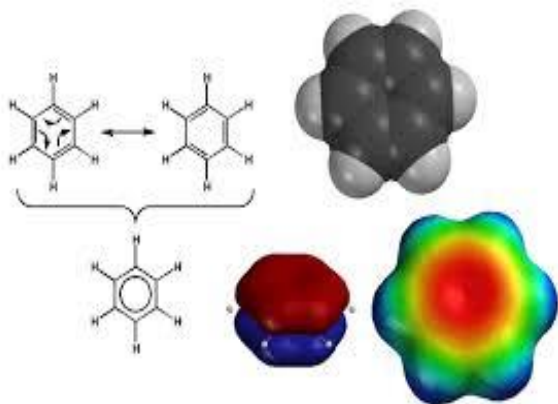
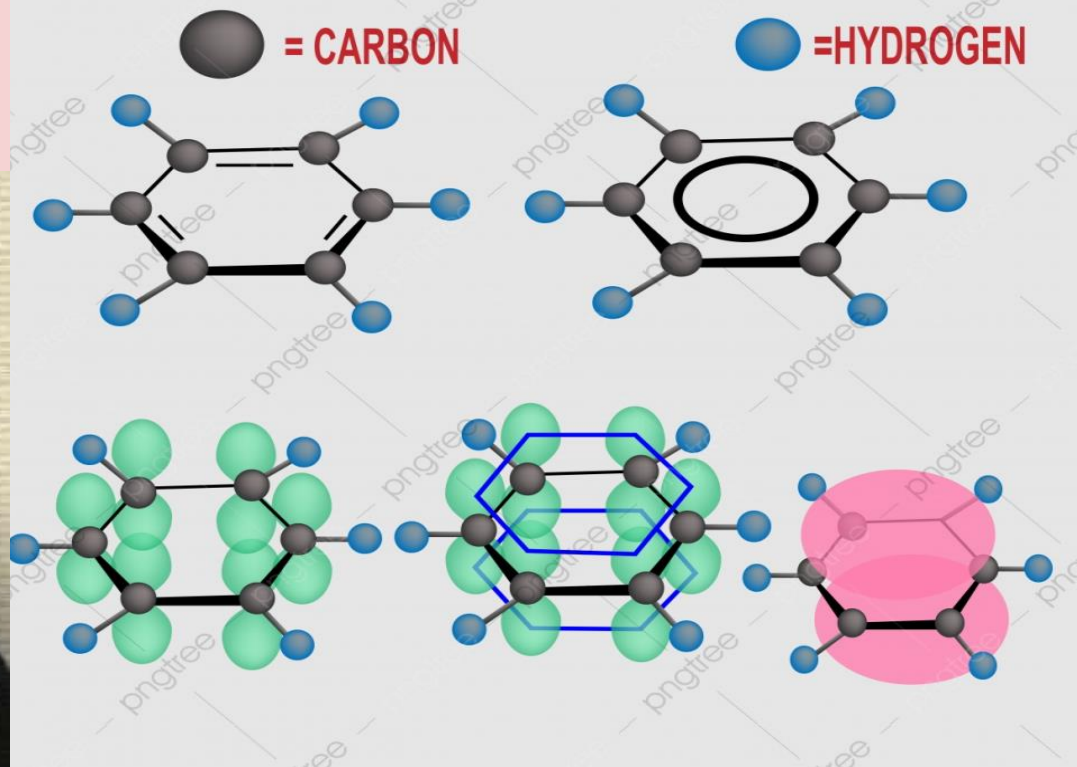


# Arenes and Aromaticity



Friedrich August Kekulé  
1829-1896 (German)

## BENZENE (C<sub>6</sub>H<sub>6</sub>)

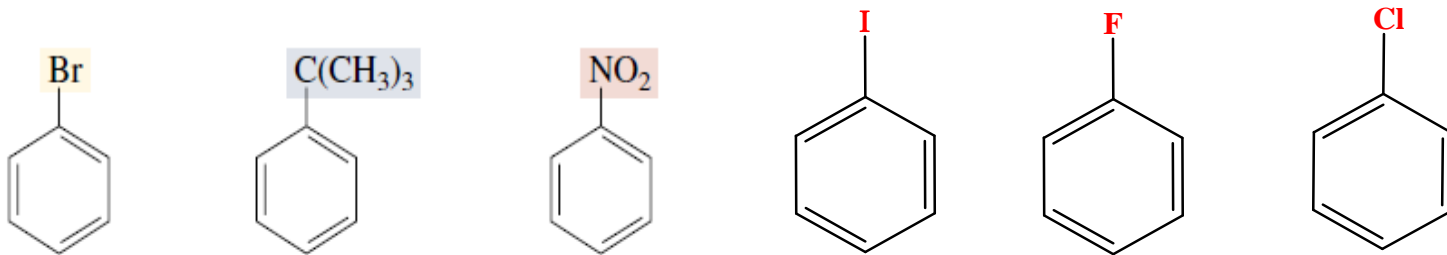


**Prof.(Dr) Suryawanshi V.S.**

Department of Chemistry,  
Shri Chhatrapati Shivaji College,  
Omerga Dist.Osmanabad.  
vssurya11@gmail.com

# Nomenclature of benzene derivatives:

A) Benzene as **parent name** and the **substituent** is indicated by a prefix...



Bromobenzene

*tert*-Butylbenzene

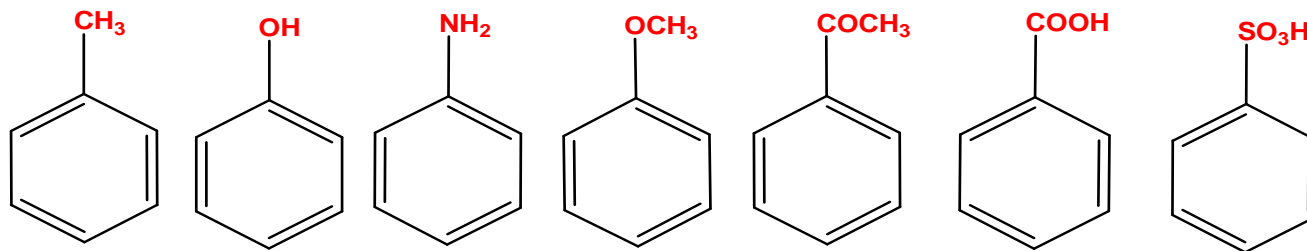
Nitrobenzene

Iodobenzene

Fluorobenzene

Chlorobenzene

B) **Substituent along with the benzene ring** are given a new name.



Toluene

Phenol

Aniline

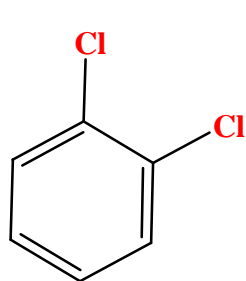
Anisole

Acetophenone

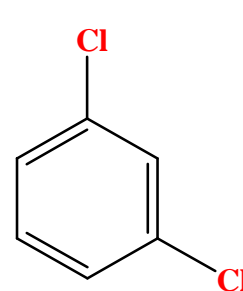
Benzoic acid

Benzene sulphonic acid

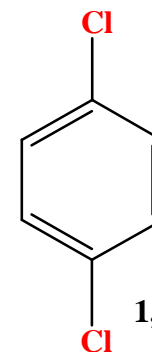
C) When substituents are present, their relative positions are indicated by the prefix **ortho, meta and Para** (abbreviated as, *o*-, *m*-, *p*-) or by the use of numbers.



