

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

Learning Objectives

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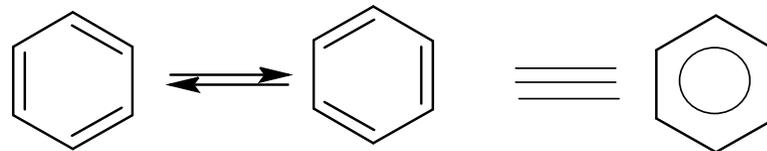
At the end of this chapter, students will be able to:

- Understand the hybridization in benzene
- Understand the resonance description of structure of benzene
- Recognize the general properties of aromatic compounds, the criteria of aromaticity and Huckel's rule
- Recognize the methods for naming aromatic compounds, including IUPAC method and common names.
- Know the types of electrophilic aromatic substitution reactions.
- Understand the reactivity of aromatic compounds and orientation of monosubstituted benzene's reactions.
- Know the reactions of alkyl side chains of aromatic compounds.

Aromatic Hydrocarbons

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- 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 electrophilic addition to double and triple bonds and free radical substitution.

The Structure of Benzene Ring

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- **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*.

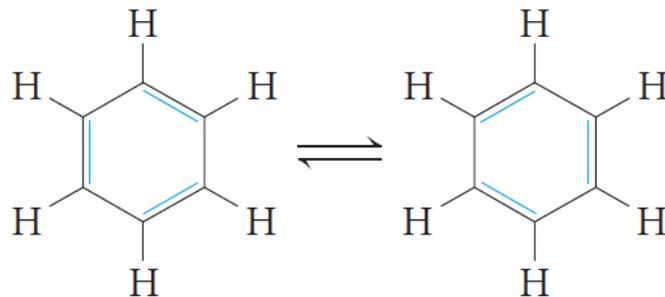
It does not undergo the typical addition reactions of alkenes or alkynes.

The Structure of Benzene Ring

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○ 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.

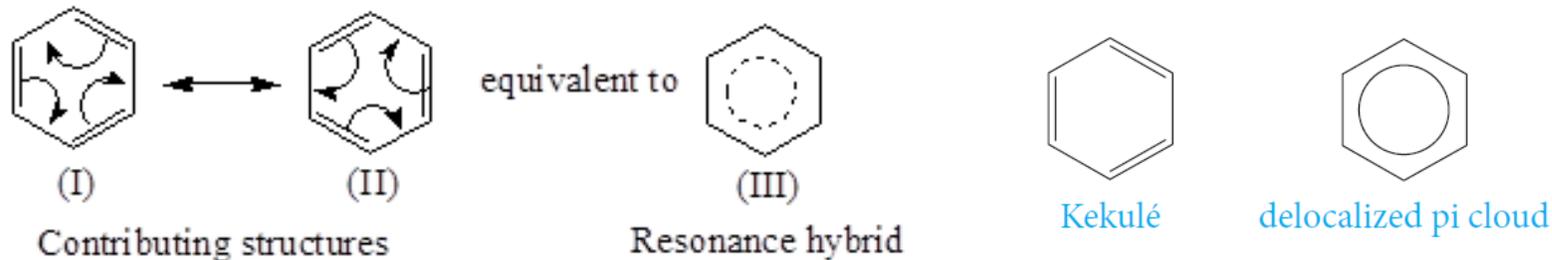


the Kekulé structures for benzene

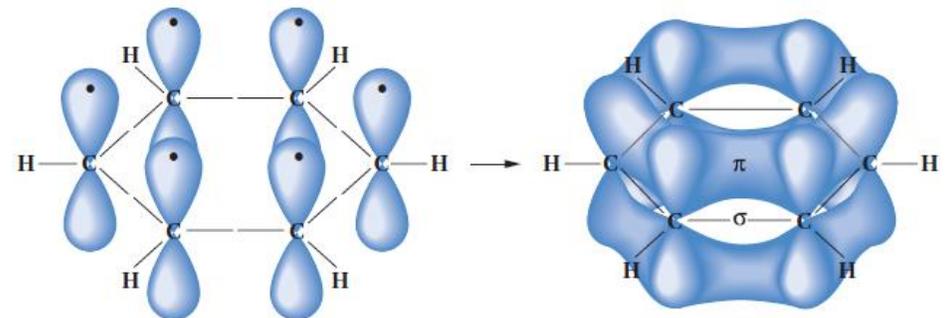
The Structure of Benzene Ring

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○ Resonance Model for Benzene.



- Benzene is *planar*.
- All of the *carbon-carbon bond lengths* are identical: 1.39 \AA , intermediate between typical *single* (1.54 \AA) and *double* (1.34 \AA) carbon-carbon bond lengths.
- Each carbon is therefore *sp²-hybridized*.
- Bond angles of 120° .



