

# Fundamentals of Organic Chemistry

## CHEM 108

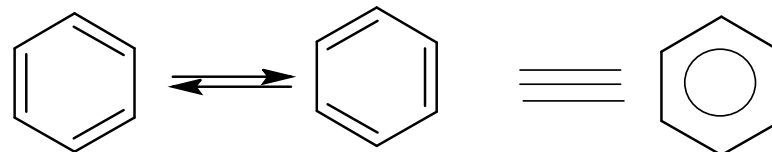
*King Saud University*

College of Science, Chemistry Department

# 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.

# The Structure of Benzene Ring

3

- **Benzene** is the *parent hydrocarbon of aromatic compounds*, because of their special chemical properties.
- Today a compound is said to be **aromatic** if it is *benzene-like in its properties*.

## Structure of Benzene

- Molecular formula =  $C_6H_6$

The carbon-to-hydrogen ratio in benzene, suggests a *highly unsaturated structure*.

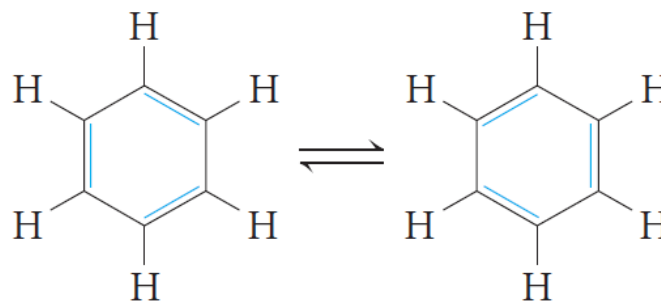
- Benzene reacts mainly by *substitution*.

It does not undergo the typical addition reactions of alkenes or alkynes.

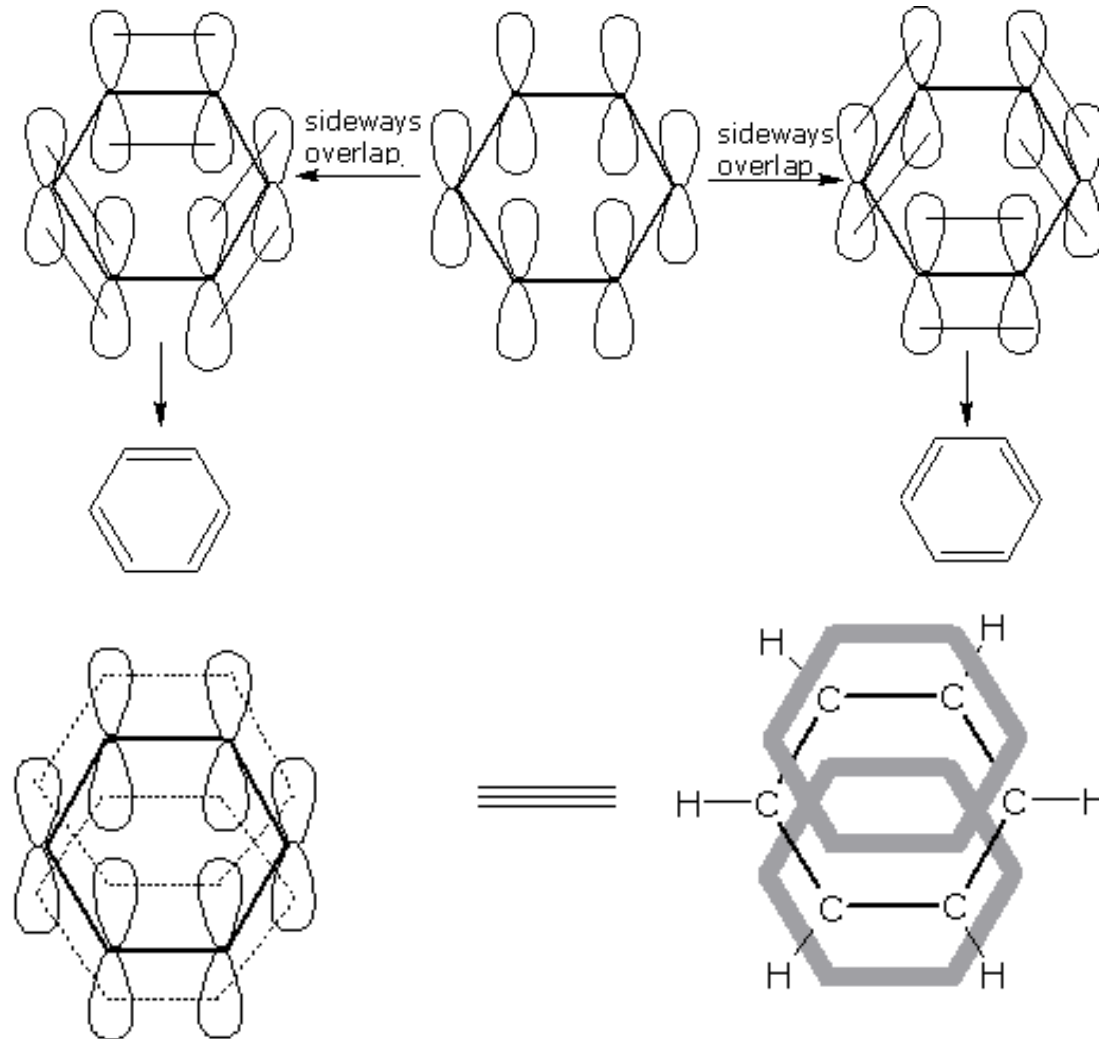
# The Structure of Benzene Ring

## ○ Kekulé structure for benzene.

- He suggested that six carbon atoms are located at the corners of **a regular hexagon**, with one hydrogen atom attached to each carbon atom.
- He suggested that **single and double bonds alternate** around the ring (conjugated system of double bonds).
- Kekulé suggested that the single and double bonds exchange positions around the ring so rapidly that the typical reactions of alkenes cannot take place.



