



# Chem 145

## Benzene & Aromatic Compounds

### Chapter 5

1434-1435  
2013-2014  
2<sup>nd</sup> semester

**Dr. Seham ALTERARY**

# Chapter Outlines

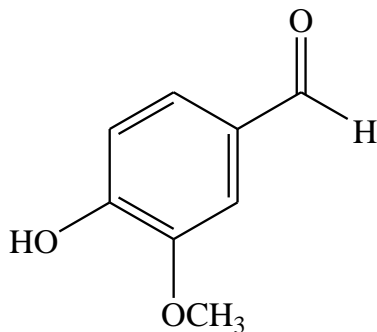
- Aromatic Compounds and Aromaticity.
- The physical properties of Benzene
- Hybridization of Benzene Ring.
- Hückel's Rule.
- Nomenclature of Benzene and Aromatic Compounds.
- Electrophilic Aromatic Substitution Reactions:
  1. *Specific Electrophilic Aromatic Substitution reactions.*
  2. *Side reaction of Aromatic compounds.*
  3. *Disubstituted Benzene “Orientation in monosubstituted”.*

# Aromaticity and Aromatic compounds

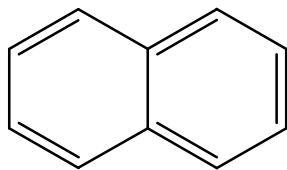
Aromatic word is derived from the Greek word '*aroma*' which means **fragrant smell**. For such reason, benzene and its derivative were originally classify as *aromatic compounds* as many of them have distinctive odors.

Here is some examples of aromatic compounds that have *distinctive odors*:

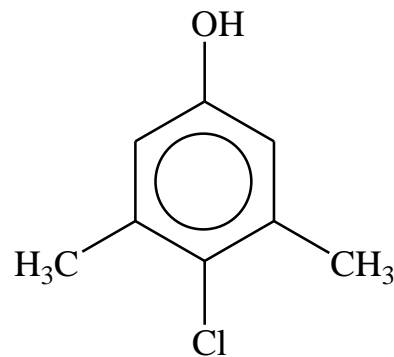
## General Information



Vanillin



Naphthalene



Dettol

4-hydroxy-3-methoxybenzaldehyde

4-chloro-3,5-dimethylphenol

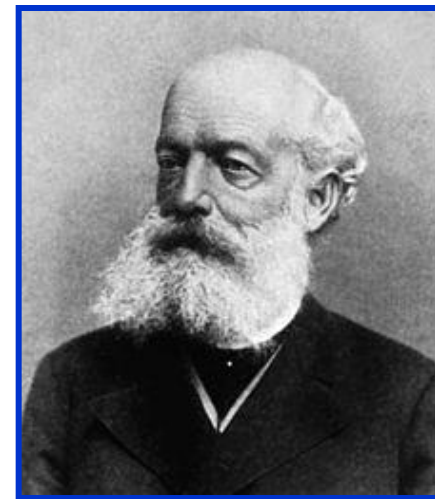
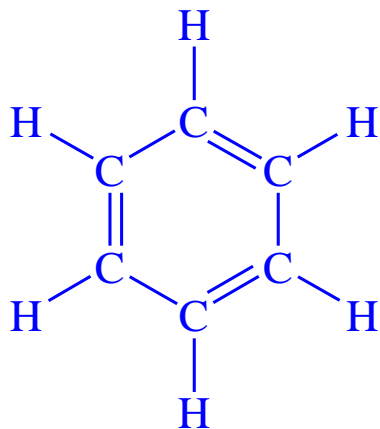


**Note**, however, that "aromatic" hydrocarbons sometimes are **odorless**.<sub>3</sub>

# Benzene Chemical structure

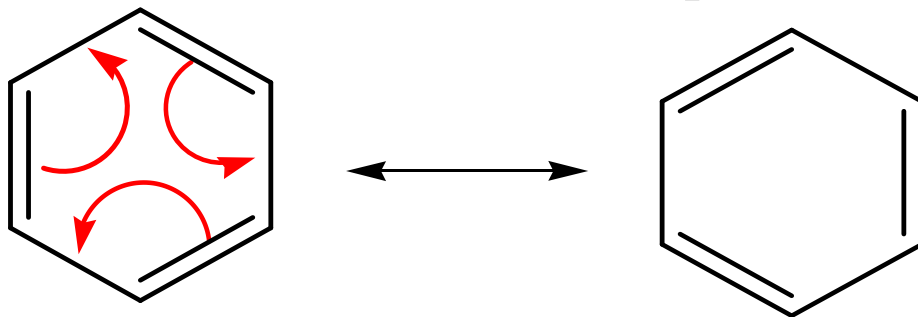


- There were several other structures proposed for **benzene**, but a much more satisfactory approach became possible when we began to understand that covalent bonds consist of **pairs of electrons** shared between atoms.
- In 1865 **Kekulé** proposed the structure for **benzene**. Which satisfied the molecular formula  $C_6H_6$  and the **valence of carbon**. It also has only a **single kind of hydrogen**.

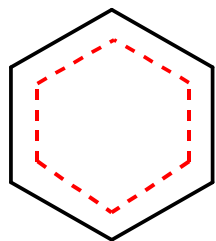


**Friedrich August Kekulé**

**Kekulé** suggested that the two compounds were in rapid equilibrium, so they could not be separated. Although this is **not exactly correct**, it was a pretty good answer for the time. Now we know that these are; the two resonance structure of the same compounds.

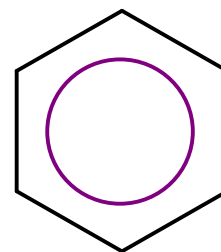


The **true** structure of benzene is a the **RESONANCE MIXTURE** or **HYBRID** of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the  $\pi$  bonds.



The electrons in the  $\pi$ -bonds are delocalized around the ring

or in an abbreviated way

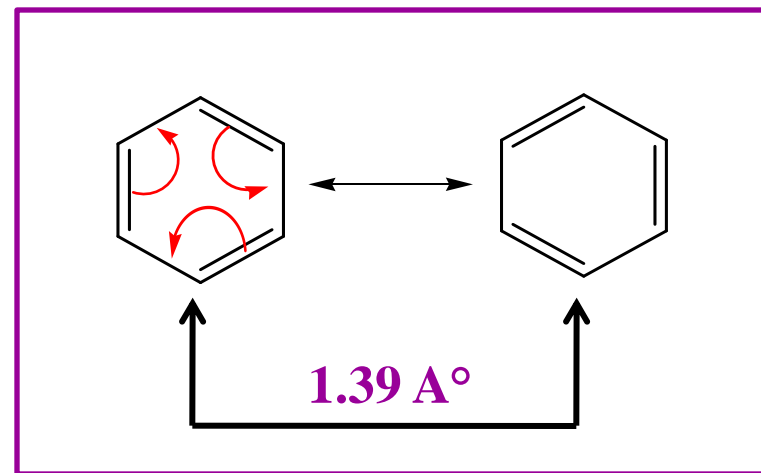
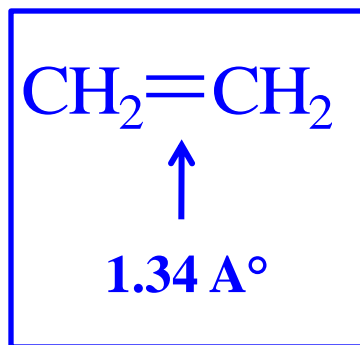
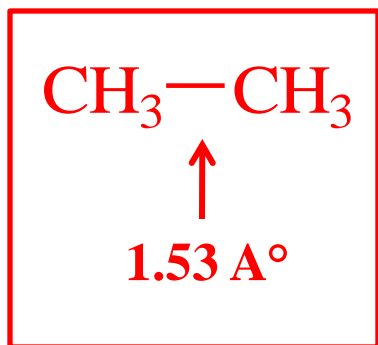


The circle represent six  $\pi$ -electrons distributed over the six atoms of the ring.

Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two **Kekulé** structures)

# Later spectroscopic evidence showed :

1. All bond lengths to be **equal** and **intermediate** between **single** and **double bond** lengths (**1.39 Å**).



2. It was also found that benzene was a **flat (planar)** molecule.
3. Further more, all **bond angles** in benzene are  $120^\circ$ ,  $p$  electrons are **delocalised**.



**Delocalized electrons** are electrons in a molecule that are not associated with a single atom or to a covalent bond. **Delocalized electrons** are contained within an orbital that extends over several adjacent atoms. <sub>6</sub>

# The physical properties of Benzene



1) Benzene is a colorless liquid.

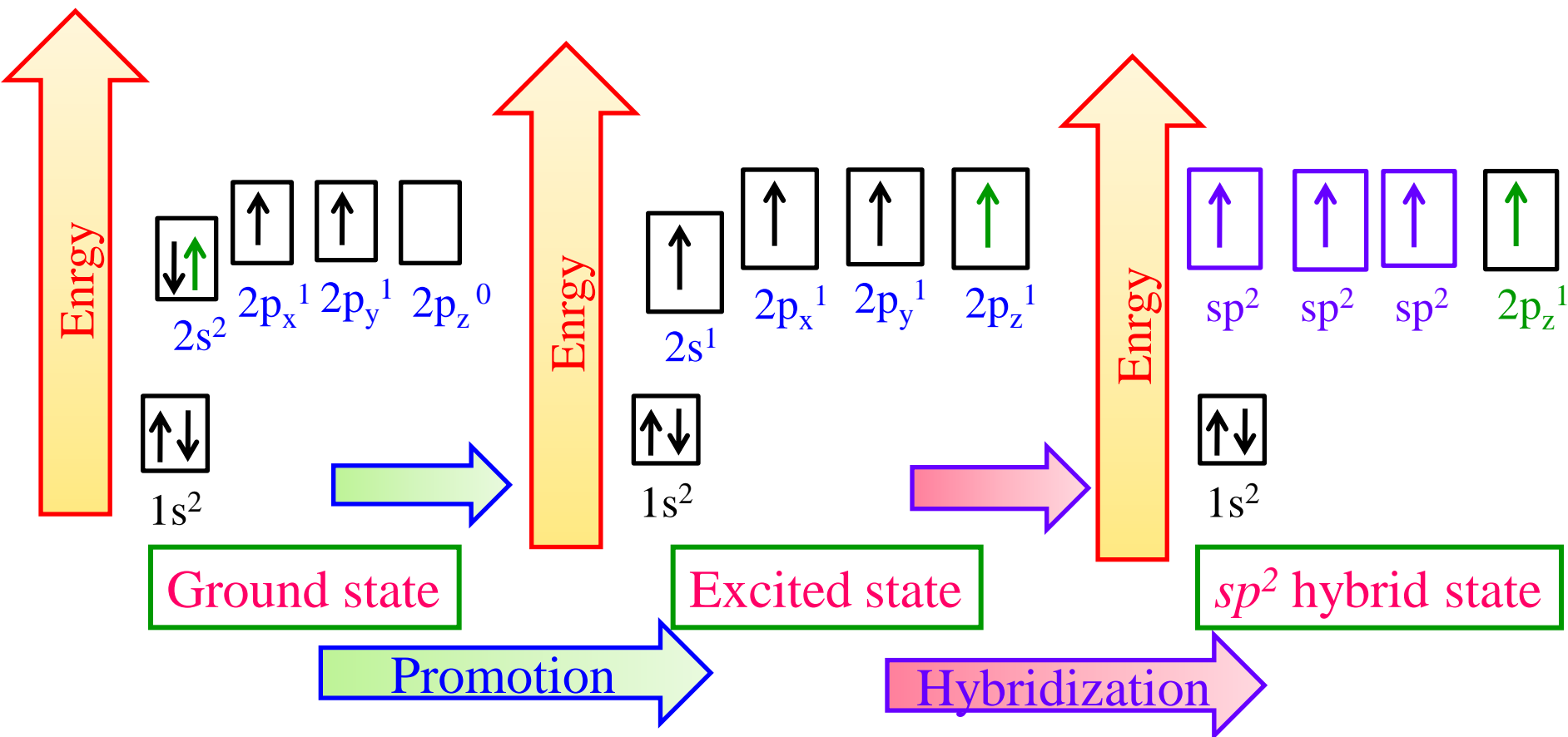
2) Benzene is soluble in organic solvents but immiscible in water.

