

# Organic Chemistry

244 CHEM

## Aromatic Hydrocarbons

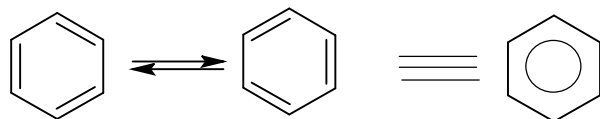
Dr. Hany El-Hamshary

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# Aromatic Hydrocarbons

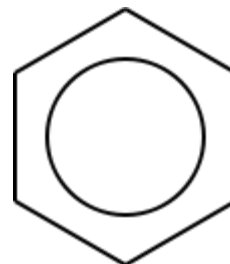
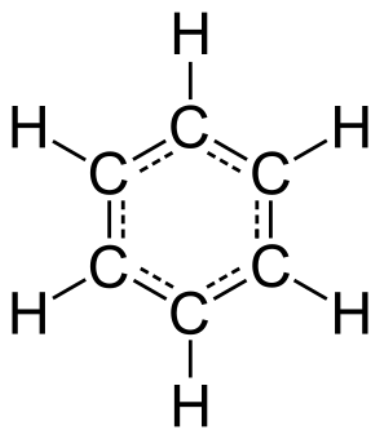
Originally called **aromatic** due to fragrant odors, although this definition seems inaccurate as many products possess distinctly non-fragrant smells!

Currently a compound is said to be aromatic if it has *benzene-like in its properties*.



Their properties differ markedly from those of aliphatic hydrocarbons.

Aromatic hydrocarbons undergo electrophilic substitution whereas aliphatic hydrocarbons undergo ionic addition to double and triple bonds and free radical substitution.



**Benzene**,  $C_6H_6$ , is a planar, cyclic compound

It was expected that benzene would be : 1,3,5-cyclohexatriene , with the shape of irregular hexagone whose bonds are:

**three C—C bond lengths of 1.54 A**

**three C=C bonds of 1.34A**

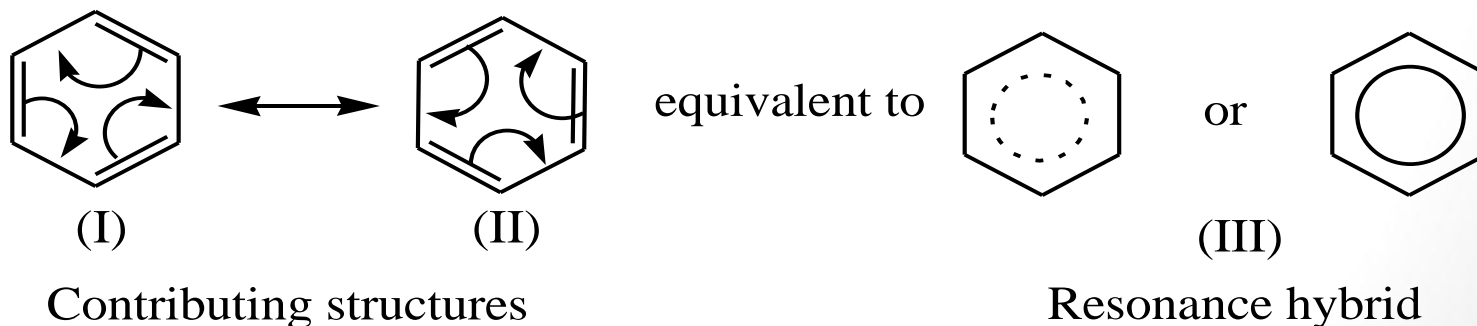
**However, it was found that all six C-C bods to be 1.39 A°**

## Structure of benzene:

X-ray diffraction experiments reveals that all carbon-carbon bonds in benzene are of **equal length, 1.39 Å**.

Benzene is expected to undergo addition reactions, however it reacts by electrophilic substitution

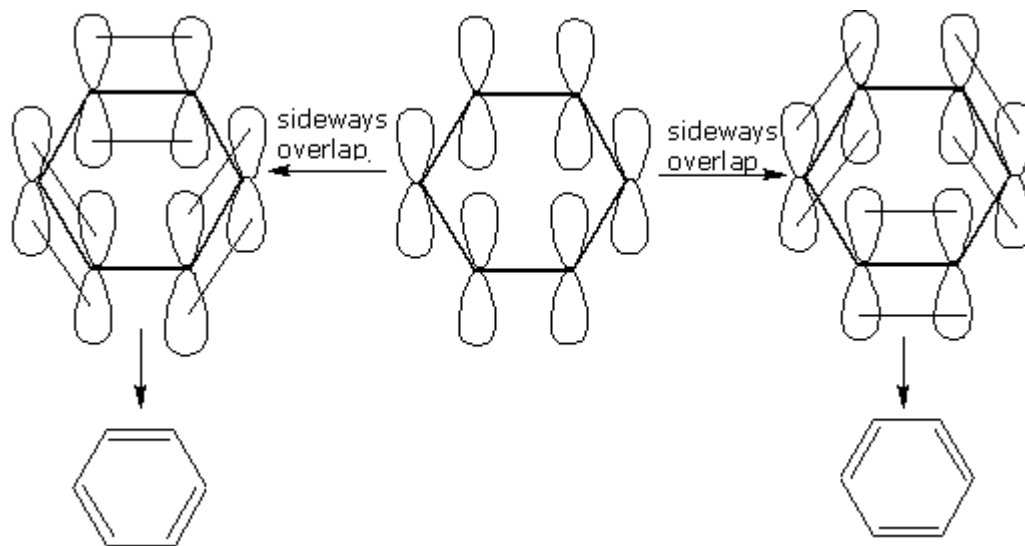
The true structure of benzene can be explained by the **concept of resonance**.



# Orbital structure of benzene

*X-ray studies show that a*

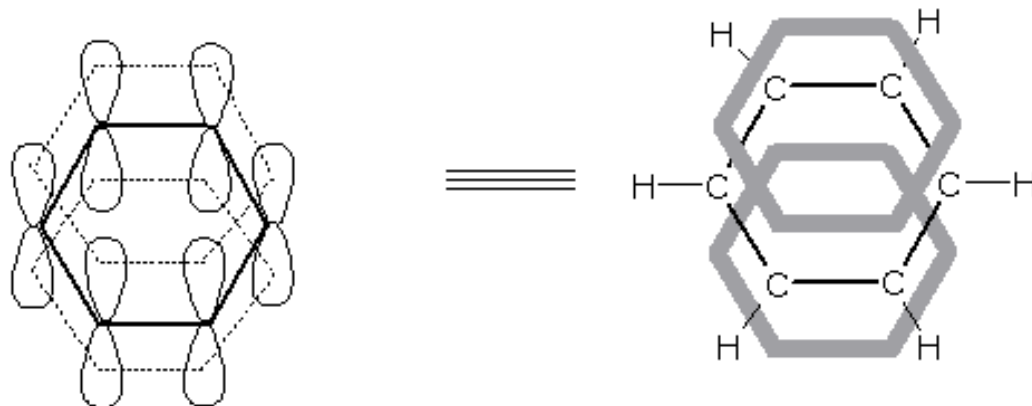
- Benzene molecule is a flat (planar) molecule. All carbon and hydrogen atoms lie in the same plane.
- It has a regular hexagon structure with all six carbon atoms lying at the corners; each carbon atom is bonded to three other atoms.
- All carbon-carbon bond lengths are equal at 139 pm.
- All CC angles (or CH angles) are equal at  $120^\circ$ .
- Each carbon atom in benzene molecule is  $sp^2$  hybridized
- All  $sp^2$  hybrid orbitals lie in the same plane (the plane of the carbon atoms) and are oriented towards the corners of an equilateral triangle.



Sideways overlap of 2p orbitals leading to formation of two sets of  $\pi$ -bonds.

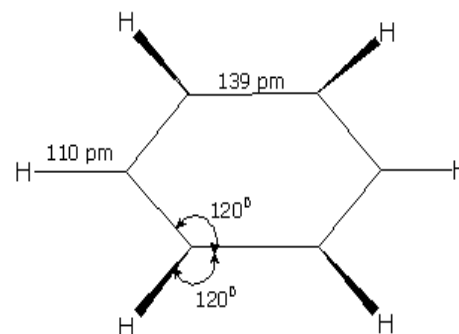
All the 'p' orbitals on the six C atoms in benzene molecule are equidistant from each other, so the 'p' orbitals of any one carbon atom are able to overlap equally well with the similar orbitals of both the carbon atoms on either sides. A continuous ring of electron cloud results because of such overlap and leads to a molecular orbital consisting to two continuous rings, one lying above, and the other below the plane of the ring as shown.

The delocalization of electrons over the six carbons may easily be seen in the molecular orbital picture of benzene.



Any pair of adjacent *p*-orbitals is capable of **side-side overlap** to form a bond.

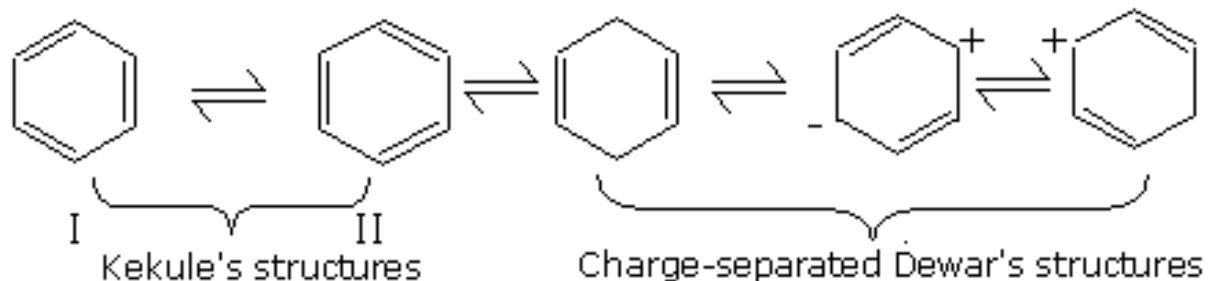
Thus, each bond in benzene has a character intermediate between a single and a double bond.



The shape and size of benzene molecule.

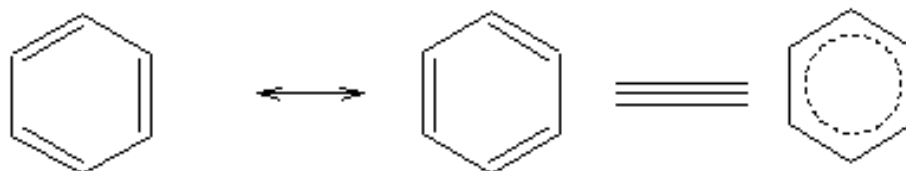
## Resonance hybrid structure of benzene

The theory of resonance states that benzene is a resonance hybrid of the following canonical forms:



This is due to delocalized pi electron clouds ; the electrons which form the double pi bond keep on "jumping " between subsequent bonds. Thus electrons for C–C bonding are distributed equally between each of the six carbon atoms. Average length between the C-C and C=C is at 0.139 nm

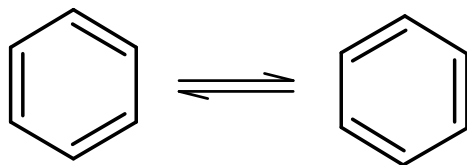
Since, the forms I and II are the most contributing, hence benzene is represented as a hybrid structure of these two structures, i.e:





## Resonance Energy and Stability of Benzene:

In the following delocalised and contributing structures of benzene

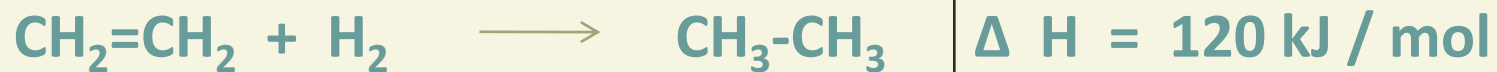


The energy required to change the delocalised structure to one of the contributing structures is called *resonance energy*.