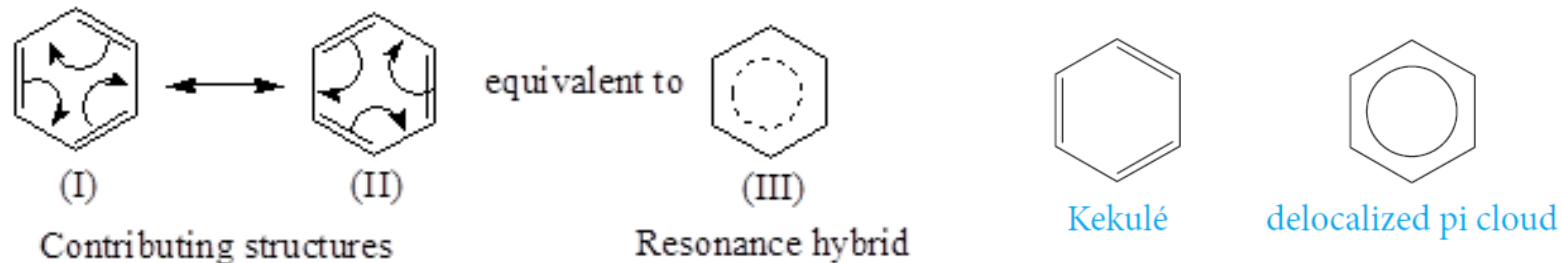
the Kekulé structures for benzene



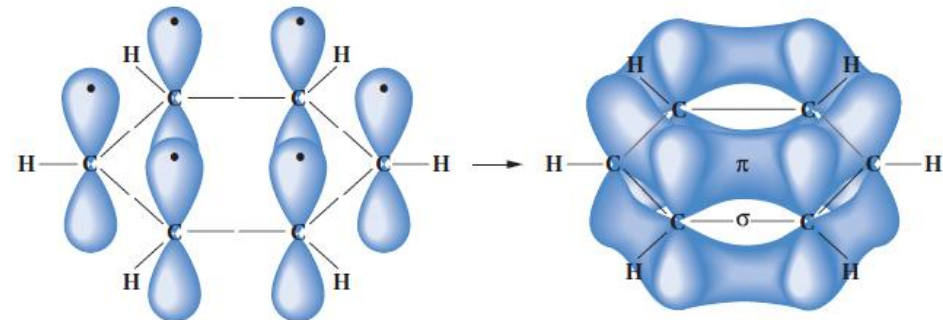
# The Structure of Benzene Ring

6

## ○ Resonance Model for Benzene.



- Benzene is *planar*.
- All of the *carbon-carbon bond lengths* are identical:  $1.39 \text{ \AA}$ , intermediate between typical *single* ( $1.54 \text{ \AA}$ ) and *double* ( $1.34 \text{ \AA}$ ) carbon-carbon bond lengths.
- Each carbon is therefore *sp<sup>2</sup>-hybridized*.
- Bond angles of  $120^\circ$ .



# Aromatic Character (Aromaticity)



**To be classified as aromatic, a compound must have:**

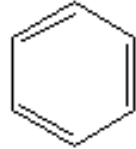
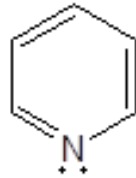
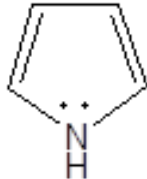
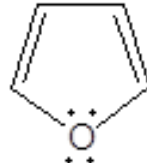
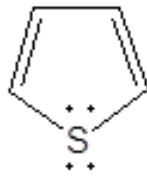
- ① Cyclic structure
- ② Cyclic structure contains what looks like a continuous system of alternating double and single bonds
- ③ Aromatic compounds must be planar
- ④ Fulfill Hückel's rule

The number of  $\pi$  electrons in the compound =  $(4n + 2)$

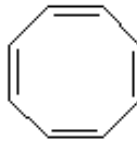
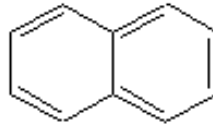




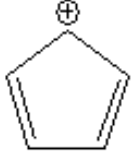
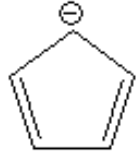

Where ( $n = 0, 1, 2, 3,$  and so on).

# Aromatic Character (Aromaticity)

8

$n$	$4n + 2$	Structure and name of aromatic compound
1	6	     Benzene      Pyridine      Pyrrole      Furan      Thiophene

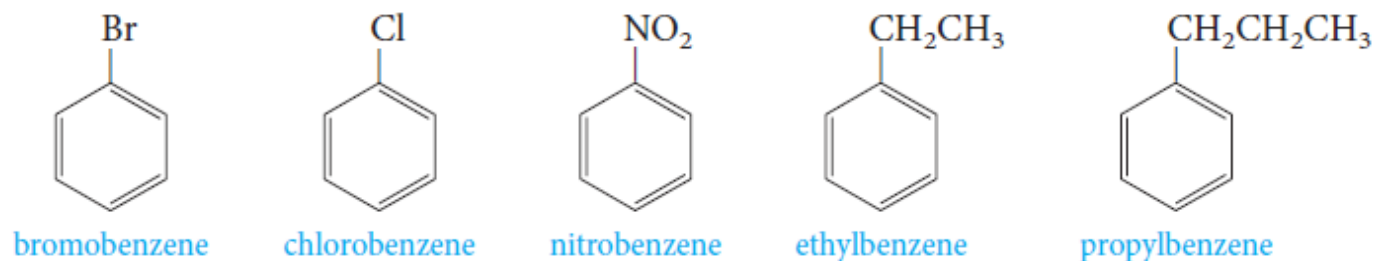
## Examples

					
$4n+2 =$	8	10	2	2	4
$n =$	1.5	2	0	0	0.5
					
$4n+2 =$	4	4	6	4	
$n =$	0.5	0.5	1	0.5	

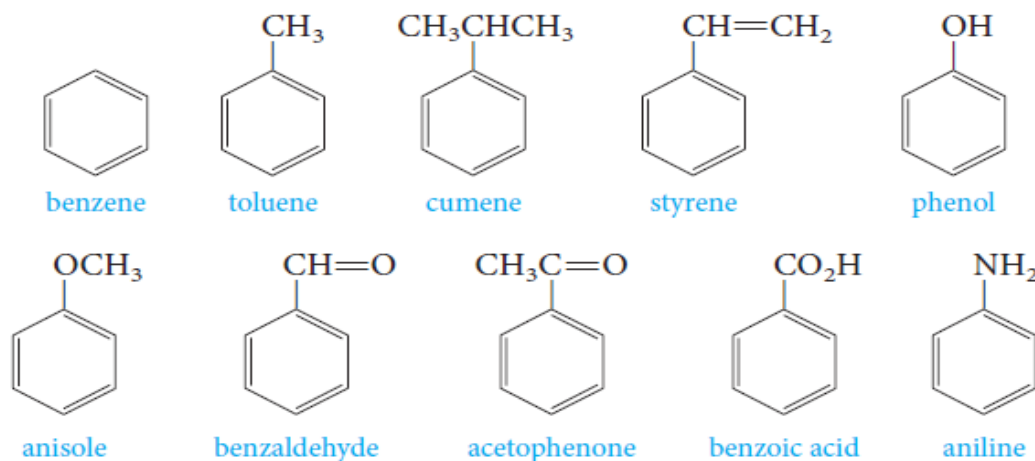


# Nomenclature of Aromatic Compounds

- **Monosubstituted benzenes** that do not have common names accepted by IUPAC are named as derivatives of benzene.

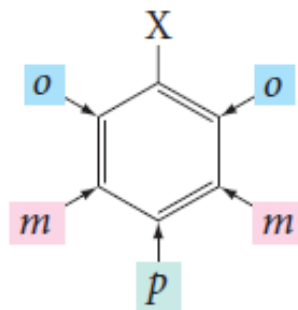


Common names are accepted by IUPAC (parent compounds).

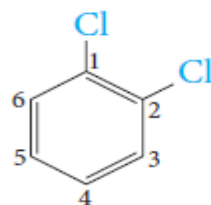


# Nomenclature of Aromatic Compounds

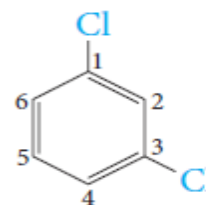
- When **two substituents** are present, *three isomeric structures are possible*.
  - They are designated by the prefixes; **ortho- (o-)**, **meta- (m-)** and **para- (p-)**.
  - If substituent X is attached to carbon 1; **o- groups** are on **carbons 2 and 6**, **m- groups** are on **carbons 3 and 5**, and **p- groups** are on **carbon 4**.



