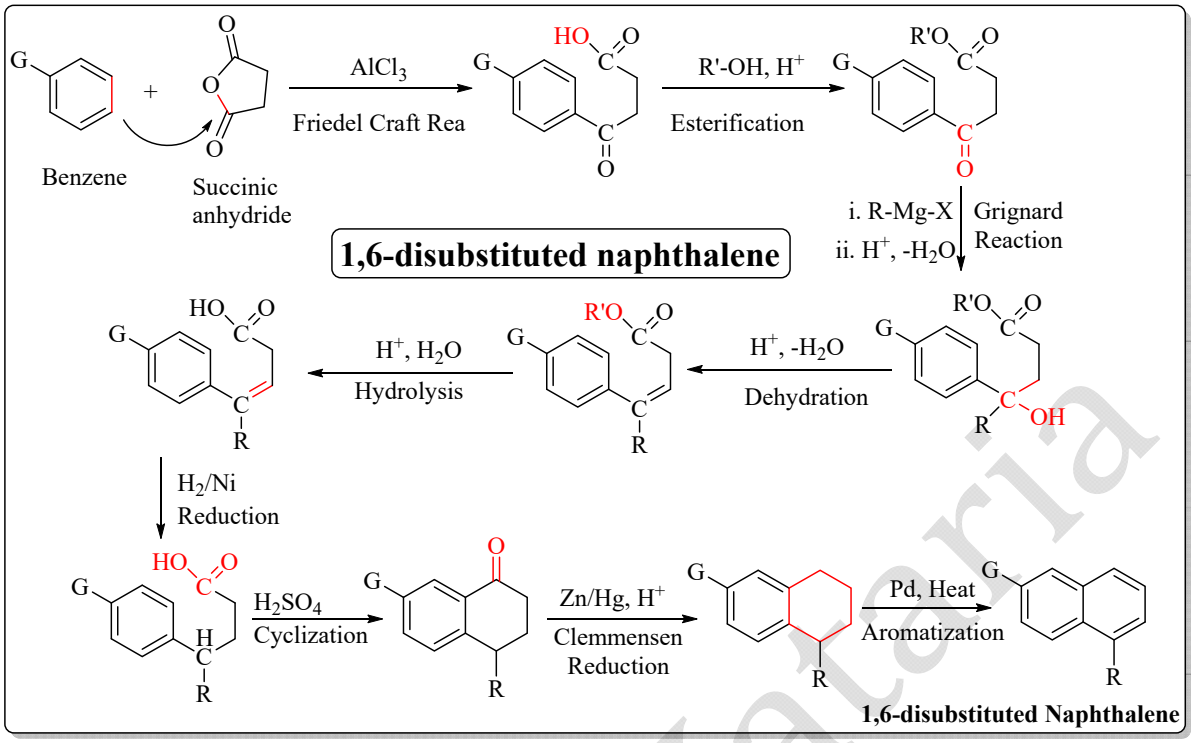
- This synthesis is very useful for synthesis of **polynuclear aromatic hydrocarbon** and its derivatives.
- This method involves (1) **Friedel-Craft acylation** (2) **Clemmensen reduction** (3) **Ring closure reaction** (4) **Clemmensen reduction** and (5) **Aromatization**
- **β-substituted naphthalene** can be synthesized by taking **substituted benzene** as a **starting material** and follow the above order of reaction.



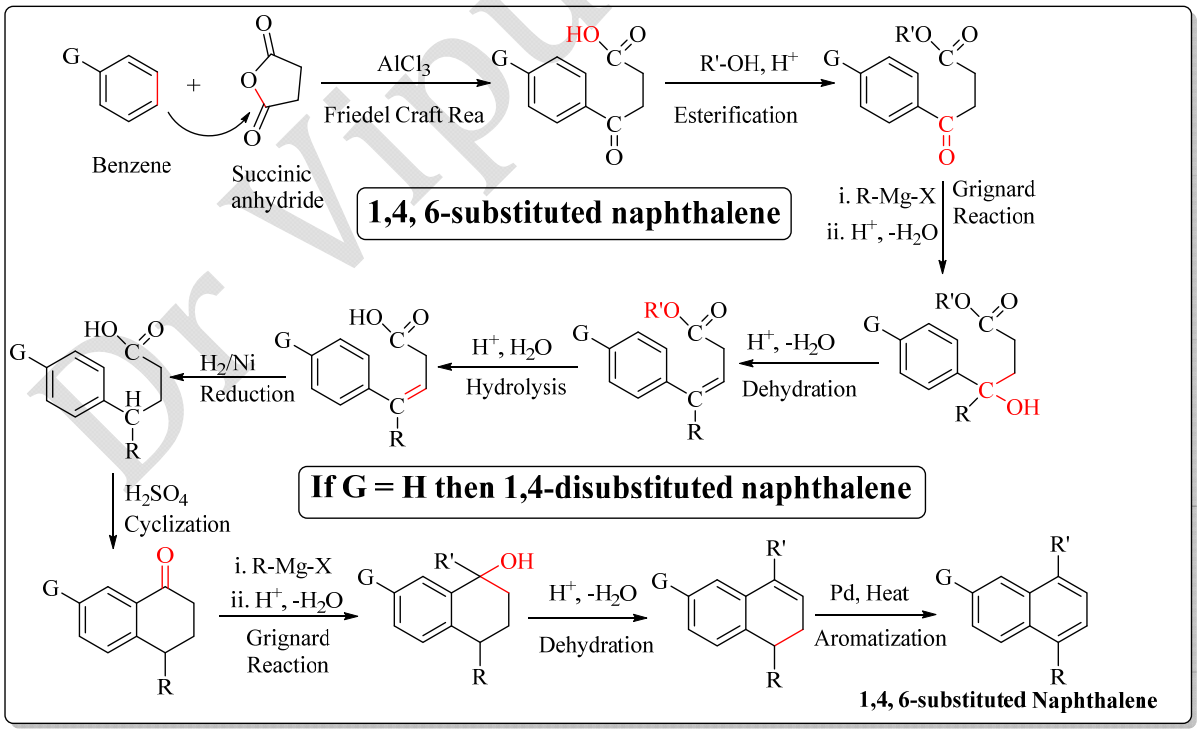
- **For β-substituted naphthalene** we can start the reaction with toluene, anisole or bromobenzene as in such starting materials Friedel craft acylation takes place at para position.



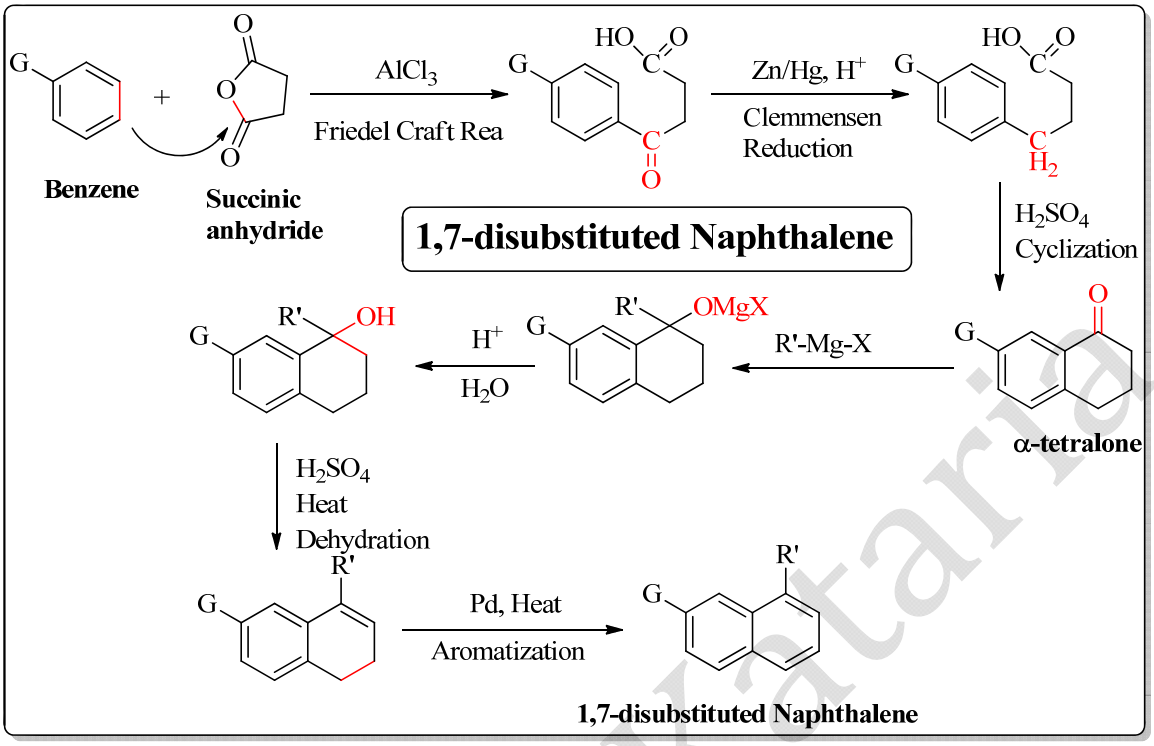
- **For α-substituted naphthalene** we can start the reaction with and applying Friedel craft acylation, clemmensen reduction, ring closure (cyclization), Grignard reaction, hydrolysis, dehydration followed by aromatization.