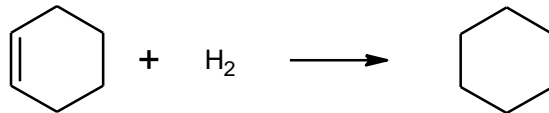
*Resonance energy* is calculated by finding the difference between heat of hydrogenation of the resonance and contributing structure.

This extra stability of benzene is due to resonance and is known as the resonance energy. It is determined by the difference between the calculated and experimental heats of hydrogenation of the cyclohexene, 1,3-cyclohexadiene and 1,3,5-cyclohexatriene (benzene)

Hydrogenation is the addition of hydrogen to a double bond compound. If, for example, you hydrogenate ethene you get ethane:

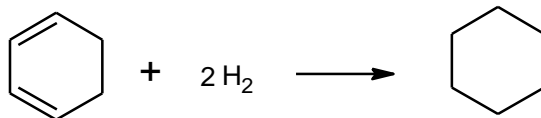


Cyclohexene



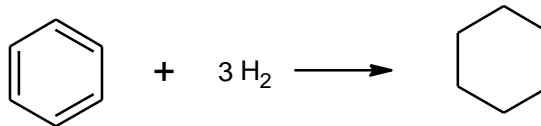
125 kJ/mol  
(≈ 30 kcal/mol)

1,3-Cyclohexadiene



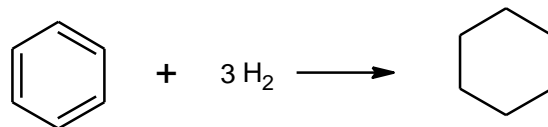
232 kJ/mol (55.7 kcal/mol)

(1,3,5-cyclohexatriene) **imaginary molecule**

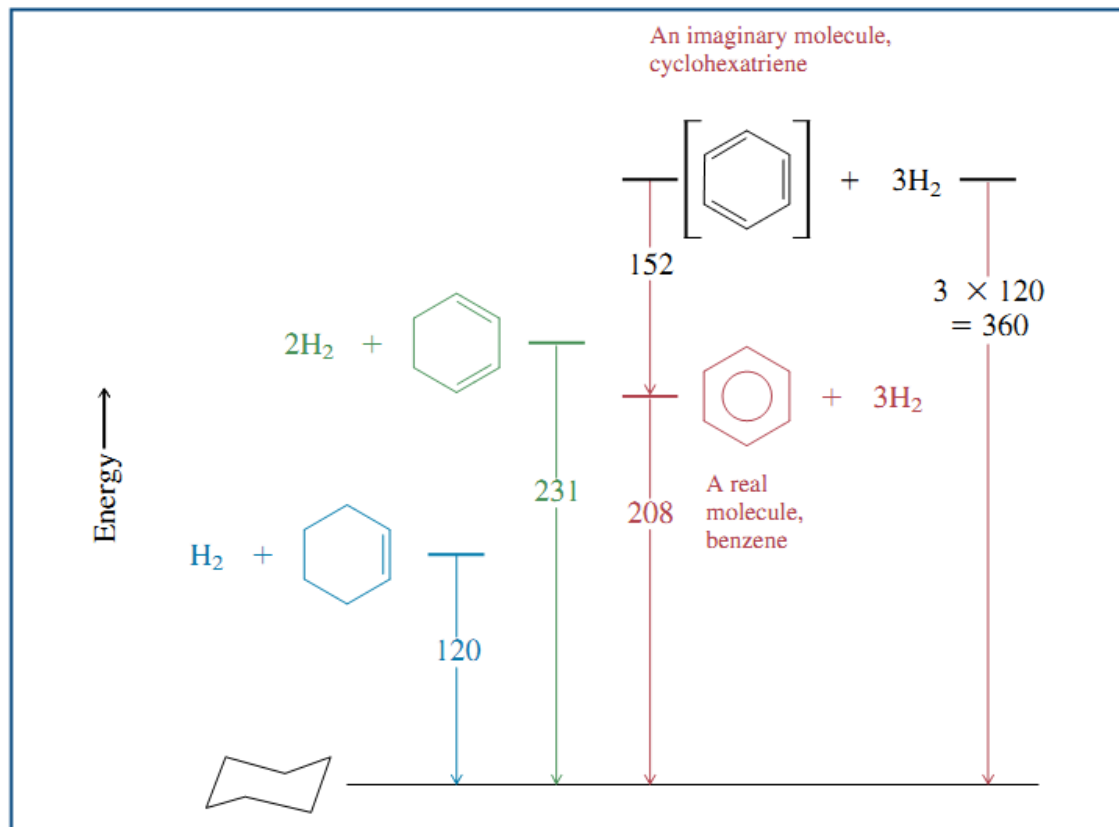


Expected heat of  
hydrogenation:  
360 kJ/mol (85.8 kcal/mol).

Benzene



Actual heat of  
hydrogenation is  
152 kJ/mol (36 kcal/mol)



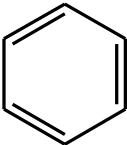
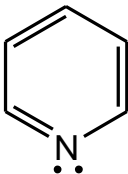
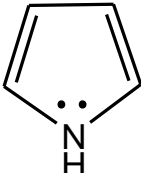
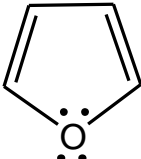
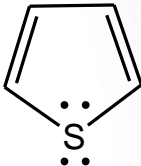
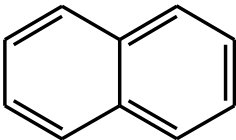
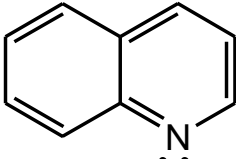
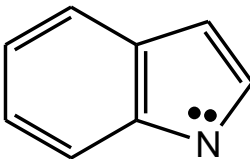
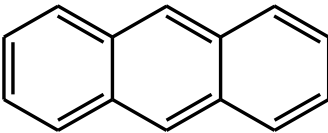
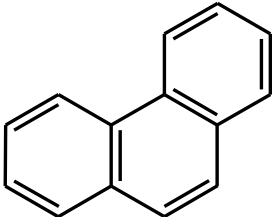
Expected heat of hydrogenation of 1,3,5-cyclohexatriene should equal to three times the heat of hydrogenation of cyclohexene, or a total of 360 kJ/mol (85.8 kcal/mol). However, the heat of hydrogenation of benzene is 152 kJ/mol (36 kcal/mol) less than expected for a hypothetical compound 1,3,5-cyclohexatriene by  $360 - 152 = 208$  kJ/mol. This difference in energy is called the **resonance energy** of benzene. It is a measure of how much more stable benzene is than would be predicted on the basis of its formulation as a pair of rapidly interconverting 1,3,5-cyclohexatrienes

# Benzene and Aromaticity: Huckel's rule

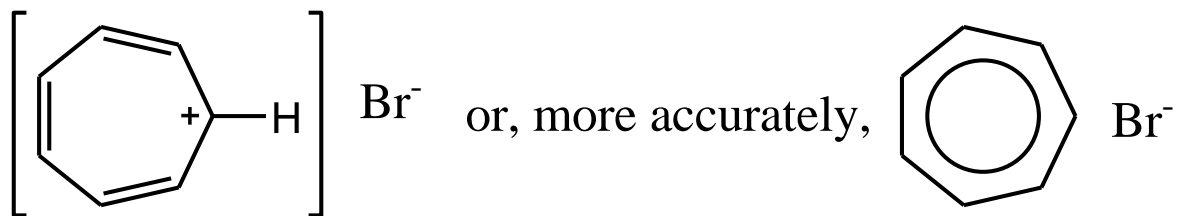
Aromatic compounds are those, which resemble benzene in chemical behavior. These compounds contain *alternate double and single bonds in a cyclic structure*. They undergo *substitution reactions* rather than addition reactions. This characteristic behavior is called aromatic character or aromaticity. Huckel formulated a rule to identify aromatic compounds that is known as **Huckel's rule**:

1. Aromatic compounds should be cyclic.
2. The compound should have a planar structure.
3. There should be delocalized  $\pi$  electrons in the compound.
4. There should be  $(4n + 2)$  pi electrons in the compound. The value of  $n = 0, 1, 2, 3, \dots$

# Aromatic Character (Aromaticity): The $(4n + 2)$ Rule

$n$	$4n + 2$	Structure and name of aromatic compound
1	6	 Benzene  Pyridine  Pyrrole  Furan  Thiophene
2	10	 Naphthalene  Quinoline  Indole
3	14	 Anthracene  Phenanthrene

## Aromatic Character (Aromaticity): The $(4n + 2)$ Rule

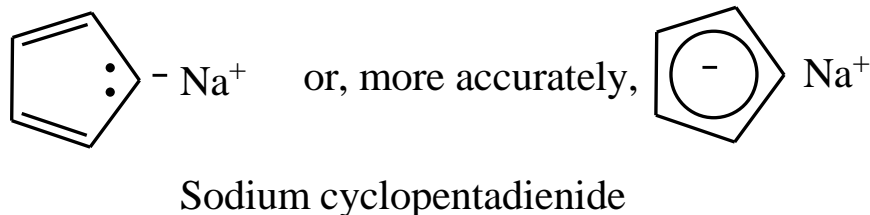


Tropylium bromide

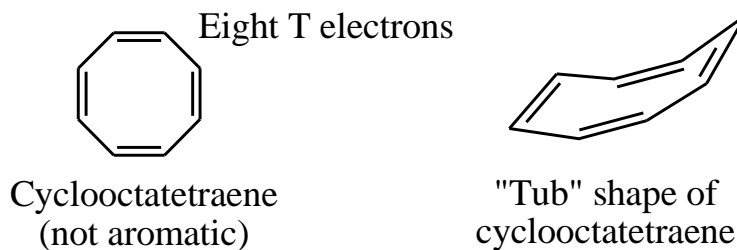
➔ **Tropylium ion** is a seven-membered ring that contains three double bonds.

The ring has a total of **six  $\pi$  electrons**,  
**It is therefore aromatic.**

## Aromatic Character (Aromaticity): The $(4n + 2)$ Rule



- ➔ **Cyclopentadienide anion** is a five-membered ring  
The ring has a sextet  $\pi$  electrons,  
**two double bonds and a pair of nonbonded electrons.**  
It is therefore aromatic



- ➔ **Cyclooctatetraene,**  
 $(4n + 2) = 8 \pi$  electrons  
no integral value of  $n$   
Cyclooctatetraene is not aromatic.

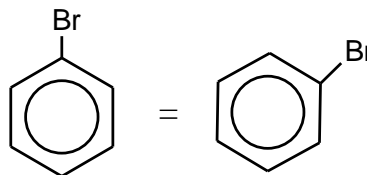


# Nomenclature

## Monosubstituted Benzenes

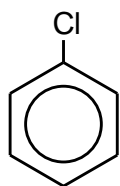
Because all six positions in benzene are equivalent,

*there is no need to specify by a number the position of a substituent for monosubstituted benzenes.*

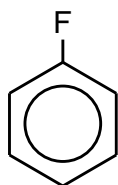


Bromobenzene

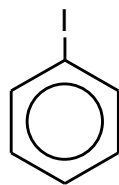
The two structures represent the same molecule because all positions are equivalent.