3) It is an aromatic compound so it has a typical aromatic odor.

# Hybridization of Benzene ring.



The Simplest Aromatic Compound; “*The parent Aromatic compound*”.



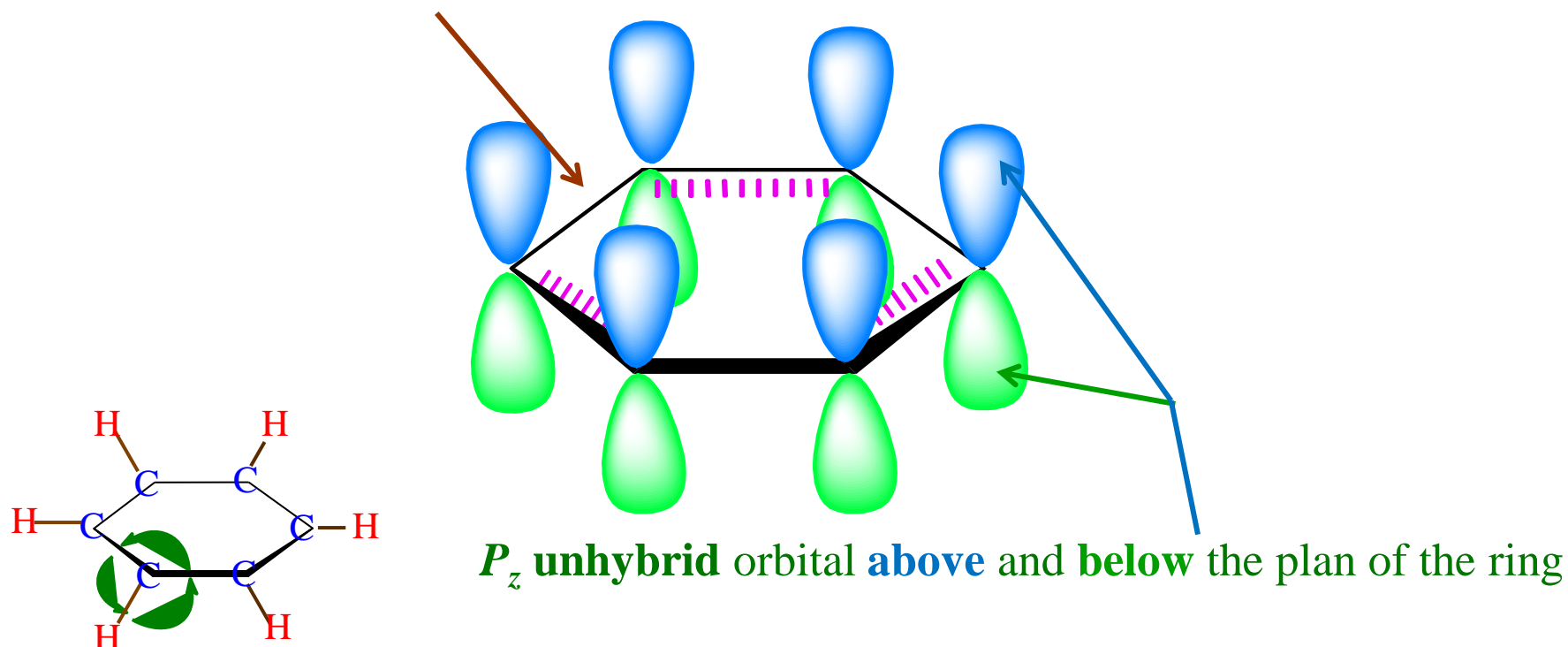
Benzene is built from **hydrogen** atoms ( $1s^1$ ) and **carbon** atoms ( $1s^2 2s^2 2p_x^1 2p_y^1$ ). Each **carbon atom** has to join to **three other atoms** (one hydrogen and two carbons) and **doesn't have enough unpaired electrons** to form the required number of bonds, so it needs **to promote** one of the  $2s^2$  pair into the empty  $2p_z$  orbital.



# Summary

- **Benzene** has **3  $sp^2$ -hybridized** for each **C** atoms.
- Each carbon atom uses the  **$sp^2$  hybrids** to form **sigma bonds** with **two other carbons** and **one hydrogen atom**.

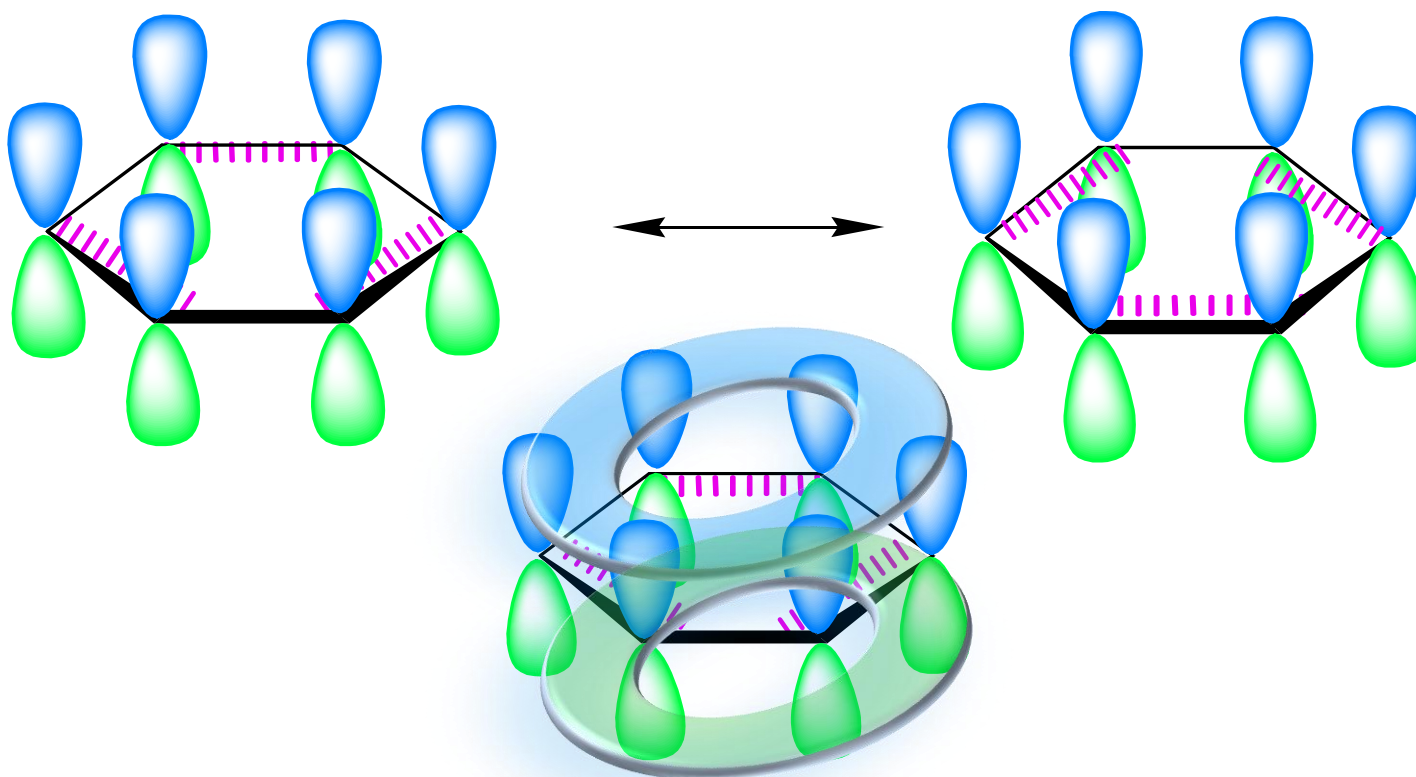
$\sigma$  bond formed from  **$sp^2$  hybrid** orbitals .



The **three  $sp^2$  hybrid** orbitals arrange themselves as far apart as possible - which is at  **$120^\circ$**  to each other in a **plane**.

# Summary

- ❑ Because the electrons are *no longer held between just two carbon* atoms, but are spread over the whole ring, the electrons are said to be *delocalised*.
- ❑ The lobes of these atomic orbitals **meld together** to form **circular rings of electron density** *above* and *below* the plane of the molecule.
- ❑ The two of these together constitute the "second half" of the *carbon-carbon double bonds* in *benzene*.



# Hückel's Rule

**Erich Hückel** proposed a series of rules that would predict whether compounds would be **unusually stable** like **benzene**. These compounds are called **aromatic**, and *if they meet these requirements* are **much more stable** than expected for a similar **non-aromatic** structure.

## Aromatic structural requirements :

- ✓ The molecule must be **cyclic**.
- ✓ Every atom in the ring must possess a **p-orbital** ( **$sp^2$**  hybridized).
- ✓ The molecule must be **planar** so that all of the **p-orbitals** are **parallel**.
- ✓ The molecule must have  **$4n+2$   $\pi$ -electrons** (electrons in the  $\pi$ -orbitals), where  **$n$**  is an **integer** (**0,1,2,3, etc**). Thus the aromatic molecule will have **2, 6, 10, 14, etc.  $\pi$ -electrons**.

# How does the $4n+2$ Rule Work?

To apply the  $4n+2$  rule,

**first** count the number of  $\pi$  electrons in the molecule.

**Then**, set this number equal to  $4n+2$  and solve for  $n$ .

If  $n$  turns out to be 0 or any positive integer (1, 2, 3,...), the rule has been met.

For;  $4n+2$   $\pi$  electrons ( $n = 0, 1, 2, 3, \dots = 2, 6, 10, 14, 18$ ) is Aromatic

 Note that;

Molecules that **doesn't follow** any of the first three *aromatic criteria* are called **Non-Aromatic**.

# Applications of Hückel rules:

(a) Homocyclic Systems.

(b) Heterocyclic Systems.

(c) Polycyclic Systems.

(1) Neutral Compounds.

(2) Aromatic Ions.

## Aromatic Ions:

Hückel's rule also applies to **ions**, as long as a compound has  $4n+2 \pi$  - **electrons**. It doesn't matter if the molecule is *neutral* or has a *charge*.

*Pi electrons are counted as follows:*

Each double bond counts as **two** pi electrons.

Each (+) charge counts as **zero** pi electrons.

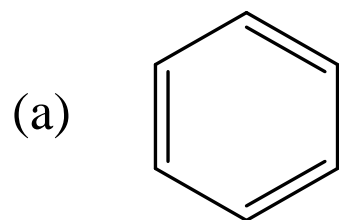
Each (-)charge counts as **two** pi electrons.

Each (•) radical counts as **one** pi electron.

Set the total number of pi electrons as equal to  $4n + 2$ ; solve for n.