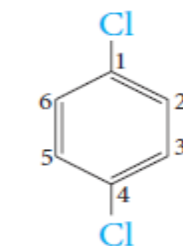
- **Examples;**



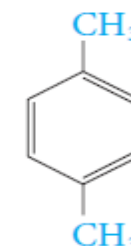
*ortho*-dichloro-  
benzene



*meta*-dichloro-  
benzene



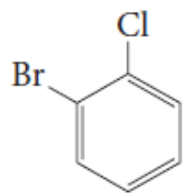
*para*-dichloro-  
benzene



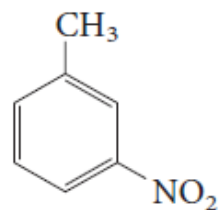
*para*-xylene\*

# Nomenclature of Aromatic Compounds

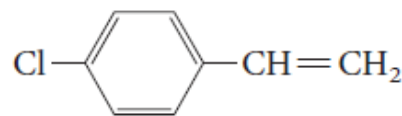
- The prefixes; *ortho-* (*o-*), *meta-* (*m-*) and *para-* (*p-*) are used when the two substituents are not identical.



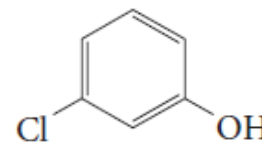
*o*-bromochlorobenzene  
(note alphabetical order)



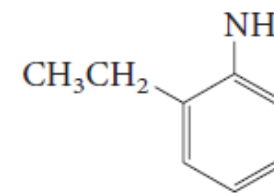
*m*-nitrotoluene



*p*-chlorostyrene

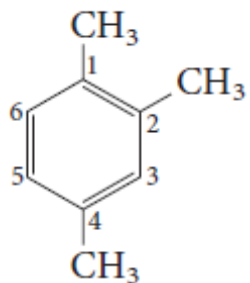


*m*-chlorophenol

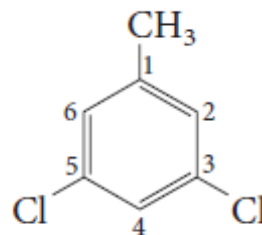


*o*-ethylaniline

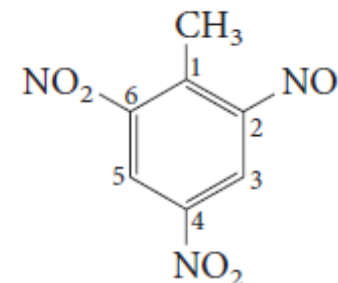
- When **more than two substituents** are present, their positions are designated by **numbering the ring**.



1,2,4-tri-  
methylbenzene



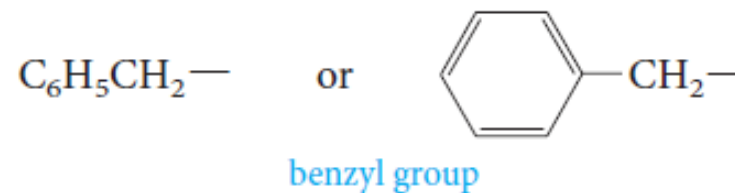
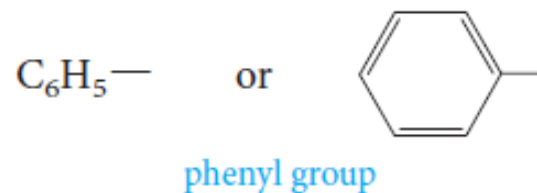
3,5-dichlorotoluene



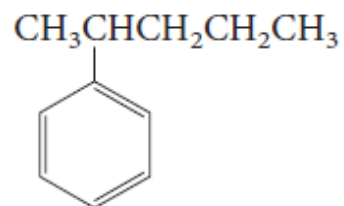
2,4,6-trinitrotoluene  
(TNT)

# Nomenclature of Aromatic Compounds

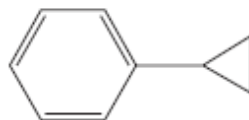
- Two groups with special names occur frequently in aromatic compounds; the **phenyl group** and the **benzyl group**.



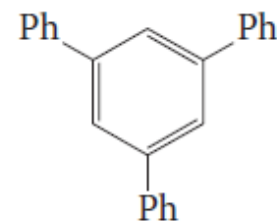
- **Examples;**



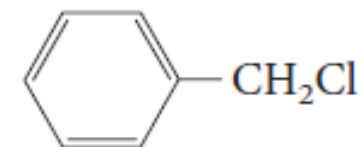
2-phenylpentane  
(or 2-pentylbenzene)



phenylcyclopropane  
(or cyclopropylbenzene)



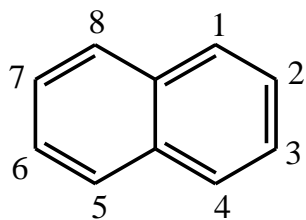
1,3,5-triphenylbenzene



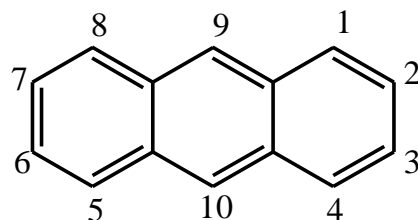
benzyl chloride

# Nomenclature of Aromatic Compounds

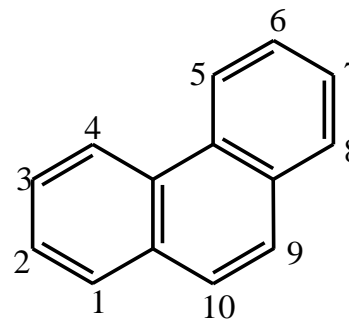
Polynuclear aromatic hydrocarbons containing two, three & four rings are :



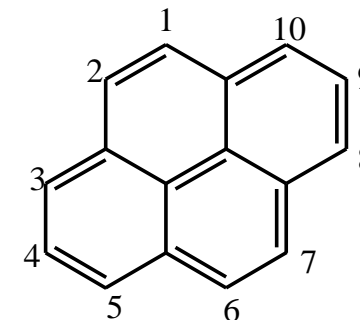
Naphthalene



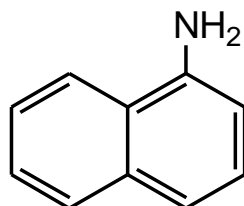
Anthracene



Phenanthrene

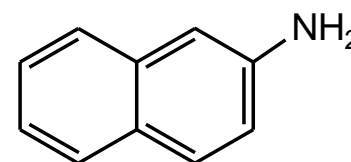


Pyrene



IUPAC name:  
Common name:

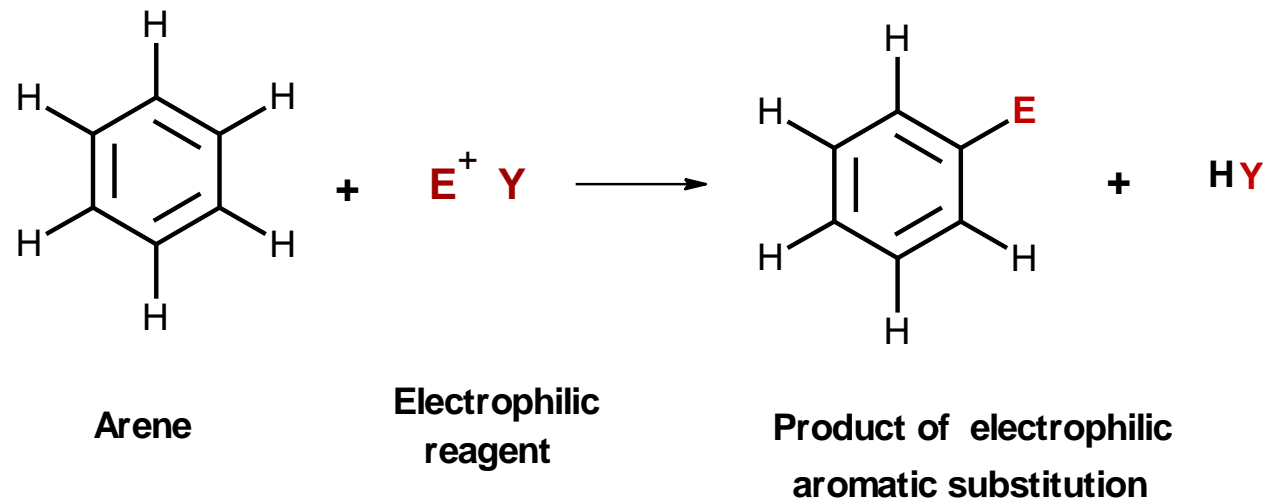
1-Aminonaphthalene  
a-Naphthylamine  
(a weak carcinogen)



2-Aminonaphthalene  
B-Naphthylamine  
(a strong carcinogen)

## Electrophilic Aromatic Substitution Reactions

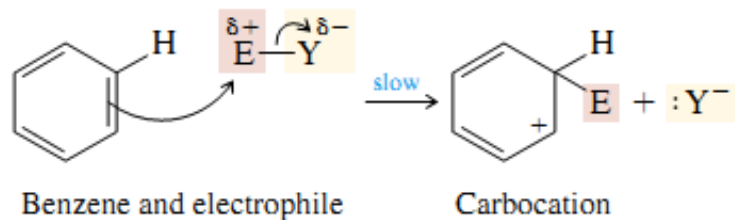
In this reaction, an electrophile  $E^+$  replaces a hydrogen atom, from the aromatic ring system.



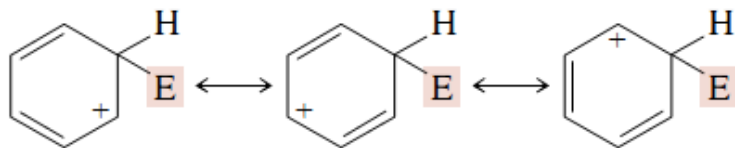
This reaction is in contrast to electrophilic addition to the double bonds of alkene



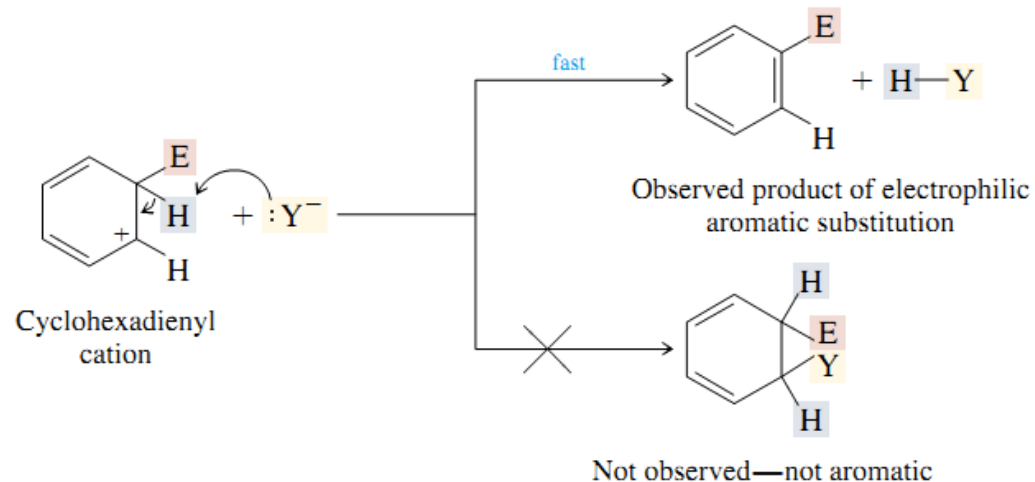
# Electrophilic Aromatic Substitution Reactions



The electrophile  $\text{E}^+$  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  $\text{Y}^-$ , which leads to the restoration of the aromatic ring

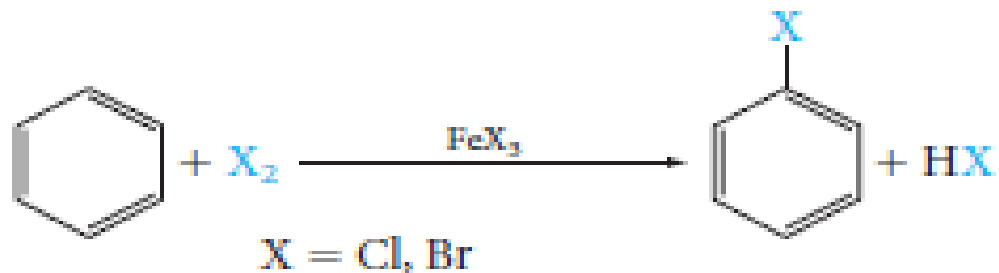


The net overall result is the substitution of the group  $\text{E}^+$  for a proton  $\text{H}^+$ .

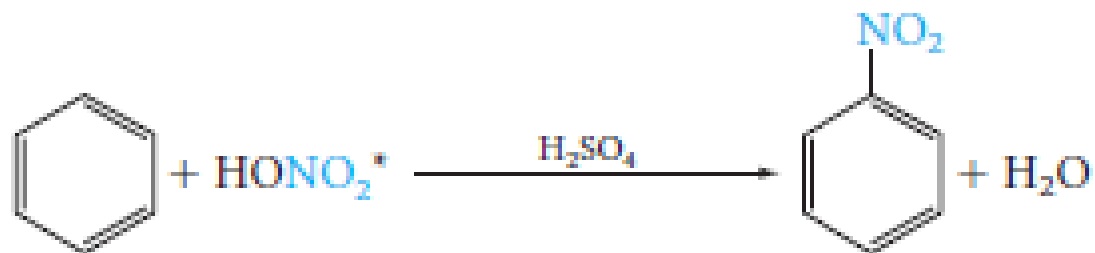
## Electrophilic Aromatic Substitution Reactions