- **1-6-disubstituted naphthalene** can be synthesized by using **substituted benzene** as a starting material followed by Friedel craft acylation, Esterification, Grignard reaction, dehydration, hydrolysis, hydrogenation (reduction), ring closure (cyclization), clemmensen reduction and aromatization.



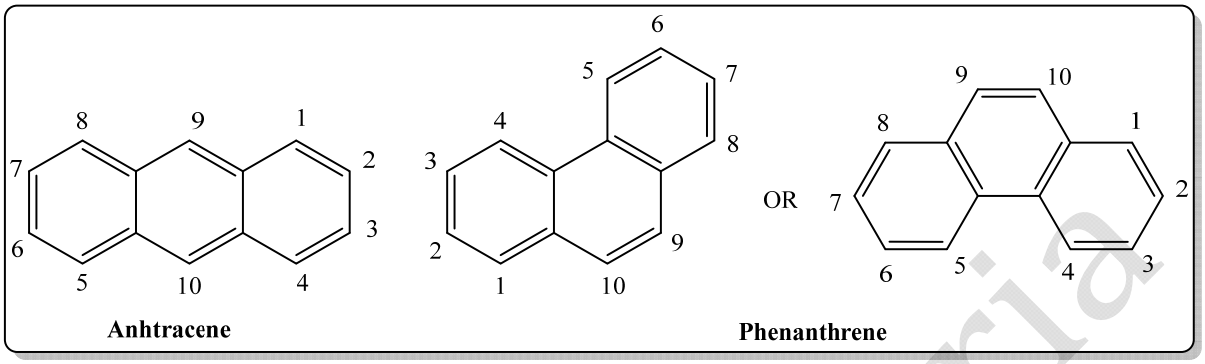
- **1,4,6-substituted or 1,4-disubstituted naphthalene** can be synthesized by using above reaction order.



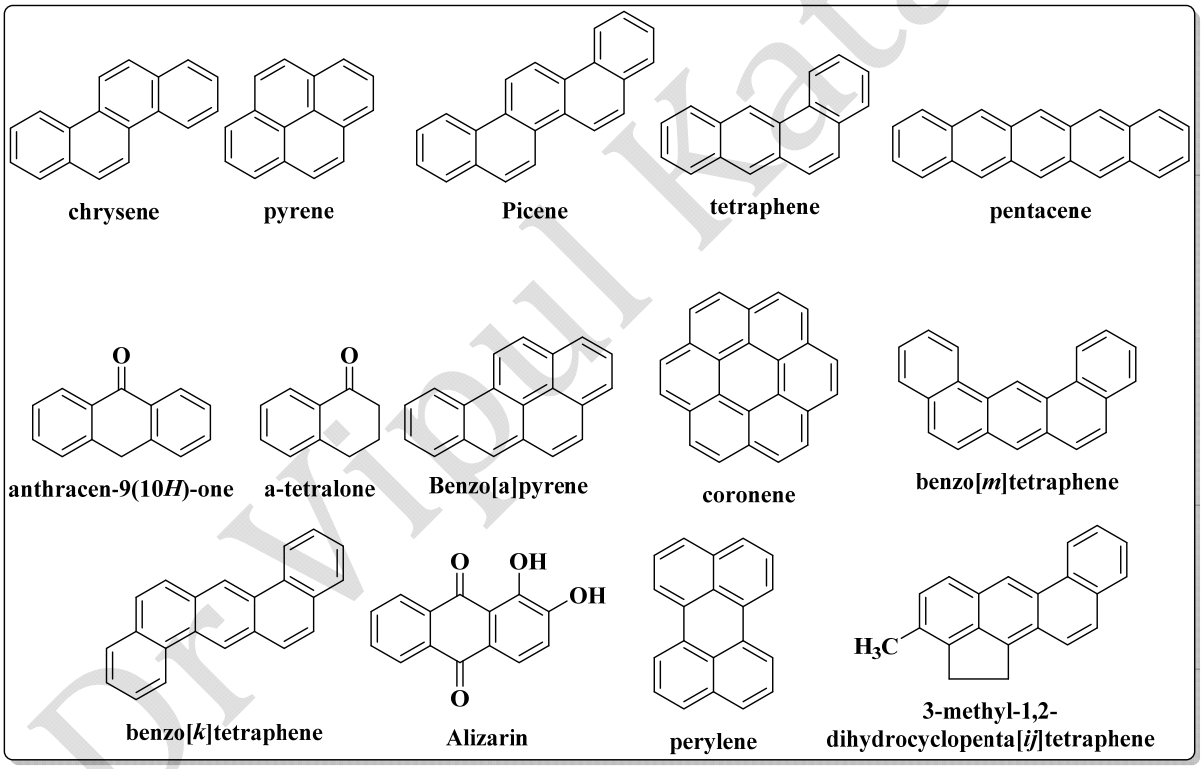
- **1,7-disubstituted naphthalene** can be synthesized by using substituted benzene as a starting material followed by Friedel craft acylation, clemmensen reduction, ring closure (cyclization), Grignard reaction, hydrolysis, dehydration and aromatization.

Anthracene and Phenanthrene

- Anthracene and phenanthrene both contain three benzene rings.
- The numbering system for Anthracene and phenanthrene is as follows.

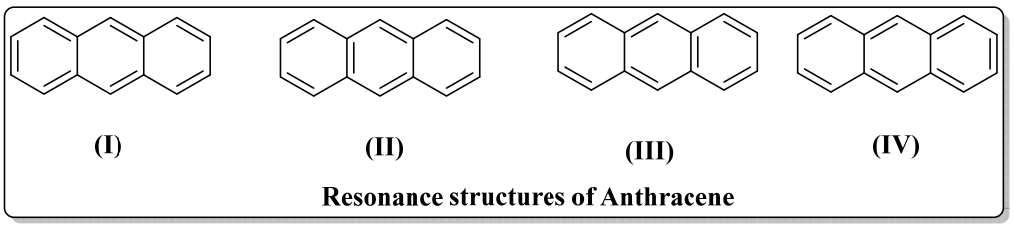


- Several other polynuclear aromatic compounds are as under.

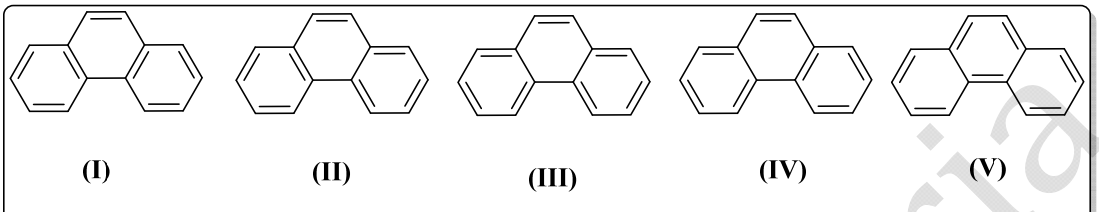


❖ Structures of Anthracene and phenanthrene

- Structures of Anthracene and phenanthrene can be explained by following resonance hybrid structures of both the compounds.