1,2 or *o*-dichlorobenzene

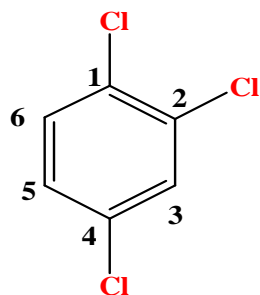
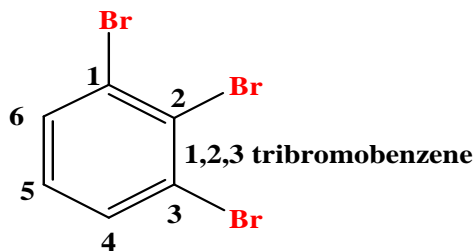


1,3 or *m*-dichlorobenzene



1,4 or *p*-dichlorobenzene

D) If **more than two substituent** are present, their relative positions are not indicated by *-o*, *m* and *-p* terms. Their **positions** are indicated by the use of **numbers only**. Benzene ring is numbered so as to get the **lowest possible sum** of the numbers.

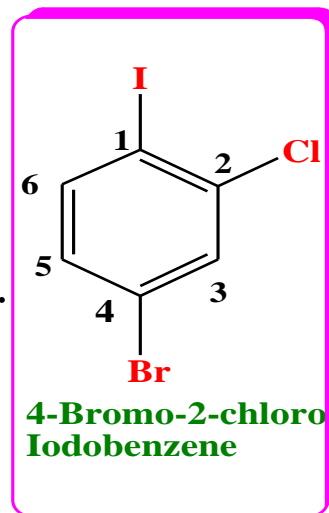
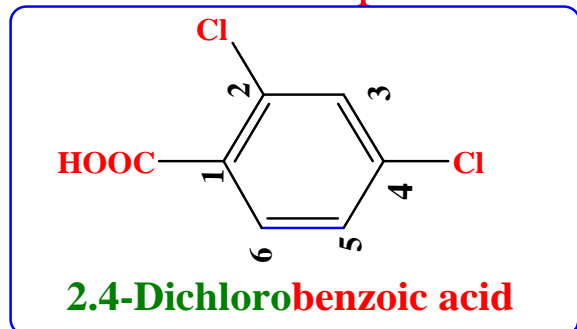
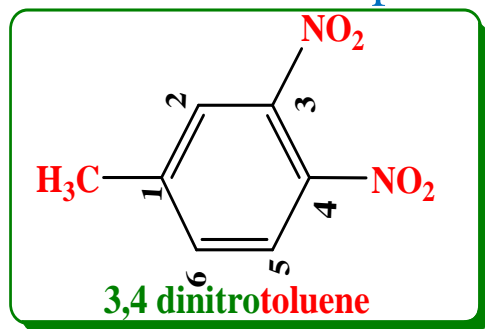


1,2,4 trichlorobenzene  
 $1+2+4=7$   
**Correct name**

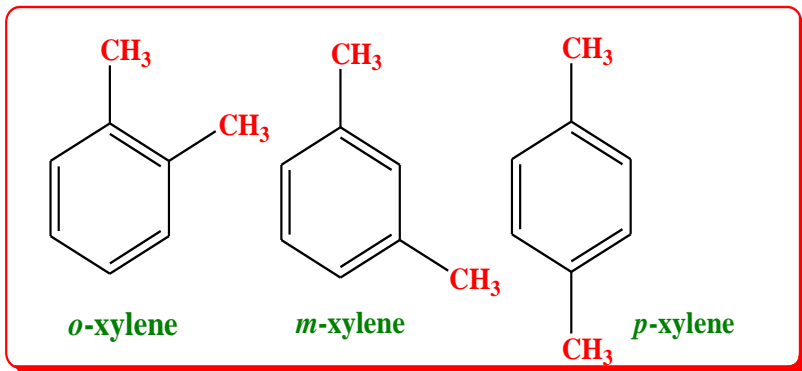
1,2,4 trichlorobenzene  
 1,4,6 trichlorobenzene  
 $1+4+6=11$   
**Incorrect/wrong name**

E) When **more than two substituent's** are present and the substituent are different, they are listed in **alphabetical order**.

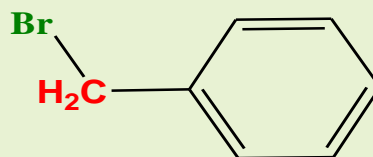
F) when a substituent is one that when taken together with the benzene ring gives a new base name that substituent is assumed to be in **position '1'** and the new **parent name is used**.



➤ Dimethyl benzenes are called as **Xylenes**.

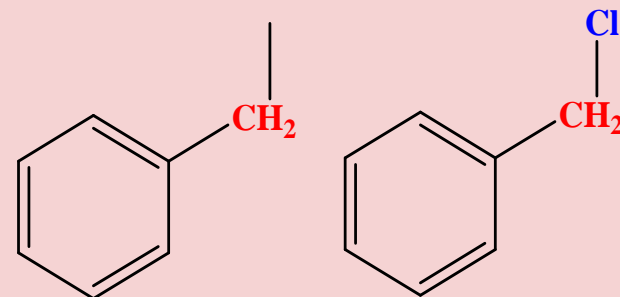


H) Organic halides in which halogen atom is directly attached to benzene ring and present in the side chain are called aralkyl halides.



**Benzyl bromide**

G) When  $-\text{C}_6\text{H}_5$  group is present as substituent. It is called as phenyl group and denoted by  $(-\text{C}_6\text{H}_5$  or Ph-).  $\text{C}_6\text{H}_5-\text{CH}_2-$  Phenyl methyl is given special name –benzyl.



**Benzyl group**

**Benzyl Chloride**

I) Alkenyl benzene has special name styrene.

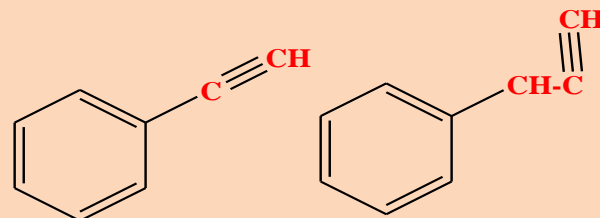


**Styrene**

**Allyl benzene**  
**(3-Phenyl propene)**

**2-phenyl-2-butene**

**Similarly,**



**Phenyl acetylene**

**Benzyl acetylene**

## Molecular formula and Kekule structure of Benzene (1865) :

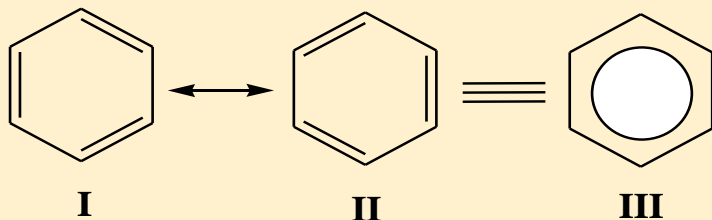


Friedrich August Kekule,  
German Organic  
Chemist (1829-1896)

1. Benzene Mol. Formula ( $C_6H_6$ ) is **hexagonal cyclic ring** structure.
2. **All six carbon** atoms are bonded to each other by **single and double bonds** and **one hydrogen** atom attached to each carbon.
3. Single and double bonds in benzene have different bond lengths, but later on proved to be wrong.
4. All **C-C bond** length in benzene is **same (1.397A)**.
5. Benzene undergoes **readily substitution** reactions rather than addition reactions, even though it possesses **unsaturated double bonds**.

### Resonance hybrid structure of benzene:

- Benzene is actually a resonance hybrid of the two Kekules structures.(I &II).
- These structures differ in the arrangement of pi electrons and
- They are delocalized over the benzene ring forms delocalized bonds.
- This delocalization of pi-electrons is represented by inscribing a circle in the hexagon.