Aromatic Character (Aromaticity)



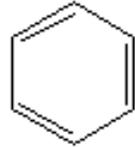
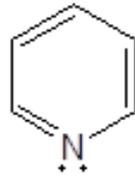
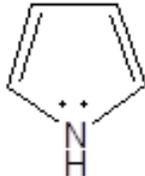
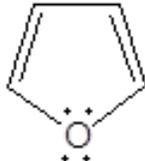
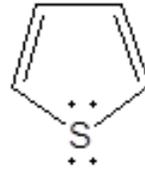
To be classified as aromatic, a compound must have:

- 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 rule

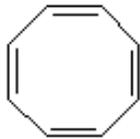
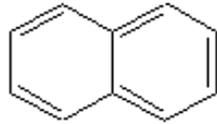
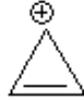
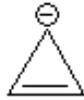
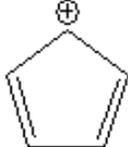
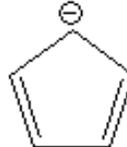
The number of π electrons in the compound = $(4n + 2)$

Where $(n = 0, 1, 2, 3, \text{ and so on})$.

Aromatic Character (Aromaticity)

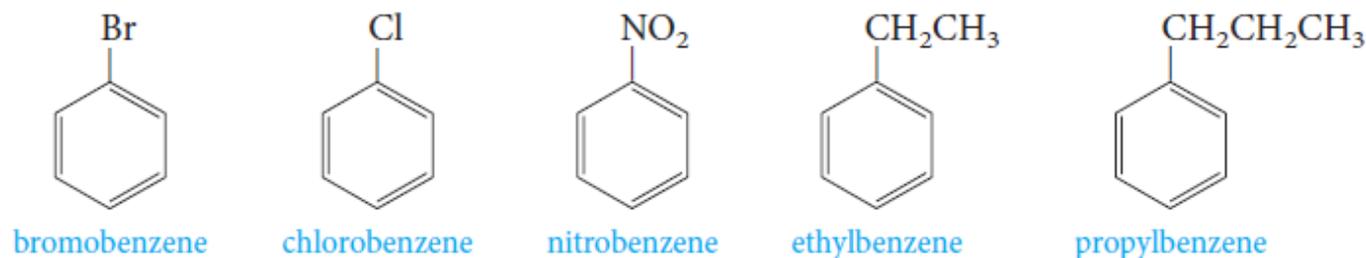
n	$4n + 2$	Structure and name of aromatic compound
1	6	 Benzene  Pyridine  Pyrrole  Furan  Thiophene

Examples

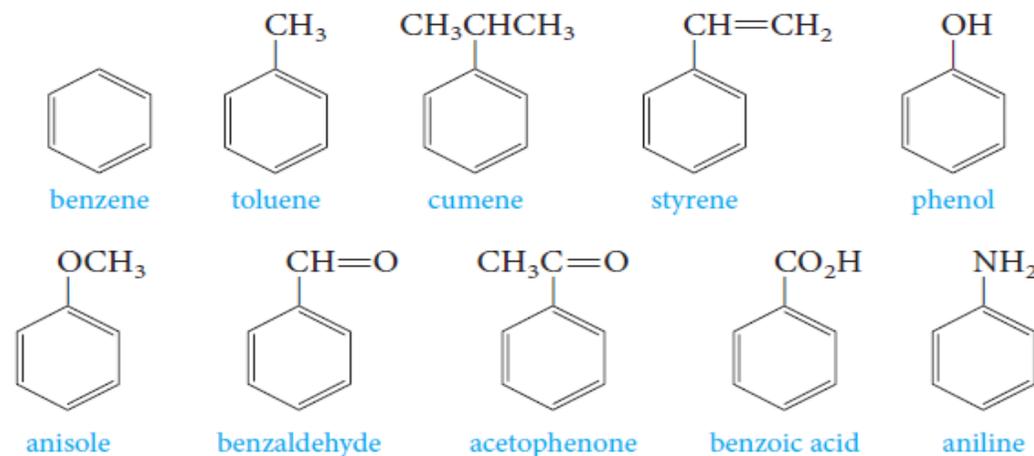
					
$4n+2 =$	8	10	2	2	4
$n =$	1.5	2	Not aromatic	0	0.5
	Not aromatic			Not aromatic	
					
$4n+2 =$	4	4	6	4	
$n =$	Not aromatic	0.5	1	Not aromatic	
		Not aromatic		Not aromatic	

Nomenclature of Aromatic Compounds

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



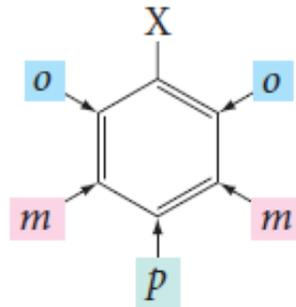
Common names are accepted by IUPAC (parent compounds).