Resonance structures of Anthracene

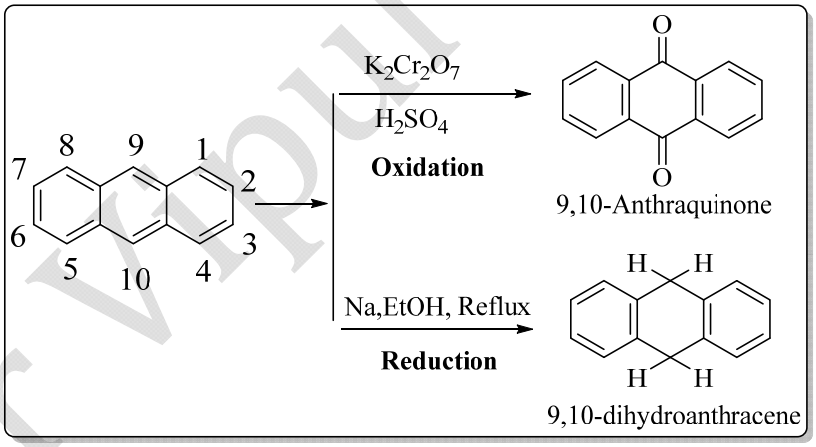


Resonance structures of Phenanthrene

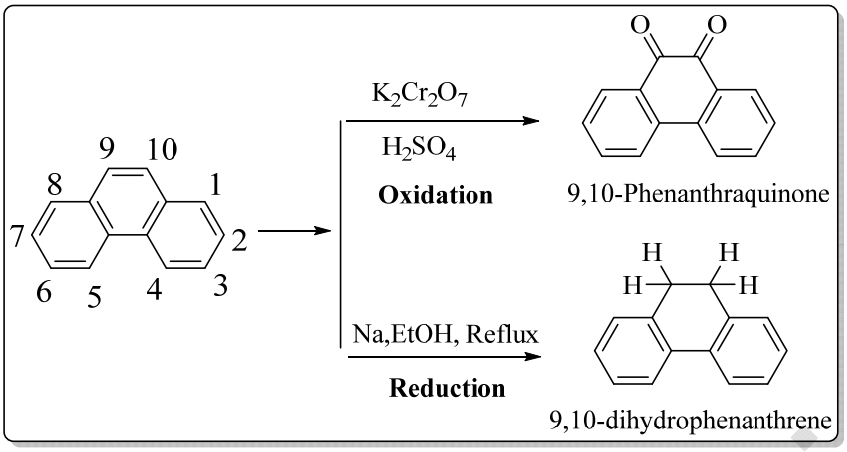
- The resonance energy for Anthracene and phenanthrene is 84 and 92 Kcal/mole respectively.

❖ Reactions of Anthracene and Phenanthrene

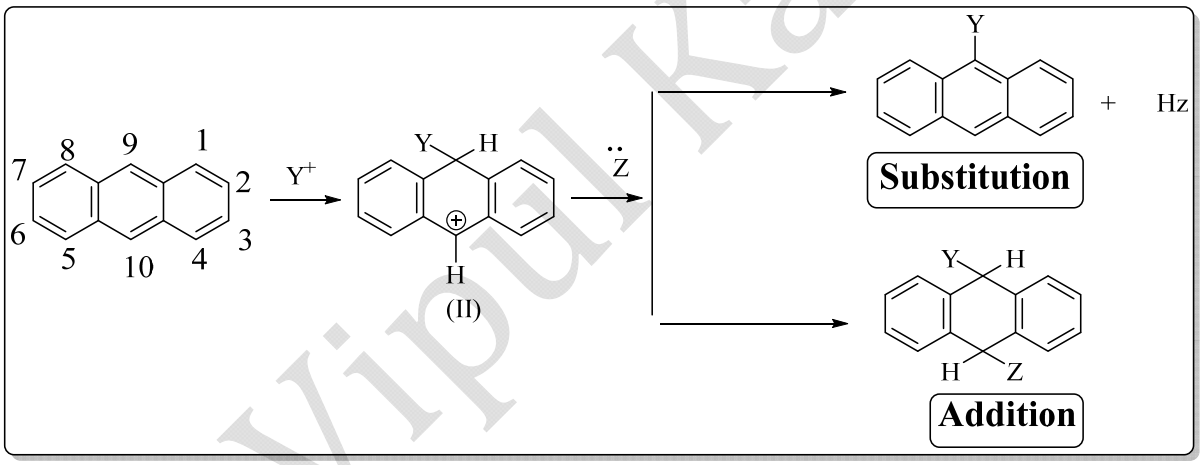
- Anthracene and phenanthrene undergo oxidation, reduction and electrophilic reactions at 9 and 10 positions due to high reactivity of C_9 and C_{10} carbons.



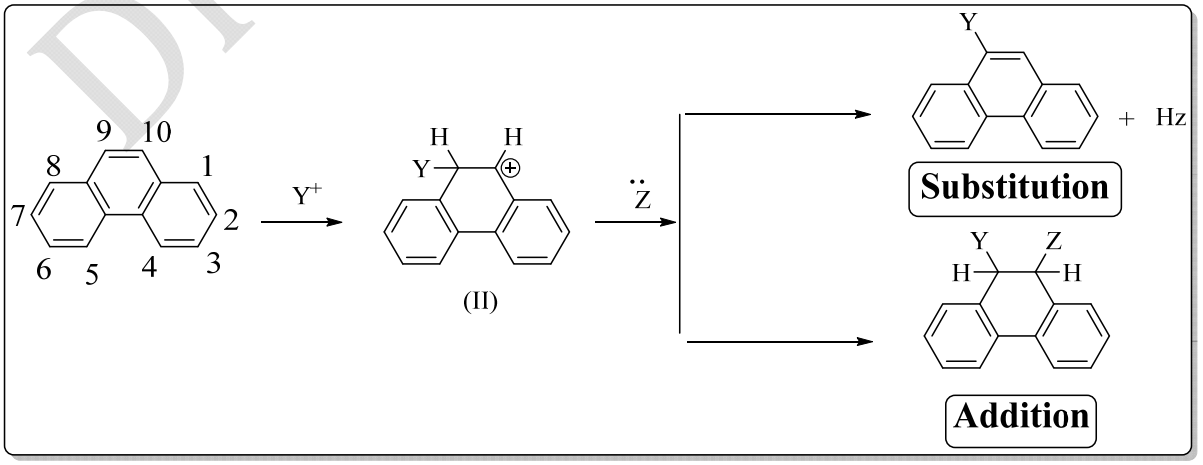
- Anthracene upon oxidation with $K_2Cr_2O_7$ and H_2SO_4 gives 9,10-anthraquinone.
- Anthracene upon reduction with Na and EtOH gives 9,10-dihydroanthracene.
- Since the resonance energy of anthracene is 84 Kcal/mole whereas resonance energy of benzene is 36 Kcal/mole.
- Upon examination of above reactions, we can see that in both the reactions only one ring get reacted and other two rings remain same. That means only 12 Kcal/mole (84 – 2 x 36 = 12 Kcal/mole) energy is getting lost.



- Since the resonance energy of Phenanthrene is 92 Kcal/mole whereas resonance energy of benzene is 36 Kcal/mole.
- Upon examination of above reactions, we can see that in both the reactions only one ring get reacted and other two rings remain same. That means only 20 Kcal/mole (92 – 2 x 36 = 20 Kcal/mole) energy is getting lost.



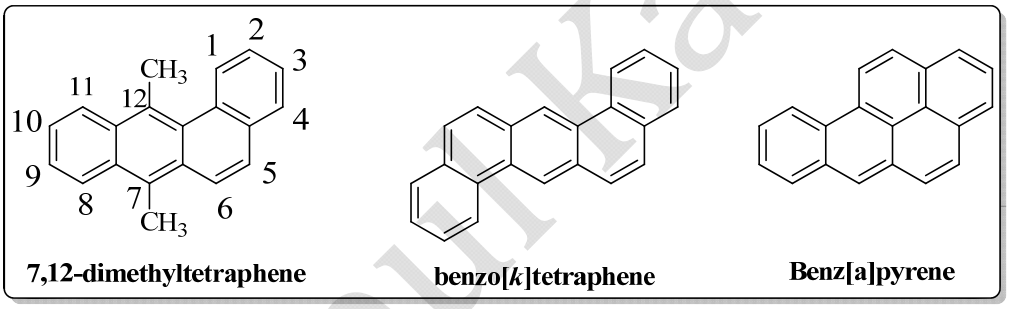
- Anthracene upon electrophilic attack can give either addition or substitution reaction.



- Phenanthrene upon electrophilic attack can give either addition or substitution reaction.
- Both Anthracene and phenanthrene undergo electrophilic reactions (either substitution or addition reaction) via formation of the carbocation (I & II).
- In both the compounds the generating carbocation is more stable and can go through substitution (losing proton) or addition reaction (accepting proton).