**C-C in Benzene = 1.39 A**

**C-C in Alkane = 1.54 A**

**C=C in Alkene = 1.33 A**

**C-H in Benzene = 1.09 A**

**C≡C in Alkyne = 1.21 A**

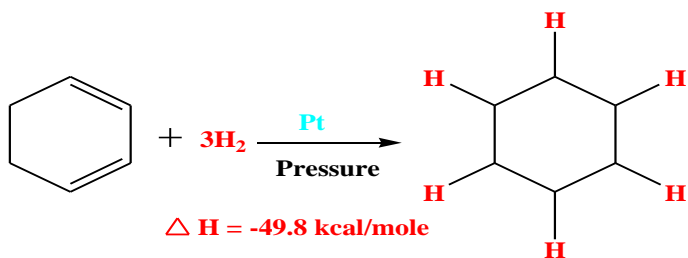
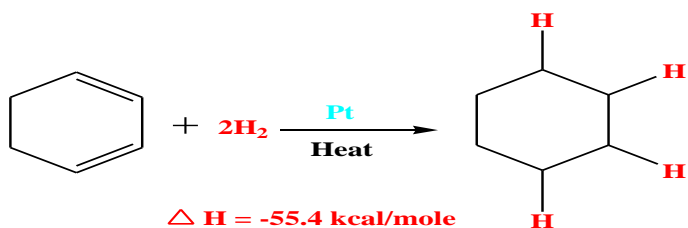
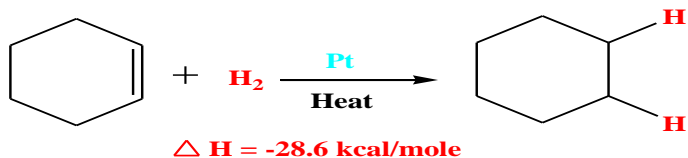
# Stability of Benzene:

**Definition:** The difference between the energy of actual molecule of Benzene (Str.III) and energy of its canonical forms (I &II) is called resonance energy or stabilization energy of Benzene.

It is calculated from heat of combustion and from heat of hydrogenation of cyclohexene.

**Heat of hydrogenation:** quantity of heat evolved when one mole of unsaturated compound is hydrogenated.

A) Cyclohexene containing one double bond gets hydrogenated readily converts to cyclohexane, similarly two and three double bonds undergoes hydrogenation with evolution of heat.



## Energy data and facts:

- We expect the heat of hydrogenation for benzene (considering three alternate double bonds-Kekules structure) is expected to be  $28.6 \times 3 = 85.8 \text{ Kcal/mole}$ .
- But actually it is  $49.8 \text{ Kcal/mole}$  which is less by  $36 \text{ Kcal/mole}$  but predicted value is  $(85.8 - 49.8 = 36 \text{ Kcal/mole})$ .
- Means benzene (Str.III-resonance hybrid) is more stable by  $36 \text{ Kcal/mole}$  than I and II canonical Kekules structures.
- Greater resonance energy gives more stability to resonance hybrid.

## Molecular orbital picture of Benzene:

- The unusual behavior towards substitution reactions can be well explained by MO picture of benzene.

According to Molecular orbital theory,

- 1) All **carbons are SP<sup>2</sup>** hybridized with **trigonal planar** structure.
- 2) Each SP<sup>2</sup> carbon atom possesses **unhybridized 2P<sub>z</sub> orbital** with one electron which remains **perpendicular** to the trigonal planar structure.
- 3) **Sidewise overlapping** takes place between upper and lower lobes of 6 P<sub>z</sub> orbitals resulting in spreading of six P<sub>z</sub> electrons in the form of π electron cloud above and below the plane of hexagonal planar benzene molecule.
- 4) This type of π overlap and π bonding is called **delocalization** and resulting bonds called as **delocalized bonds**.
- 5) Due to delocalization of π electrons **C-C length is 1.39 Å**, which is intermediate between single bond in alkane (1.54 Å) and C=C in alkene (1.33 Å).
- 6) **Axial overlapping** between SP<sup>2</sup> hybrid orbitals of each carbon atom results in the formation of **six C-C sigma** bond, similarly axial overlapping of between **spherical 1S orbitals** of six hydrogen atoms and SP<sup>2</sup> hybrid orbitals of six carbon atoms forms **six C-H sigma** bonds.
- 7) All six carbon atoms are SP<sup>2</sup> hybridized, bond angle between H-C-C and C-C-C remains **120 degree**. Geometry of the molecule is cyclic, planar with delocalization of 6 π electrons. i.e. and **obeys Huckel rule** for aromaticity (4n+2) π electrons.

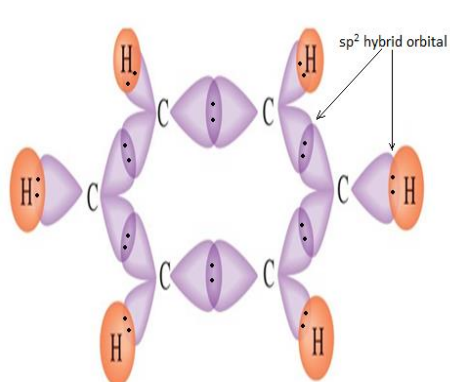


Fig. Sigma bond formation

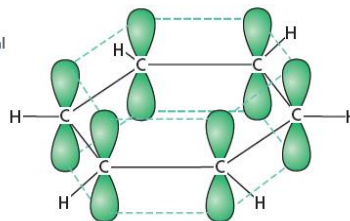


Fig. Sidewise overlap of unhybridized p orbitals to form  $\pi$  bonds

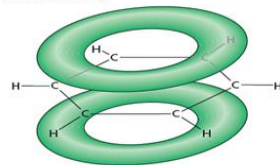


Fig.  $\pi$  electrons cloud lying above and below the plane.

## Aromaticity

- It is a property of the **conjugated cycloalkenes** and **aromatic** which enhances the **stability** of a molecule due to the **delocalization** of electrons present in the  $\pi$ - $\pi$  orbitals.
- Aromatic molecules (**Benzene**) are said to be very **stable**, and they **do not break** so easily and also reacts with other types of substances.
- The organic compounds which are not said to be aromatic are known as aliphatic compounds. These might be in **cyclic form**, but only the aromatic rings have a **special kind of stability**.



- Benzene is **ideal** compounds possessing aromatic character. **Benzene and other compounds** which are **similar to benzene** in certain characteristics are called **aromatic** compounds.
- There are some physical and chemical properties of aromatic compounds are collectively known as **aromaticity or aromatic** character. These areas follows,
  - 1) Geometry of molecule must be **cyclic, planar(flat)** and contains some no.of **conjugated 'π' bonds**.
  - 2) 'π' bonds should cyclically be delocalized forming **'π' electron cloud** above and below the plane of molecule.
  - 3) Molecule should follow **Huckel rule (4n+2) π** electrons rule where n is an integer and may be 0,1,2,3,4etc.
  - 4) Must have unusual **thermal stability** with low heat of hydrogenation and low heat of combustion.
  - 5) Readily undergoes **substitution reactions** than addition reactions.
  - 6) Must **resist to oxidation** reactions with  $\text{KMnO}_4$ ,  $\text{HNO}_3$  and others.
  - 7) Compound should have **diamagnetic** susceptibility.

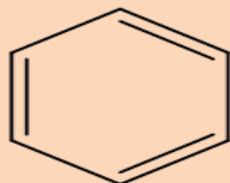
## Huckel rule: Erich Hückel 1931 (German chemist and physicist)

If a cyclic, planar molecule has  $4n+2$   $\pi$  electrons, it is considered **aromatic**. This **rule** would come to be known as **Hückel's Rule**.

When the number of its  $\pi$ -electrons equals  $(4n+2)$  where  $n$  is a non-negative integer, although clear-cut **examples** are really only established for values of  $n = 0$  up to about  $n = 6$ .