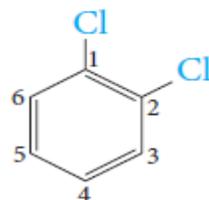
Nomenclature of Aromatic Compounds

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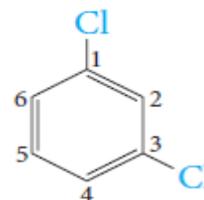
- When **two substituents** are present, *three isomeric structures are possible*.
 - They are designated by the prefixes; **ortho- (o-)**, **meta- (m-)** and **para- (p-)**.
 - If substituent X is attached to carbon 1; **o- groups** are on **carbons 2 and 6**, **m- groups** are on **carbons 3 and 5**,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



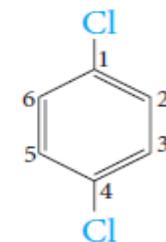
- **Examples;**



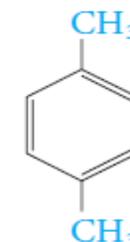
ortho-dichloro-
benzene



meta-dichloro-
benzene



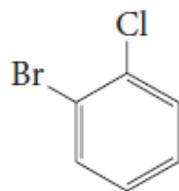
para-dichloro-
benzene



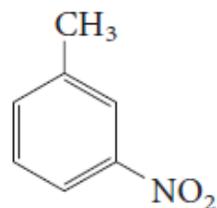
para-xylene*

Nomenclature of Aromatic Compounds

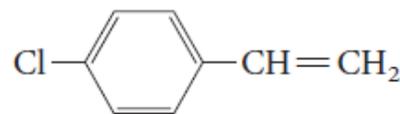
- The prefixes; *ortho-* (*o-*), *meta-* (*m-*) and *para-* (*p-*) are used when the two substituents are not identical.



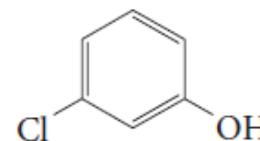
o-bromochlorobenzene
(note alphabetical order)



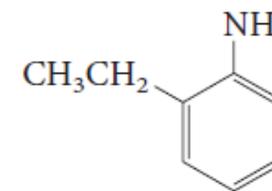
m-nitrotoluene



p-chlorostyrene

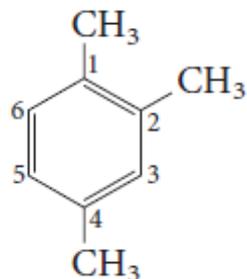


m-chlorophenol

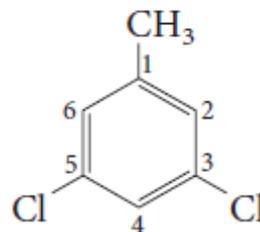


o-ethylaniline

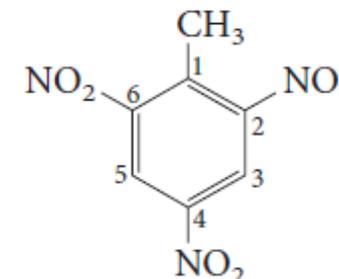
- When **more than two substituents** are present, their positions are designated by **numbering the ring**.



1,2,4-trimethylbenzene



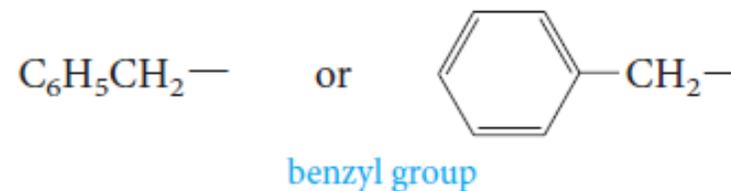
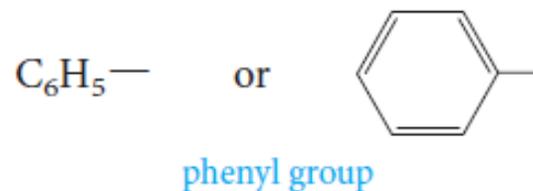
3,5-dichlorotoluene



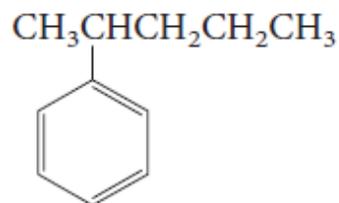
2,4,6-trinitrotoluene
(TNT)

Nomenclature of Aromatic Compounds

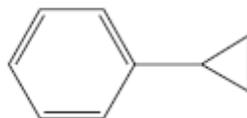
- Two groups with special names occur frequently in aromatic compounds; the **phenyl group** and the **benzyl group**.