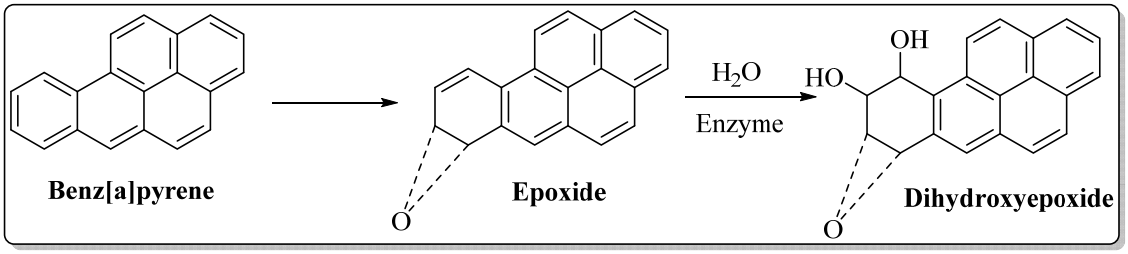
❖ Carcinogenic hydrocarbons (Arene oxides)

- There are number of organic compounds that produce cancer, are referred as carcinogenic compounds.
- One can have exposure of such organic compounds from environment.
- It is necessary to eliminate such carcinogenic compounds from environment.
- The most potent carcinogenic compounds are as under.

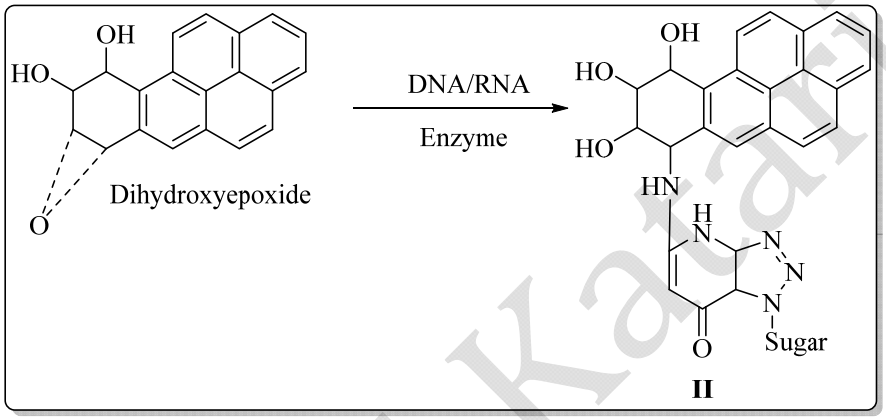


7,12-dimethyltetraphene **benzo[*k*]tetraphene** **Benz[a]pyrene**

- These compounds are produced by incomplete combustion of coal, petroleum and tobacco.
- These compounds can cause cancer to human beings.
- It is found from the experiments that applying such compounds on the skin of animals can produce carcinogenic effects.
- When such compounds enter in organism, the organism tries to eliminate it.
- If the compounds have lower solubility in water then elimination takes place by conversion of such compounds in water soluble compounds.
- Polynuclear aromatic compounds are converted into arene oxides in which one ring of compounds loses its aromaticity.
- An epoxide is hydrolysed in presence of enzymes to diols.

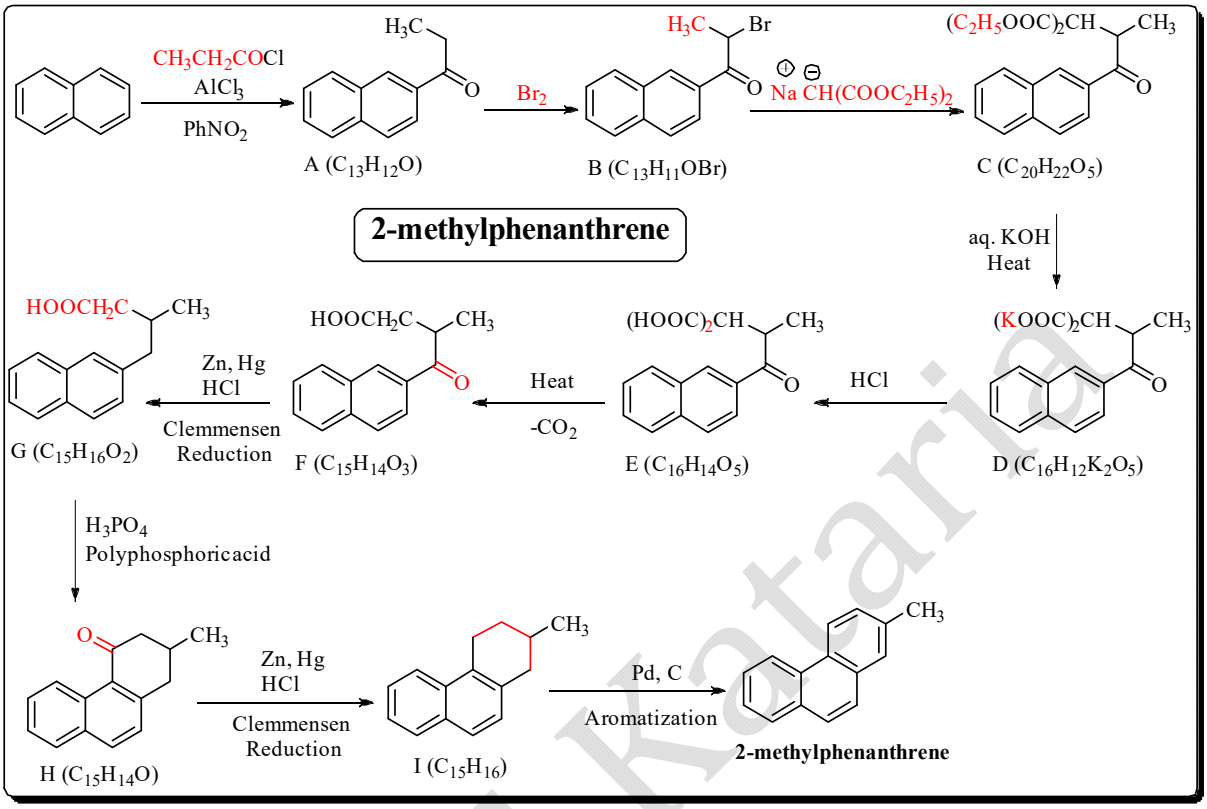


- These compounds excreted from the organism but in some cases some diols undergo further epoxidation in region and stereo selective way to for benz[a]pyrene diol epoxide. These epoxides are carcinogenic.

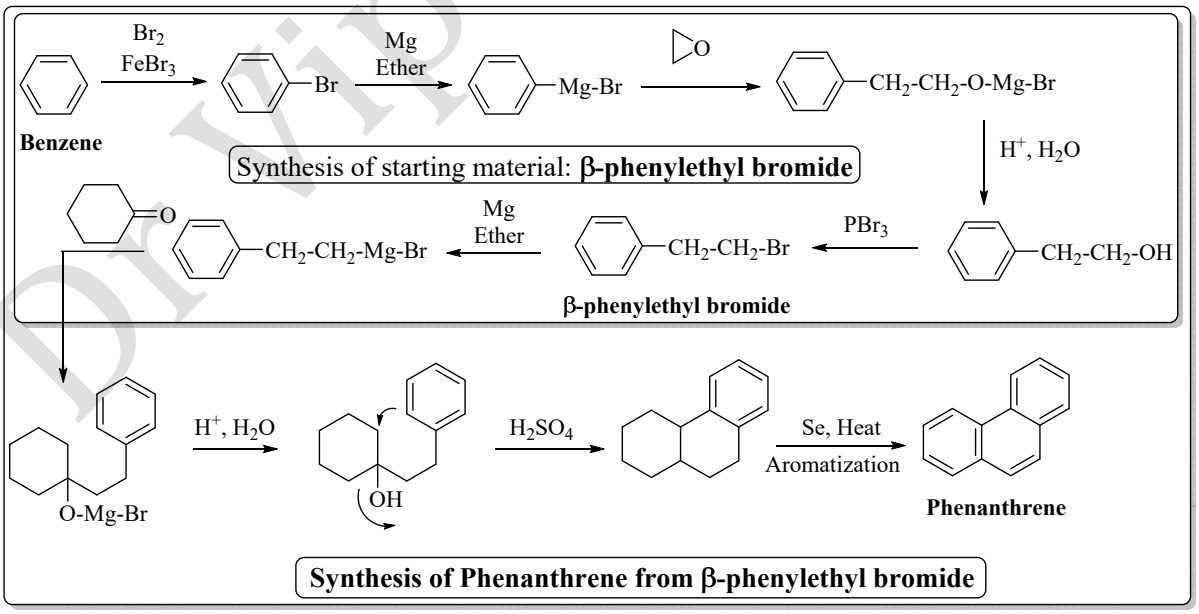


- The diol epoxide reacts with DNA to form II.
- This large hydrocarbon attached to the guanine prevents it from fitting in to the double helox of DNA and from H-bonding to cytosine in the opposite strand. This damage leads to mutations and increases probability of cancer.