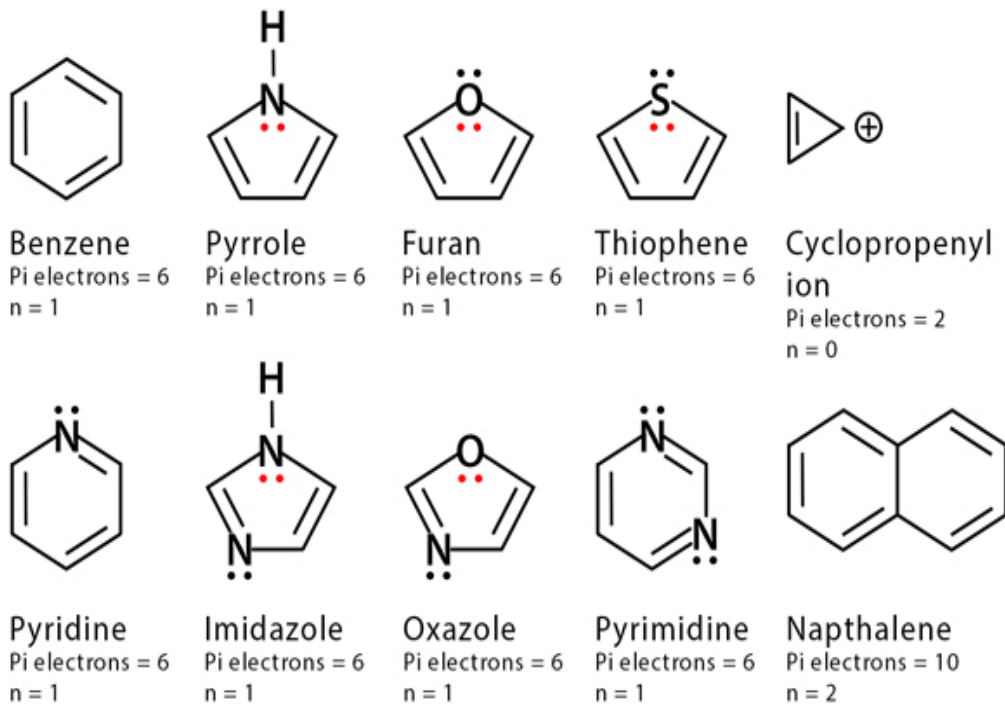
Example: 1) **Benzene**

No. of pi bonds = 3



- So no. of delocalized pi electrons =  $3 \times 2 = 6$   $\pi$  e so,  $(4n+2)$   $\pi$  electrons =  $(4n+2) = 6$
- Therefore,  $4n = 6 - 2 = 4$  and  $4n = 4$  Hence  $n = 1$  (non negative integer) so compound is Aromatic.

### Huckel's Rule for Aromatic Compounds (Number of Pi Electrons = $4n + 2$ )



Note: Red dots indicate pi electrons



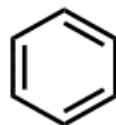
2  $\pi$  electrons

Aromatic



4  $\pi$  electrons

Not Aromatic



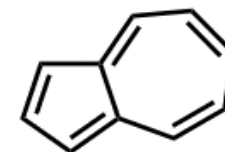
6  $\pi$  electrons

Aromatic



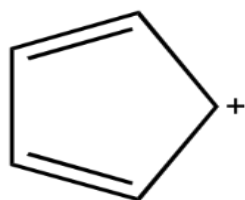
8  $\pi$  electrons

Not Aromatic



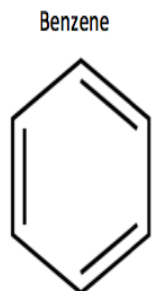
10  $\pi$  electrons

Aromatic



Cyclopentadienyl cation  
(four pi electrons)

Qu. Using the criteria for aromaticity, determine if the following molecules are aromatic:



Since benzene has 6 pi electrons:

$$4n + 2 = 6$$

Find n:

$$4n + 2 = 6$$

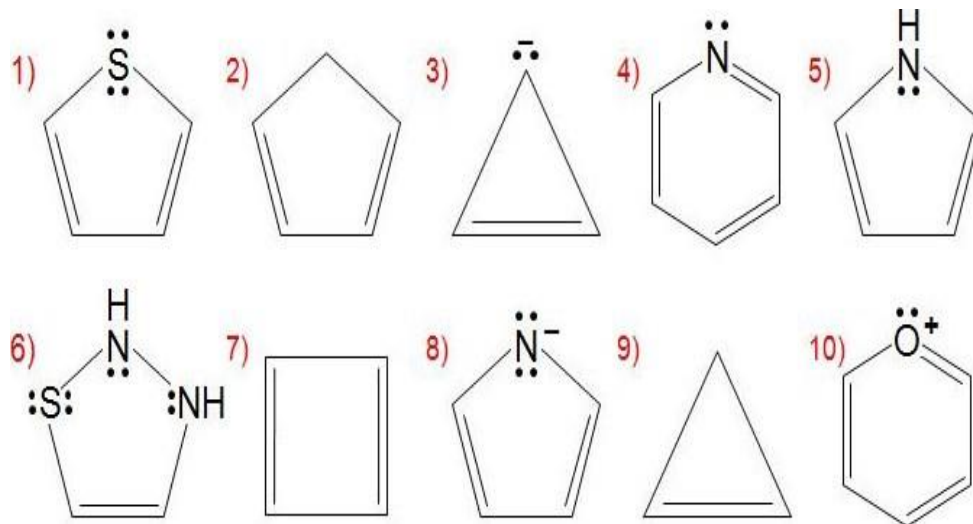
$$4n = 6 - 2$$

$$4n = 4$$

$$n = 1$$

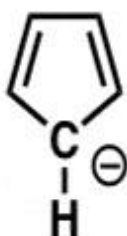
An aromatic compound follows Huckel's rule if n is equal to zero or a positive whole number.

Benzene is aromatic

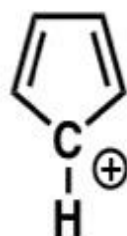




6 pi electrons



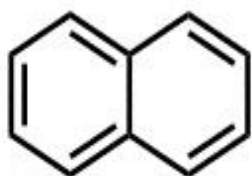
6 pi electrons



4 pi electrons



2 pi electrons



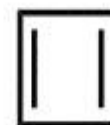
10 pi electrons



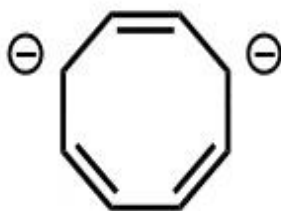
6 pi electrons



8 pi electrons



4 pi electrons



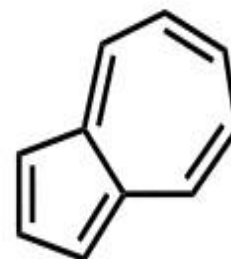
10 pi electrons



4 pi electrons



6 pi electrons



10 pi electrons

## Aromatic Electrophilic Substitution Reaction:

➤ Benzene has pi electron cloud above and below its sigma bond framework. Hence benzene is susceptible to Electrophilic attack, thus undergoes substitution reactions.

➤ Mechanism of aromatic Electrophilic substitution reaction involves following two steps.

**Step-I : a)** Electrophile ( $E^+$ ) approaches one of the carbon atom of benzene to form initially partial bonding which represents Transition state-I (T.S.)