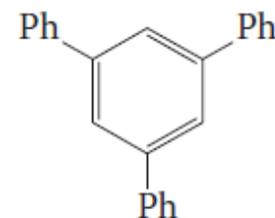
- **Examples;**



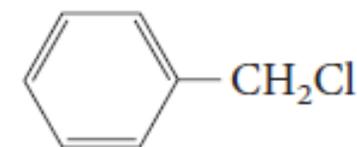
2-phenylpentane
(or 2-pentylbenzene)



phenylcyclopropane
(or cyclopropylbenzene)



1,3,5-triphenylbenzene

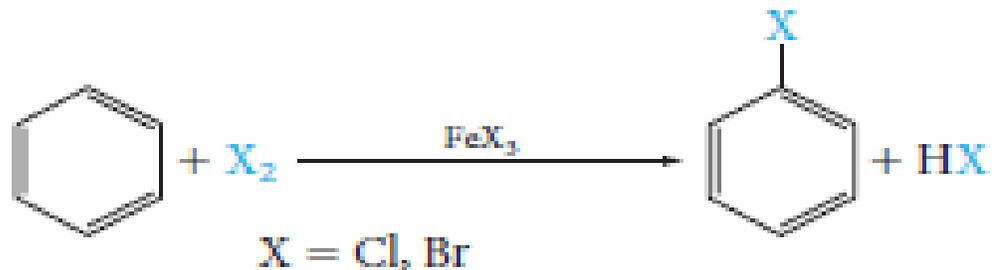


benzyl chloride

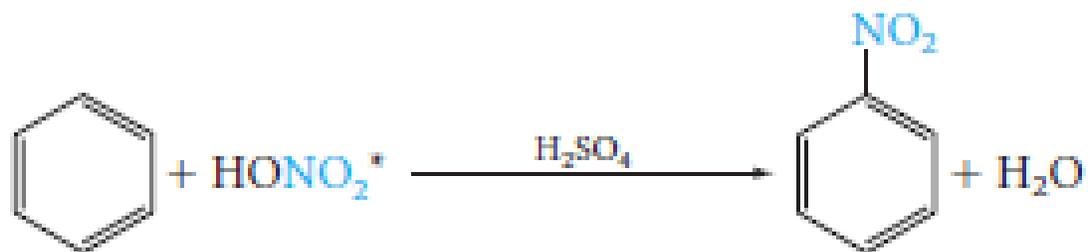
Electrophilic Aromatic Substitution Reactions

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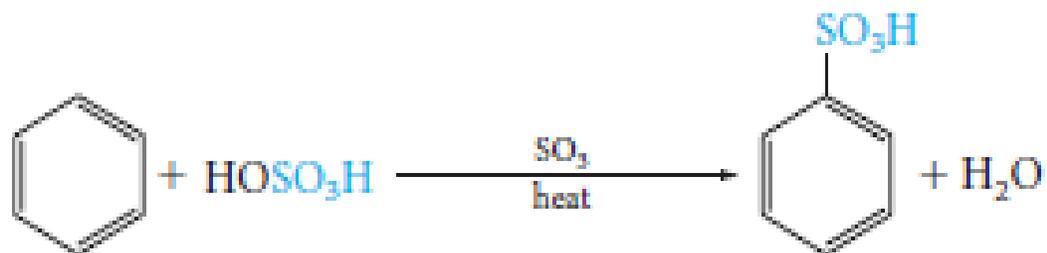
1) Halogenation



2) Nitration



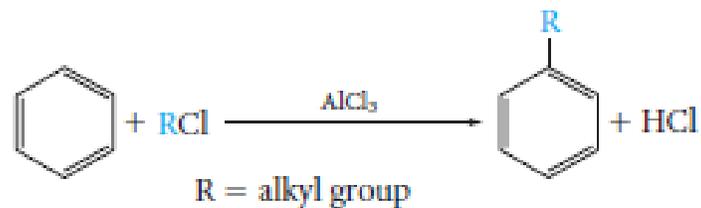
3) Sulfonation



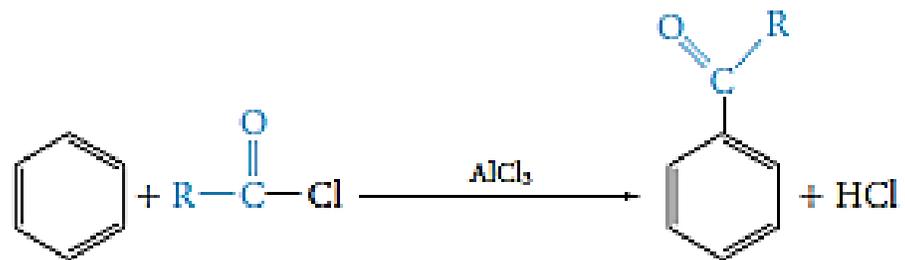
Electrophilic Aromatic Substitution Reactions

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4) Alkylation (Friedel-Crafts)

