

# Fundamentals of Organic Chemistry

## CHEM 109

*For Students of Health Colleges*

Credit hrs.: (2+1)

*King Saud University*

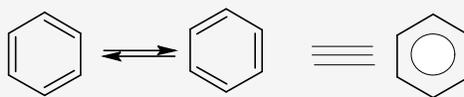
College of Science, Chemistry Department

### CHAPTER 3: Aromatic Hydrocarbon

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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**.

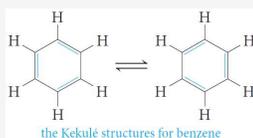


- **Benzene** is the **parent hydrocarbon of aromatic compounds**, because of their special chemical properties.

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## The Structure of Benzene Ring

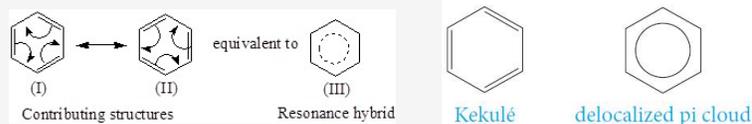
- Molecular formula =  $C_6H_6$   
The carbon-to-hydrogen ratio in benzene, suggests a *highly unsaturated structure*.
- Benzene reacts mainly by *substitution*.  
It does not undergo the typical addition reactions of alkenes or alkynes.
- **Kekulé Structure for Benzene**
  - He suggested that
    - *six carbon atoms* are located at the corners of a *regular hexagon*, with one hydrogen atom attached to each carbon atom.
    - *single and double bonds alternate* around the ring (conjugated system of double bonds) and exchange positions around the ring.



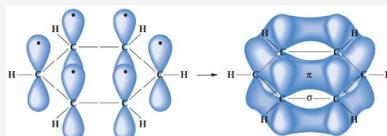
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## The Structure of Benzene Ring

### ○ 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  *$sp^2$ -hybridized*.
- Bond angles of  $120^\circ$ .



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## Aromatic Character (Aromaticity)

To be classified as aromatic, a compound must have:

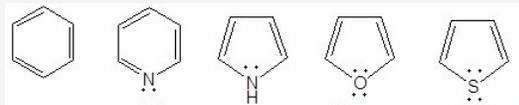
- ① Cyclic structure
- ② Cyclic structure contains what looks like a continuous system of alternating double and single bonds
- ③ Aromatic compounds must be planar
- ④ Fulfill Huckel's rule

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

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

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## Aromatic Character (Aromaticity)

$n$	$4n + 2$	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	

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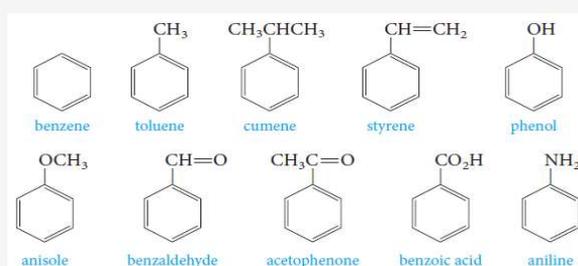
## Monosubstituted Benzenes

## 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).



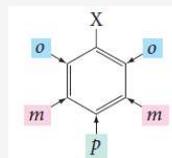
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## Disubstituted Benzenes

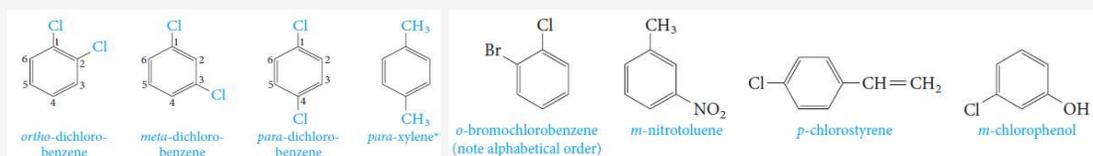
## Nomenclature of Aromatic Compounds

- 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;