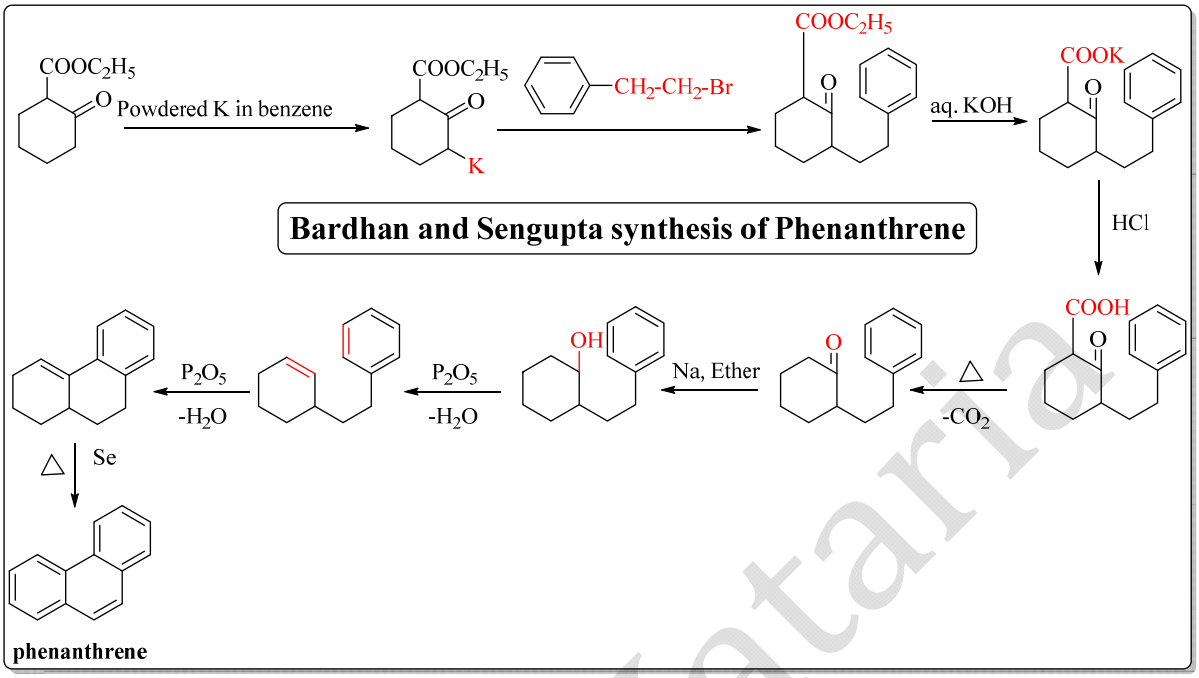
❖ 2-Methyl Phenanthrene



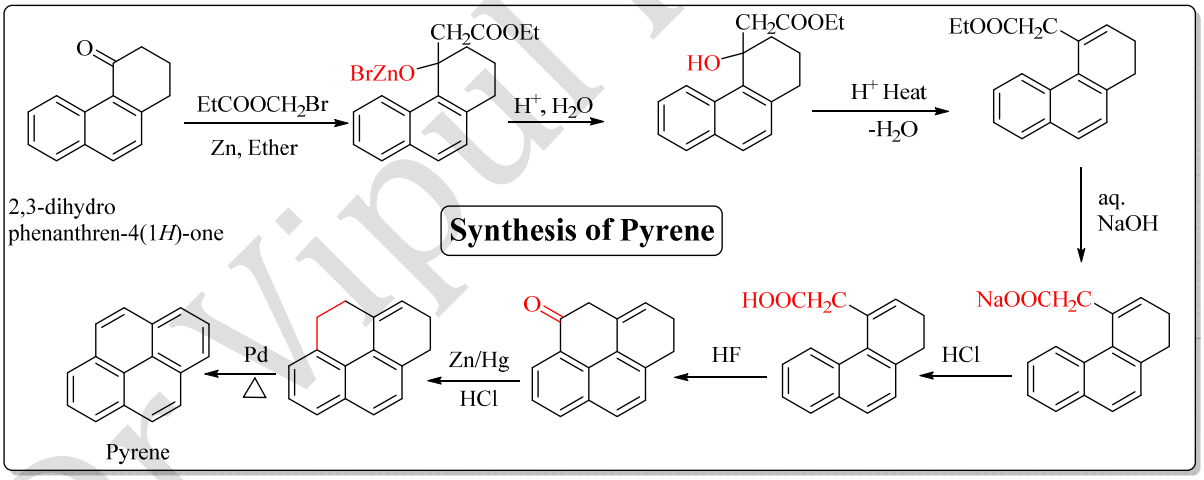
❖ Synthesis of Phenanthrene from β-phenylethyl bromide (Bogert Cook Synthesis)



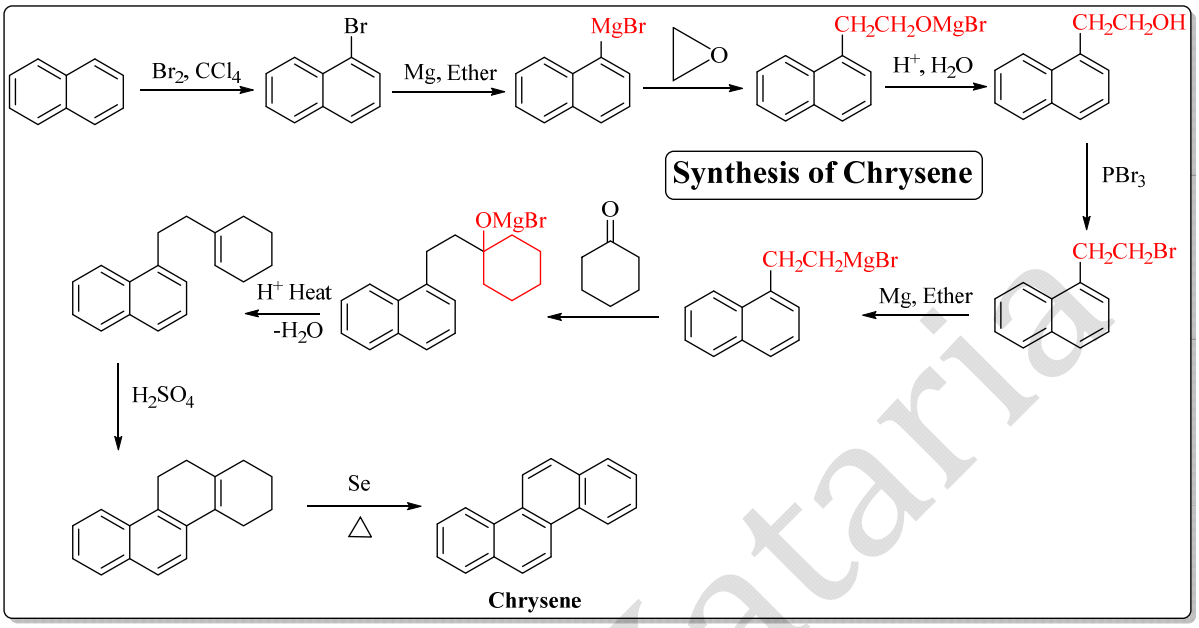
❖ Bardhan and Sengupta synthesis of Phenanthrene