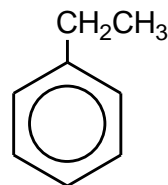
Chlorobenzene



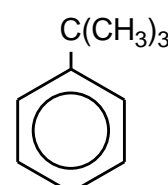
Fluorobenzene



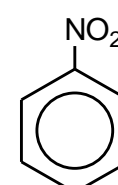
Iodobenzene



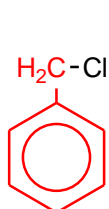
Ethylbenzene



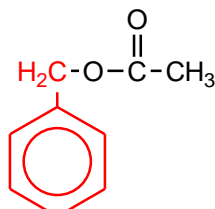
*t*-Butylbenzene



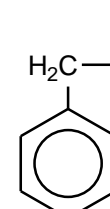
Nitrobenzene



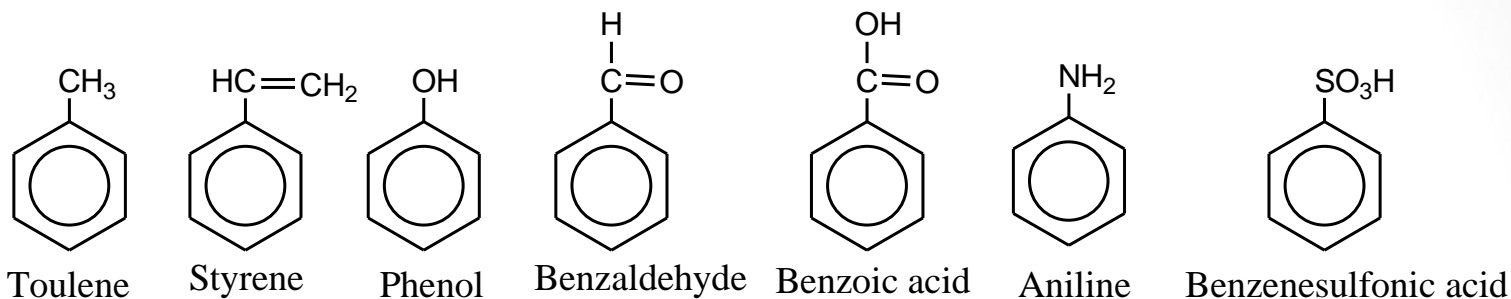
Benzyl chloride



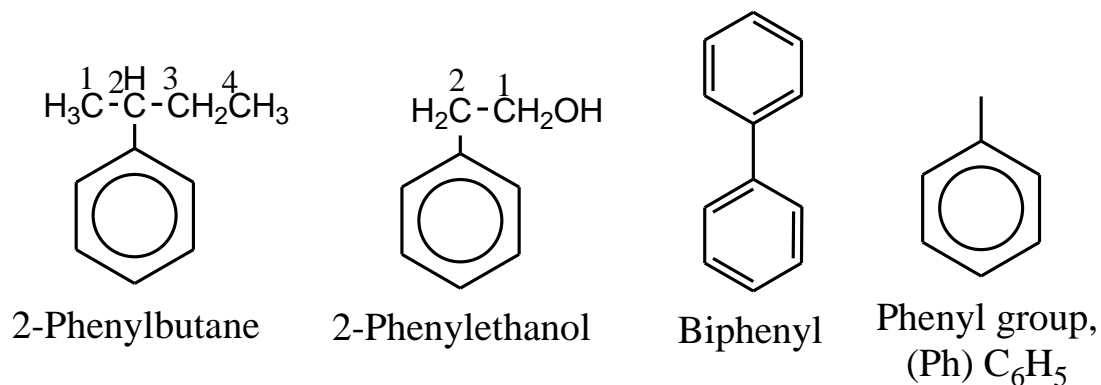
Benzyl acetate



Benzyl group,  
(PhCH<sub>2</sub>-)



Sometimes it is more convenient to **name the benzene ring as a substituent**, as in the following structures.

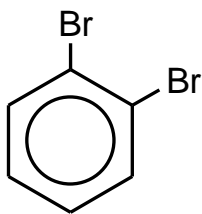


## Disubstituted Benzenes

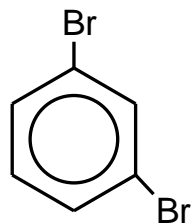
All disubstituted benzenes, no matter what the substituents, can give rise to three possible isomers.

the relative positions of the substituents are designated by numbers

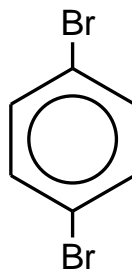
More commonly, by the prefixes **ortho (*o*-)**, **meta (*m*-)**, or **para (*p*-)**.



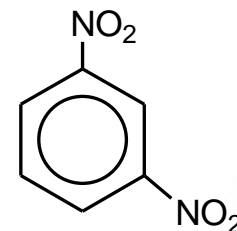
1,2-Dibromobenzene  
*o*-Dibromobenzene



1,3-Dibromobenzene  
*m*-Dibromobenzene



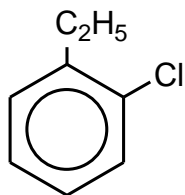
1,4-Dibromobenzene  
*p*-Dibromobenzene



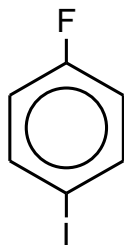
1,3-Dinitrobenzene  
*m*-Dinitrobenzene

# Disubstituted Benzenes

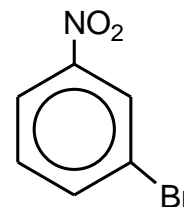
When the substituents are different, they are listed in alphabetical order.



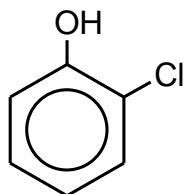
1-Chloro-2-ethylbenzene  
(*o*-Chloroethylbenzene)



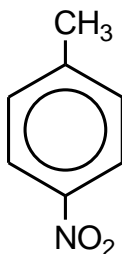
1-Fluoro-4-iodobenzene  
(*p*-Fluoroiodobenzene)



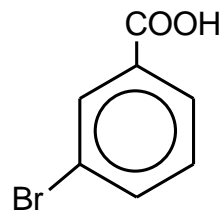
1-Bromo-3-nitrobenzene  
*m*-Bromonitrobenzene



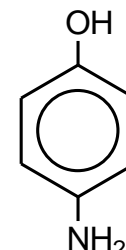
2-Chlorophenol  
(*o*-Chlorophenol)



4-Nitrotoulene  
(*p*-Nitrotoulene)



1-Bromobenzoic acid  
*m*-Bromobenzoic acid)

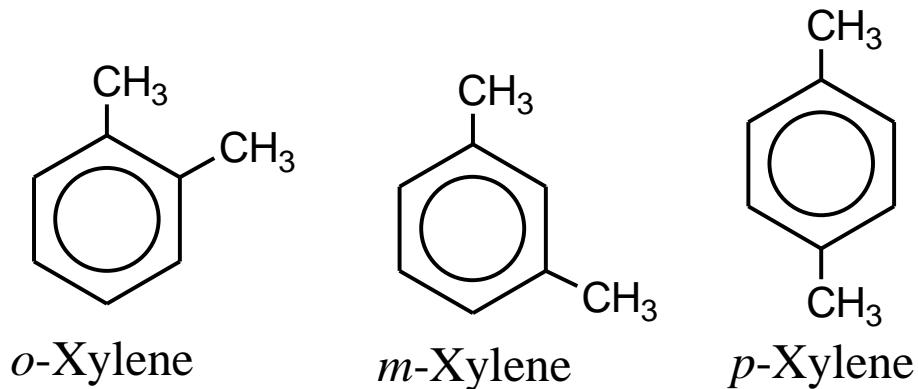


4-Aminophenol  
(*p*-Aminophenol)  
or  
4-Hydroxyaniline  
(*p*-Hydroxyaniline)

Like monosubstituted benzenes, certain disubstituted benzenes are referred to by their common names.

Example:

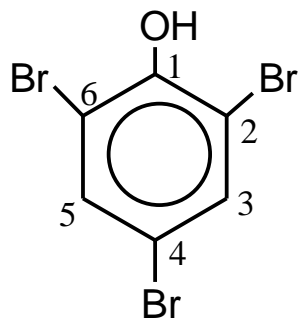
*The dimethylbenzenes are known as xylenes.*



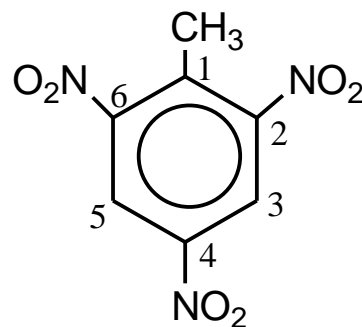
## Polysubstituted Benzenes

As with disubstituted benzenes,

If one of the group is part of the parent compound, the carbon that bears the functional group of the parent compound is assigned the number 1.



2,4,6-Tribromophenol  
(OH on carbon 1)

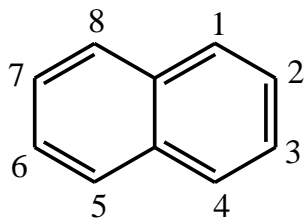


2,4,6-Trinitrotoulene (TNT)  
(CH<sub>3</sub> on carbon 1)

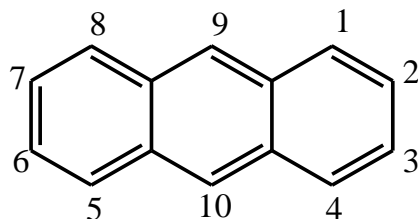
# Polynuclear Aromatic

## Hydrocarbons

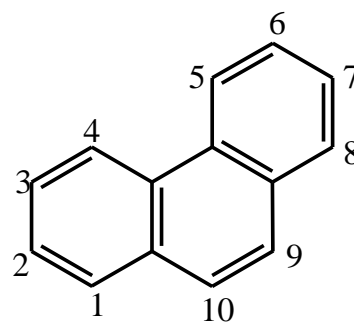
Polynuclear aromatic hydrocarbons containing two, three & four rings are :



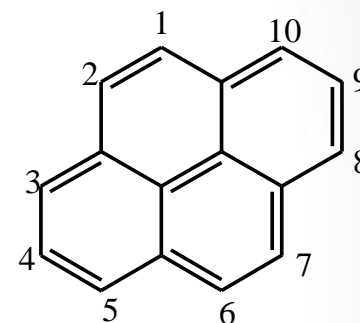
Naphthalene



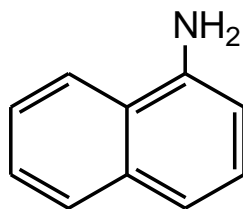
Anthracene



Phenanthrene

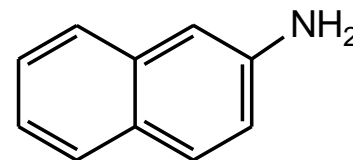


Pyrene



IUPAC name:  
Common name:

1-Aminonaphthalene  
a-Naphthylamine  
(a weak carcinogen)

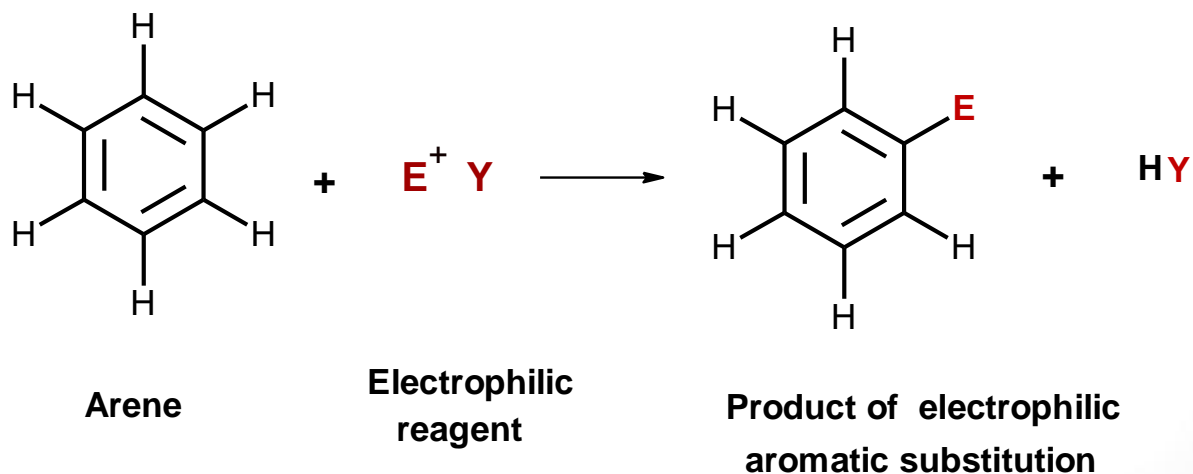


2-Aminonaphthalene  
B-Naphthylamine  
(a strong carcinogen)