# Examples

## “Neutral Aromatic compounds”

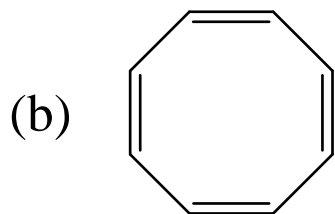


Benzene

$3\pi\text{-bonds} = 6 \text{ pi electrons}$

$$4n+2 = 6 ; n = 1$$

☺ **Aromatic**

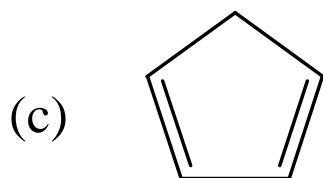


Cyclooctatetraene

$4\pi\text{-bonds} = 8 \text{ pi electrons}$

$$4n+2 = 8 ; n = 3/2$$

☹ **Anti-aromatic**

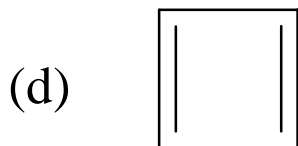


Cyclopentadiene

The hybridization of the top C is  $sp^3$

**Not planar, not fully conjugated**

☹ **Non-aromatic**



Cyclobutadiene

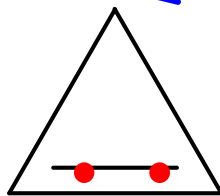
$2\pi\text{-bonds} = 4 \text{ pi electrons}$

$$4n+2 = 4 ; n = 1/2$$

☹ **Anti-aromatic**

# Exercise

## Case 1

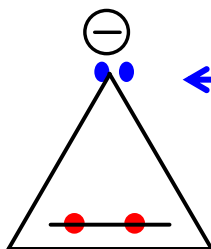


The hybridization of the top "C" is  $sp^3$   
i.e. No p-orbital

Cyclopropene

The compound is **Non-aromatic**

## Case 2

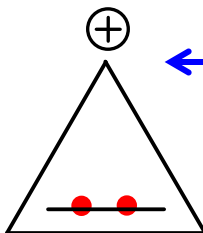


-ve charge atom  
has **2 pi** electrons

$$4n+2 = 4 ; n = 1/2$$

☹ **Anti-aromatic**

## Case 3



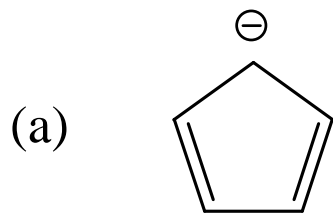
+ve charge atom  
empty p orbital.

$$4n+2 = 2 ; n = 0$$

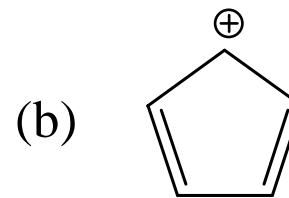
☺ **Aromatic**

# Examples

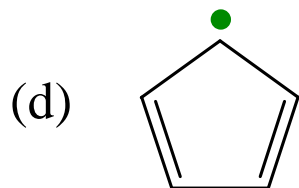
## “Aromatic Ions”



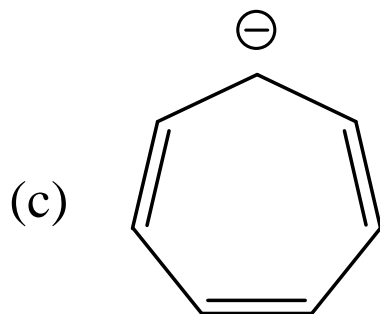
Cyclopentadienylanion



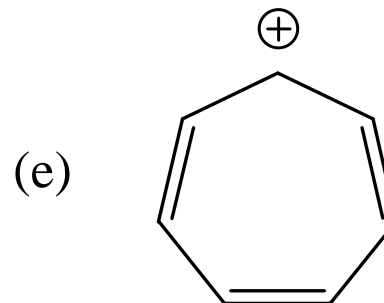
Cyclopentadienylcation



Cyclopentadienylradical



Cycloheptatrieneanion



Cycloheptatrienecation  
(*tropylium ion*)



# Heterocyclic Systems

- **Heterocyclic compounds** are compounds in which one or more carbons in the ring are replaced by other atoms (*heteroatoms*).
- **Heteroatoms** in organic compounds are usually nitrogen “N”, oxygen “O”, or sulfur “S” atoms.
- **Heterocyclic aromatic compounds** are heterocycles that are *planar*, *cyclic*, *fully conjugated* molecules that follow Hückel's rule.

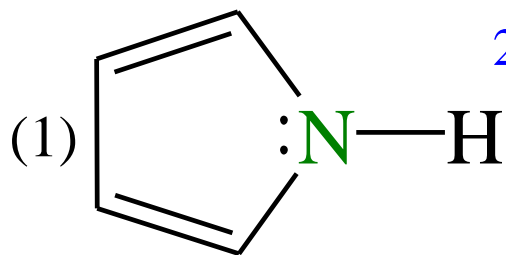
## How to count the # lone pair(s) on hetero atom?

- A **single lone pair** can be found with atoms in the nitrogen group such as **nitrogen** in ammonia,
- **Two lone pairs** can be found with atoms in the **chalcogen** group such as **oxygen** , **sulfur** in water

# Examples

## “Heterocyclic compounds”

Predict which of the following structures accord to Hückels rule for aromaticity

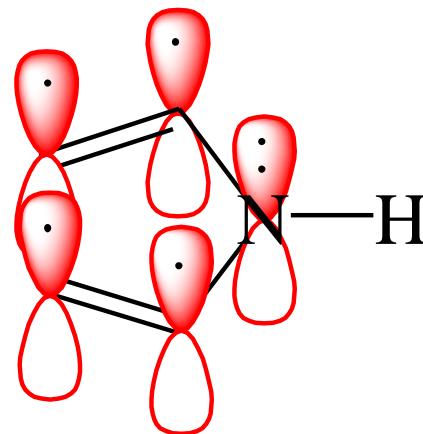


**Pyrrol**

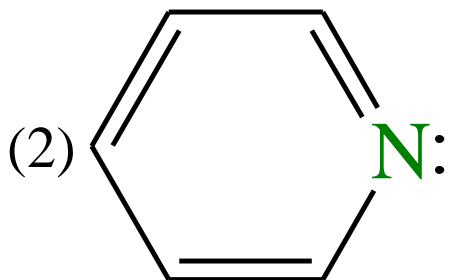
$2\pi\text{-bonds} + 1 \text{ lone pair} = 6 \text{ pi electrons}$

$$4n+2=6; n=1$$

☺ **Aromatic**



The lone pair of electrons are in the  $p$  orbital. They contribute to the  $\pi$ -aromatic system.

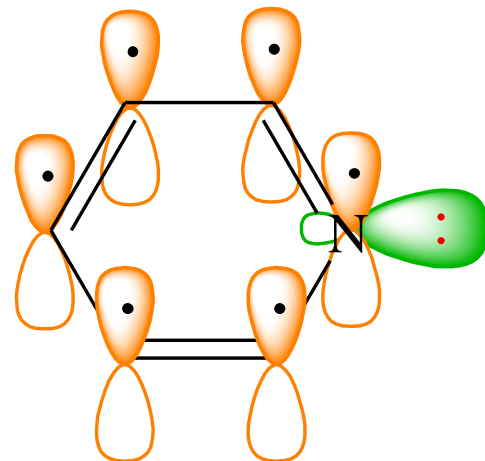


**Pyridine**

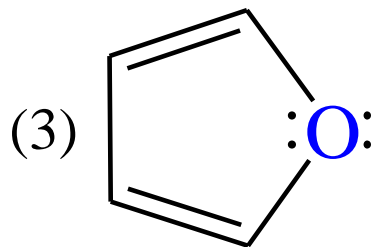
$3\pi\text{-bonds} + 0 \text{ lone pair} = 6 \text{ pi electrons}$

$$4n+2=6; n=1$$

☺ **Aromatic**



The lone pair occupies an  $sp^2$  orbital. They are perpendicular to the  $p$  orbitals they **don't** contribute to the  $\pi$ -aromatic system.

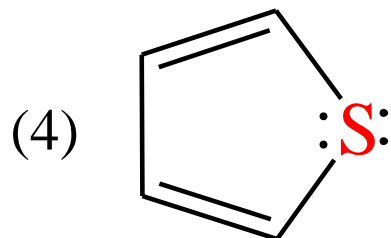
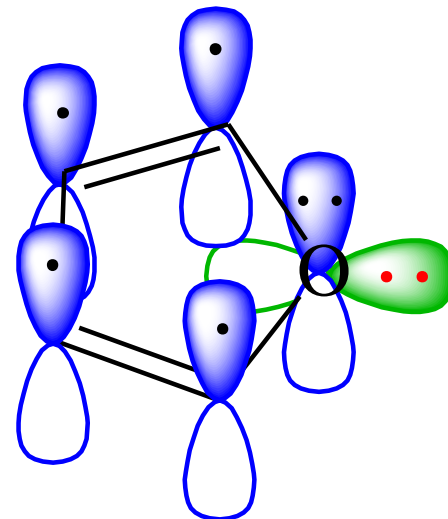


**Furan**

$2\pi\text{-bonds} + 1 \text{ lone pair} = 6 \text{ pi electrons}$

$$4n+2 = 6 ; n = 1$$

☺ **Aromatic**

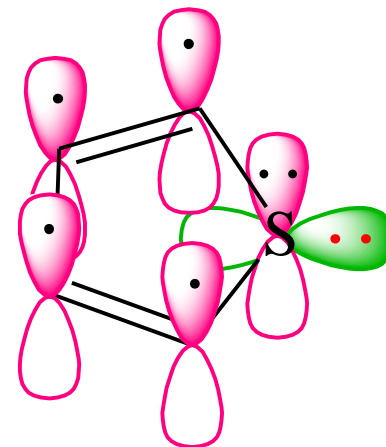


**Thiophene**

$2\pi\text{-bonds} + 1 \text{ lone pair} = 6 \text{ pi electrons}$

$$4n+2 = 6 ; n = 1$$

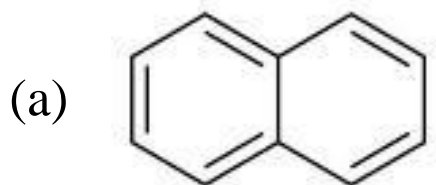
☺ **Aromatic**



Both **Furan** & **Thiophene** have **two pairs** of *nonbonding electrons* but **only** one pair is in the **unhybridized** *p* orbital and is **able to overlap** with the **carbons** of the ring. The **second lone pair** of electrons is *in the plan* of the ring.

# Polycyclic Systems

Predict which of the following structures accord to *Hückels rule* for aromaticity

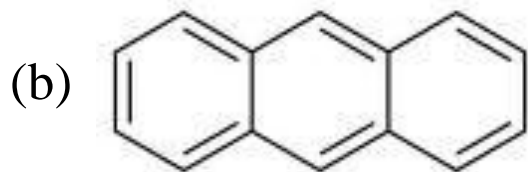


**Naphthalene**

$5\pi$ -bonds = 10 pi electrons

$$4n+2 = 10 ; n = 2$$

☺ **Aromatic**

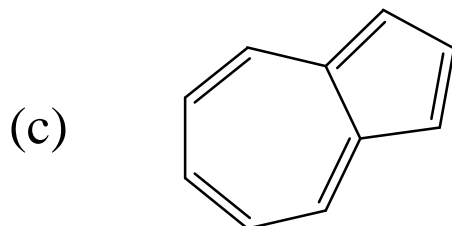


**Anthracene**

$7\pi$ -bonds = 14 pi electrons

$$4n+2 = 14 ; n = 3$$

☺ **Aromatic**



**Azulene**

$5\pi$ -bonds = 10 pi electrons

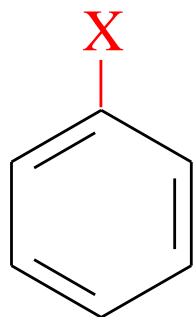
$$4n+2 = 10 ; n = 2$$

☺ **Aromatic**

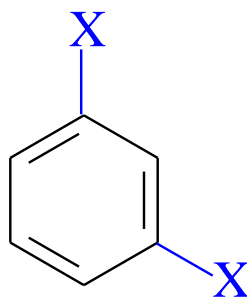
# Nomenclature of Benzene derivatives

Benzene derivatives are divided into three classes :

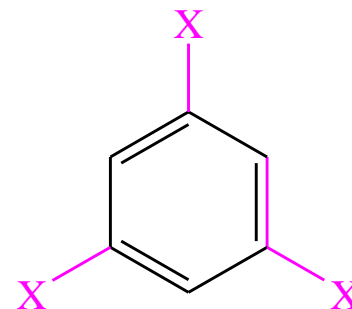
MonoSubstituted  
Benzene



DiSubstituted  
Benzene



Tri or Poly-  
Substituted  
Benzene



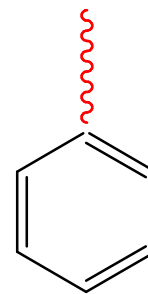
# IMPORTANT NOTES:

- **Aryl = Ar = Aromatic group**

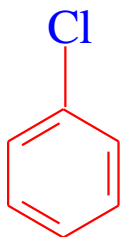
“ It is a broad term, and includes *any aromatic* rings”

- **Phenyl =  $\Phi$  or Ph =  $C_6H_5-$**

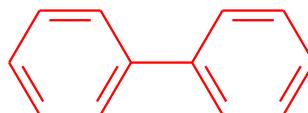
You get a phenyl group,  $C_6H_5$ , by removing a **hydrogen** from a benzene ring,  $C_6H_6$ .



e.g.