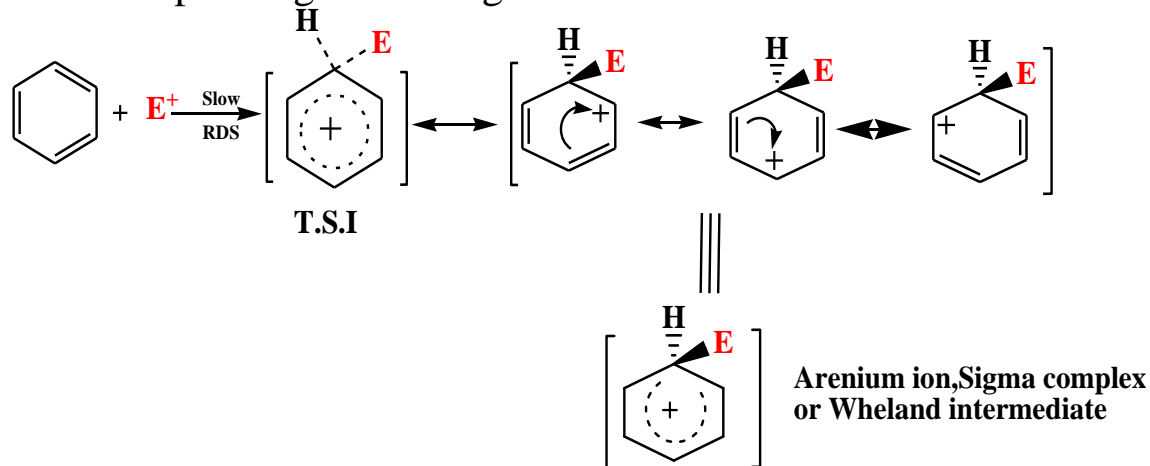
**b)** then two electrons of the six electrons ' $\pi$ ' (pi) system form a ' $\sigma$ ' (sigma) bond to one carbon atom of benzene ring.

**c)** Resulting +vely charged species is called as ' $\sigma$ ' (sigma) complex or **Wheland intermediate** or **Arenium ion**.

**d)** The carbon of benzene that forms a ' $\sigma$ ' bond to the Electrophile becomes **SP<sup>3</sup> hybridized** and remaining five carbon atoms remain still **SP<sup>2</sup> hybridized** with p orbital's.

**e)** The four ' $\pi$ ' electrons of the arenium ion are delocalized through these five p-orbitals.

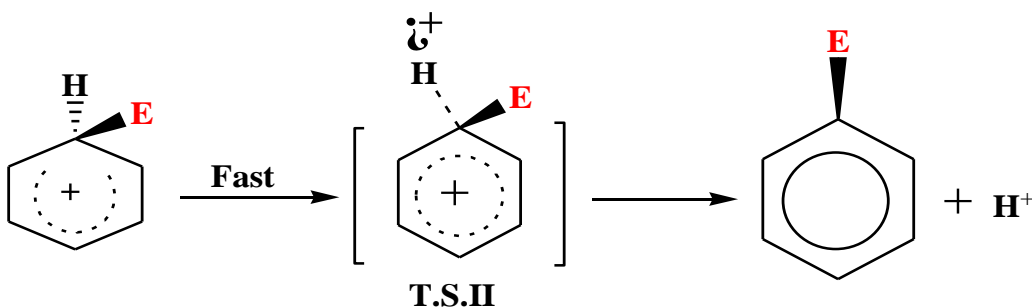
**f)** The arenium ion gets stabilized due to delocalization of positive charge over the ring forming corresponding resonating structure.



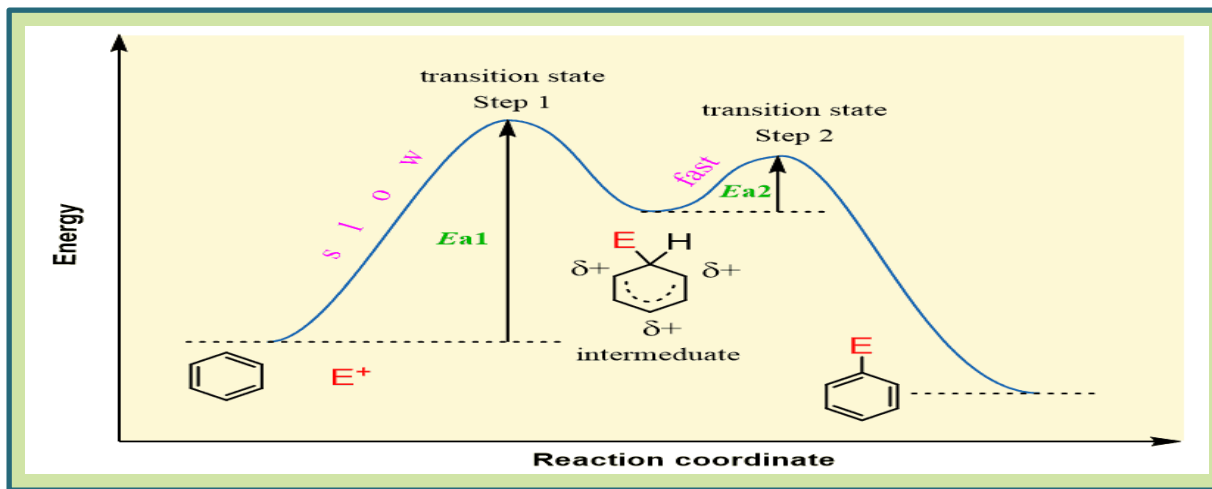
The formation of arenium ion is slow step hence it is rate determining step.

## Step-I :

- Bonding** between carbon and hydrogen becomes weak forming partial bonding, It represents **T.S.-II**.
- Arenium ion **loses a proton** from the carbon atom that bears the Electrophile. Benzene ring regains its two electrons.
- The carbon atom that bears the electrophile becomes **SP<sup>2</sup> hybridized again** and a benzene with six fully delocalized 'π' electrons is formed.
- In **step-II**, the **loss of a proton** takes place **rapidly** relative to step-I. Hence it is a fast step and has **no effect on the overall rate of reaction**.



Graph of energy V/s reaction coordinate

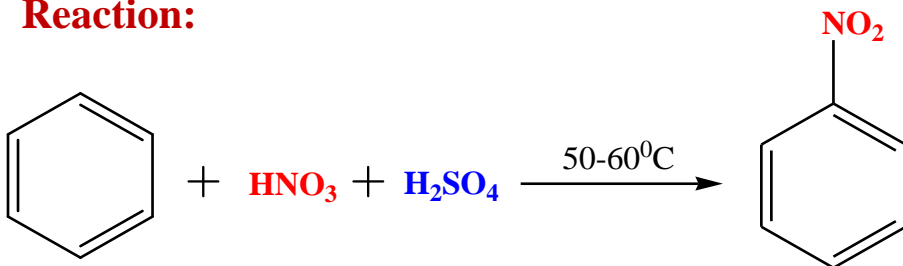


Energy profile diagram for aromatic electrophilic substitution reaction.

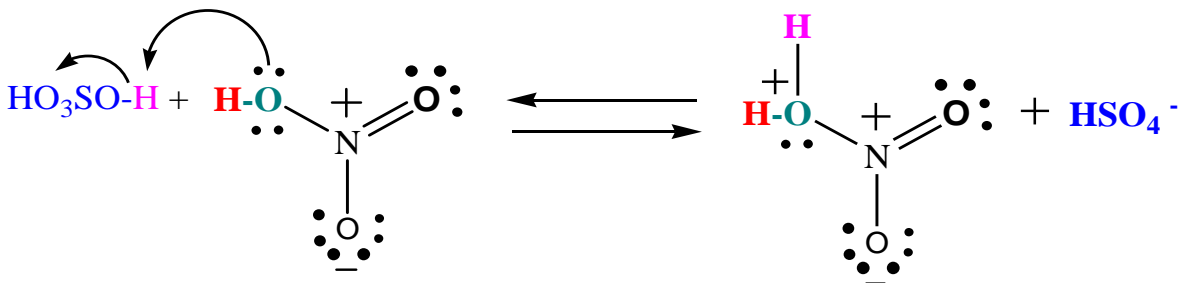
## Nitration reaction:

Benzene on heating with a mixture of conc. nitric acid and conc. sulphuric acid at 50-60 degree forms nitrobenzene. Conc. sulphuric acid increases the rate of reaction by increasing the concentration of electrophile  $\text{NO}_2^+$ .