## Reactions of Benzene :

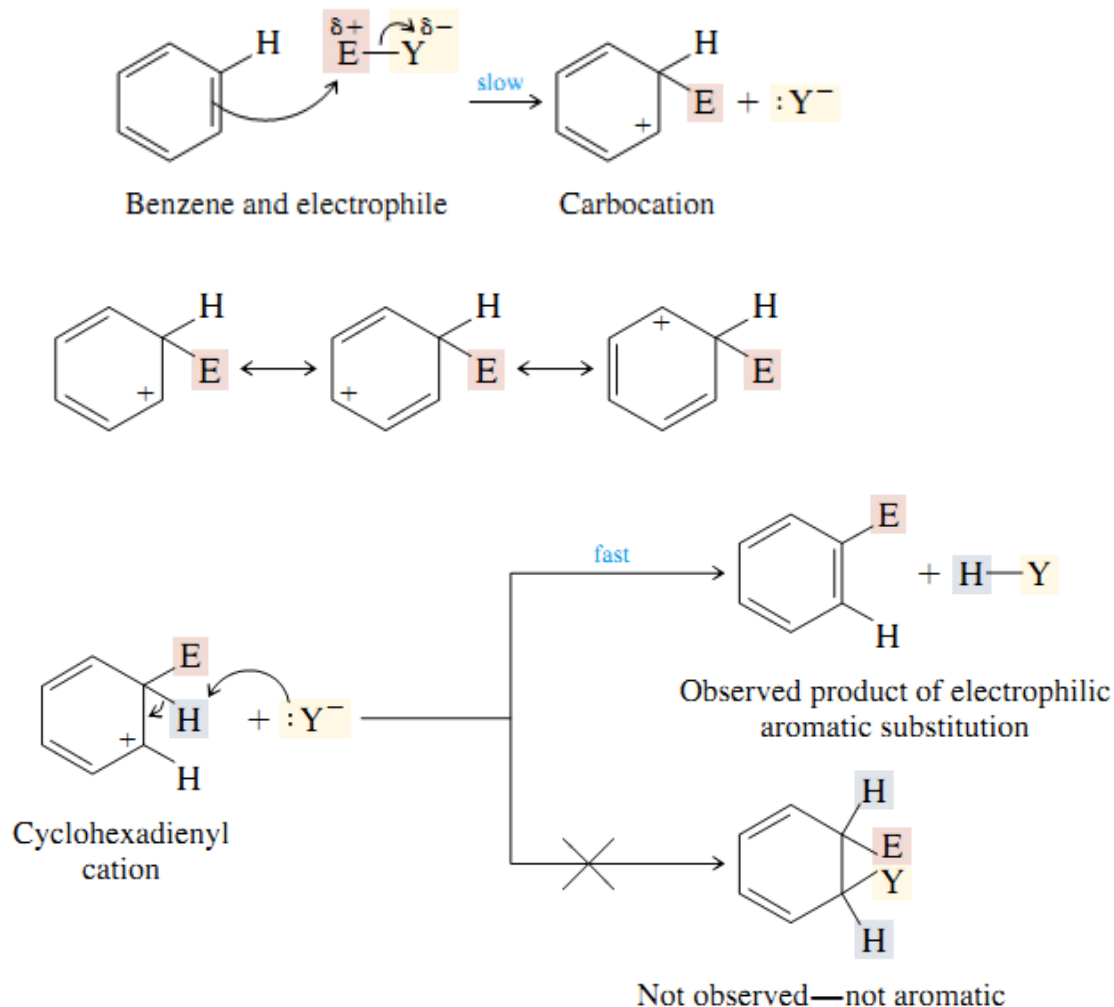
### Electrophilic substitution reactions

In this reaction, an electrophile  $E^+$  replaces a hydrogen atom, from the aromatic ring system.





# General Mechanism

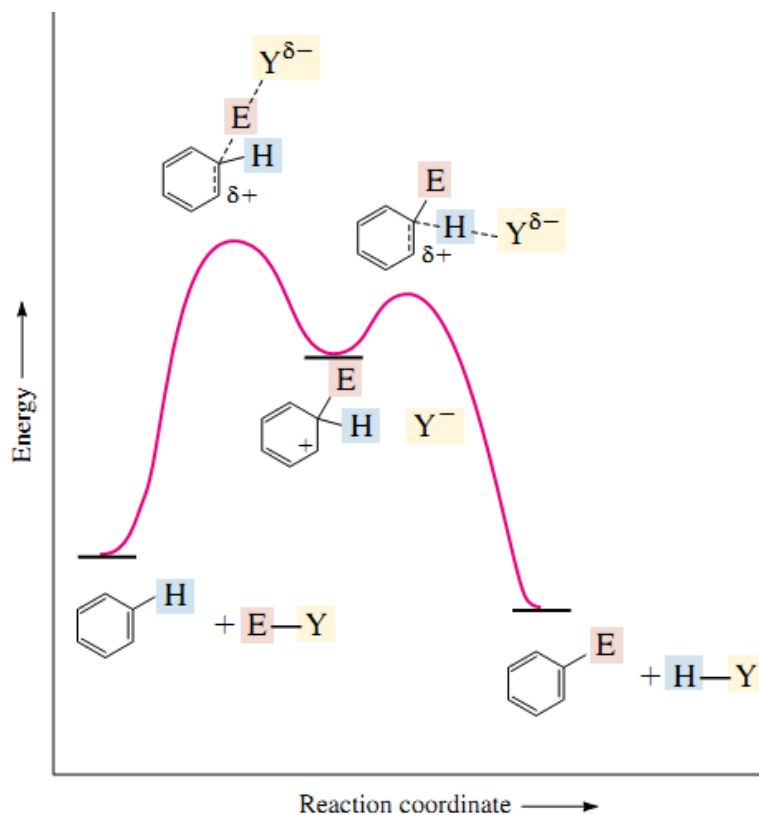


The electrophile  $E^+$  approaches the cloud of the aromatic ring and forms a bond to carbon, creating a +ve charge in the ring

The removal of the proton by the nucleophile  $Y^-$ , which leads to the restoration of the aromatic ring

The net overall result is the substitution of the group  $E^+$  for a proton  $H^+$ .

The following is the potential energy diagram describing the general mechanism of electrophilic aromatic substitution. In order for electrophilic aromatic substitution reactions to overcome the high activation energy that characterizes the first step, the electrophile must be a fairly reactive one.



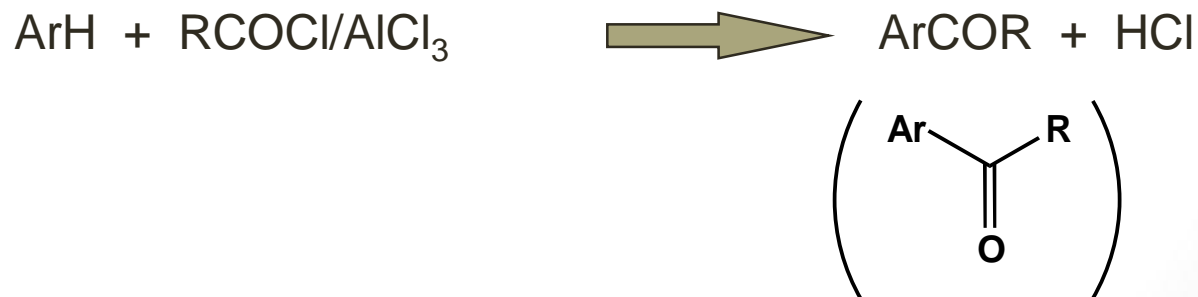
## Examples of electrophilic substitution:

Alkylation & acylation of benzene: **Friedel-Crafts Reaction**

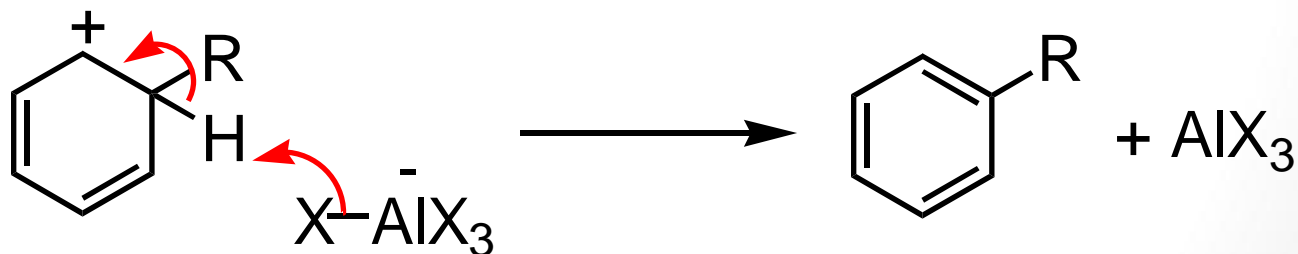
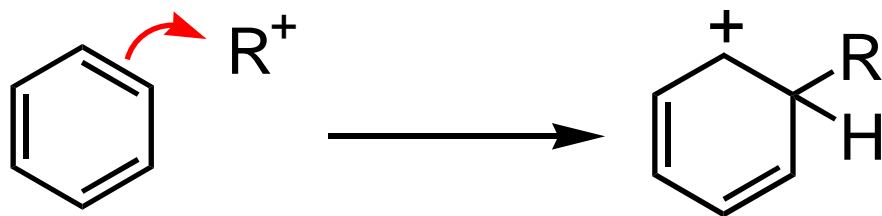
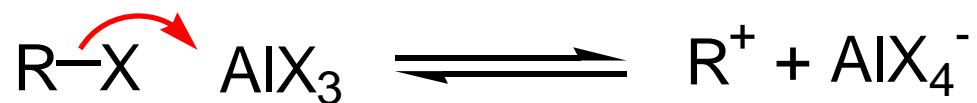
Friedel - Crafts alkylation

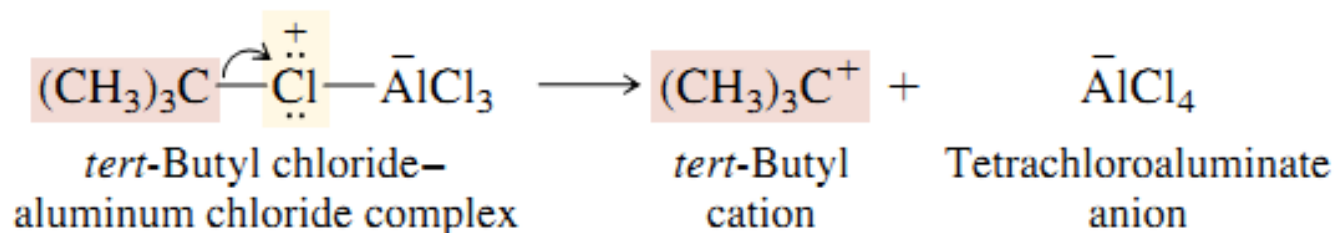
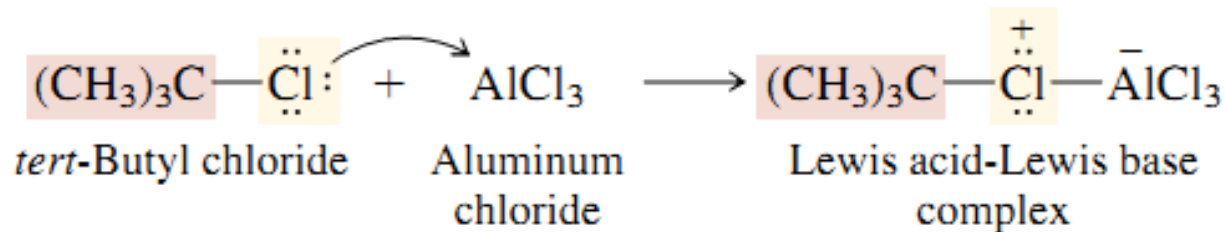
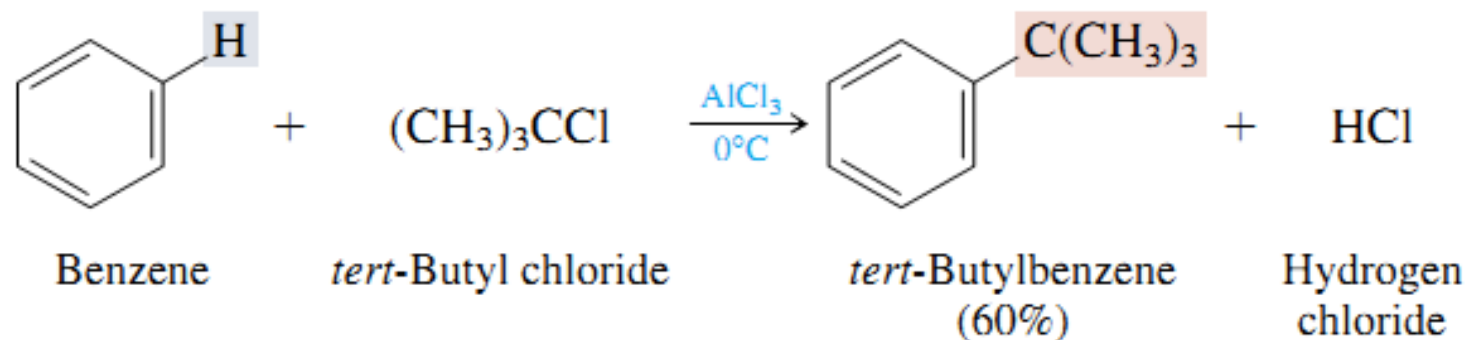