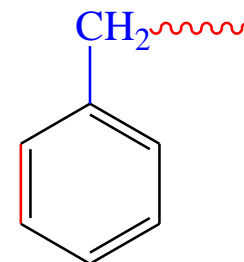
**Phenylchloride**



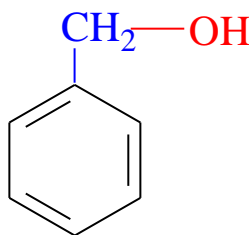
**biphenyl**

- **Benzyl = Bn =  $C_6H_5CH_2-$**

You get a benzyl group,  $C_6H_5CH_2-$ , by removing a **hydrogen** from the **methyl** on the benzene ring.



e.g.



**Benzylalcohol**

## (a) Monosubstituted Benzene

**Two systems** are used in naming *monosubstituted* benzene.

Case 1.

Benzene is a **parent name** for some *monosubstituted* benzenes the substituent name is added as prefix. (**Combined name**).

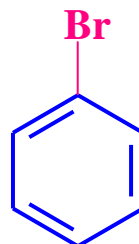
Case 2.

For other *monosubstituent* benzenes, the presence of substituent result in a *new parent name*. (**Singular Name**)

### For the 1<sup>st</sup> Case

There are usually **two equivalent names** for each **benzene-based compound**, one with *phenyl* as the root and one with *benzene*.

(a) Functional group suffix = **-benzene**



**Bromobenzene**

(b) Functional group prefix = **phenyl-**



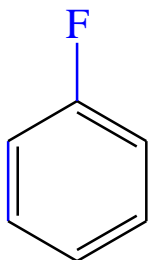
**Phenylbromide**

# (1) Benzene as a Parent Name

(Combined name).

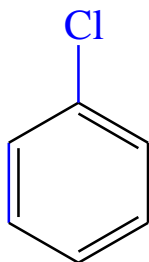
The IUPAC system of naming **mono-substituted** benzene derivatives uses the name of the **substituent** as a **prefix** to the name benzene.

## Examples



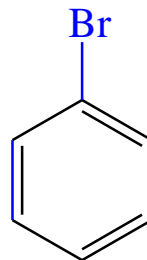
Fluorobenzene

Phenyl fluoride



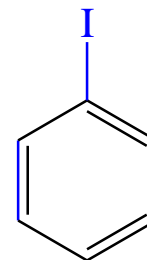
Chlorobenzene

Phenyl chloride



Bromobenzene

Phenyl Bromide

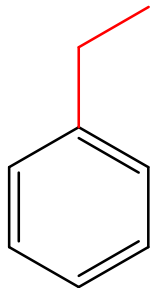


Iodobenzene

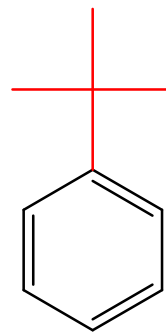
Phenyl iodide



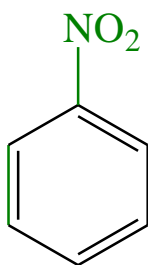
## Examples



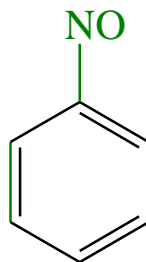
Ethylbenzene



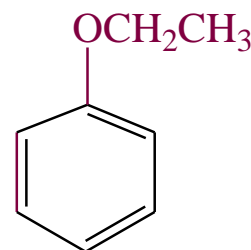
*t*-Butylbenzene



Nitrobenzene



Nitrosobenzene



Ethoxybenzene



**Note:**

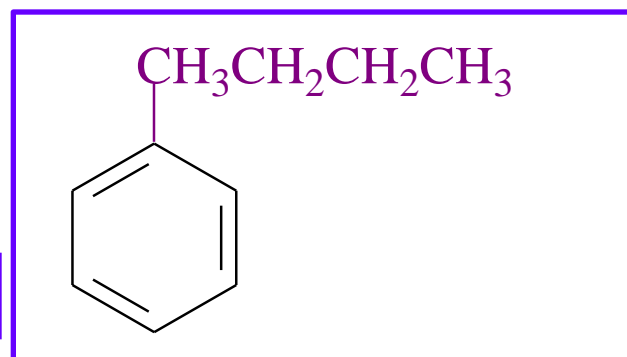
Because all six positions in benzene are *equivalent*, there is no need to specify by a **position number of a substituent** for **monosubstituted benzene**.

## Notes that:

When the **aliphatic part** of a molecule is **more complex** than **the aromatic**. The name of the compound may be derived from the aliphatic part using prefix, **Phenyl**, to indicate benzene substitution.

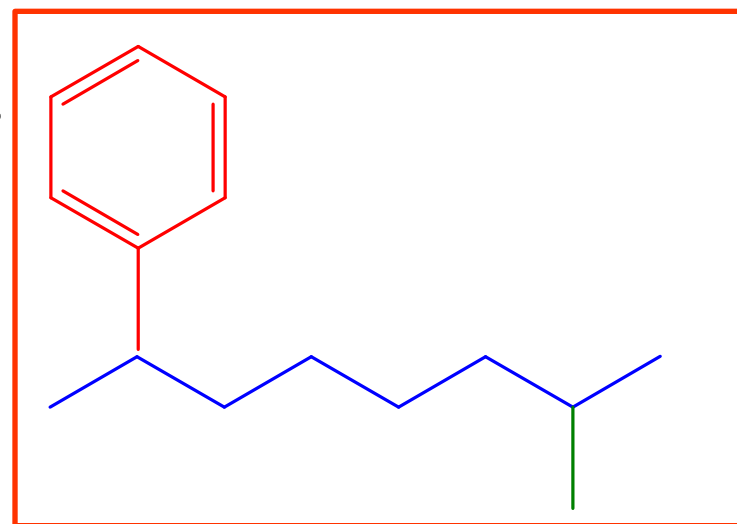
1.  $R \leq 6$  benzene ring as parent name  
“alkyl-substituted benzene”

Butylbenzene



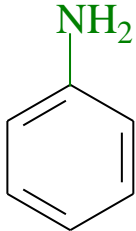
- $R > 6$  or  $R$  containing a functional group,  
2. benzene ring as substituent.  
“Phenyl-substituted hydrocarbon”

2-methyl-7-phenyloctane

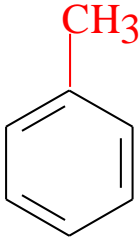
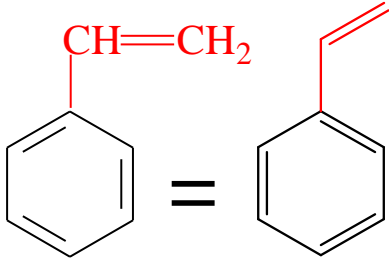
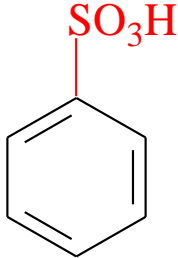


## (2) Benzene Derivatives Common Name (Singular Name)

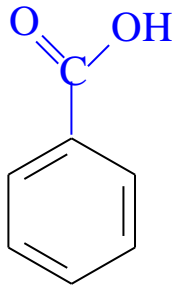
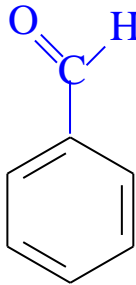
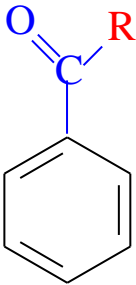
A few **mono-substituted benzene** have names wherein the substituent and benzene ring taken together constitute a ***new parent name***.

Function group	Structure	Name
$\text{—NH}_2$		<b>Aniline</b>
<b>Amino</b>		

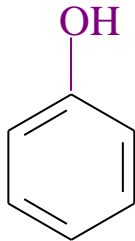
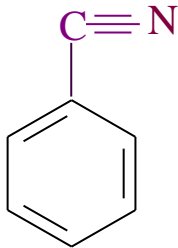
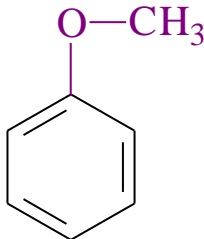
# Examples

Function group	Structure	Name
$-\text{CH}_3$		<b>Toluene</b>
<b>Methyl</b>		
$-\text{CH}=\text{CH}_2$		<b>Styrene</b>
<b>Vinyl</b>		
$-\text{SO}_3\text{H}$		<b>Benzenesulfonic acid</b>
<b>Sulfo</b>		

# Examples

Function group	Structure	Name
$\text{—C(=O)OH}$		<b>Benzoic acid</b>
<b>Carboxyl group</b>		
$\text{—C(=O)H}$		<b>Benzaldehyde</b>
<b>Aldehyde group</b>		
$\text{—C(=O)R}$		<b>R</b> = ph <b>Benzophenone</b>
<b>Carbonyl group</b> <b>“ Keton ”</b>		<b>or</b> <b>R</b> = CH <sub>3</sub> <b>Acetophenone</b>

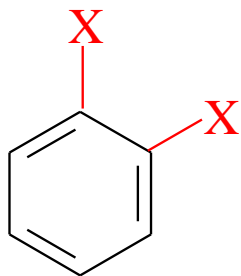
# Examples

Function group	Structure	Name
$\text{—OH}$		<b>Phenol</b>
<b>Hydroxyl</b>		
$\text{—C}\equiv\text{N}$		<b>Benzonitrile</b>
<b>Nitrile</b>		
$\text{—O—CH}_3$		<b>Anisol</b>
<b>Methoxy</b>		

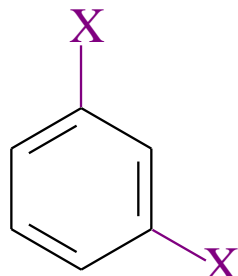
# Disubstituted Benzene

□ When two substituents, either the *same* or *different*, are attached to benzene ring, three isomeric structures are possible.