16

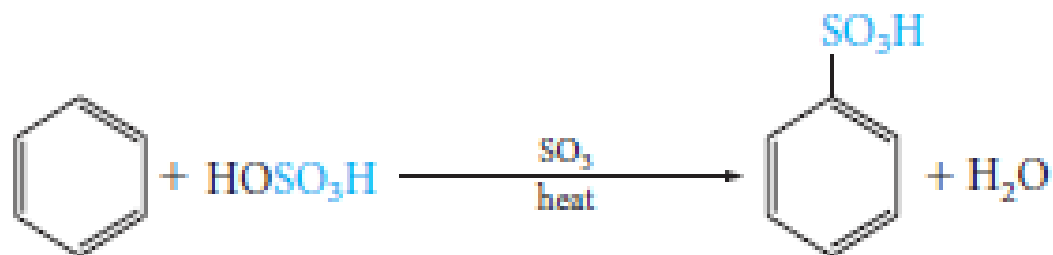
### 1) Halogenation



### 2) Nitration



### 3) Sulfonation

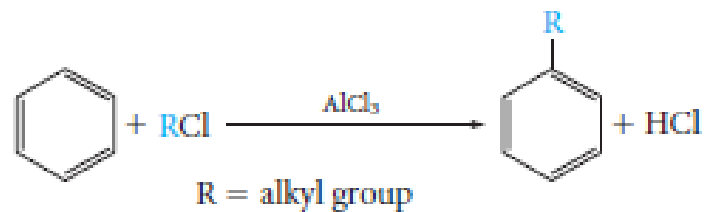




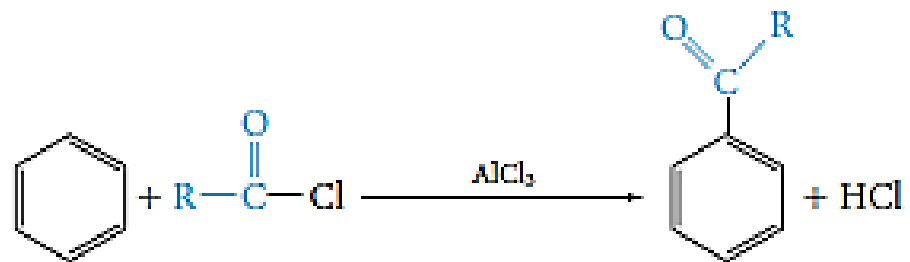
## Electrophilic Aromatic Substitution Reactions

17

### 4) Alkylation (Friedel-Crafts)

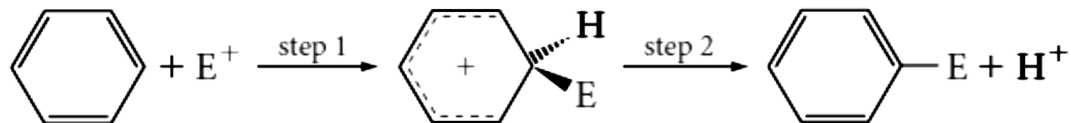


### 5) Acylation (Friedel-Crafts)



## The Mechanism of Electrophilic Aromatic Substitution

We can generalize this two-step mechanism for all the electrophilic aromatic substitutions.

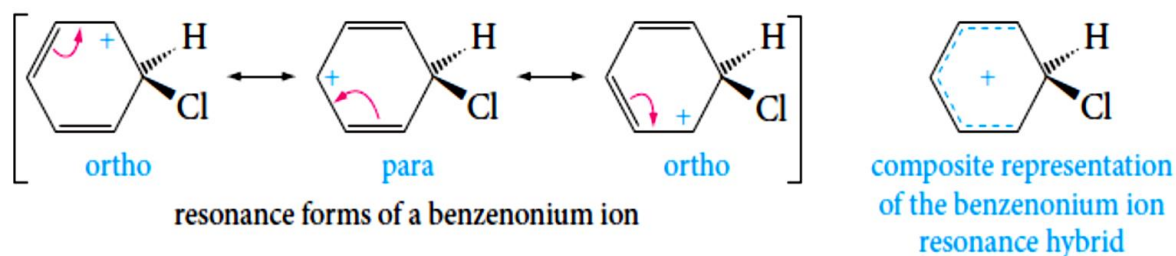
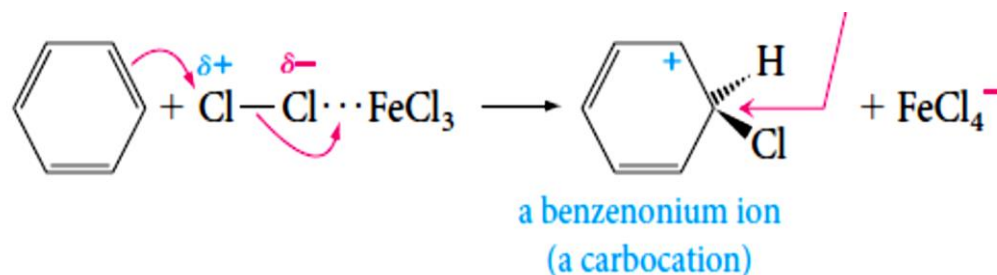
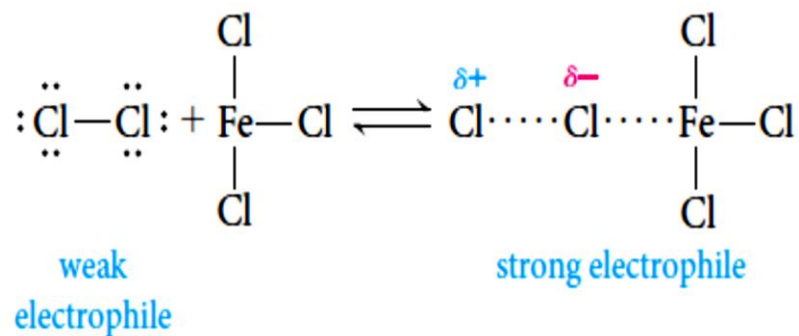


## Electrophilic Aromatic Substitution Reactions

18

### The Mechanism of Electrophilic Aromatic Substitution

#### ➤ Halogenation



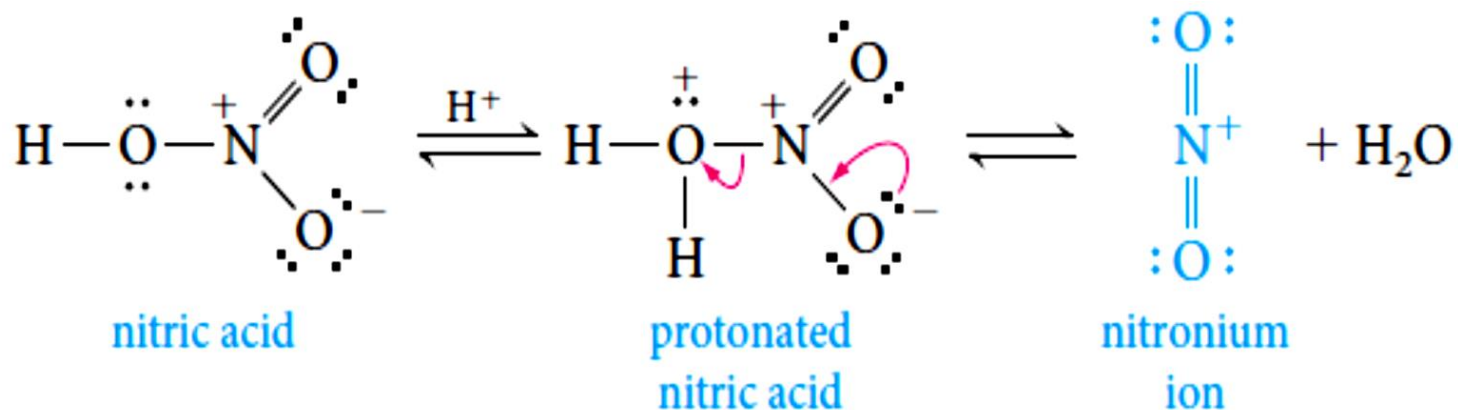
## Electrophilic Aromatic Substitution Reactions

19

### The Mechanism of Electrophilic Aromatic Substitution

#### ➤ Nitration

In aromatic nitration reactions, the *sulfuric acid catalyst* protonates the *nitric acid*, which then loses water to generate the *nitronium ion* ( $\text{NO}_2^+$ ), which contains a positively charged nitrogen atom.