Friedel - Crafts acylation

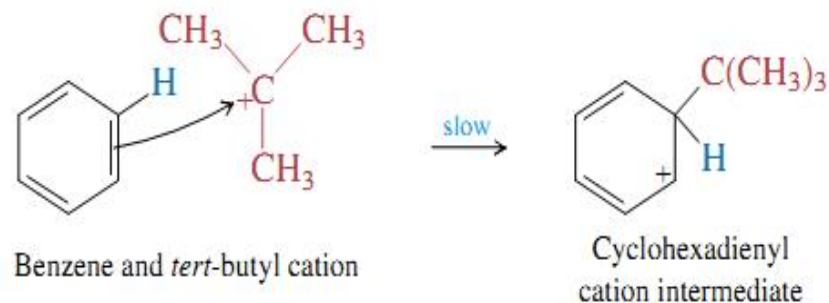


# Friedel - Crafts alkylation

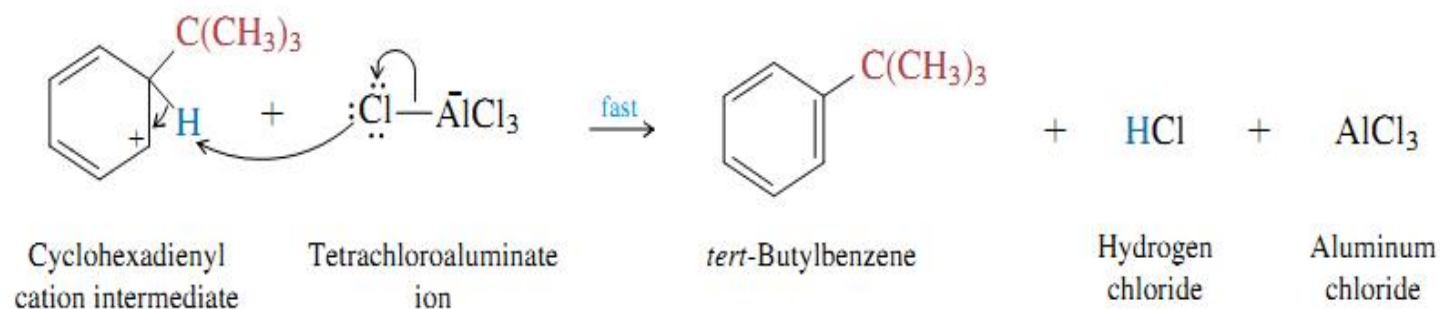




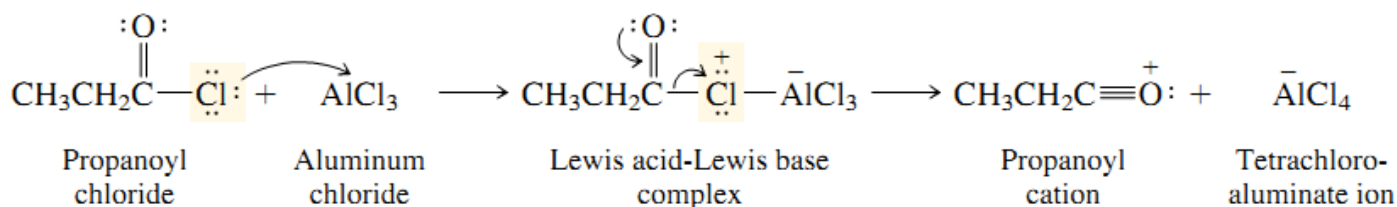
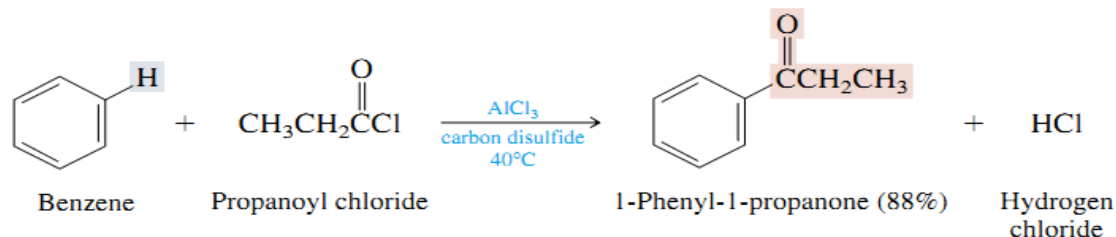
**Step 1:** Once generated by the reaction of *tert*-butyl chloride and aluminum chloride, *tert*-butyl cation attacks the  $\pi$  electrons of benzene, and a carbon-carbon bond is formed.



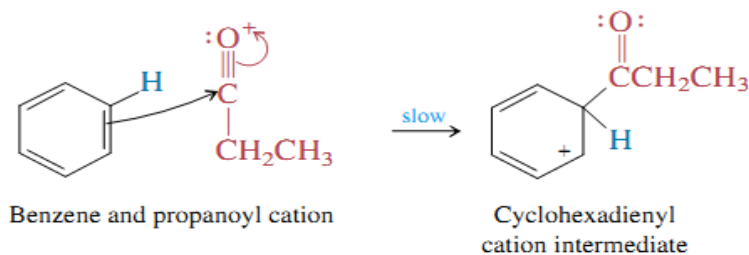
**Step 2:** Loss of a proton from the cyclohexadienyl cation intermediate yields *tert*-butylbenzene.



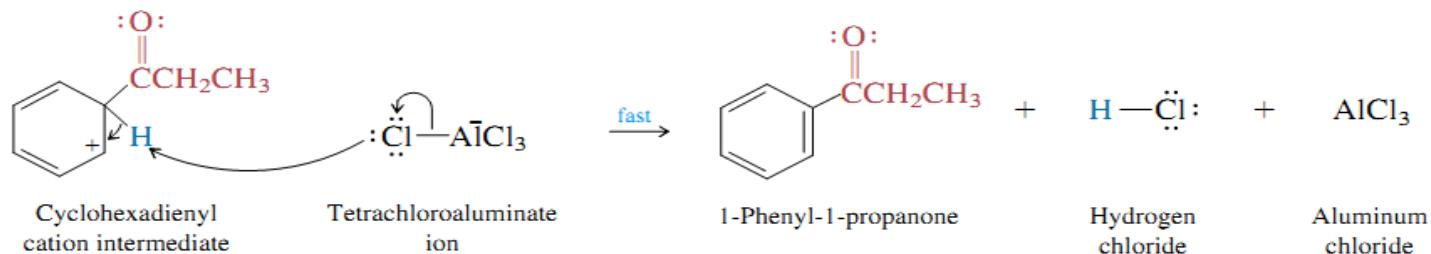
# Friedel-Crafts acylation of benzene



**Step 1:** The acyl cation attacks benzene. A pair of  $\pi$  electrons of benzene is used to form a covalent bond to the carbon of the acyl cation.

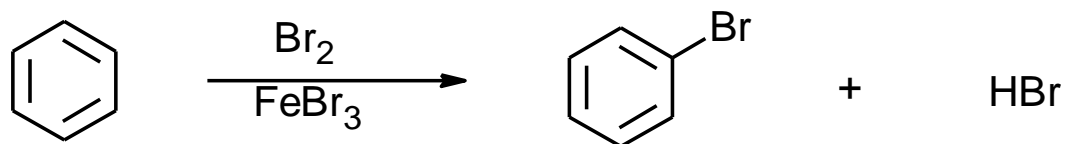


**Step 2:** Aromaticity of the ring is restored when it loses a proton to give the acylbenzene.



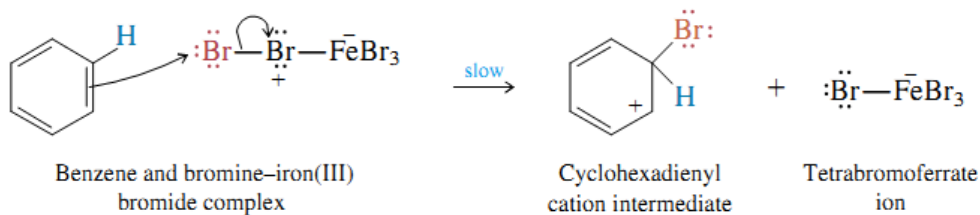
# Bromination of benzene

It requires the presence of a Lewis acid catalyst, ferric bromide. Ferric bromide will help to generate a highly reactive electrophile, the bromonium ion ( $\text{Br}^+$ ).

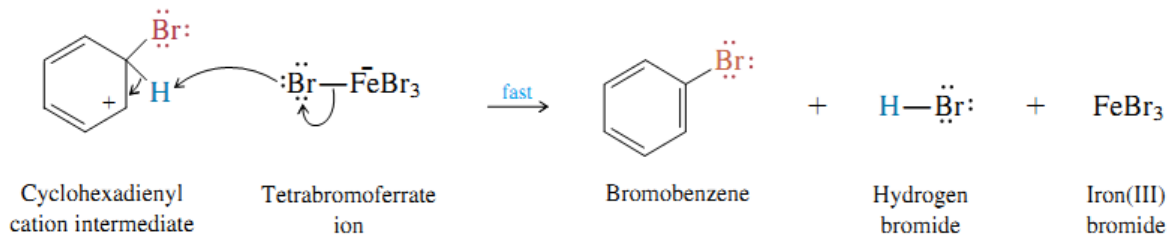


**Step 1:** The bromine–iron(III) bromide complex is the active electrophile that attacks benzene.

Two of the  $\pi$  electrons of benzene are used to form a bond to bromine and give a cyclohexadienyl cation intermediate.