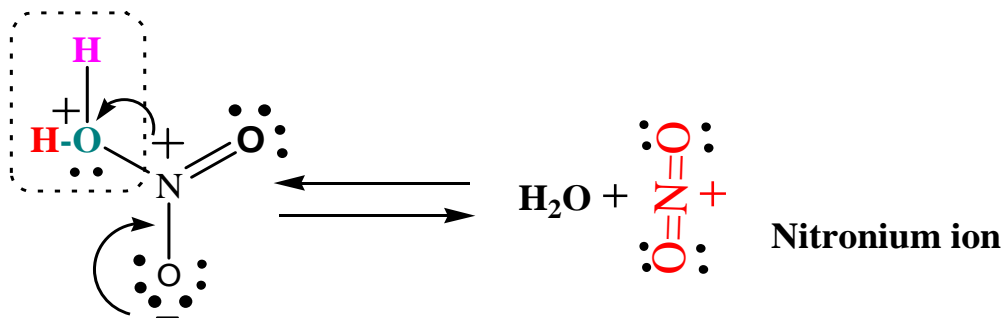
### Reaction:



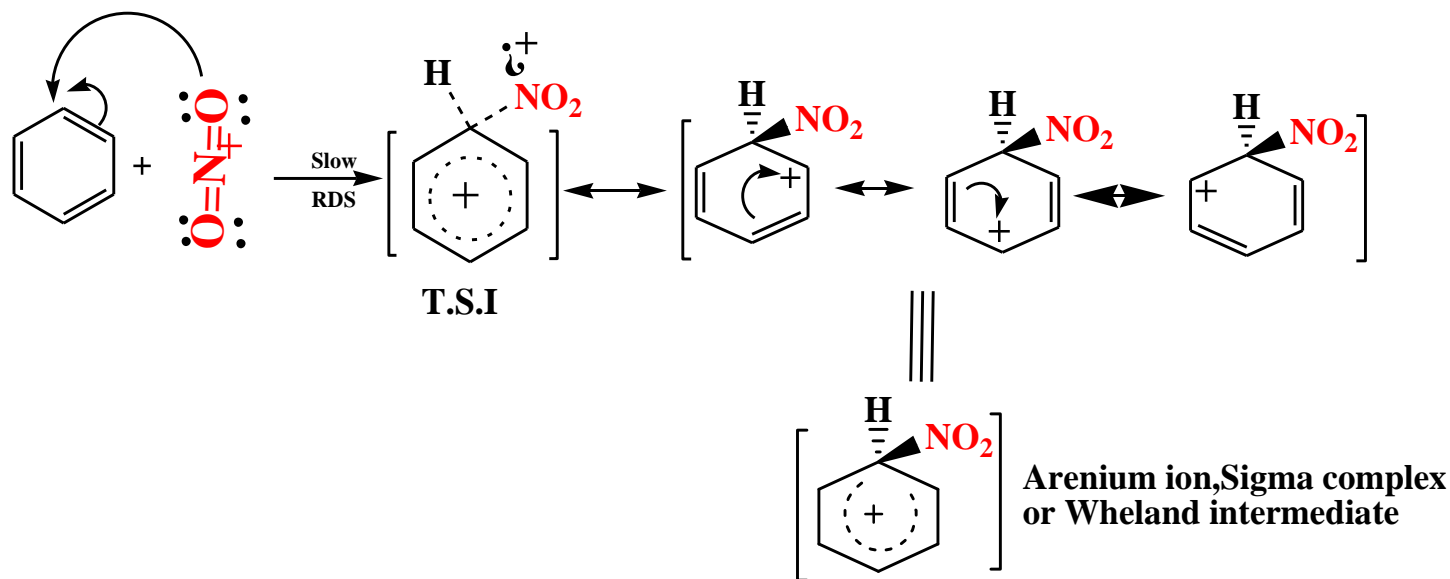
**Step-I :** Nitric acid accepts proton from the stronger Sulphuric acid.



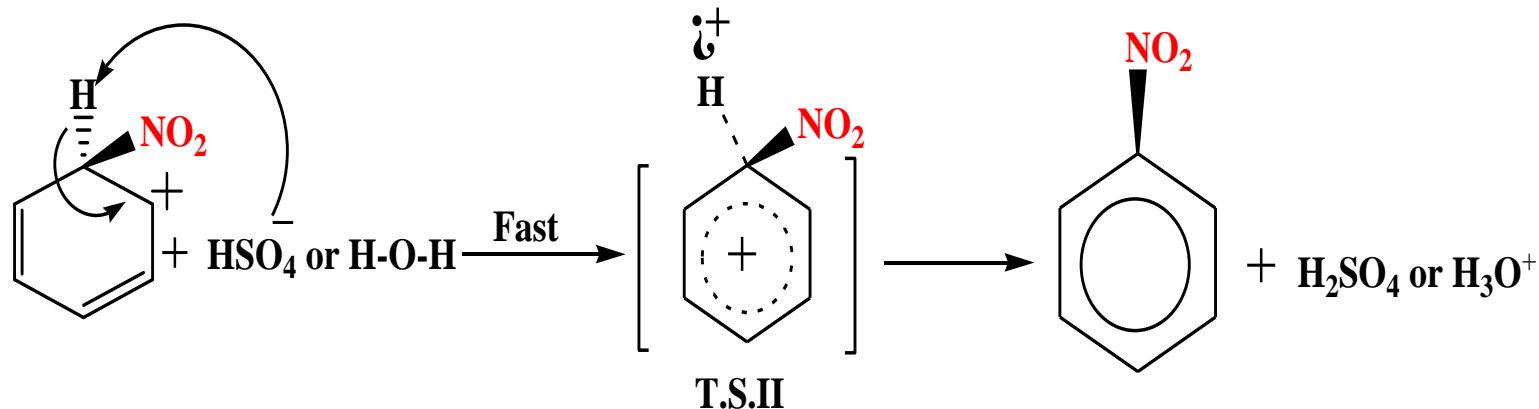
**Step-II :** Protonated Nitric acid dissociates to form a Nitronium ion.



**Step-III** :Nitronium ion acts as an electrophile and attacks one of the carbon atoms of benzene to form a resonance stabilized arenium.



**Step-IV** :Proton from arenium ion is abstracted by base  $\text{HSO}_4^-$  or  $\text{H}_2\text{O}$  to form nitrobenzene.

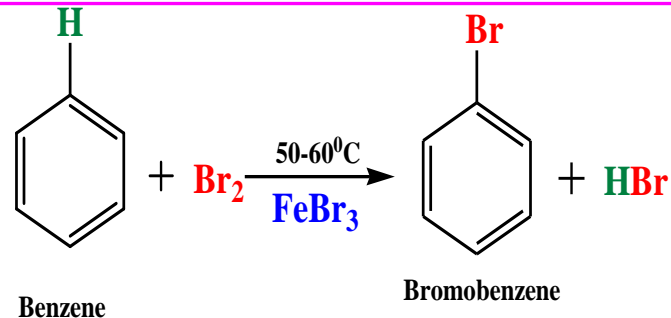
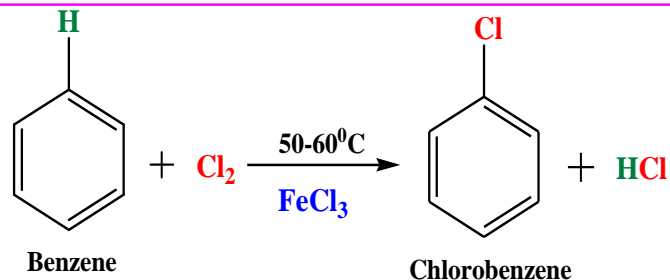




## Halogenations reaction:

Benzene reacts with  $\text{Cl}_2$  and  $\text{Br}_2$  in the presence of Lewis acids like  $\text{FeCl}_3, \text{FeBr}_3$  and  $\text{AlCl}_3$  to form chlorobenzene and bromobenzene respectively.