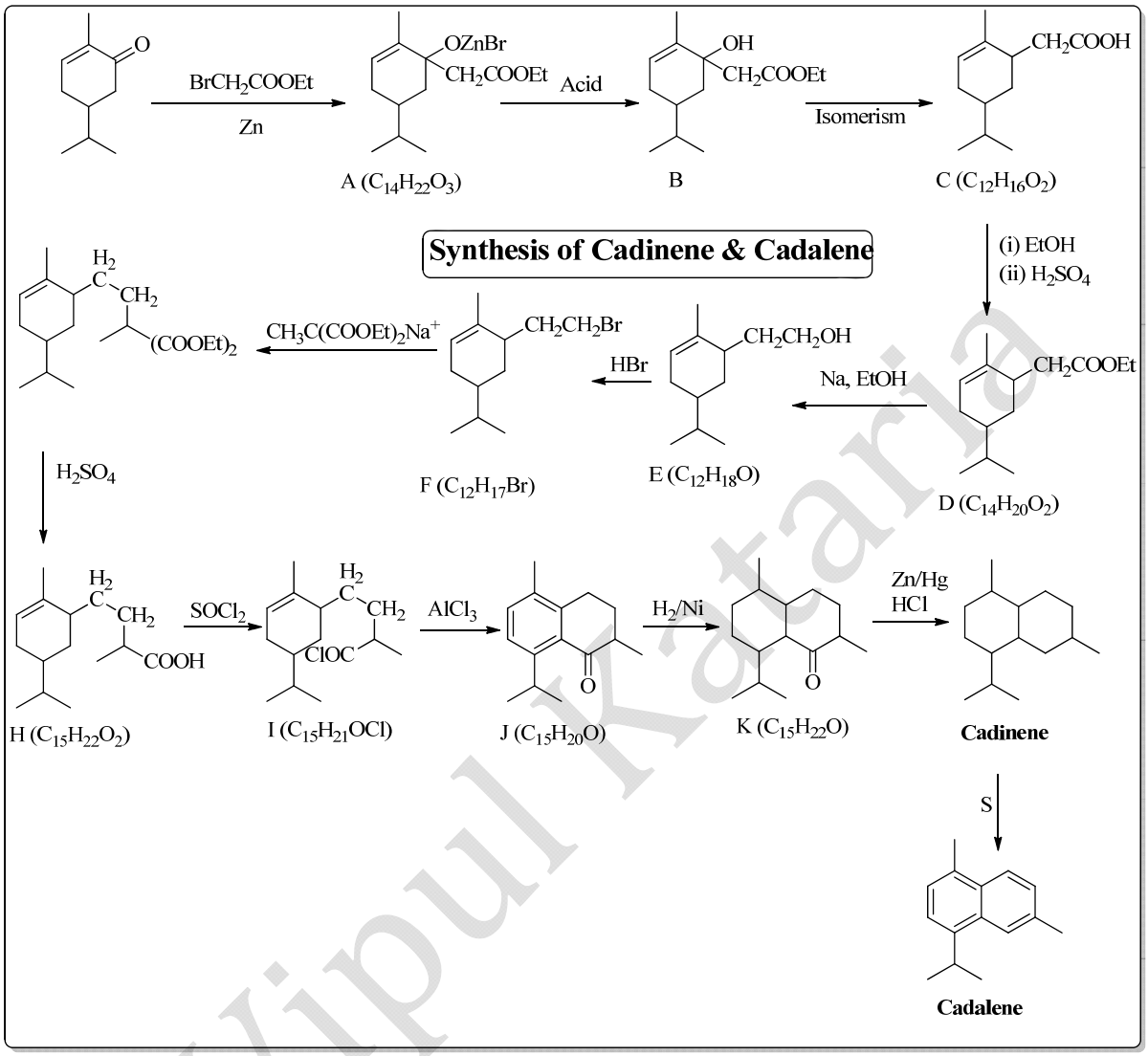
❖ Synthesis of Pyrene



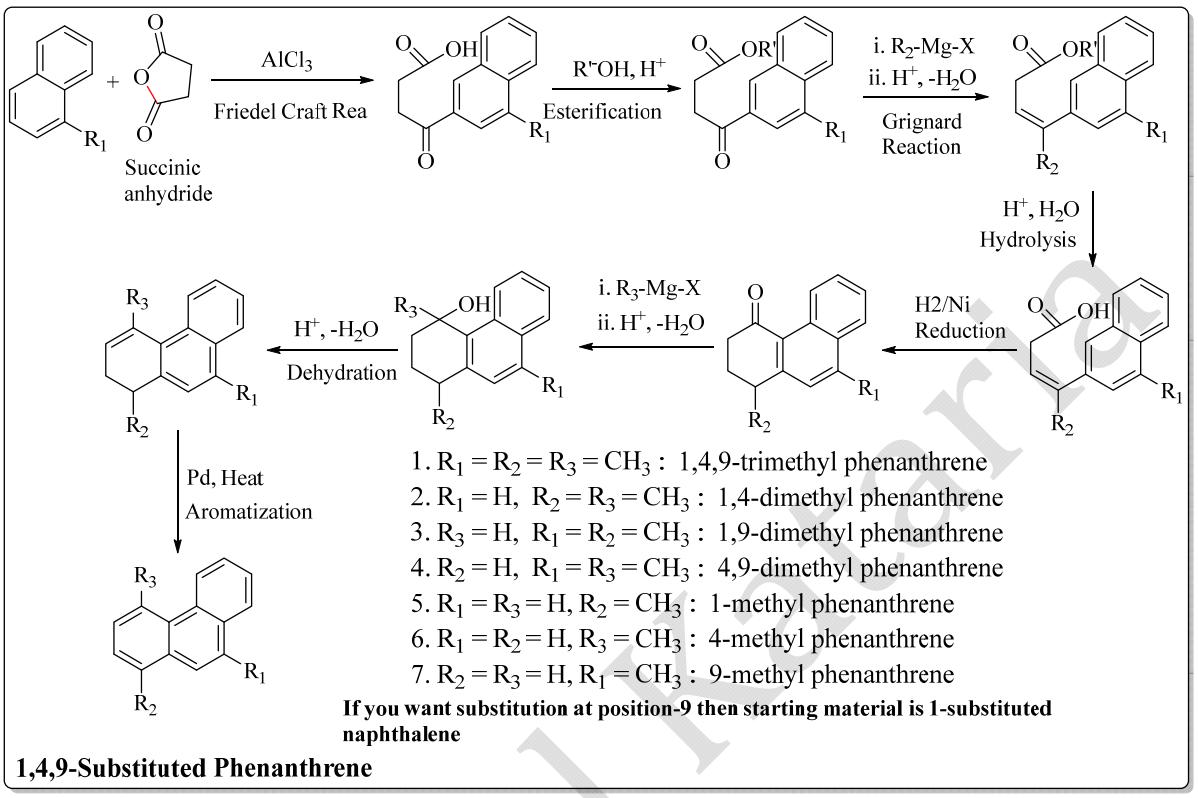
❖ Synthesis of Chrysene



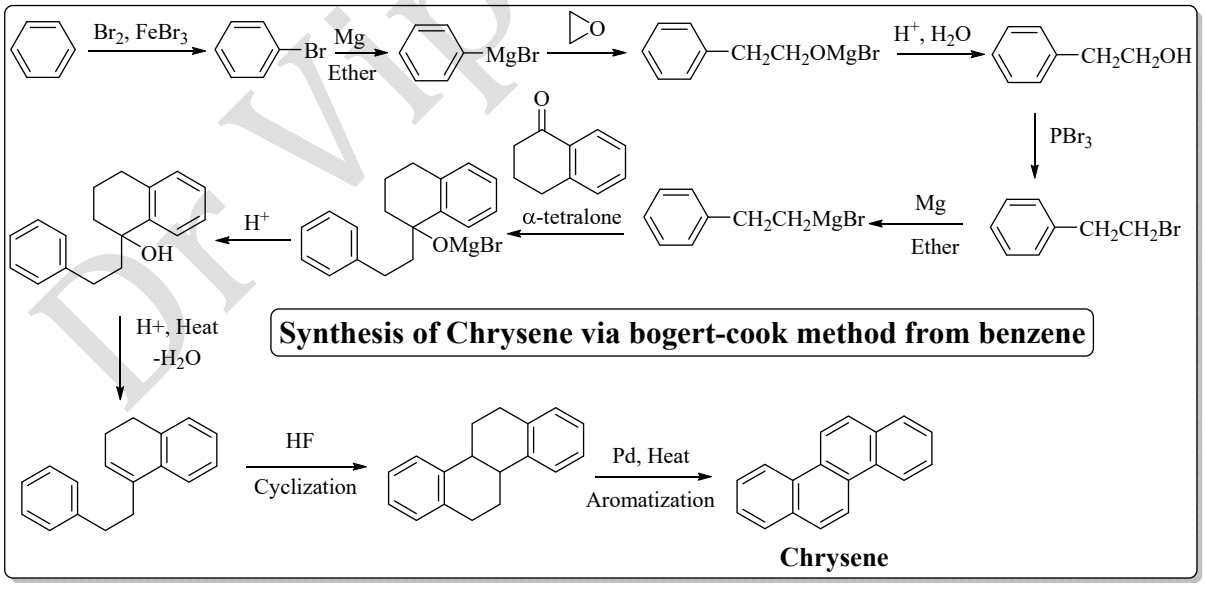
❖ Synthesis of Cadalene



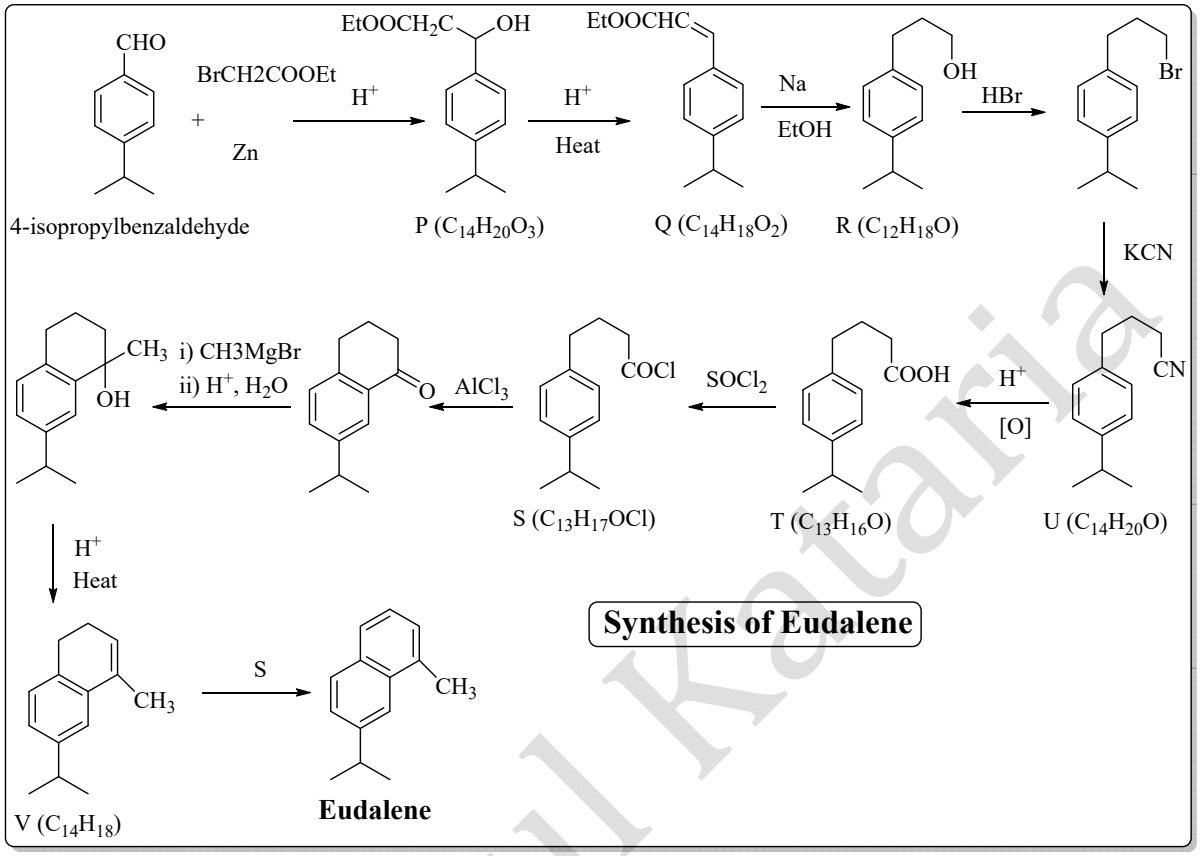
❖ Haworth Synthesis of different substituted phenanthrene from naphthalene or mono substituted naphthalene



❖ Synthesis of Chrysene via bogert-cook method from benzene

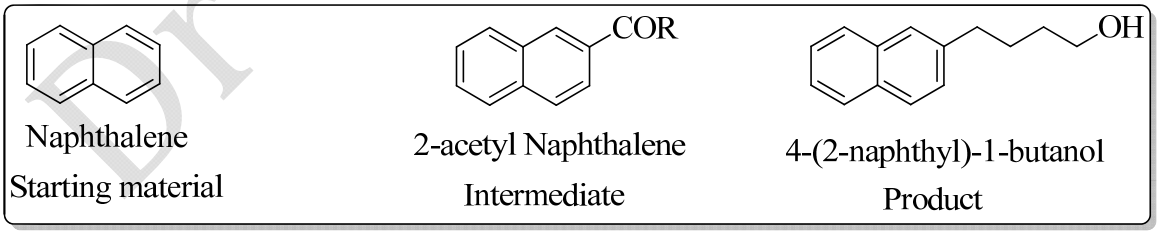


❖ Synthesis of Eudalene found in Eucalyptus oil



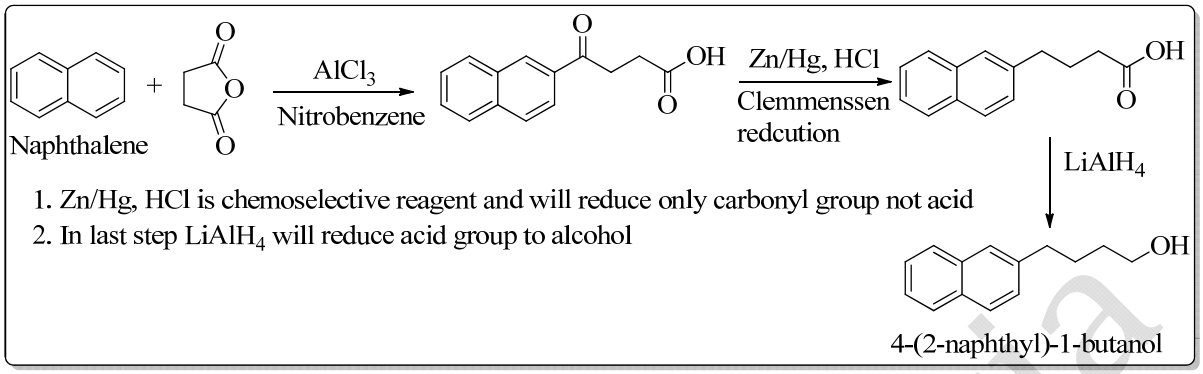
Question: Give the synthesis of 4-(2-naphthyl)-1-butanol by initial acylation of naphthalene.

For such question you need to understand or remind the structure of product and starting material.



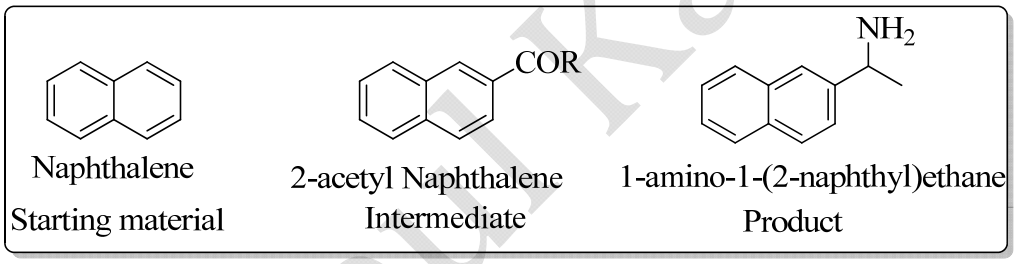