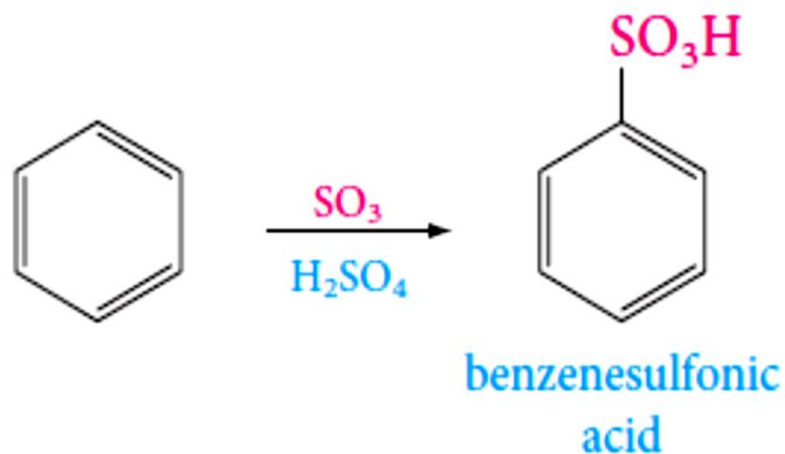
## Electrophilic Aromatic Substitution Reactions

20

## The Mechanism of Electrophilic Aromatic Substitution

## ➤ Sulfonation

We use either concentrated or *fuming sulfuric acid*, and the electrophile may be sulfur trioxide,  $\text{SO}_3$ , or *protonated sulfur trioxide*,  $^+\text{SO}_3\text{H}$ .



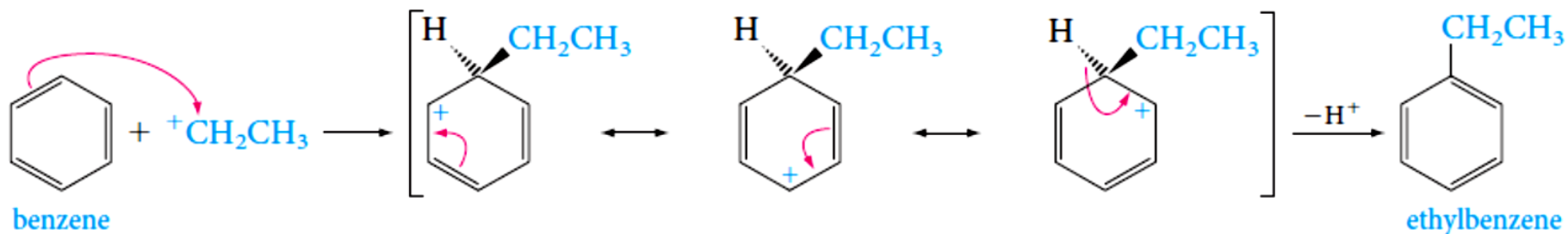
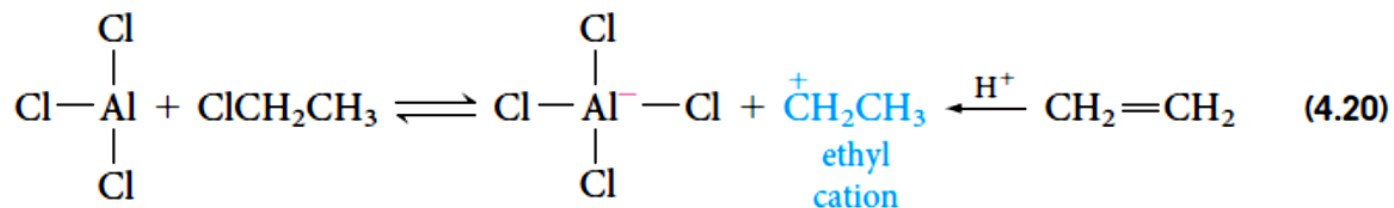
## Electrophilic Aromatic Substitution Reactions

21

### The Mechanism of Electrophilic Aromatic Substitution

#### ➤ Friedel–Crafts Alkylation

The *electrophile is a carbocation*, which can be formed either by removing a halide ion from an *alkyl halide* with a *Lewis acid catalyst* (for example,  $AlCl_3$ ).



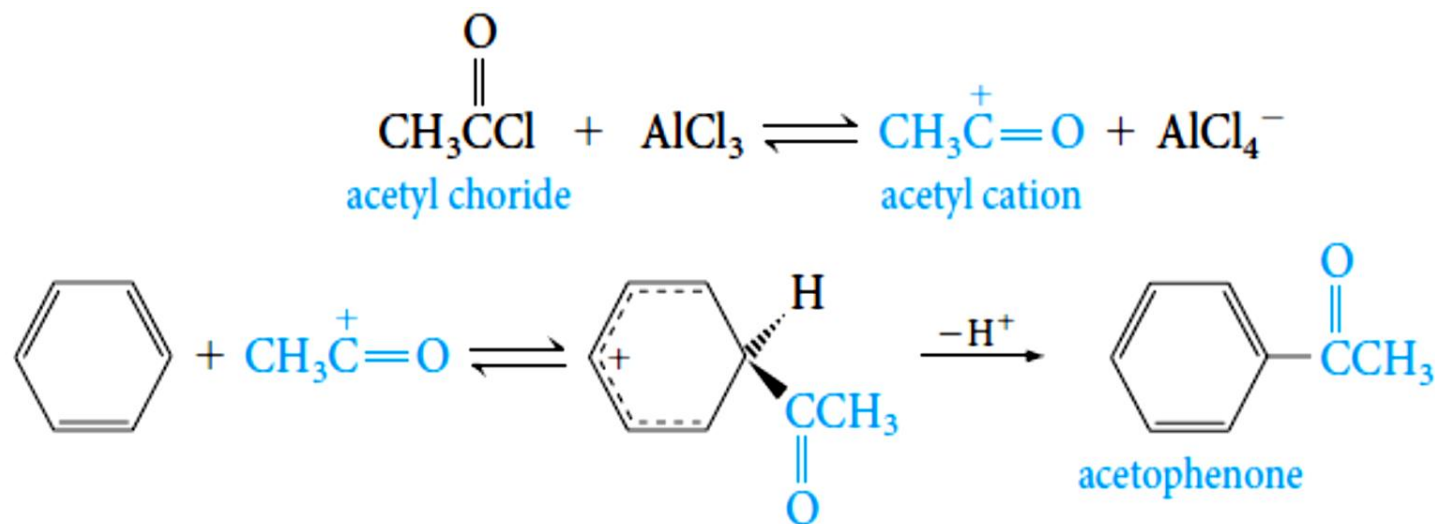
## Electrophilic Aromatic Substitution Reactions