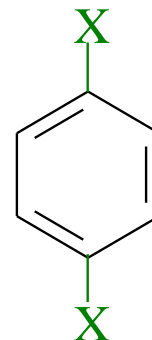
The prefix system uses the prefixes:



1,2- = *ortho*-  
(abbreviated, *o*- )

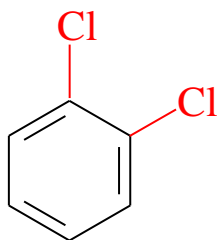


1,3- = *meta*-  
(abbreviated, *m*- )

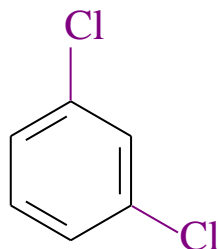


1,4- = *para*-  
(abbreviated, *p*- )

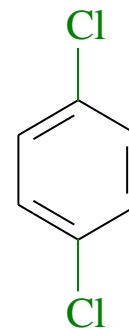
## Examples:



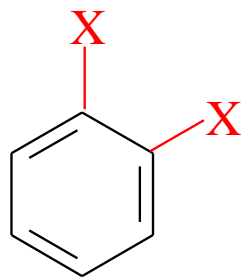
*ortho*-chlorobenzene  
or 1,2- Dichlorobenzene



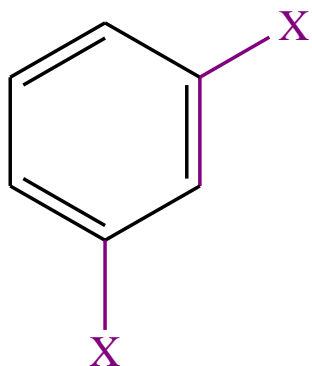
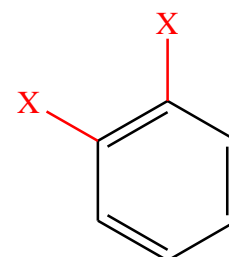
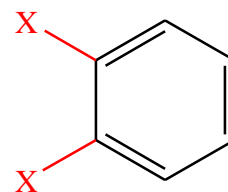
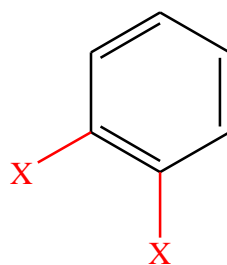
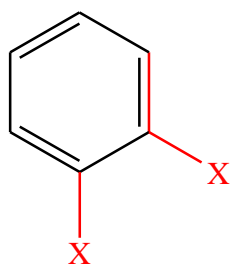
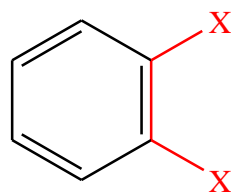
*meta*-chlorobenzene  
or 1,3- Dichlorobenzene



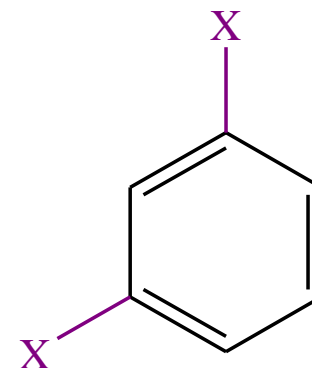
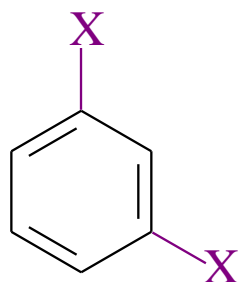
*para*-chlorobenzene  
or 1,4- Dichlorobenzene



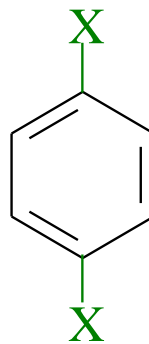
1,2- = *ortho*-  
(abbreviated, *o*- )



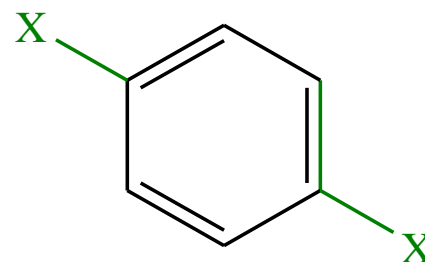
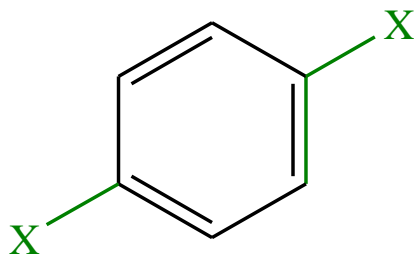
1,3- = *meta*-  
(abbreviated, *m*- )



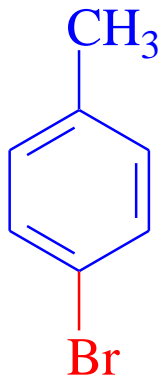




1,4- = *para*-  
(abbreviated , *p*- )

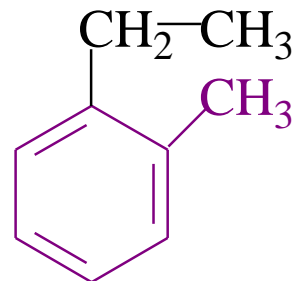


□ When **one of the two substituents** in a disubstituted benzene impart a *special name* to the compound (as example; *toluene*), the compound is named **as a derivative of that parent molecule**. The special substituent is assumed to be at ring position 1.



4-Bromotoluene

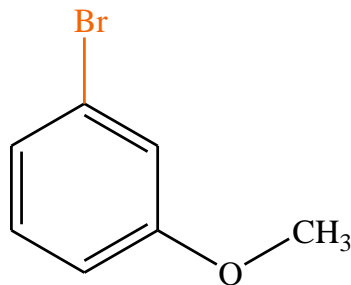
(Not; 1-Bromo-4-toluene)



2-Ethyltoluene

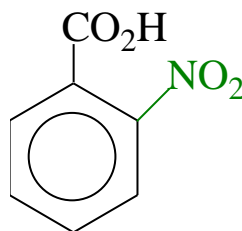
(Not; 1-Ethyl-2-methylbenzene)

## Examples



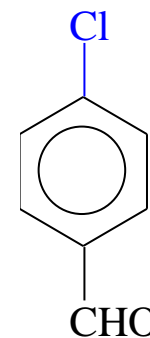
1-Bromo-anisol

*m*-Bromoanisol



2-Nitrobenzoic acid

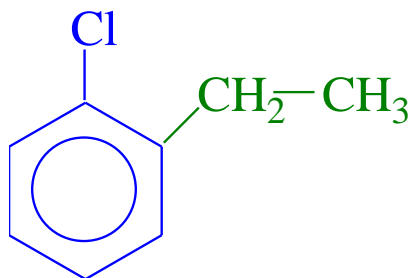
*o*-Nitrobenzoic acid



4-Chlorobenzaldehyde

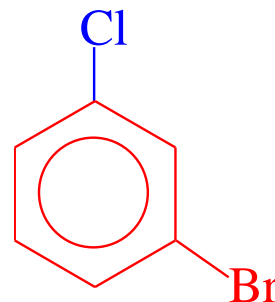
*p*-Chlorobenzaldehyde

❑ When neither substituent group impart a special name, the substituents are cited in **alphabetical order** before the ending **-benzene**. The **carbon of the benzene ring** bearing the substituent with **alphabetical priority** becomes **carbon 1**.



1-Chloro-2-ethylbenzene

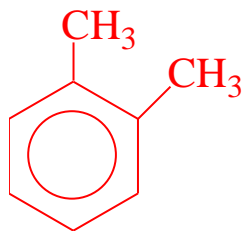
Not; 2-Chloro-1-ethylbenzene



1-Bromo-3-chlorobenzene

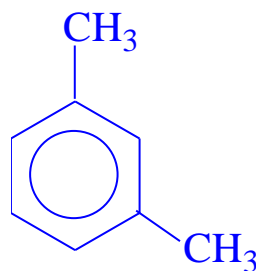
Not; 3-Bromo-1-chlorobenzene

❑ A benzene ring bearing **2 methyl groups** is a situation that generates a new special base name. such compounds ( has three isomers) are **not named as** 2-methylbenzene or Methyl toluene.



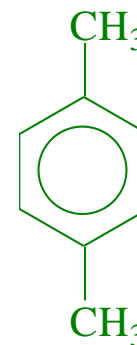
***o*-Xylene**

or 1,2- Dimethylbenzene



***m*-Xylene**

or 1,3- Dimethylbenzene



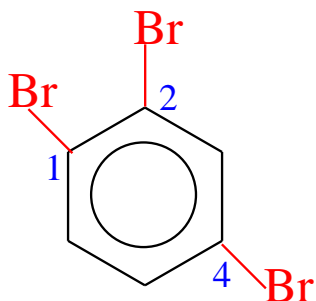
***p*-Xylene**

or 1,4- Dimethylbenzene

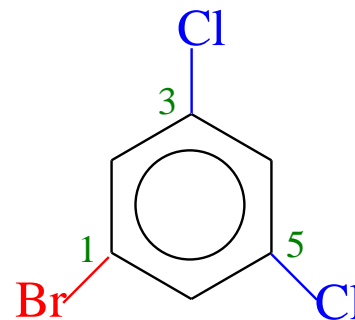
## Benzene derivatives with three or more substituents

- ❑ When **more than two** groups are present on the benzene ring, their positions are indicated by **numbers**.
- ❑ The ring is numbered in such **a way** as to obtain **the lowest possible numbers** for the carbon atoms that have substituents.
- ❑ If there is a choice of numbering (**two systems give the same lowest set**), then the group that **came first alphabetically** is given **the lower number**.

### Examples:

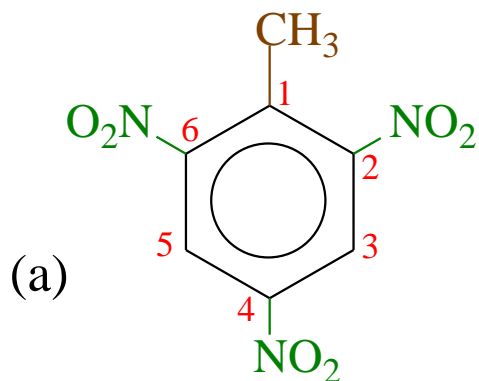


1,2,4-Tribromobenzene



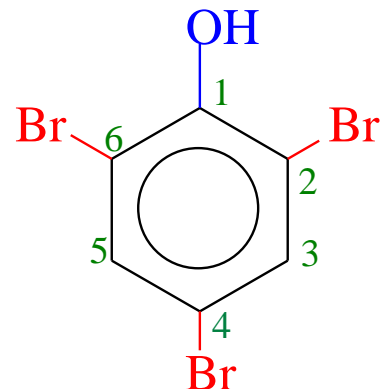
1-Bromo-3,5-dichlorobenzene

## Examples:



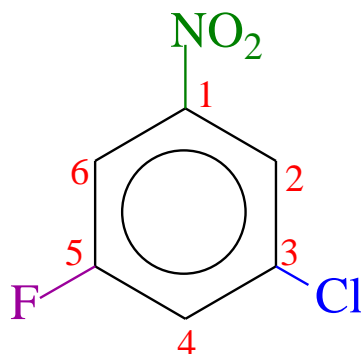
2,4,6-Trinitrotoluene (TNT)  
“CH<sub>3</sub> on Carbon 1”

(b)



2,4,6-Tribromophenol  
“OH on Carbon 1”

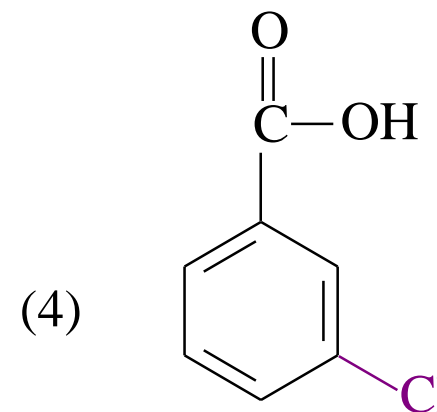
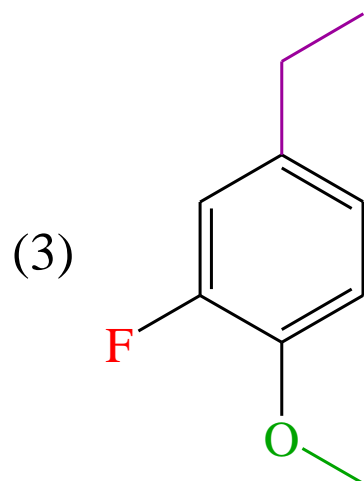
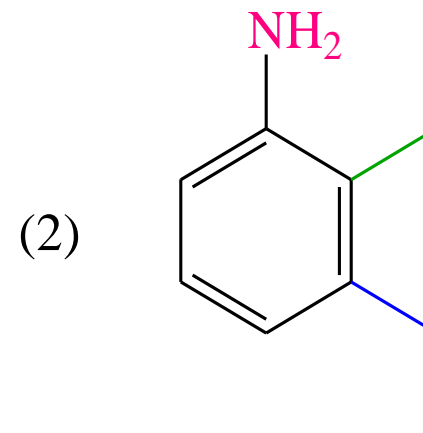
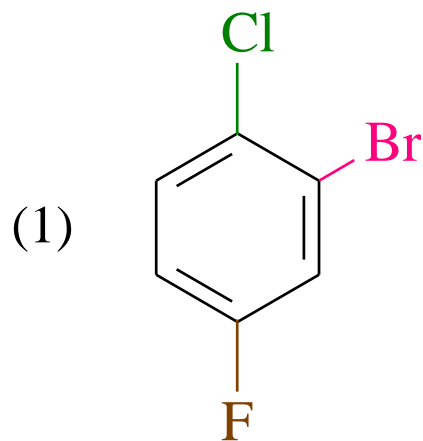
(c)



3-Chloro-5-fluoronitrobenzene  
“Nitro on Carbon 1”

# Exercises

Give an IUPAC or COMMON for each of the following:



# Reactions of Benzene

## Electrophilic Substitution Reactions:

- 1. Specific Electrophilic Aromatic Substitution reactions.*
- 2. Side reaction of Aromatic compounds.*
- 3. Disubstituted Benzene “Orientation in monosubstituted”.*

# Electrophilic Substitution Reactions:

In *electrophilic substitution reactions*, an electrophile ( $E^+$ ) is substituted for a **hydrogen** in the aromatic( benzene) ring.