## Reaction:

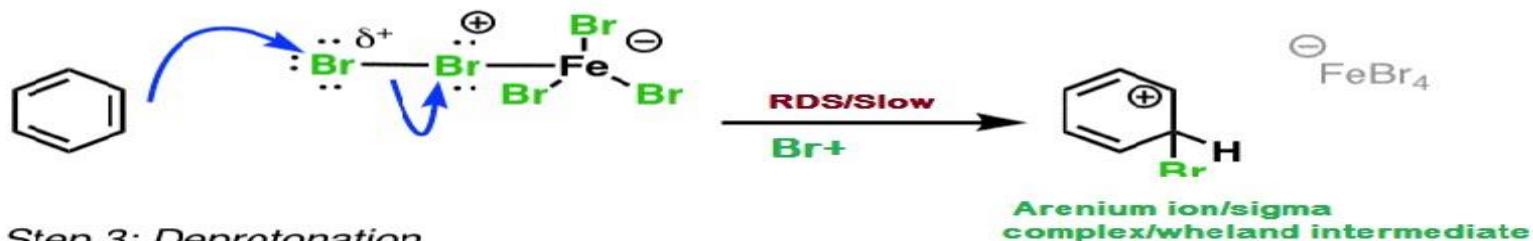


### Bromination of Benzene: The Mechanism

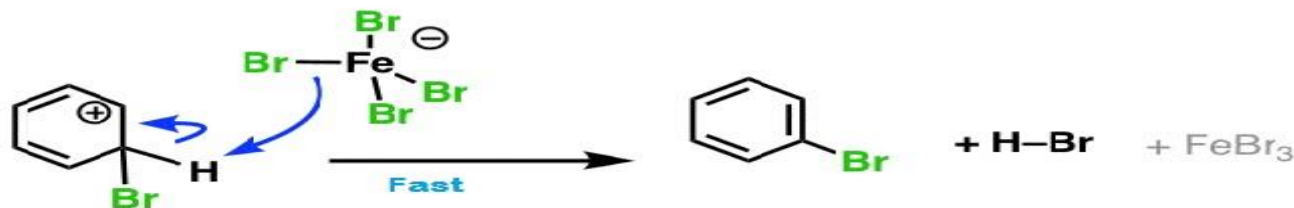
Step 1: Activation of Lewis acid



Step 2: Attack of electrophile by the benzene ring



Step 3: Deprotonation



**Iodination of benzene:** Iodine is very **unreactive**. The reaction of iodine with aromatic compound is highly **reversible**. **Loss of iodine** occurs more often from arenium ion than **loss of hydrogen** (last step).

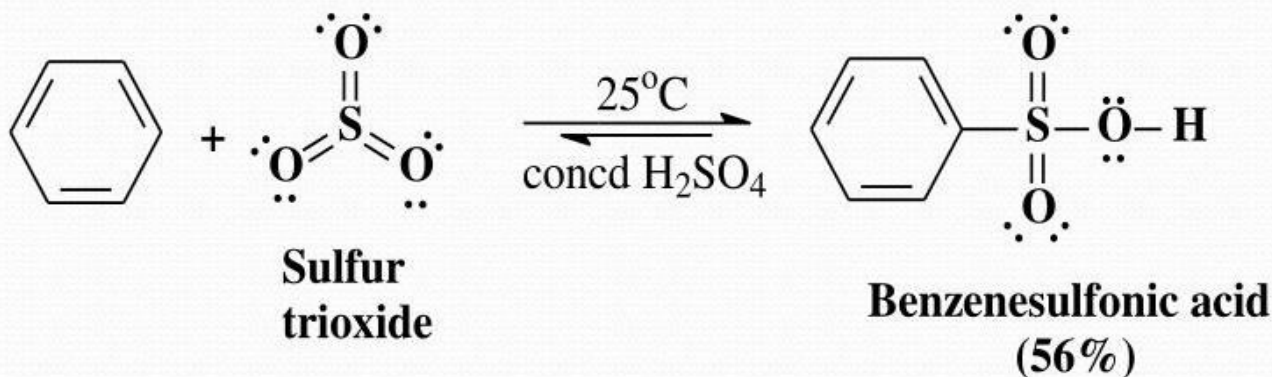
**Fluorination of benzene:** Benzene reacts with fluorine **vigorously**, hence direct fluorination of benzene is **not possible**.

❖ **Sulphonation of Benzene:**

❖ Benzene reacts with **fuming sulfuric acid** (Conc.  $\text{H}_2\text{SO}_4$  **saturated with  $\text{SO}_3$** ) at room temp. to produce benzene sulphonic acid.

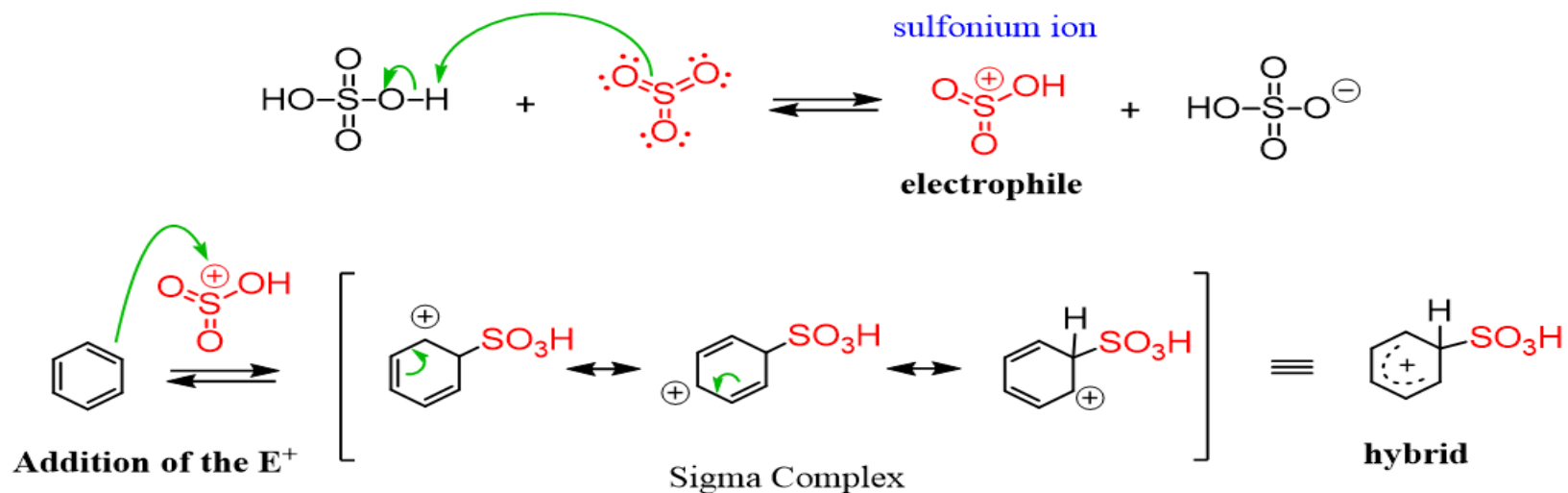
❖ Sulphonation also takes place in **Conc.  $\text{H}_2\text{SO}_4$**  alone but the **reaction is very slow**. In both cases  **$\text{SO}_3$  acts as electrophile**.