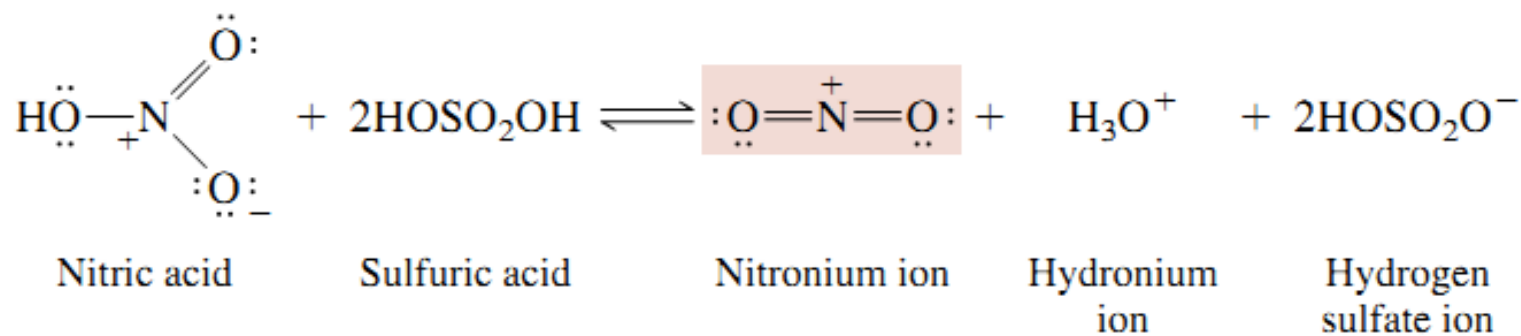
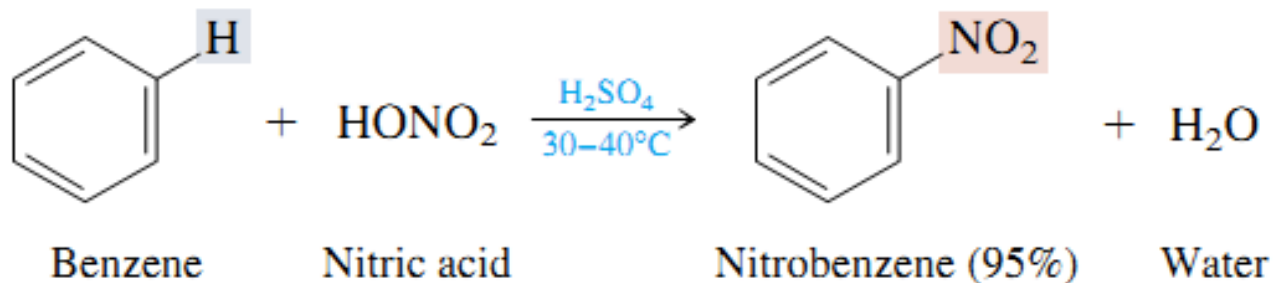
**Step 2:** Loss of a proton from the cyclohexadienyl cation yields bromobenzene.



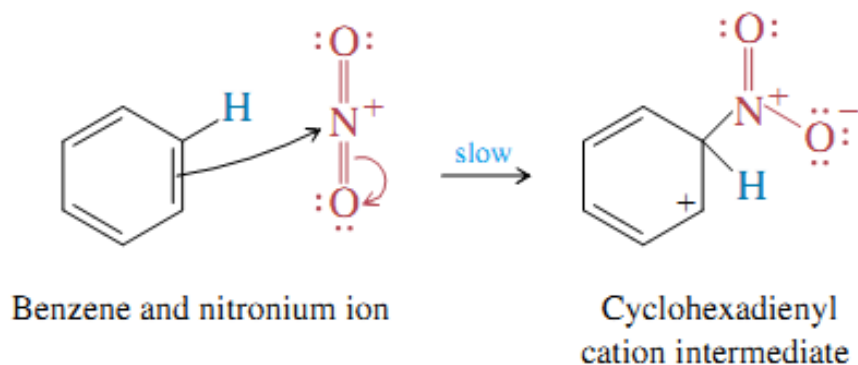


## Nitration of benzene

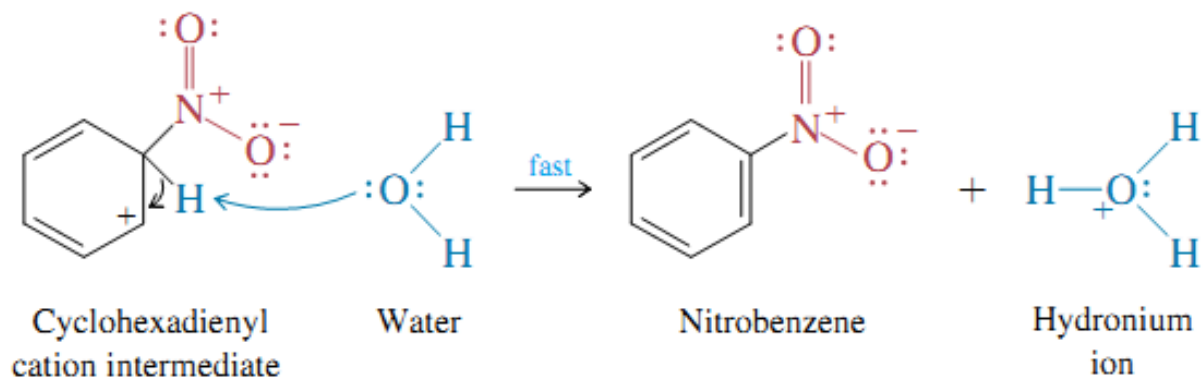
It requires the presence of a protonated acid, sulfuric acid. The attacking electrophile in nitration is the **nitronium ion** ( $\text{NO}_2^+$ )



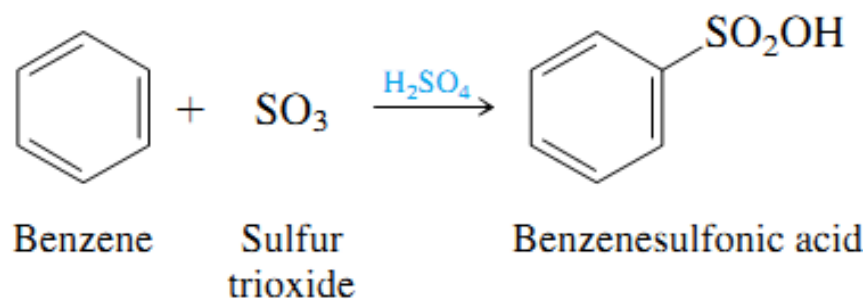
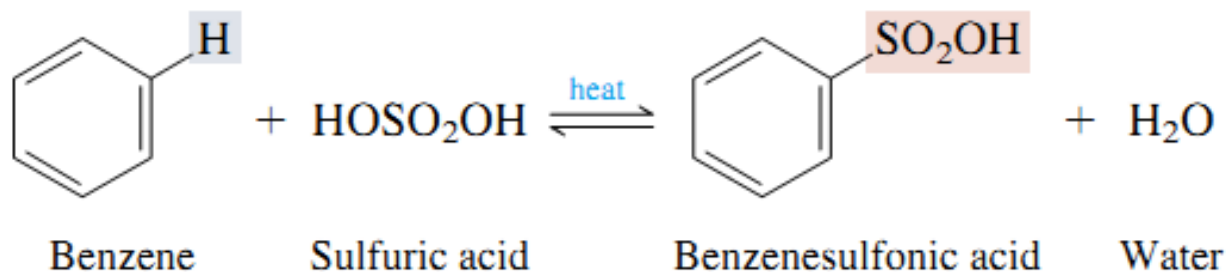
**Step 1:** Attack of nitronium cation on the  $\pi$  system of the aromatic ring



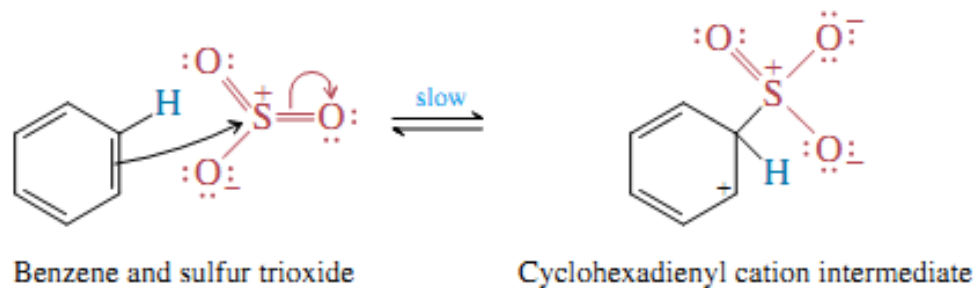
**Step 2:** Loss of a proton from the cyclohexadienyl cation



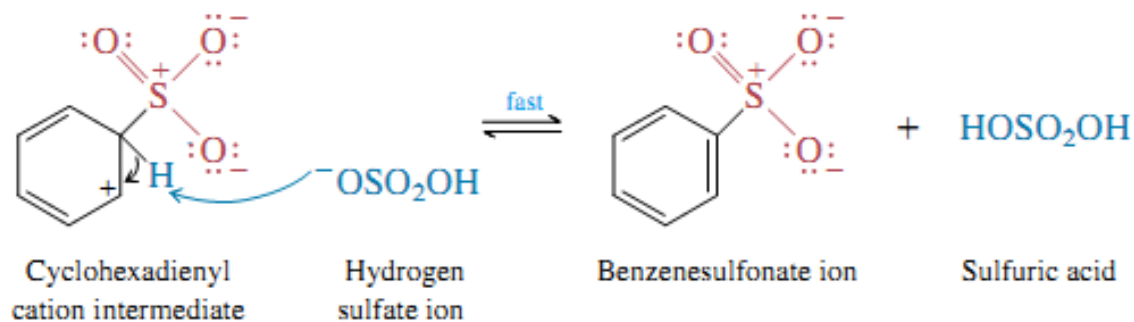
## Sulfonation of benzene



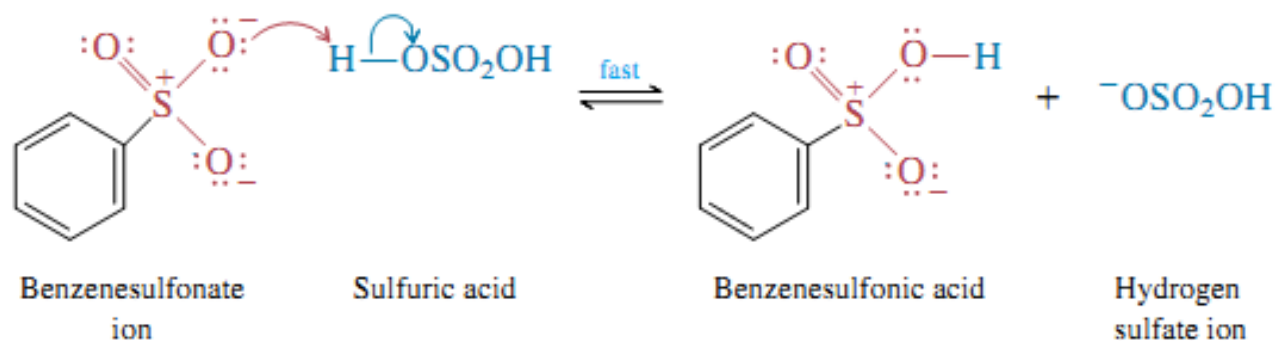
**Step 1:** Sulfur trioxide attacks benzene in the rate-determining step