The Electrophiles in Common Aromatic Substitution Reactions:

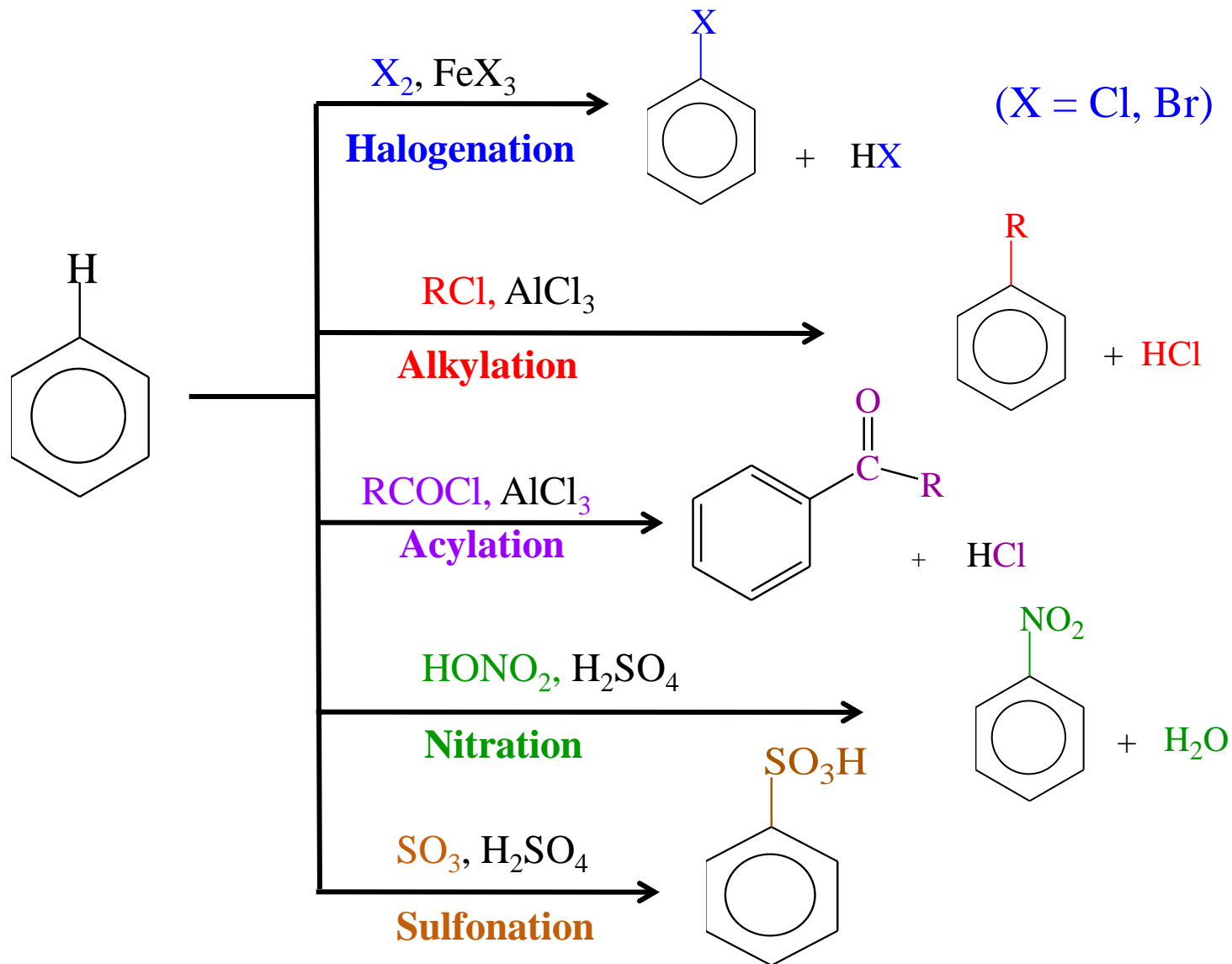
Electrophile	Name of Reaction
$Cl^+$ or $Br^+$	Halogenation
$R^+$	Alkylation
$RC\equiv O^+$	Acylation
$NO_2^+$	Nitration
$SO_3H^+$	Sulfonation

*Note that;* in each reaction **the net result** of replacement of a hydrogen in benzene By **one of the electrophiles**



# 1. Specific Electrophilic Aromatic Substitution reactions.

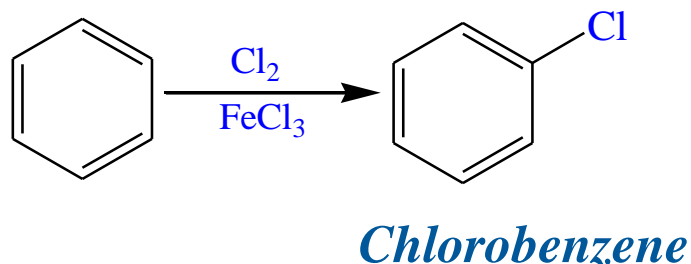
**Halogenation**, **alkylation**, **acylation**, **nitration**, and **sulfonation** are the typical electrophilic aromatic substitution reactions.



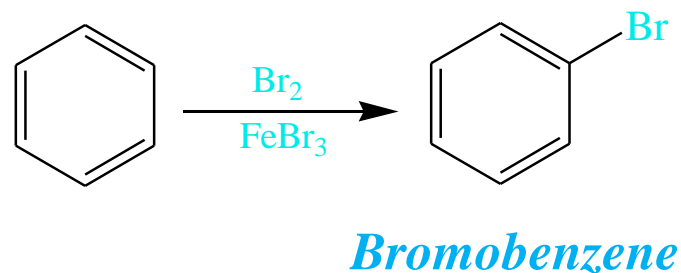
## (a) Halogenation

In **halogenation**, benzene reacts with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of a **Lewis acid catalyst**, such as  $\text{FeCl}_3$  or  $\text{FeBr}_3$ , to give the **aryl halides** chlorobenzene or **bromobenzene** respectively.

### *Chlorination*



### *Bromination*



### **Note:**

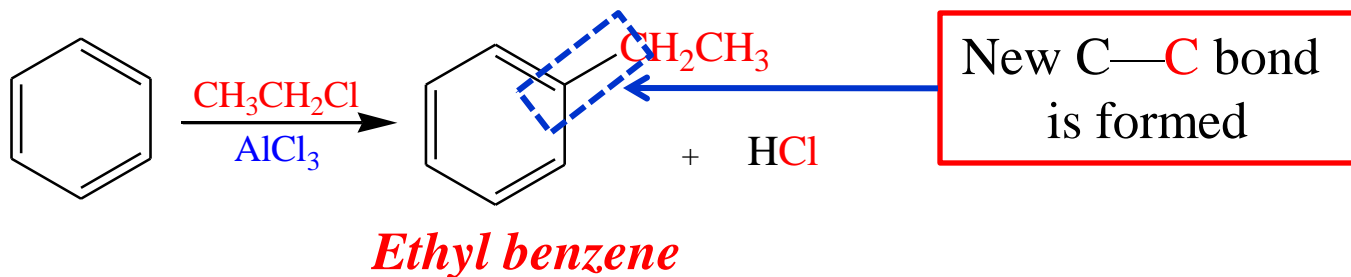
Analogous reactions with  $\text{I}_2$  and  $\text{F}_2$  are **not synthetically useful** because  $\text{I}_2$  is too unreactive and  $\text{F}_2$  reacts too violently.

# Friedel-Crafts Reaction

This reaction is used for introducing an alkyl (R-) or acyl (RCO-) group into the benzene ring.

## (b) Alkylation

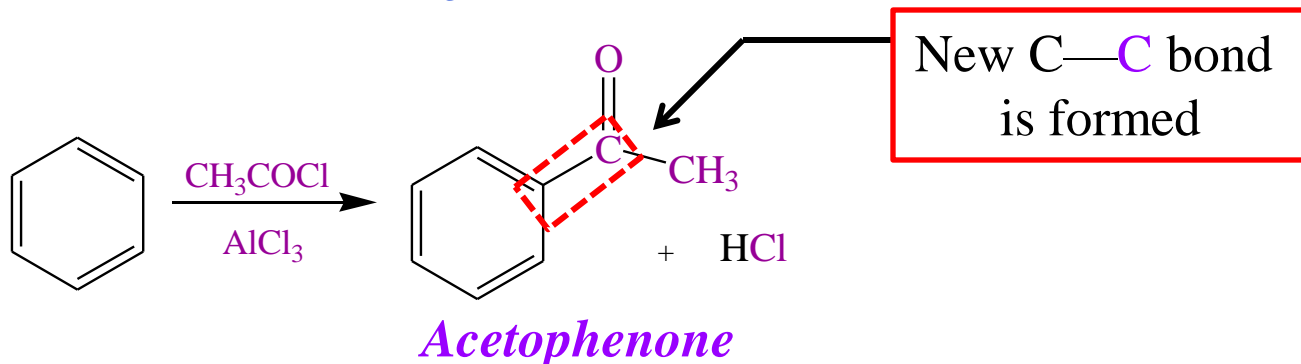
The treatment of benzene with alkyl halide (RX) in the presence of a Lewis acid aluminum trichloride ( $\text{AlCl}_3$ ) catalyst yields, an alkyl benzene.



## (c) Acylation

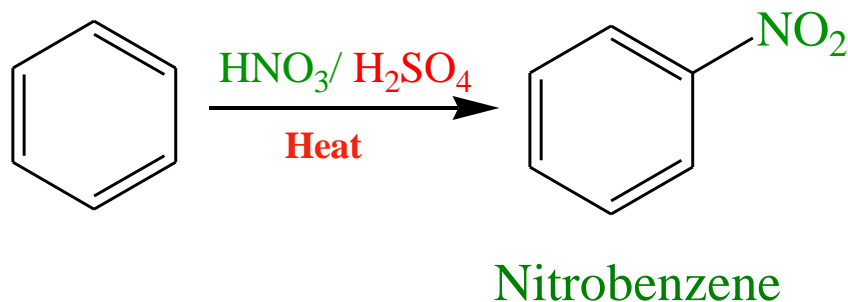
The treatment of benzene with acid chloride ( $\text{RCOCl}$ ) in the presence of a Lewis acid aluminum trichloride ( $\text{AlCl}_3$ ) catalyst yields, a ketone.