22

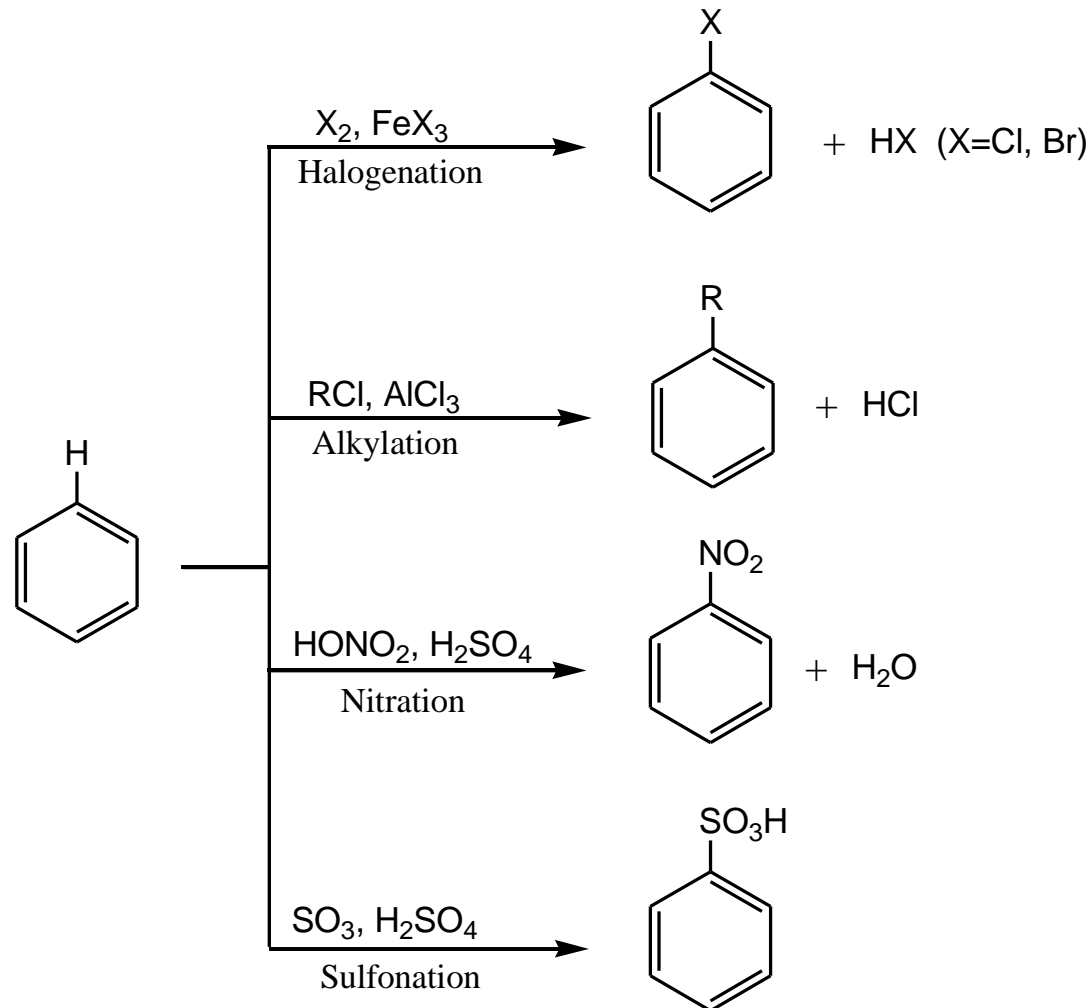
### The Mechanism of Electrophilic Aromatic Substitution

#### ➤ Friedel–Crafts Acylation

The *electrophile is an acyl cation* generated from an acid derivative, usually an *acyl halide*. The reaction provides a useful general route to aromatic ketones.

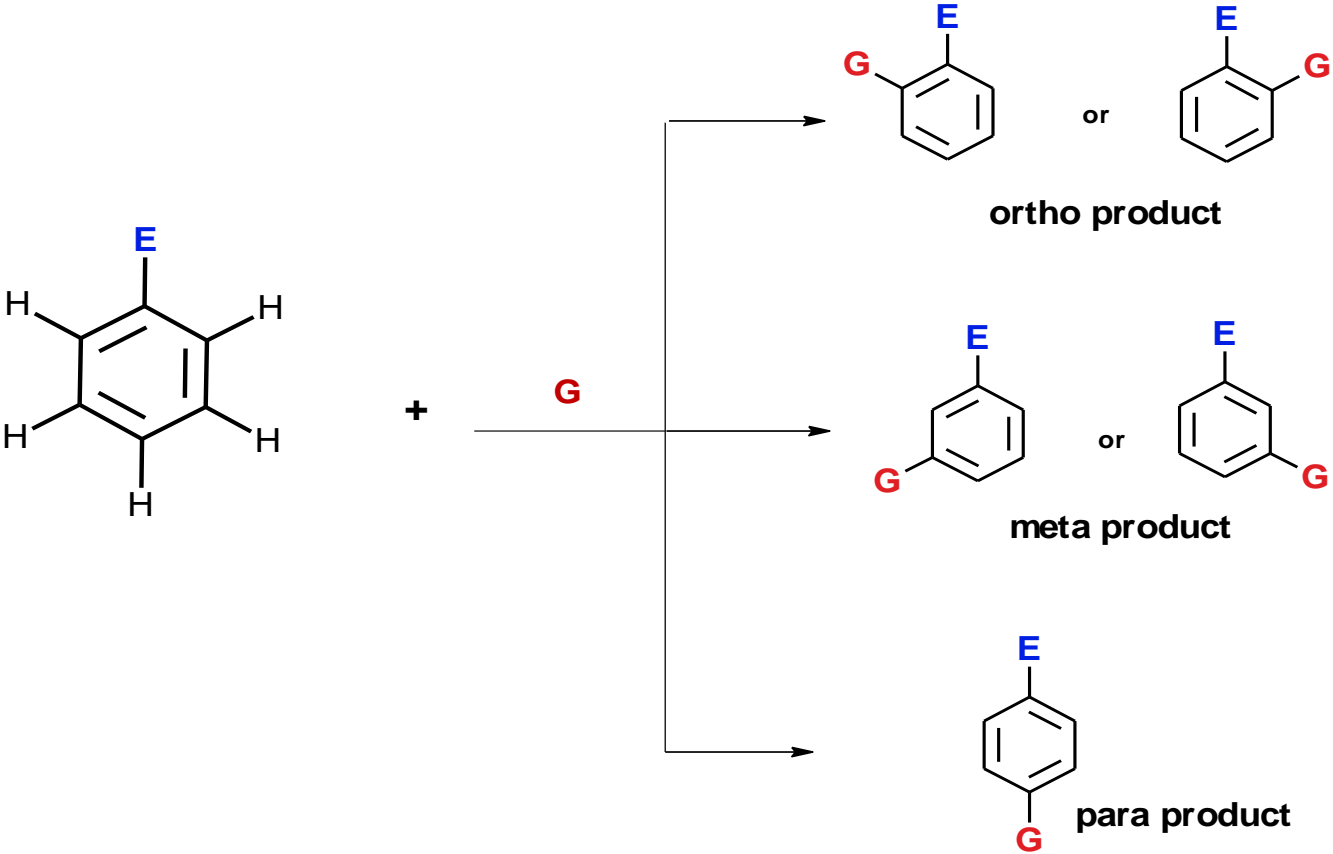


# Electrophilic Aromatic Substitution Reactions



# Disubstituted Benzenes: Orientation

Introduction of a second group,  
G, into a monosubstituted  
benzene,  $C_6H_5 - E$



