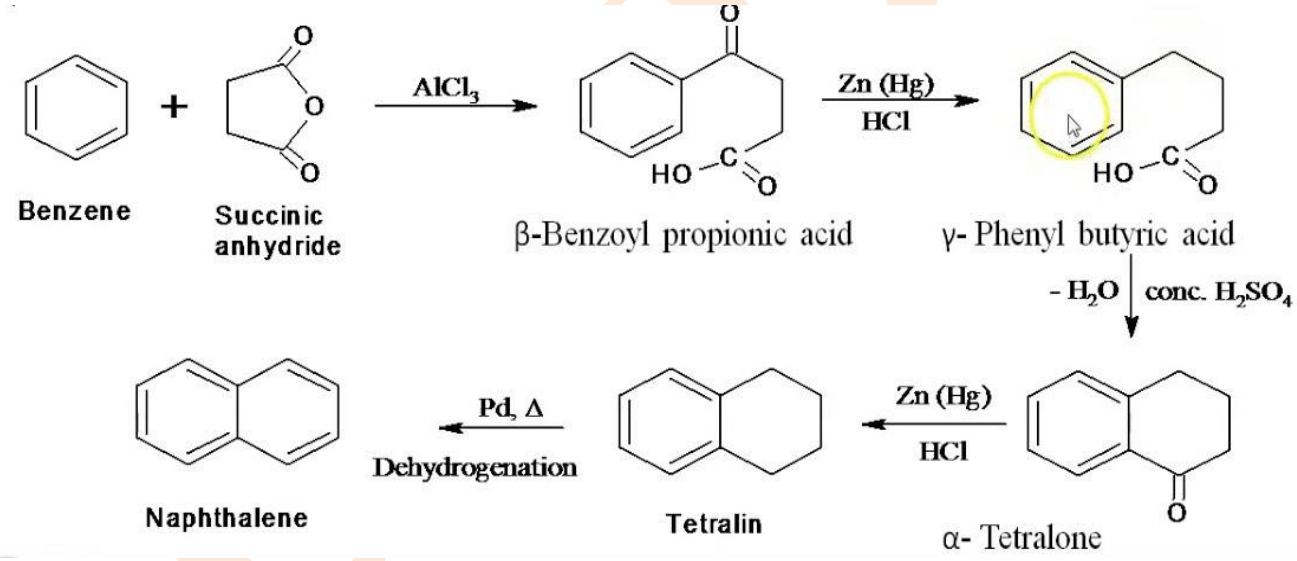
PHARMACEUTICAL ORGANIC CHEMISTRY-II- BP301T

UNIT: 4 Polynuclear hydrocarbons

CLASS:2

TOPIC: Naphthalene

Synthesis of Naphthalene:



Benzene on reaction with succinic anhydride in the presence of $AlCl_3$ to form Benzoyl propanoic acid.

Benzoyl propanoic acid which undergo reduction reaction to form phenyl butyric acid.

phenyl butyric acid is reacting with concentrate Sulphuric acid to form alpha tetralone.

Alpha tetralone undergo reduction reaction to form tetralin.

Tetralin undergo dehydrogenation to form naphthalene.

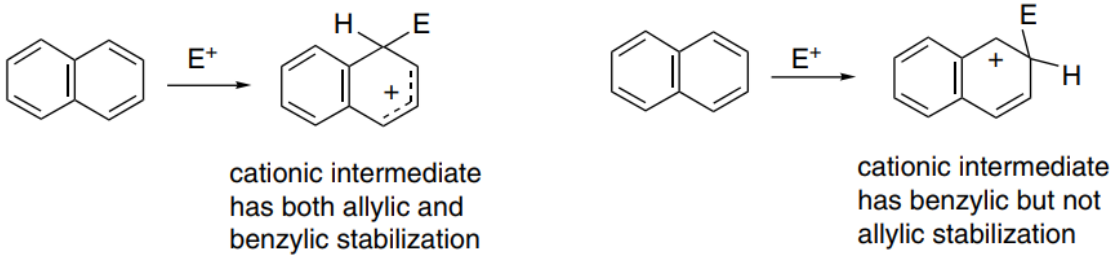
Physical properties of naphthalene:

- Naphthalene is a colourless crystalline solid
- Naphthalene is insoluble in water and soluble in organic solvents like ether, alcohol, benzene.

- Naphthalene having high melting point and low boiling point.

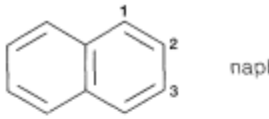
Electrophilic substitution reactions:

The first explanation which I have come across and which is also the one I am able to make sense of is given by Hepworth, Waring and Waring . They explain it by using the concept of Clar's rule. With an attack at the αα-position, there would be two resonance structures in the intermediate with preservation of the aromatic sextet. With an attack at the ββ-position, there would only be one resonance structure in the intermediate with preservation of the aromatic sextet. As such, the αα attack would be more preferable since the resultant intermediate would be more stable.
The second explanation which I have come across just today comes from Carey and Sundberg . An image of the section of the text discussing the issue is shown below.

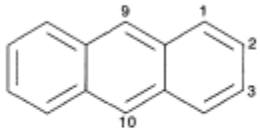


naphthalene, phenanthrene, and anthracene resemble benzene in many respects, they are more reactive than benzene in both substitution and addition reactions. This increased reactivity is expected on theoretical grounds because quantum-mechanical calculations show that the net loss in stabilization energy for the first step in electrophilic substitution or addition decreases progressively from benzene to anthracene; therefore the reactivity in substitution and addition reactions should increase from benzene to anthracene.

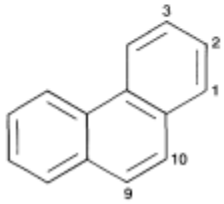
In considering the properties of the polynuclear hydrocarbons relative to benzene, it is important to recognize that we neither expect nor find that all the carbon-carbon bonds in polynuclear hydrocarbons are alike or correspond to benzene bonds in being halfway between single and double bonds.



naphthalene



anthracene



phenanthrene

The 1,2 bonds in both naphthalene and antracene are in fact shorter than the other ring bonds, whereas the 9,10 bond in phenanthrene closely resembles an alkene double bond in both its length and chemical reactivity.