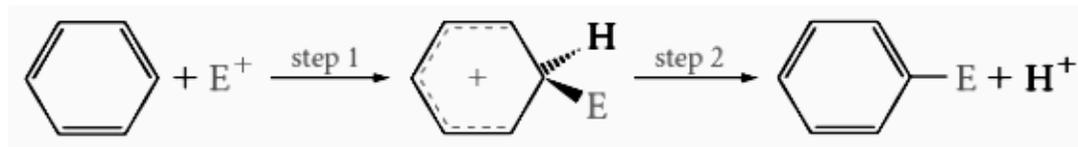


5) Acylation (Friedel-Crafts)



The Mechanism of Electrophilic Aromatic Substitution

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

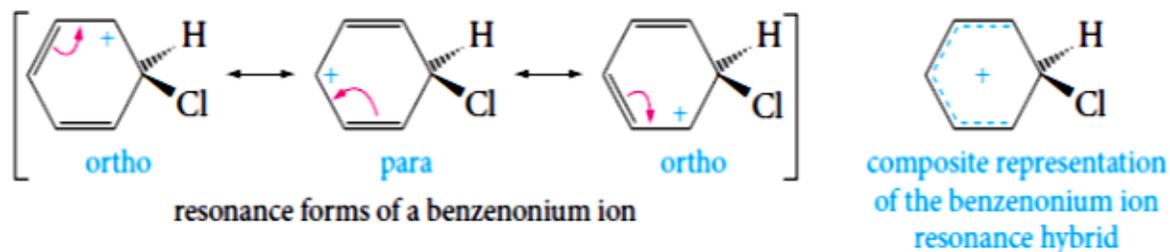
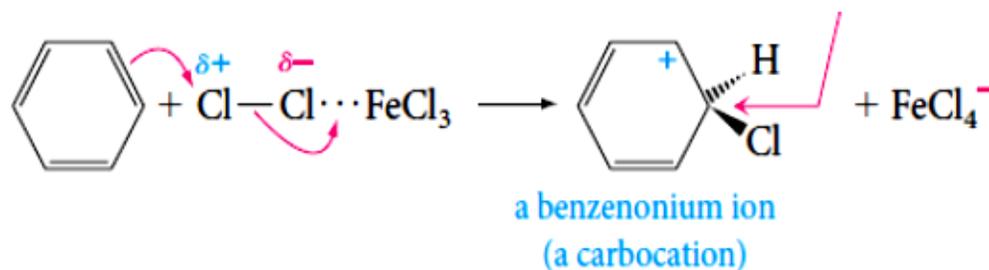
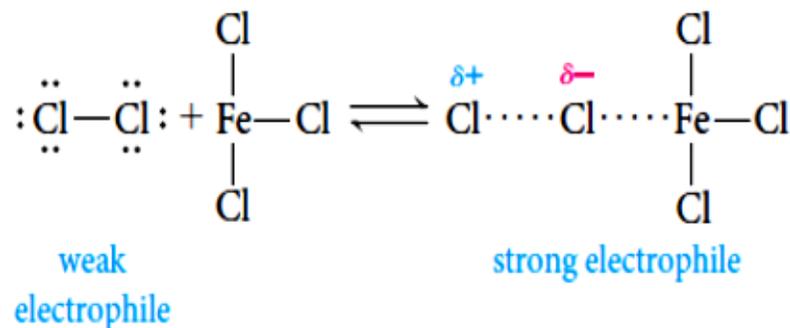


Electrophilic Aromatic Substitution Reactions

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The Mechanism of Electrophilic Aromatic Substitution

➤ Halogenation



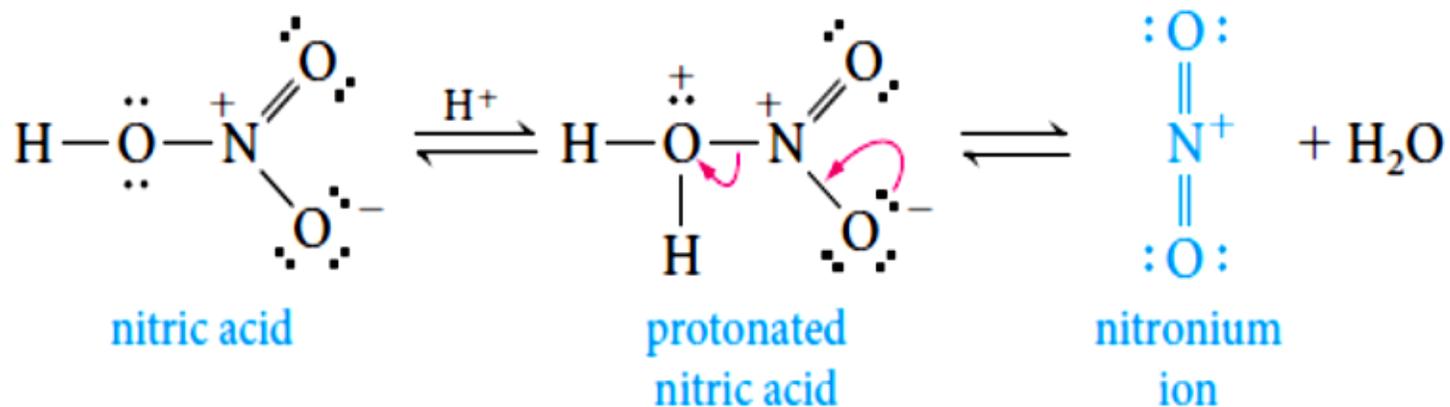
Electrophilic Aromatic Substitution Reactions