 **Note:**



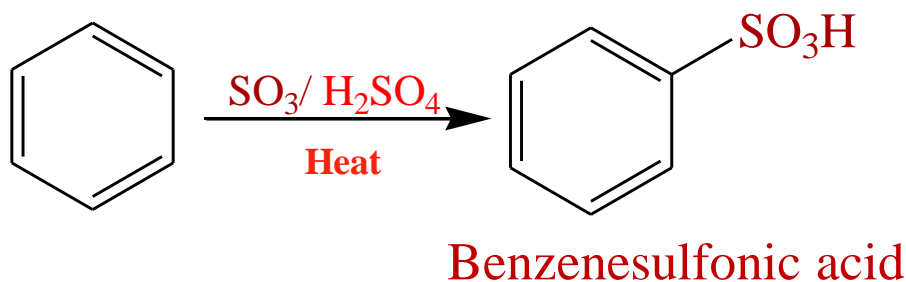
### (d) Nitration

When benzene is **heated** with concentrated **HNO<sub>3</sub>** in presence of concentrated **sulphuric acid; H<sub>2</sub>SO<sub>4</sub>** at **60° C**, we get **nitrobenzene**.



### (e) Sulfonation

When benzene is **heated** with concentrated **sulphuric acid; H<sub>2</sub>SO<sub>4</sub>** at **80° C** for 8 hours, **benzene sulphonic acid** is formed.

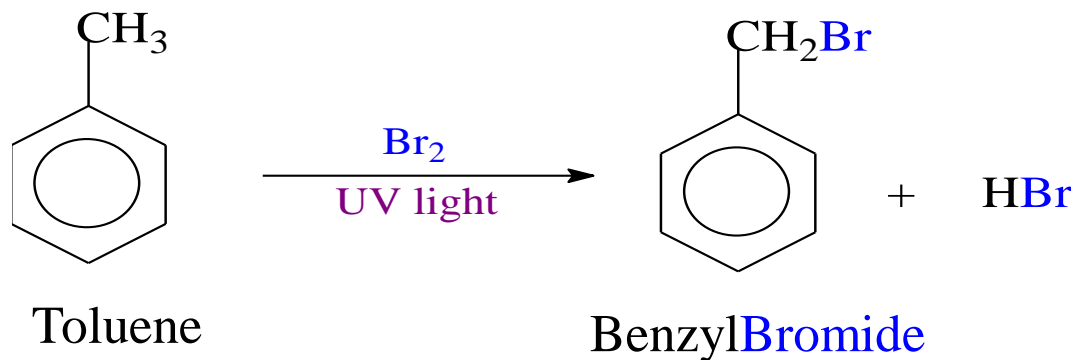


## 2. Side reaction of Aromatic compounds.

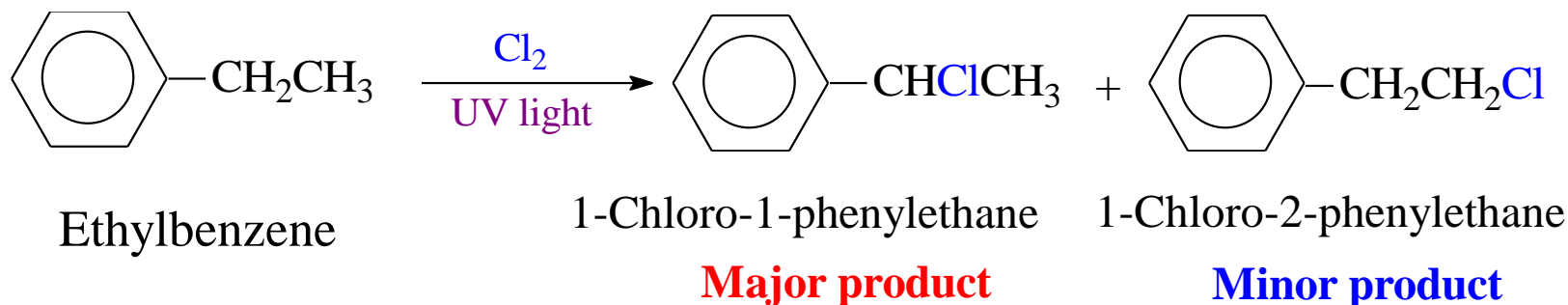
### A. Halogenation of an alkyl Side chain

An **alkylbenzene** contains both an **aliphatic** and **aromatic** portion, we may expect the aliphatic portion (the alkyl side chain) to undergoes **the alkane substitutions**.

#### Example 1. Bromination of toluene in the presence of UV light



#### Example 2. Chlorination of ethylbenzene in the presence of UV light

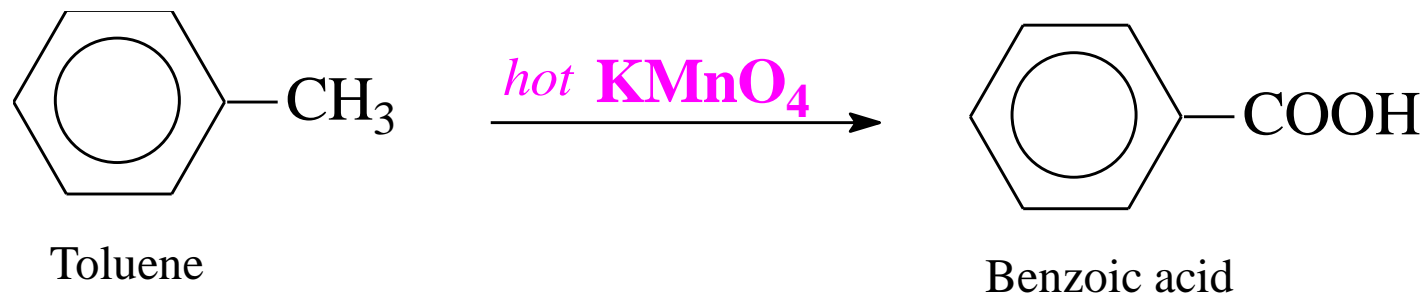


## 2. Side reaction of Aromatic compounds.

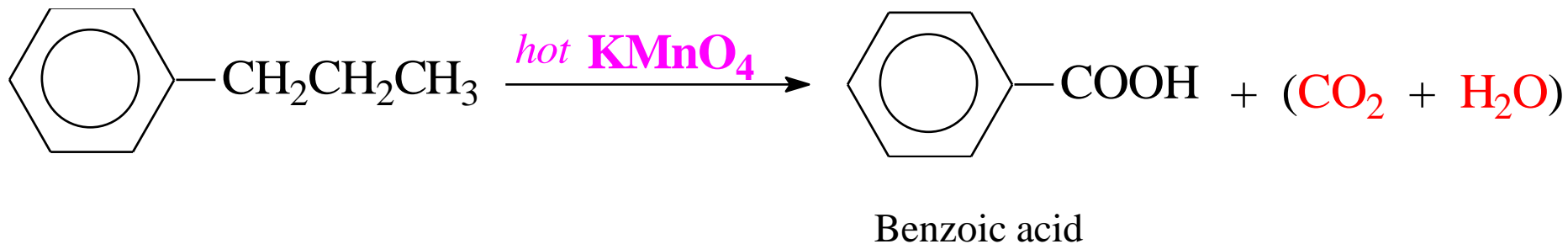
### B. Oxidation of an alkyl Side chain

Another reaction of the alkyl side chain is the conversion into a *carboxyl group*,  $\text{COOH}$ , by treatment with hot potassium permanganate.

#### Example 1.

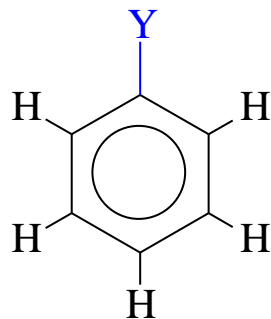


#### Example 2.

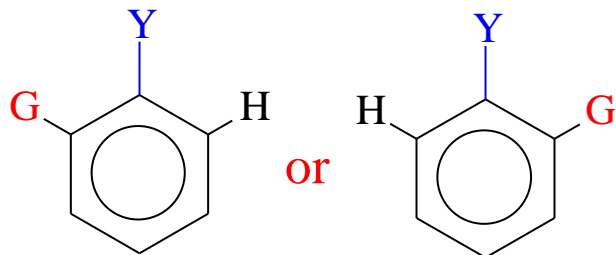


### 3. Disubstituted Benzene “Orientation in monosubstituted”.

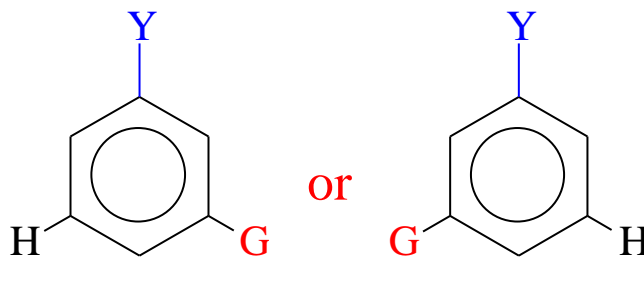
The monosubstituted benzene  $\text{C}_6\text{H}_5\text{—Y}$ , has **5 replaceable hydrogens**.



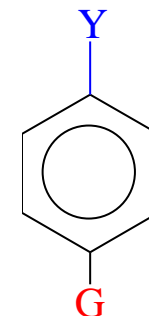
**Further substitution**  
**G = second substituent**



**Ortho product**



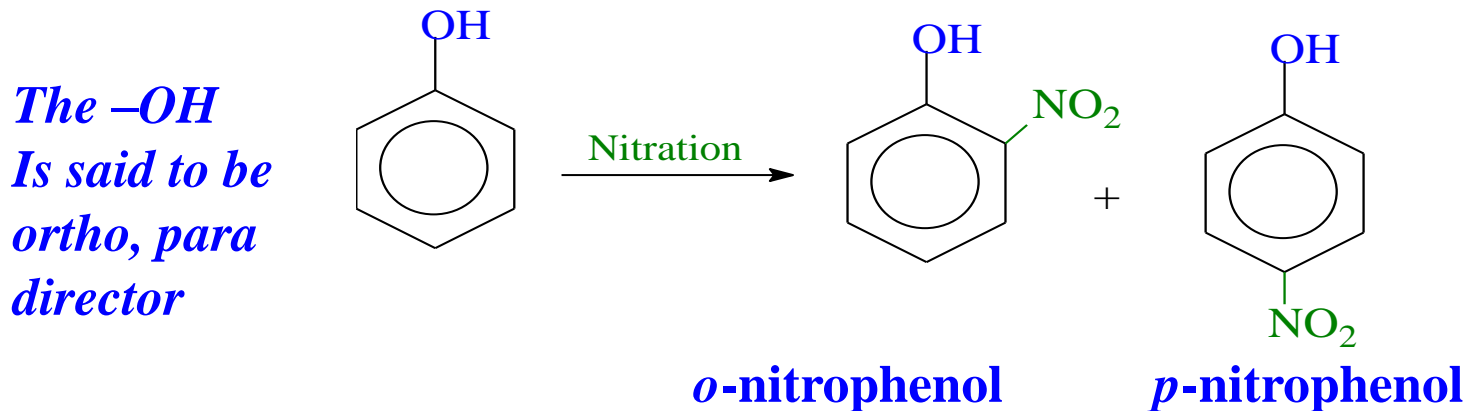
**Meta product**



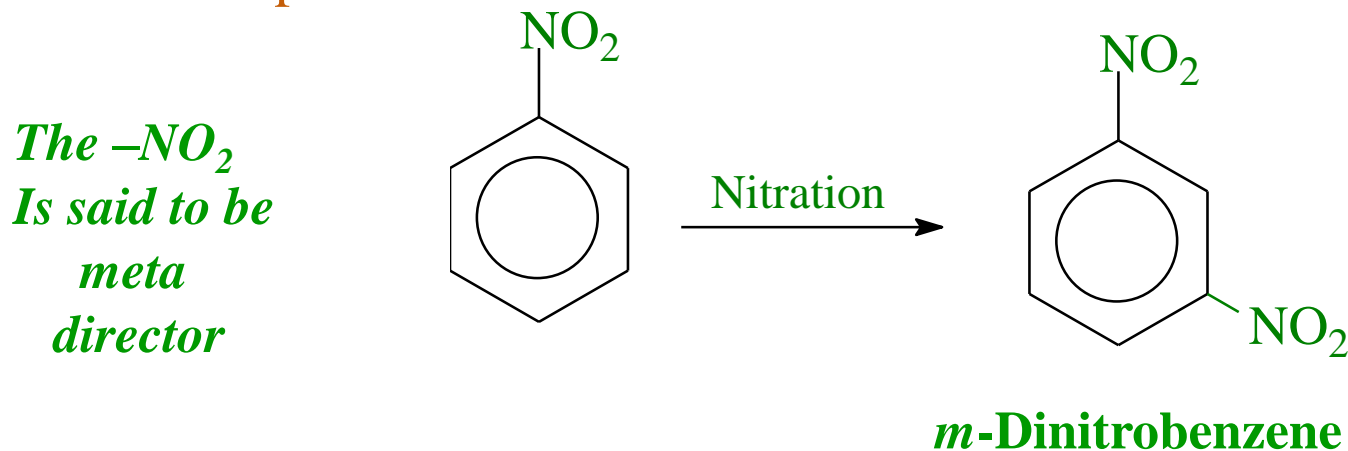
**Para product**

The actual **distribution** depends on *the nature of the first substituents*, Y, and Falls into only two categories.