Here keep in mind the question. You have been asked to prepare 4-(2-naphthyl)-1-butanol (remember its structure). Second point the starting material that is naphthalene. Third point is acylation of naphthalene so first step will be friedel craft acylation. Acylation of naphthalene depends upon the product. You need to select appropriate compound to be acylated with naphthalene. The position of substitution in product is on second (beta) position so you need to select nitrobenzene as a solvent (here remember that acylation of naphthalene is dependent

upon solvent used, if you use tetrachloro ethane as a solvent then you will get substitution at position-1, if you use nitrobenzene as a solvent then you will get substation at position-2).

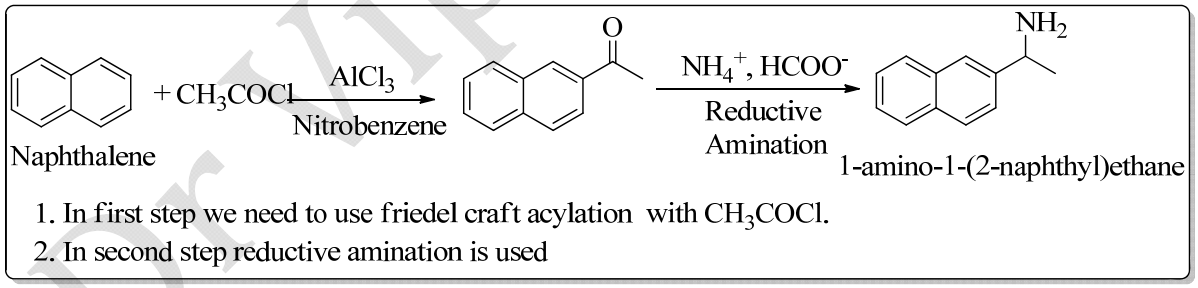


Question: Give the synthesis of 1-amino-1-(2-naphthyl)ethane by initial acylation of naphthalene.