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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* (NO_2^+), which contains a positively charged nitrogen atom.



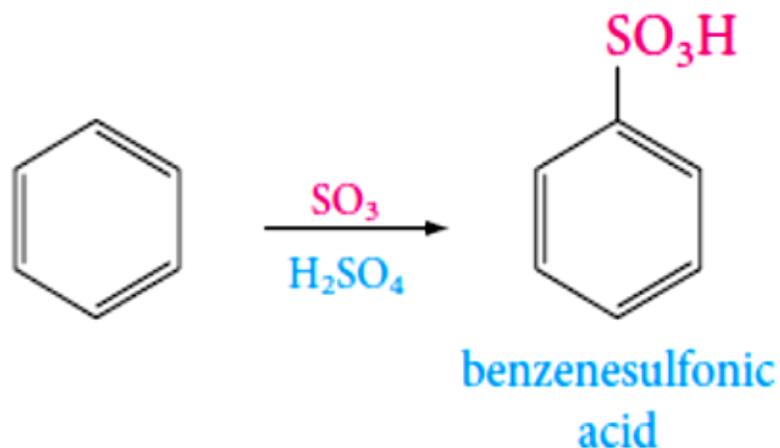
Electrophilic Aromatic Substitution Reactions

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The Mechanism of Electrophilic Aromatic Substitution

➤ Sulfonation

We use either concentrated or *fuming sulfuric acid*, and the electrophile may be sulfur trioxide, SO_3 , or *protonated sulfur trioxide*, $^+\text{SO}_3\text{H}$.



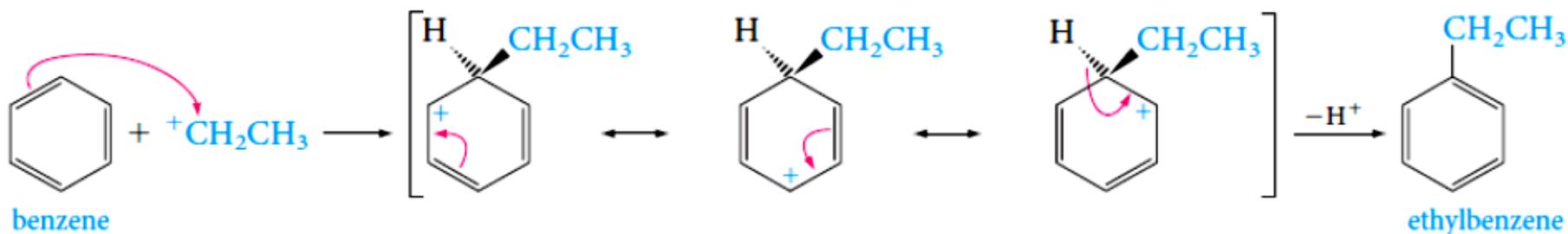
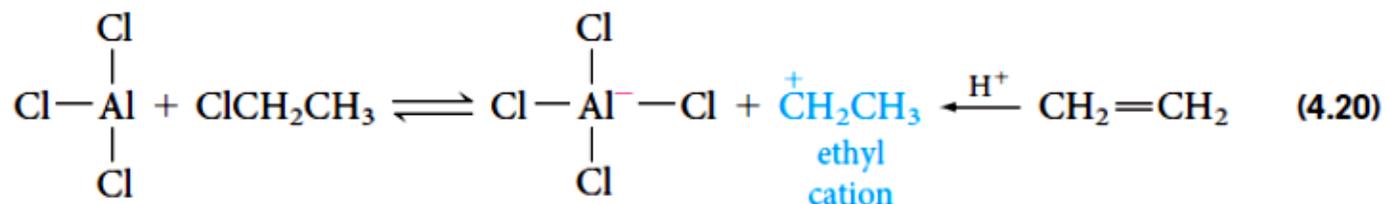
Electrophilic Aromatic Substitution Reactions

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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, $AlCl_3$).