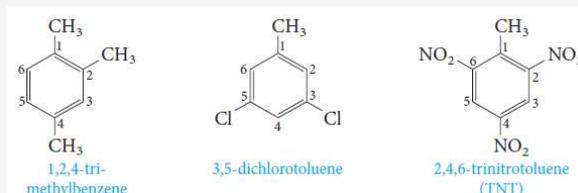


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## Polysubstituted Benzenes

## Nomenclature of Aromatic Compounds

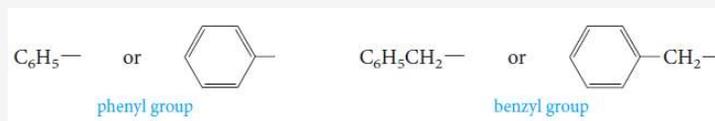
- When **more than two substituents** are present, their positions are designated by **numbering the ring**.



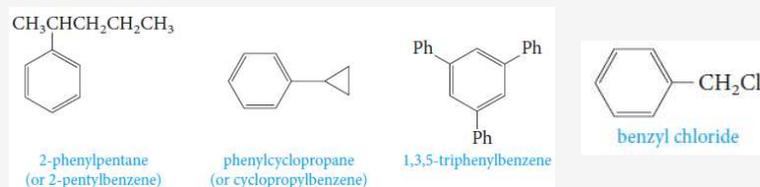
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## Nomenclature of Aromatic Compounds

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



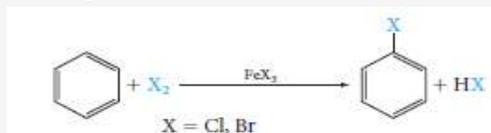
- Examples;



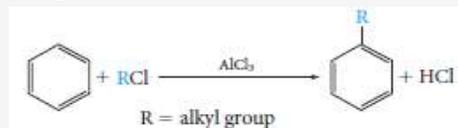
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## Electrophilic Substitution Reactions      Reactions of Benzene

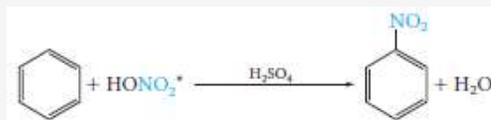
### 1) Halogenation



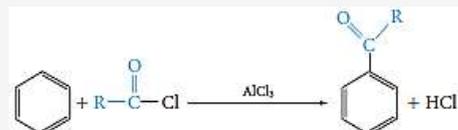
### 4) Alkylation (Friedel-Crafts)



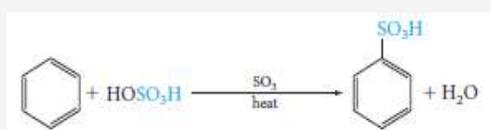
### 2) Nitration



### 5) Acylation (Friedel-Crafts)



### 3) Sulfonation

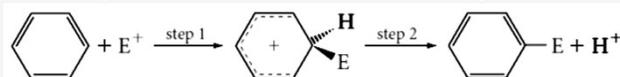


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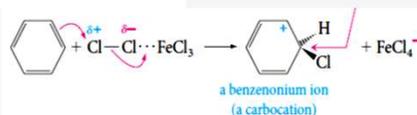
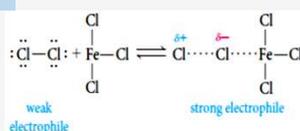
## The Mechanism of Electrophilic Substitution Reactions

## Reactions of Benzene

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



### 1) Halogenation



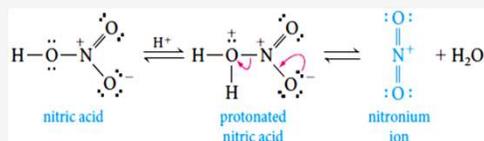
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## The Mechanism of Electrophilic Substitution Reactions