- Certain Ys direct the second substituent G, regardless of what G, into **ortho** and **para** positions.



- Other Ys direct the second substituent G, regardless of the nature of G, into **meta** positions.



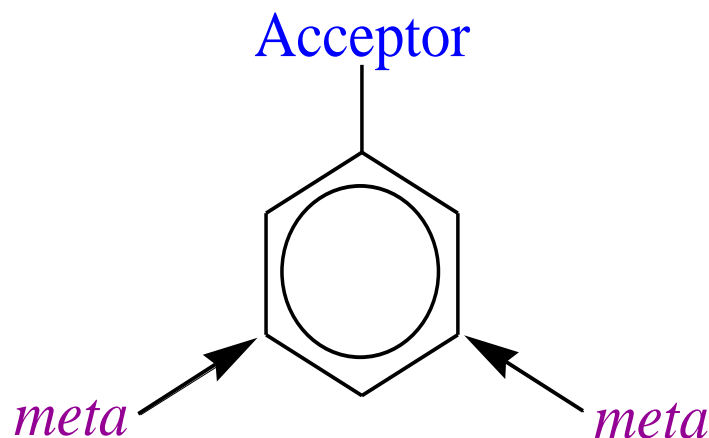
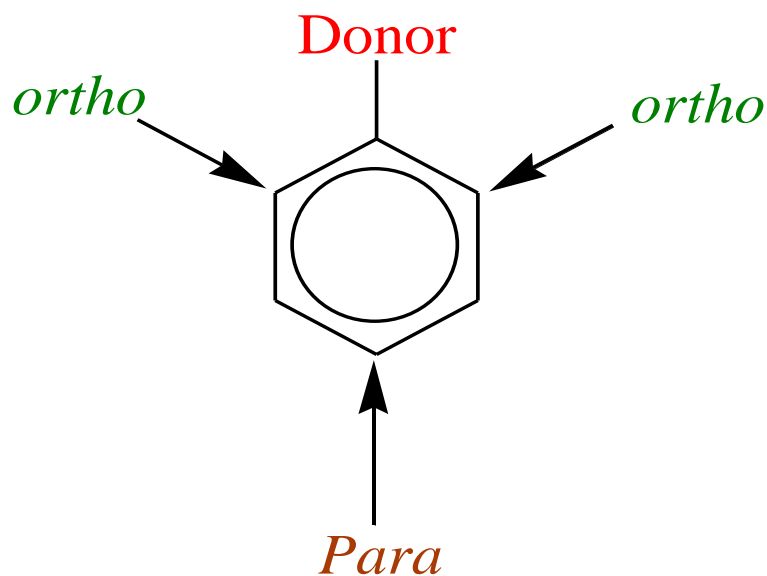


In addition to the orientation effect, the presence of a substituent also affects the rate of electrophilic substitution reactions.

➤ Substituents are classified according to their directing effect and influence on reaction rate:

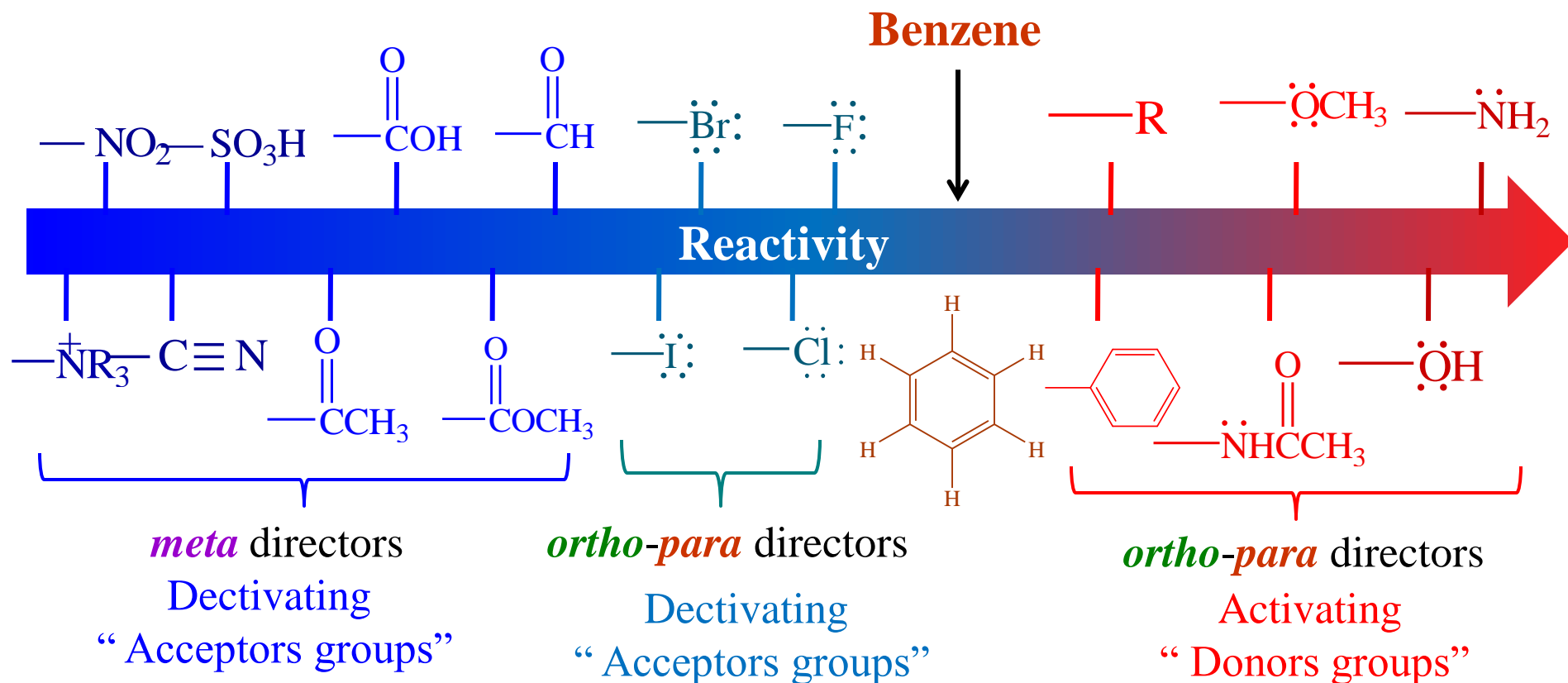
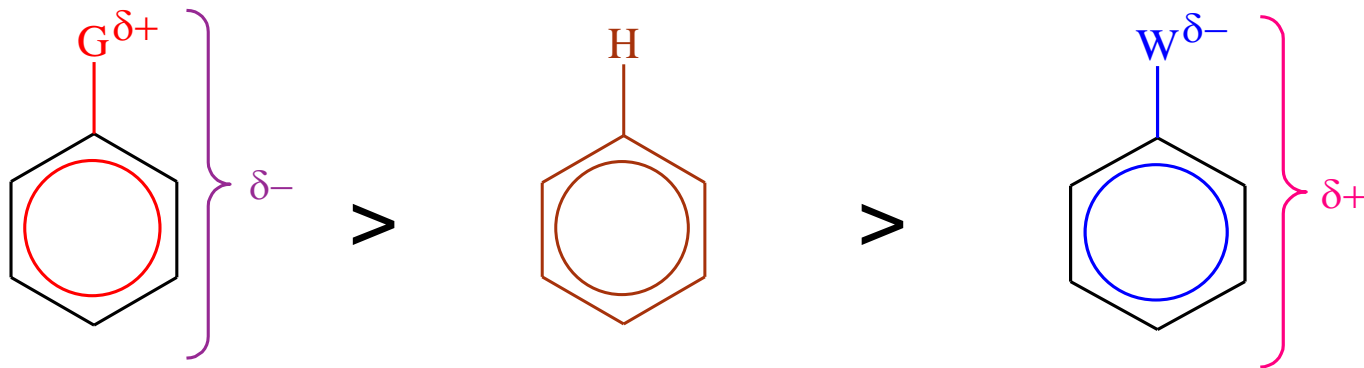
**Activator**; (electron donors): which generally direct a second electrophilic attack to the *ortho* and *para* positions.

**Deactivator**; (electron acceptors): which generally direct a second electrophilic attack to the *meta* positions.



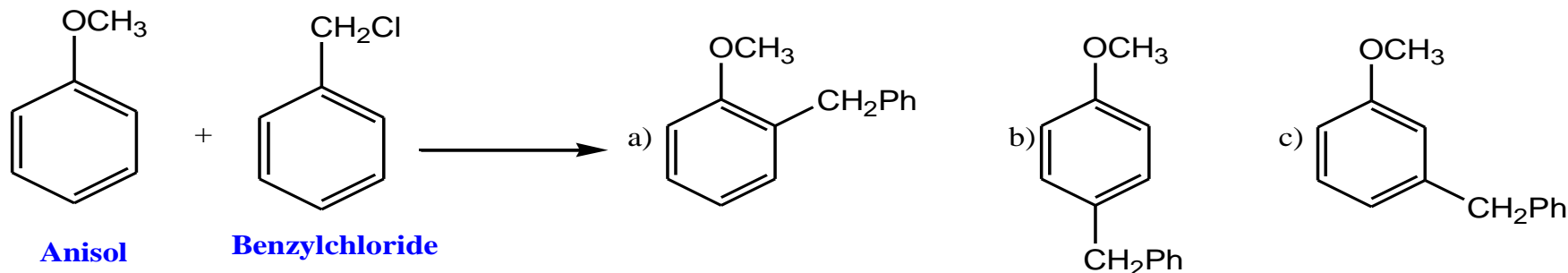
Substituent **G** donates electrons to the ring, **activating** it relative to **benzene**

Substituent **W** withdraws electrons from the ring, i.e. **deactivate** it



## Exercise:

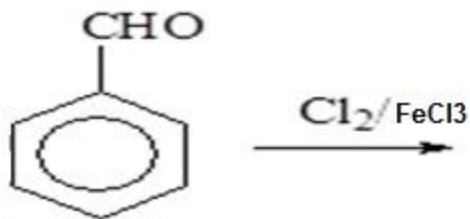
**Q1: What are the major products of the following reaction?**



**Q2: What is the empirical formula of the following compound:  
(p-methyl-toluene):**

- a)  $C_8H_{10}$       b)  $C_8H_{12}$       c)  $C_8H_{14}$       d)  $C_6H_{14}$

**Q3: What is the final product of the following reaction?**



- a) *o*-chlorobenzaldehyde      b) *m*-chlorobenzaldehyde  
c) *p*-chlorobenzaldehyde      d) a & c

*Thank you for listing*