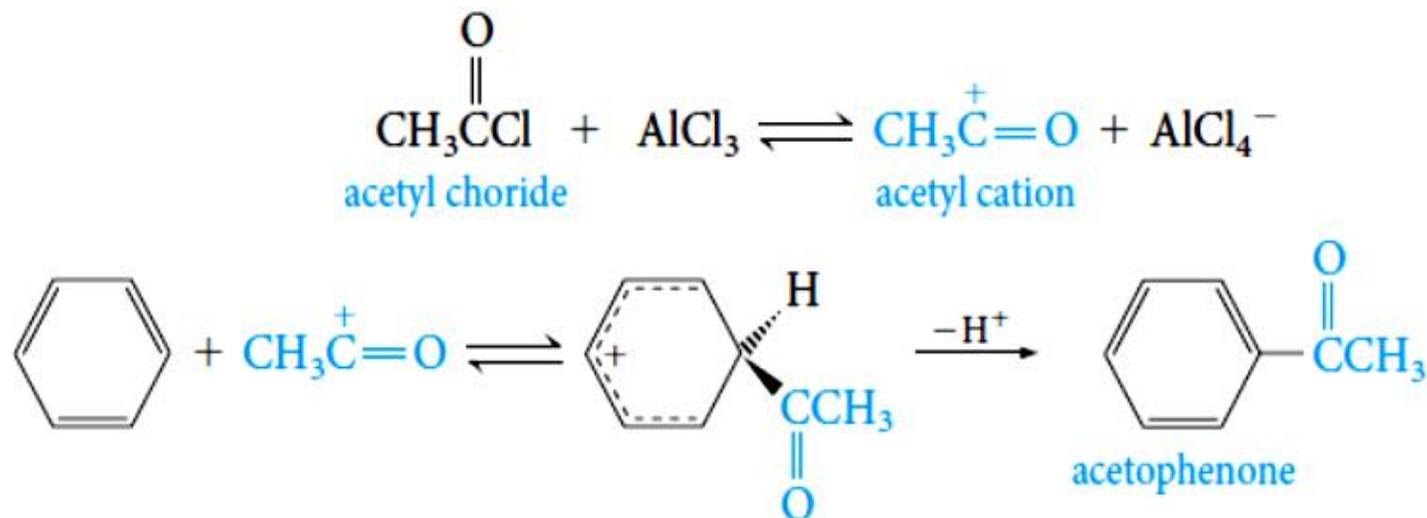
Electrophilic Aromatic Substitution Reactions

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The Mechanism of Electrophilic Aromatic Substitution

➤ Friedel–Crafts Acylation

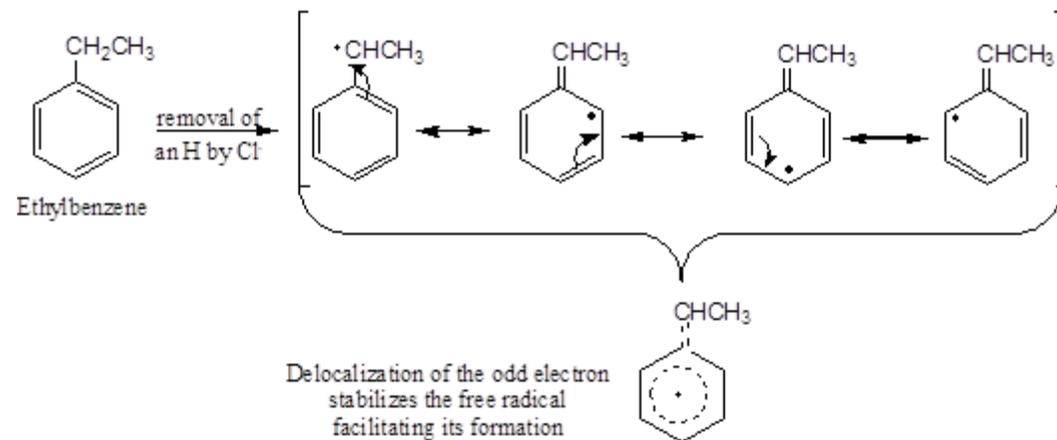
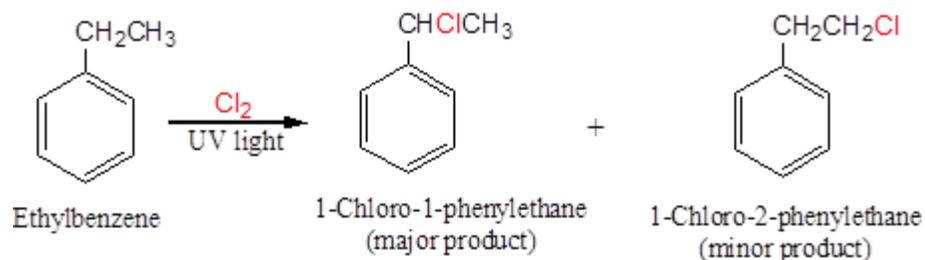
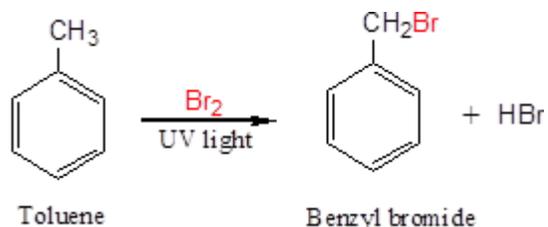
The *electrophile is an acyl cation* generated from an acid derivative, usually an *acyl halide*. The reaction provides a useful general route to aromatic ketones.