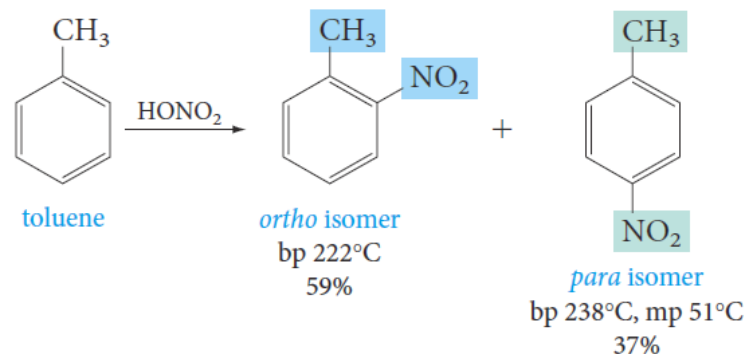
Three possible products  
for second substitution



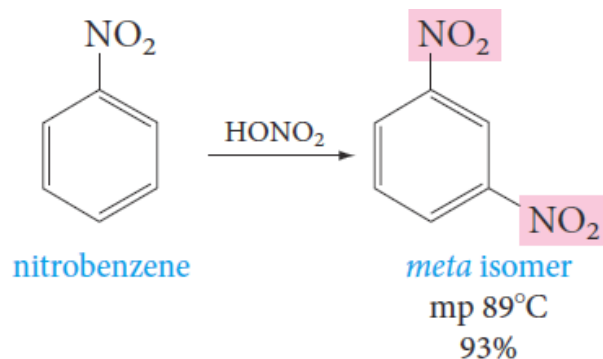
## Disubstituted Benzenes: Orientation

25

- Substituents already present on an aromatic ring determine the position taken by a new substituent.
- **Example; nitration of toluene** gives mainly a mixture of *o*- and *p*-nitrotoluene.



- On the other hand, **nitration of nitrobenzene** under similar conditions gives mainly the *meta* isomer.



## Disubstituted Benzenes: Orientation & Reactivity

26

### Directing and Activating Effects of Common Functional Groups

- 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.

	Substituent group	Name of group	
Ortho, Para-Directing	$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{HR}, -\ddot{\text{N}}\text{R}_2$	amino	Activating
	$-\ddot{\text{O}}\text{H}, -\ddot{\text{O}}\text{CH}_3, -\ddot{\text{O}}\text{R}$	hydroxy, alkoxy	
	$\begin{array}{c} \text{O} \\    \\ -\ddot{\text{N}}\text{HC}-\text{R} \end{array}$	acylamino	
	$-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$	alkyl	
	$-\ddot{\text{F}}:, -\ddot{\text{Cl}}:, -\ddot{\text{Br}}:, -\ddot{\text{I}}:$	halo	
Meta-Directing	$\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\text{R} \end{array}$	acyl, carboxy	Deactivating
	$\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\ddot{\text{O}}\text{H} \end{array}$		
	$\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$	carboxamido, carboalkoxy	
	$\begin{array}{c} \text{:O:} \\    \\ -\text{C}-\ddot{\text{O}}\text{R} \end{array}$		
	$\begin{array}{c} \text{:O:} \\    \\ -\text{S}-\ddot{\text{O}}\text{H} \\ \text{:O:} \end{array}$	sulfonic acid	
	$-\text{C}\equiv\text{N:}$	cyano	
$\begin{array}{c} \text{:O:} \\    \\ -\text{N}^+ \\ \text{:O:}^- \end{array}$	nitro		

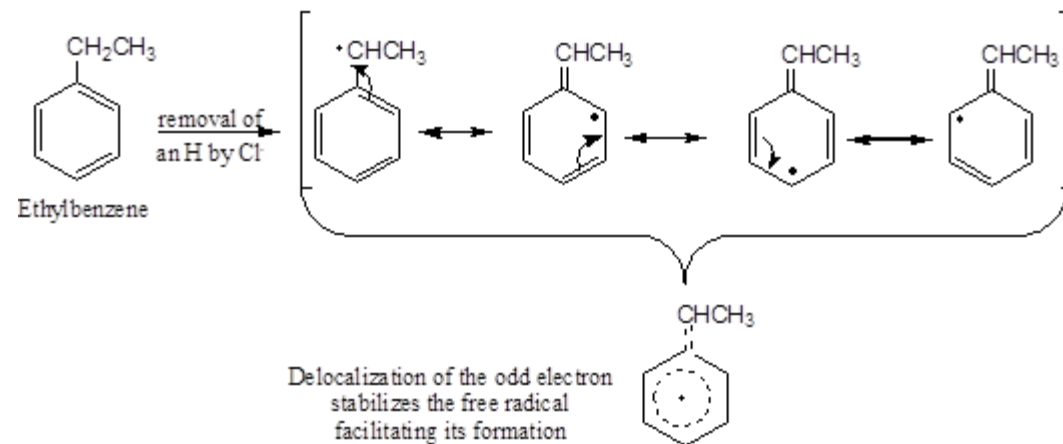
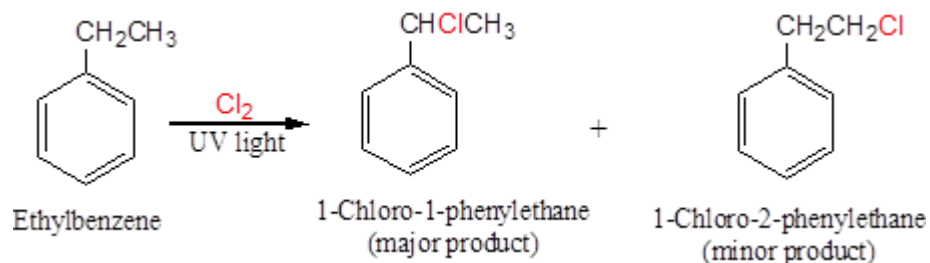
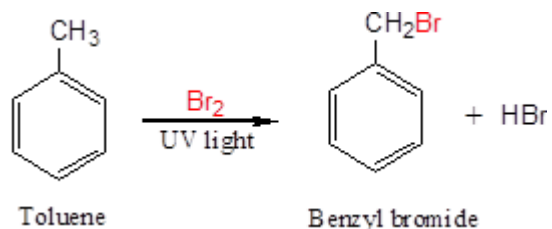
## Disubstituted Benzenes: Orientation

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

## Side-Chain Reactions of Benzene-Derivatives

28

### 1. Halogenation of an Alkyl Side Chain



## Side-Chain Reactions of Benzene-Derivatives

29

### 2. 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.