### Reactions of Benzene

#### 2) 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.



#### 3) Sulfonation

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



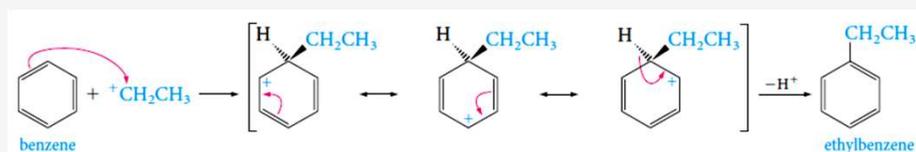
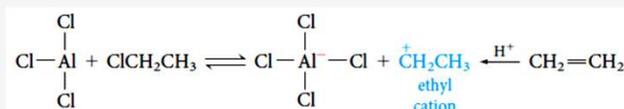
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## The Mechanism of Electrophilic Substitution Reactions

### Reactions of Benzene

#### 4) 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,  $\text{AlCl}_3$ ).



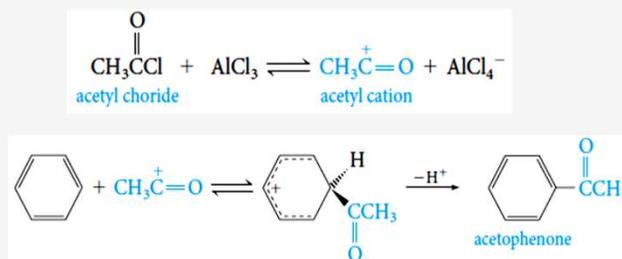
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## The Mechanism of Electrophilic Substitution Reactions

## Reactions of Benzene

### 5) Friedel–Crafts Alkylation

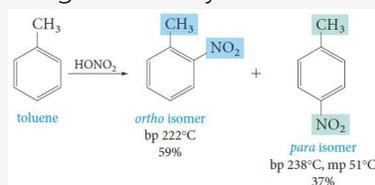
The *electrophile is an acyl cation* generated from an acid derivative, usually an *acyl halide*. The reaction provides a useful general route to aromatic ketones.



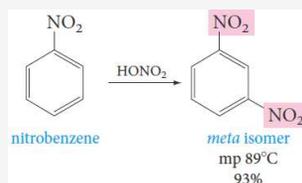
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## Disubstituted Benzenes: Orientation Reactions of Benzene

- 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.



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## Disubstituted Benzenes: Orientation & Reactivity

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.

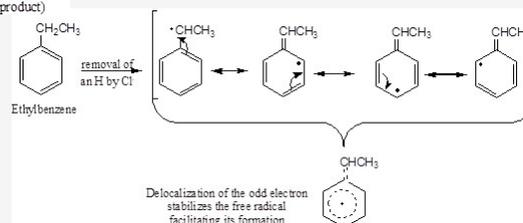
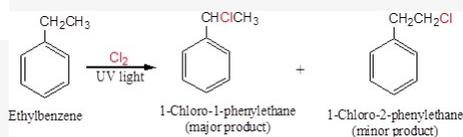
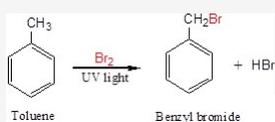
## Reactions of Benzene

	Substituent group	Name of group	
Ortho, Para-Directing	$-\text{NH}_2, -\text{NHR}, -\text{NR}_2$	amino	Activating
	$-\text{OH}, -\text{OCH}_3, -\text{OR}$	hydroxy, alkoxy	
	$-\text{NHC}(=\text{O})\text{R}$	acylamino	
	$-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$	alkyl	
	$-\text{F}, -\text{Cl}, -\text{Br}, -\text{I}$	halo	
Meta-Directing	$-\text{C}(=\text{O})\text{R}$	acyl, carboxy	Deactivating
	$-\text{C}(=\text{O})\text{NH}_2$	carboxamido, carboalkoxy	
	$-\text{C}(=\text{O})\text{OR}$	carboxamido, carboalkoxy	
	$-\text{S}(=\text{O})_2\text{OH}$	sulfonic acid	
	$-\text{C}\equiv\text{N}$	cyano	
	$-\text{N}(=\text{O})_2$	nitro	

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## 1. Halogenation of an Alkyl Side Chain

## Side-Chain Reactions of Benzene-Derivatives



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## 2. Oxidation of an Alkyl Side Chain

## Side-Chain Reactions of Benzene-Derivatives

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