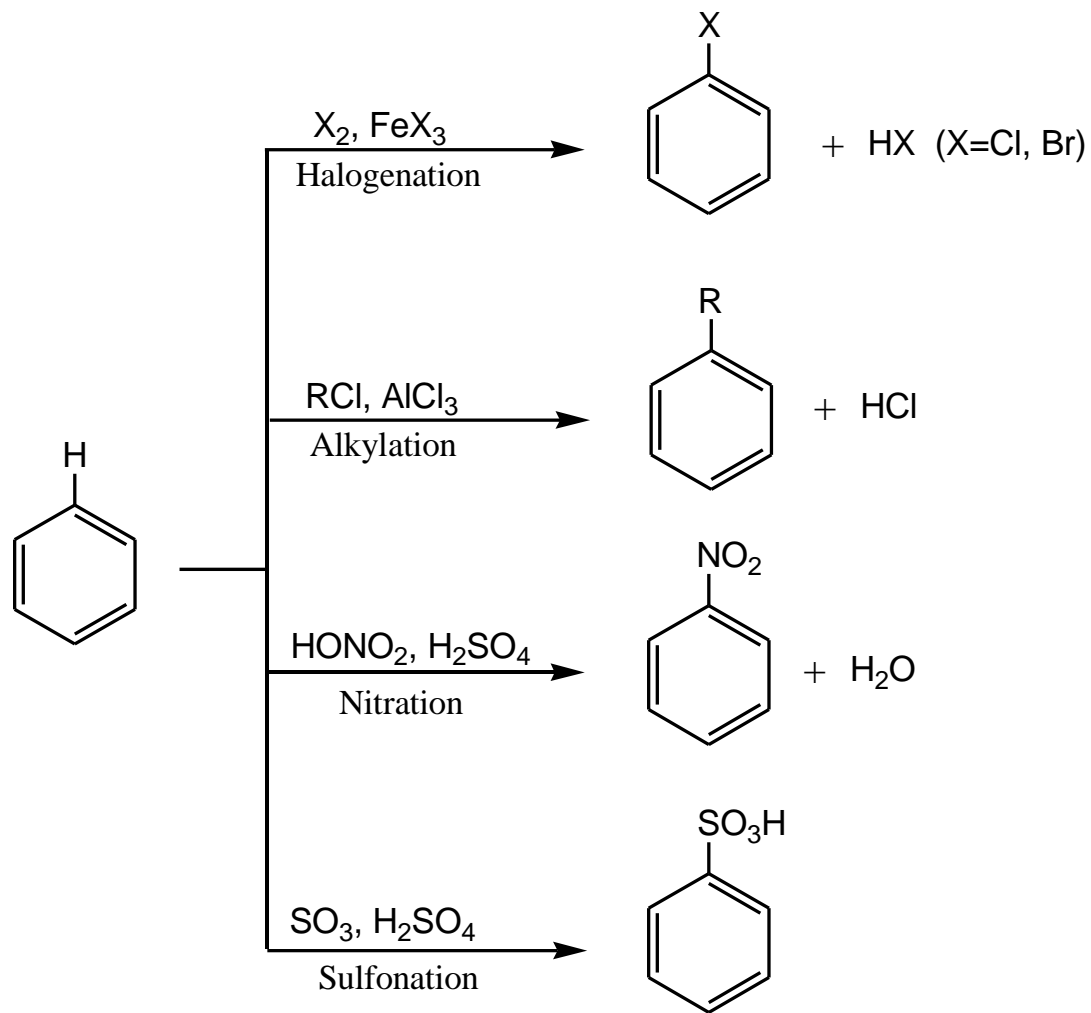
**Step 2:** A proton is lost from the  $sp^3$  hybridized carbon of the intermediate to restore the aromaticity of the ring. The species shown that abstracts the proton is a hydrogen sulfate ion formed by ionization of sulfuric acid.



**Step 3:** A rapid proton transfer from the oxygen of sulfuric acid to the oxygen of benzenesulfonate completes the process.



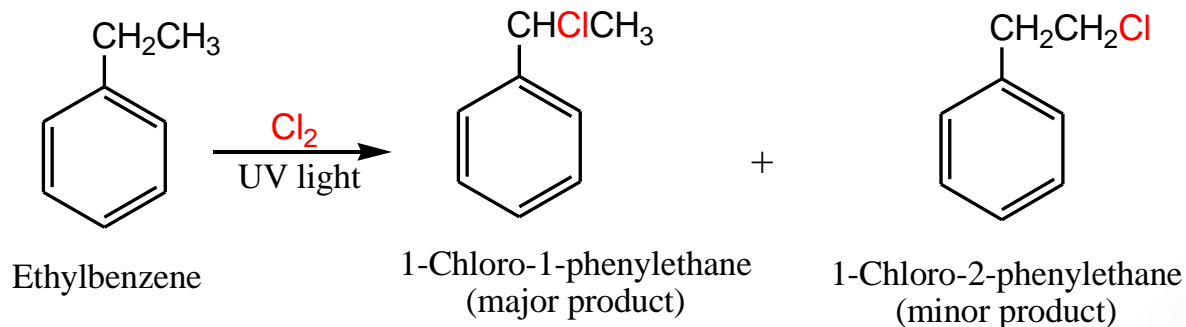
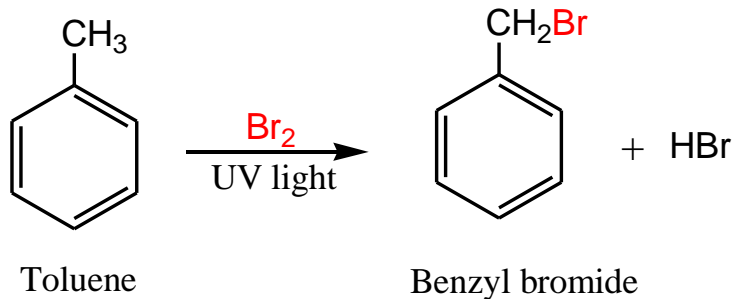
# Specific Electrophilic Aromatic Substitution Reactions



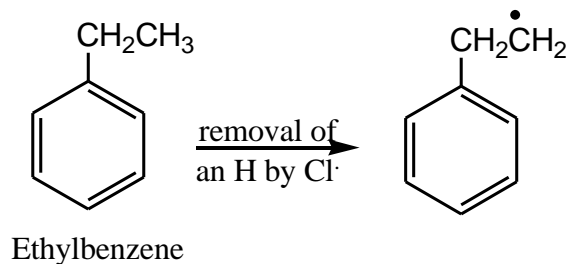
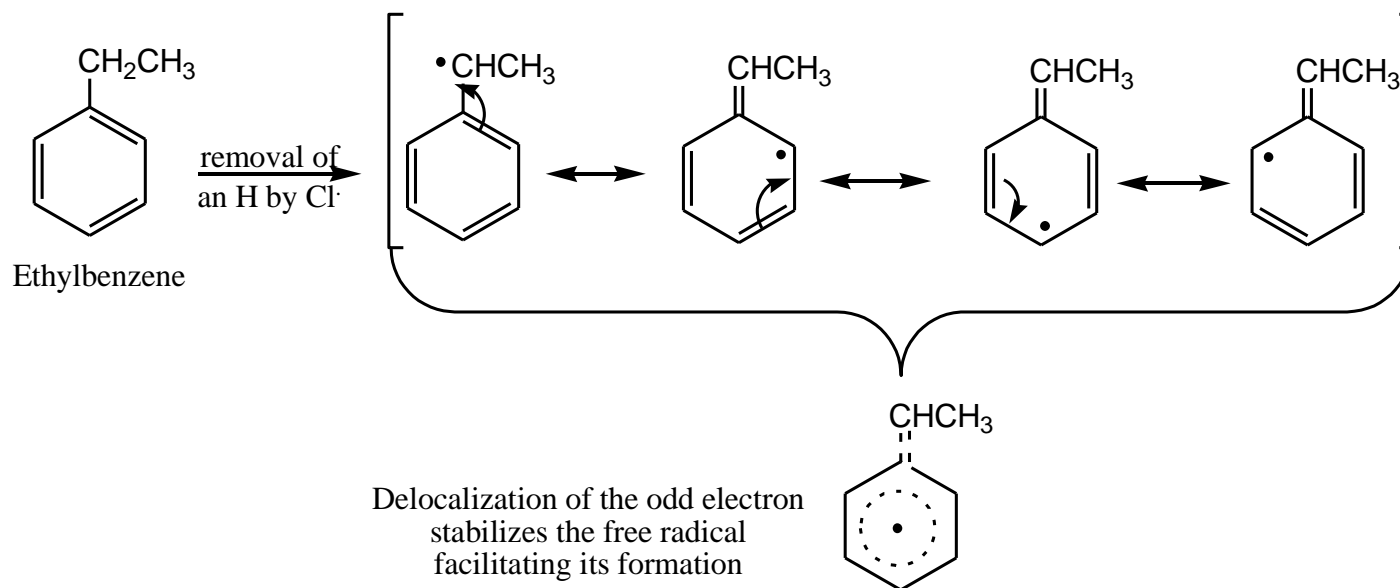
# Side-Chain Reactions of Aromatic

## A. Halogenation of an Alkyl Side Chain

Free radical substitution on alkane.  
No substitution in the aromatic ring.



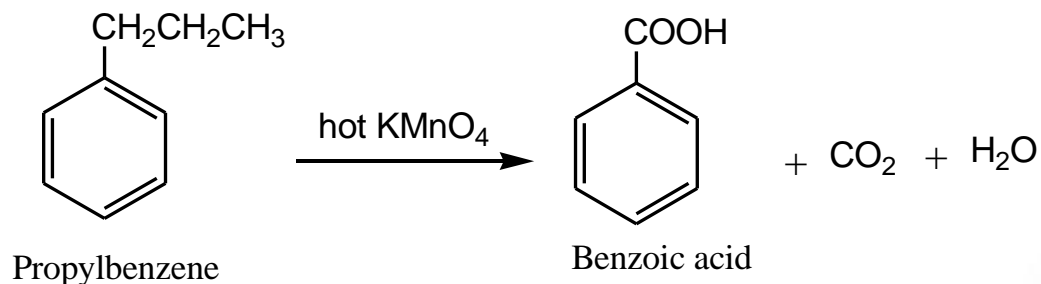
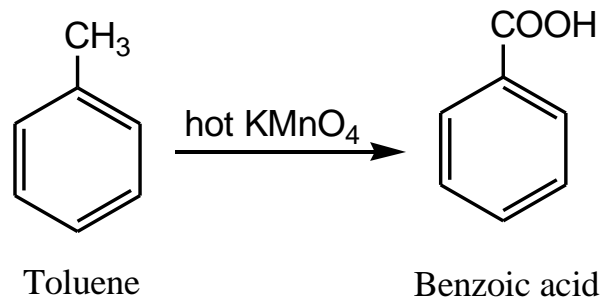
# A. Halogenation of an Alkyl Side Chain



The odd electron cannot be stabilized; therefore the free radical is more difficult to form

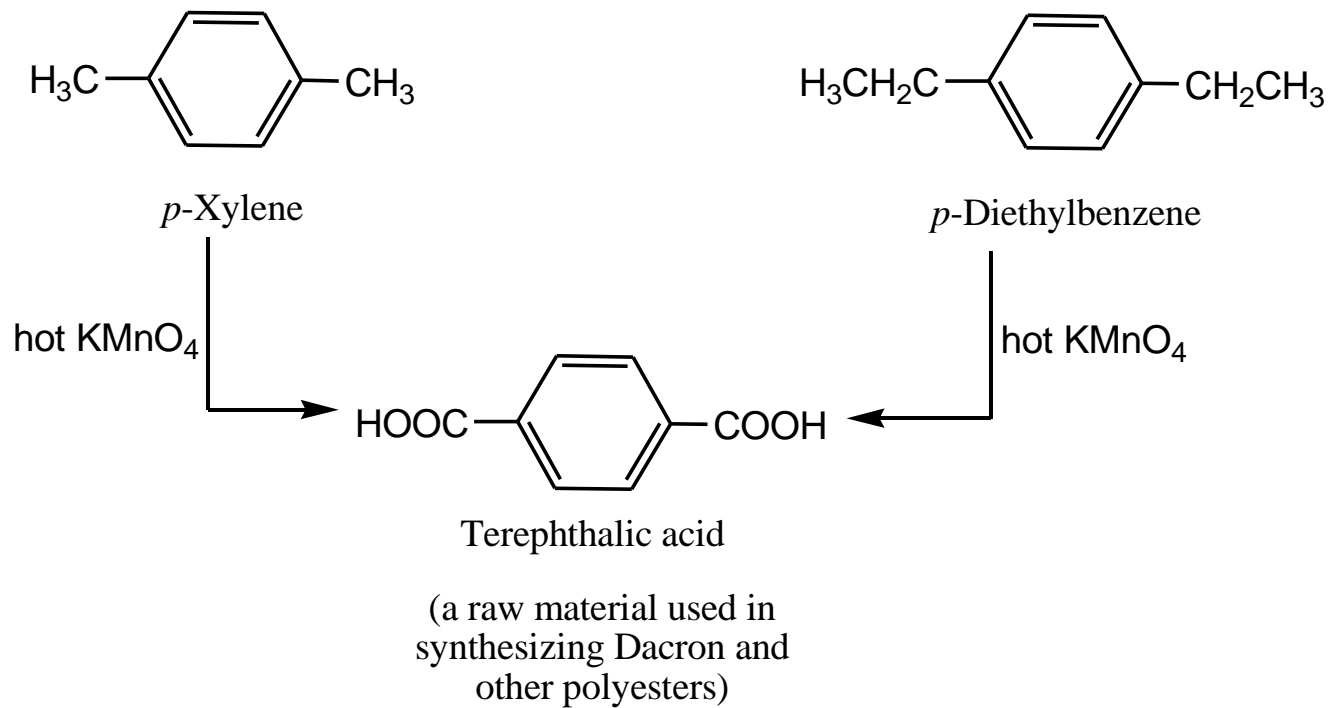
## B. Oxidation of an Alkyl Side Chain

- Conversion into a carboxyl group,  $-\text{COOH}$ , by treatment with **hot potassium permanganate**.
- Regardless the **length of the alkyl chain**, the product is always the same, **Benzoic acid**.