In this question, the final product is **1-amino-1-(2-naphthyl)ethane** and starting material is naphthalene. The intermediate is acetyl naphthalene.

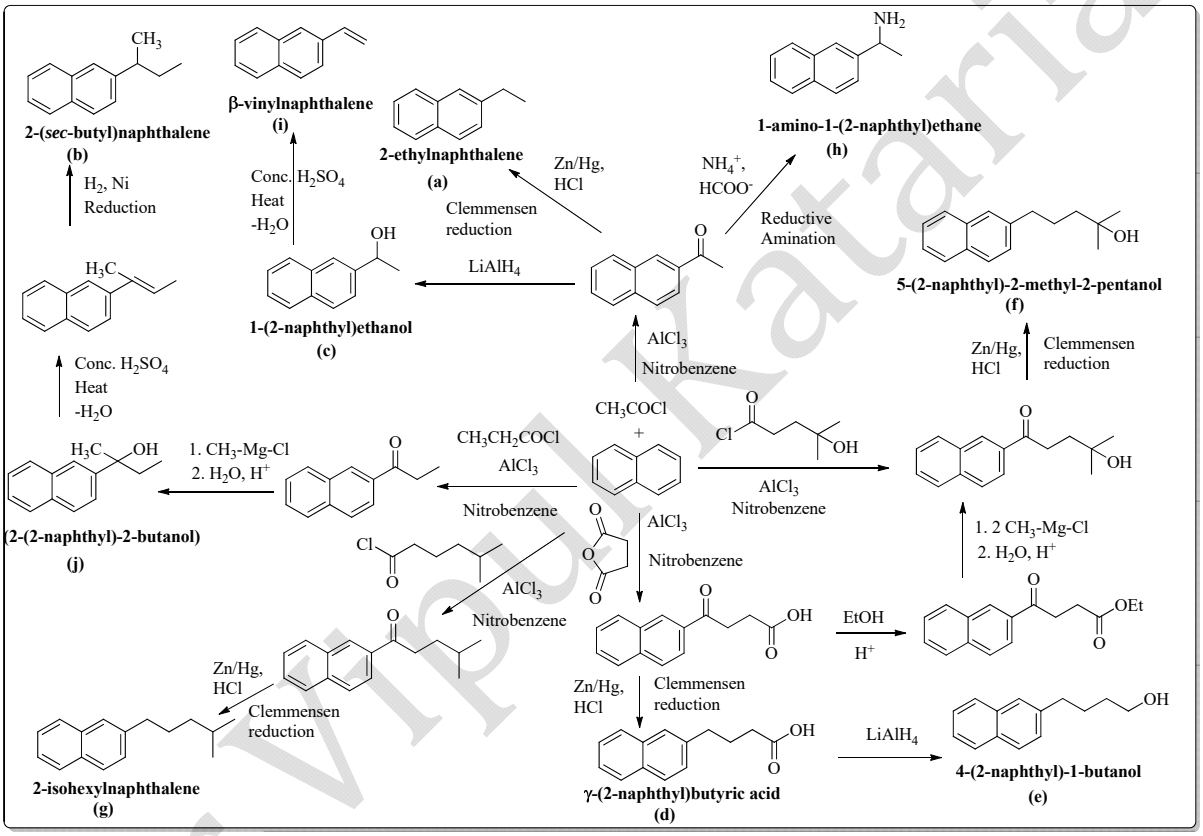


Keep in mind that how we perform acylation.



Question: Outline synthesis of following compounds from naphthalene via an initial acylation.

(a) 2-ethylnaphthalene
(b) 2-(sec-butyl)naphthalene
(c) 1-(2-naphthyl)ethanol
(d) γ-(2-naphthyl)butyric acid
(e) 4-(2-naphthyl)-1-butanol
(f) 5-(2-naphthyl)-2-methyl-2-pentanol
(g) 2-isohexylnaphthalene
(h) 1-amino-1-(2-naphthalene)ethane
(i) β-vinylnaphthalene
(j) methylethyl-2-naphthylcarbinol or (2-(2-naphthyl)-2-butanol)



Question: Starting with 1-nitronaphthalene, and using any inorganic or aliphatic reagent, prepare following products.

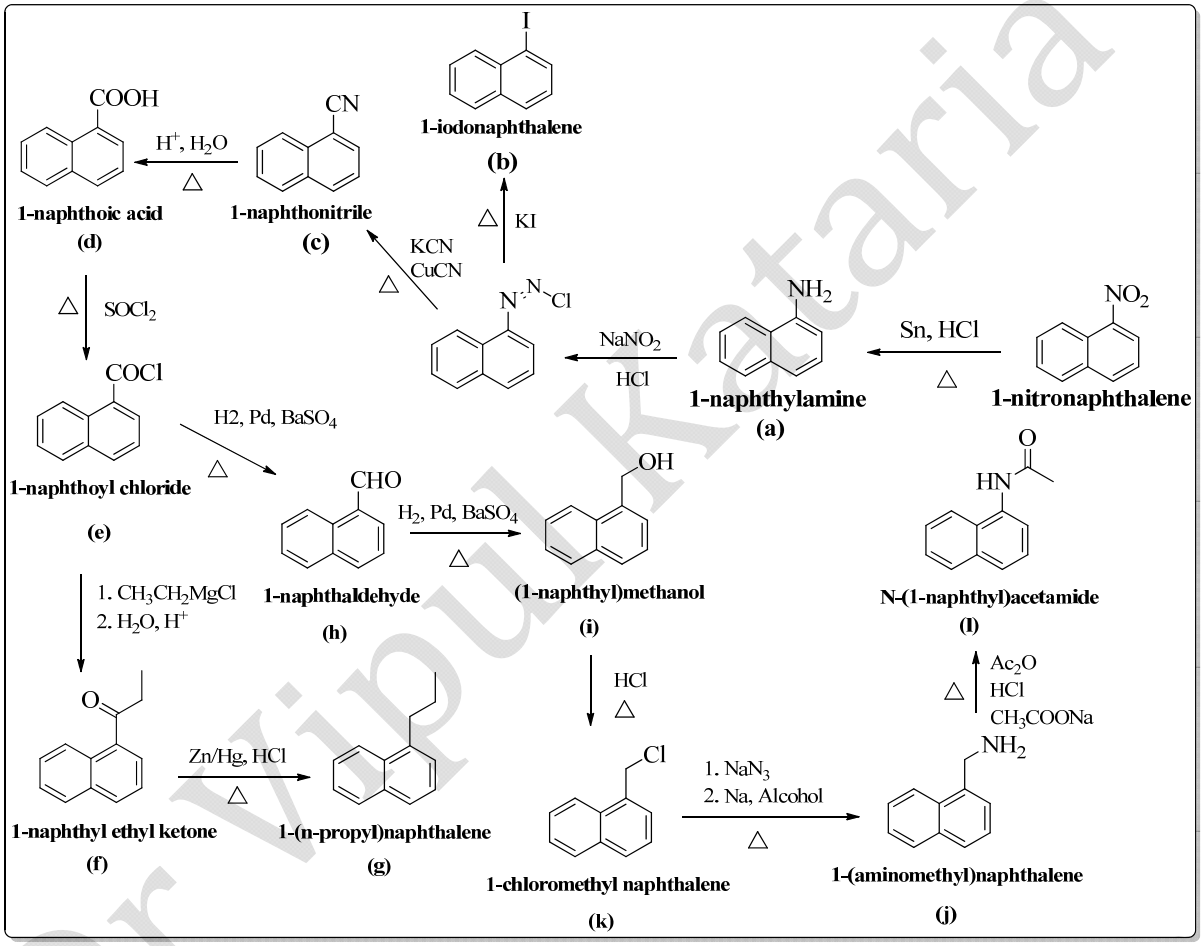
(a) 1-naphthylamine (b) 1-iodonaphthalene (c) 1-naphthonitrile

(d) 1-naphthoic acid (e) 1-naphthoyl chloride (f) 1-naphthyl ethyl ketone

(g) 1-(n-propyl)naphthalene (h) 1-naphthaldehyde

(j) (1-naphthyl)methanol (j) 1-(aminomethyl)naphthalene

(k) 1-chloromethyl naphthalene (l) N-(1-naphthyl)acetamide



I have work hard preparing this material.....

You also work hard preparing from this material!!!!

Best Luck....