❖ **Reaction:**

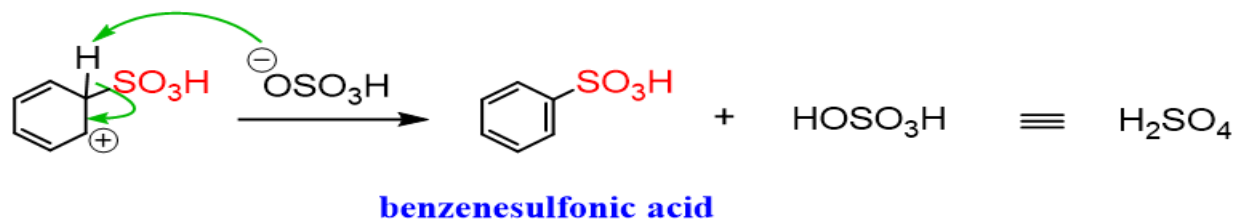


## Mechanism:

The  $^+\text{SO}_3\text{H}$  strong electrophile is formed by protonation of  $\text{SO}_3$



Loss of a proton - restoring the aromaticity



## ❖ Friedel-Crafts reaction:

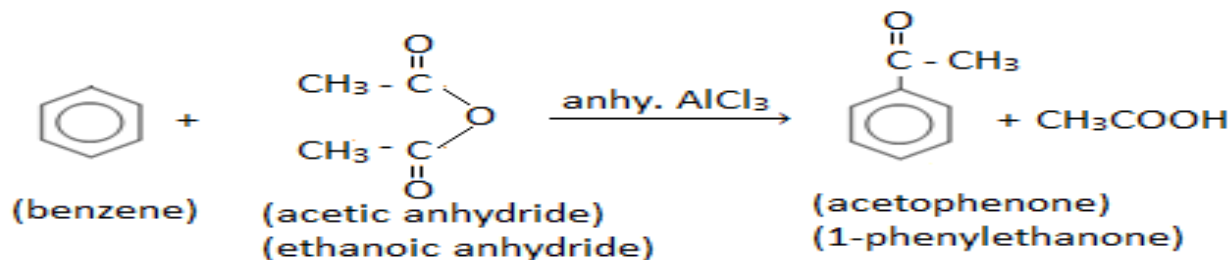
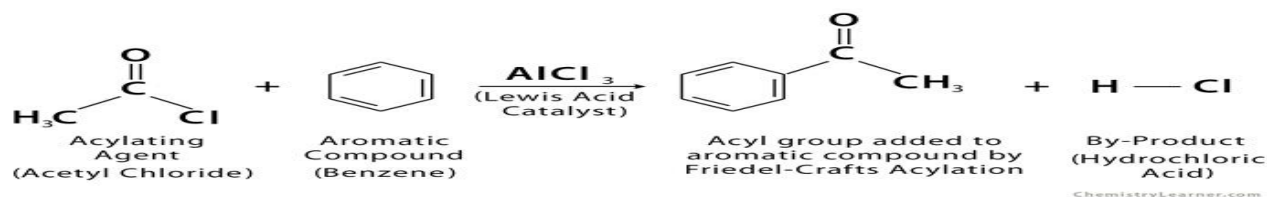
This reaction divides into two types:

- 1) Friedel-Crafts Acylation
- 2) Friedel-Crafts Alkylation

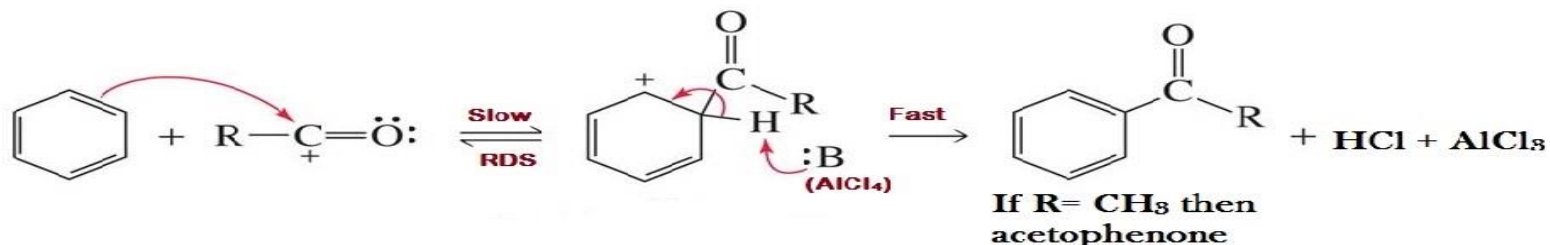
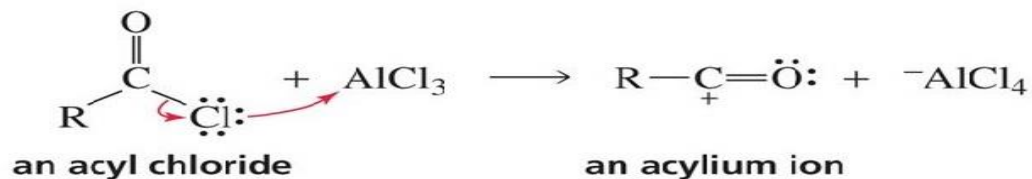
## ❖ Friedel-Crafts Acylation:

**Acylation of Benzene:** Benzene in the presence of Lewis acid like anhydrous aluminum chloride reacts with acetyl chloride or acetic anhydride at 80 C using benzene as solvent to form acyl chloride that is **acetophenone**.

### Friedel-Crafts Acylation



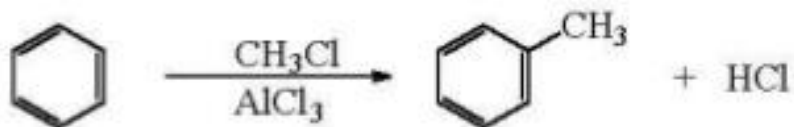
### Mechanism:



**Alkylation of Benzene:** Benzene in the presence of **anhydrous AlCl<sub>3</sub>** reacts with alkyl halide to form **alkyl benzene**. Lewis acid AlCl<sub>3</sub> enhances electrophilicity of alkylating agents.

**Example:** Benzene in presence of **anhydrous AlCl<sub>3</sub>** react with **methyl chloride** to form **methyl benzene (Toluene)**.

### Friedel craft's alkylation reaction's mechanism

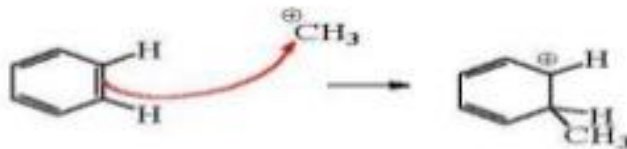


It occurs in 3 steps

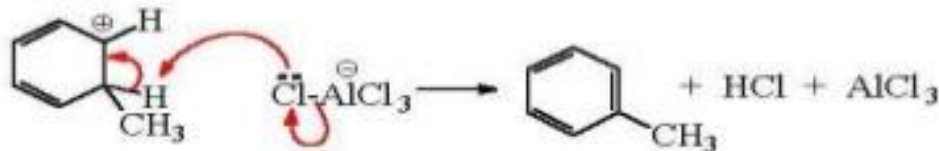
**Step-1- Generation of Electrophile methyl carbonium.**



**Step-2- Attack the electrophile to benzene ring and form sigma complex which is stabilized by resonance.**



**Step-3- The abstraction of H<sup>+</sup> from sigma complex to form electrophilic substitutions products .**





*Thank You for  
attention.....*