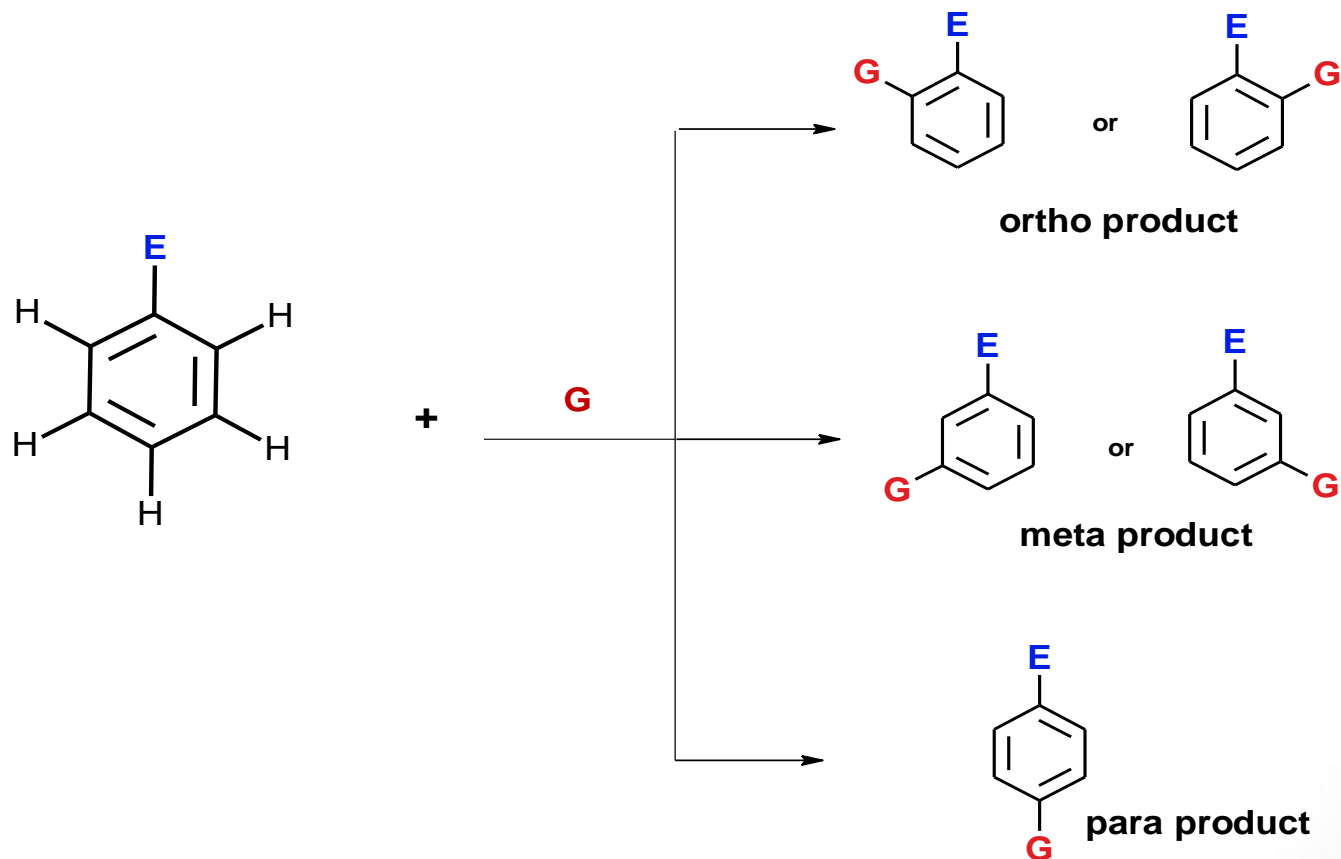


## B. Oxidation of an Alkyl Side Chain



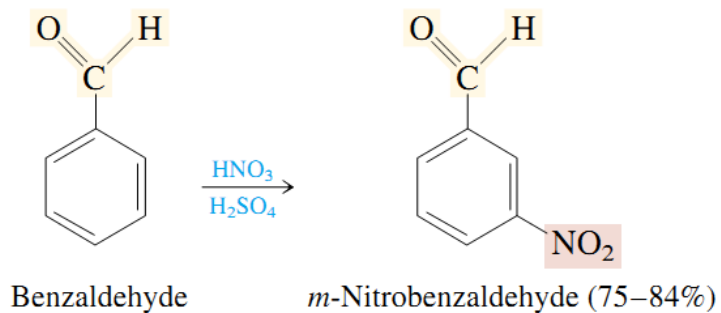
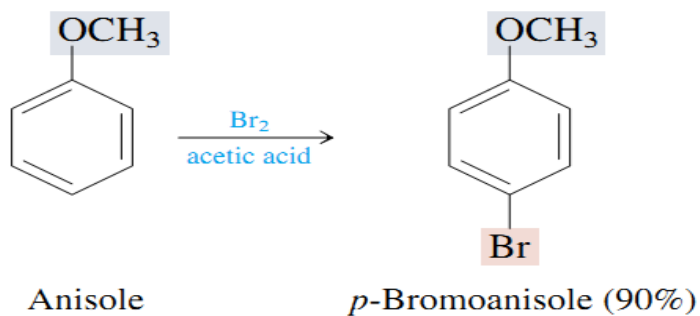
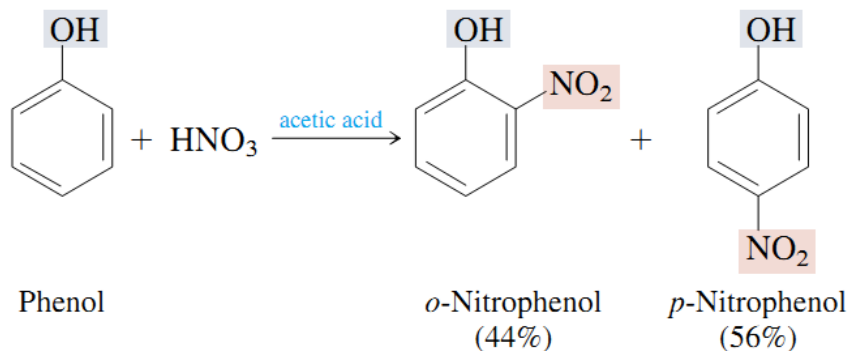
# Disubstituted Benzenes: Orientation

## Introduction of a second group, **G**, into a monosubstituted benzene, **C<sub>6</sub>H<sub>5</sub> - E**



Three possible products  
for second substitution

The actual distribution depends on **the nature of the first substituent, Y.**



# Disubstituted Benzenes:

## Orientation

### Orientation Effects of Substituents Y in Electrophilic Aromatic Substitution.

<i>ortho, para</i> directors	<i>meta</i> directors
-OH, -OR	-NO <sub>2</sub>
-NH <sub>2</sub> , -NHR, -NR <sub>2</sub>	-SO <sub>3</sub> H
-C <sub>6</sub> H <sub>5</sub>	-COOH, -COOR
-CH <sub>3</sub> , -R (Alkyl)	-CHO, -COR
-F, -Cl, -Br, -I	-CN

## Disubstitution: Reactivity

### The orientation Effect

- The presence of a substituent also affects the rate of electrophilic substitution reactions.
- Substituents that **release electrons** to the ring will **activate the ring** toward electrophilic substitution.
- Substituents that **withdraw electrons** from the ring will **deactivate the ring** toward electrophilic substitution.

The main features of orientation and reactivity can be summarized as follows:

1. All activating substituents are *ortho*, *para* directors.
2. Halogen substituents are slightly deactivating but are *ortho*, *para*-directing.
3. Strongly deactivating substituents are *meta* directors.

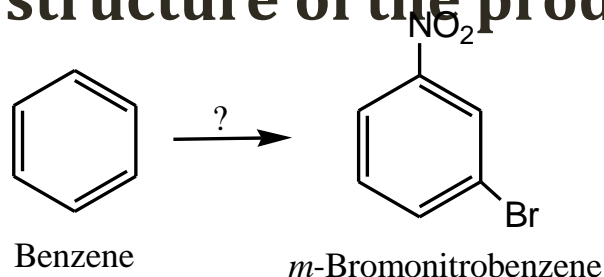
Substituent	Effect on reactivity
<b><i>ortho, para directors</i></b>	
-NH <sub>2</sub> , -NHR, -NR <sub>2</sub> , -OH, -NHCOR, OR -C <sub>6</sub> H <sub>5</sub> , -CH <sub>3</sub> , -R (Alkyl), CH <sub>2</sub> =CHR <b>H</b>	Very strongly activating Strongly activating Moderately activating <b>Standard for comparison</b>
-F, -Cl, -Br, -I	Deactivating
<b><i>meta directors</i></b>	
-SO <sub>3</sub> H, -COOH, -COOR , -CHO, -COR, -CN	Strongly deactivating
-NO <sub>2</sub> , -CF <sub>3</sub>	Very strongly deactivating

# Planning an Aromatic Synthesis

- **Example;**  
Starting from benzene, synthesize *m*-bromonitrobenzene.

➔ **Solution**

- 1) Draw the structure of the starting material and the structure of the product.



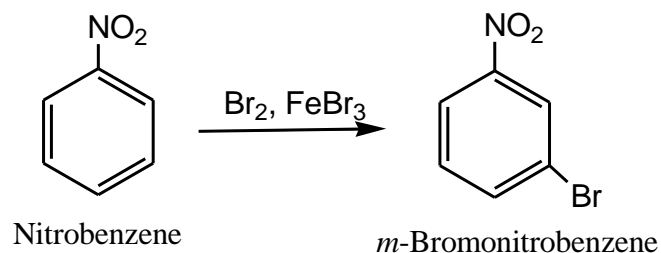
- 2) Decide what reaction leads to the product.
- NO<sub>2</sub> group is a meta director.
  - Br group is an ortho, para-directing group.

# Planning an Aromatic

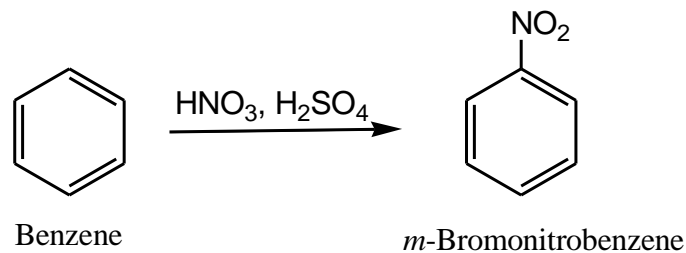
## ➤ Example;

Starting from benzene, synthesize *m*-bromonitrobenzene.

**i.e. the last reaction is bromination of nitrobenzene**



3) The reactants leading to nitrobenzene are





## Planning an Aromatic Synthesis

- **Example;**  
Starting from benzene, synthesize *m*-bromonitrobenzene.

4) Write the overall synthesis in the right order.