Side-Chain Reactions of Benzene-Derivatives

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1. Halogenation of an Alkyl Side Chain

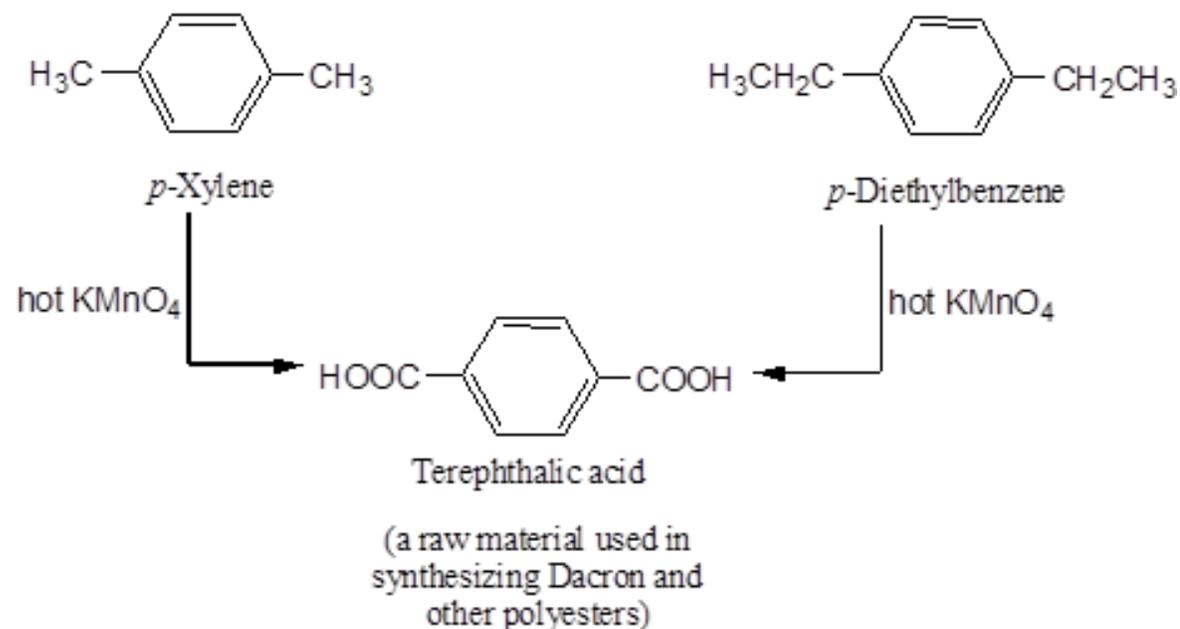
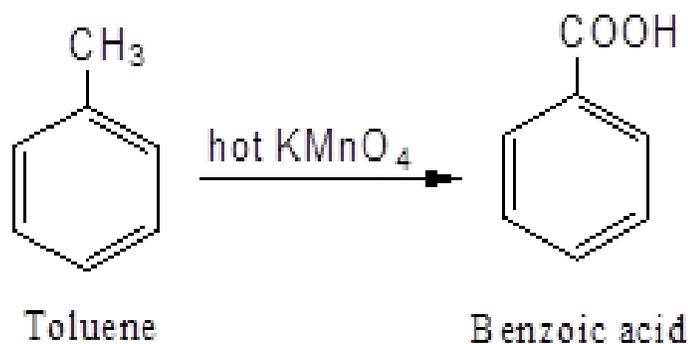


Side-Chain Reactions of Benzene-Derivatives

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2. Oxidation of an Alkyl Side Chain

- 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.



- Side-chain oxidation of alkylbenzenes is important in certain metabolic processes.
- One way in which the body rids itself of foreign substances is by oxidation in the liver to compounds more easily excreted in the urine. Toluene, for example, is oxidized to benzoic acid by this process and is eliminated rather readily.
- Benzene, with no alkyl side chain, undergoes a different reaction in the presence of these enzymes, which convert it to a substance capable of inducing mutations in DNA. This difference in chemical behavior seems to be responsible for the fact that benzene is carcinogenic but toluene is not.

Disubstituted Benzenes: Orientation & Reactivity

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Directing and Activating Effects of Common Functional Groups

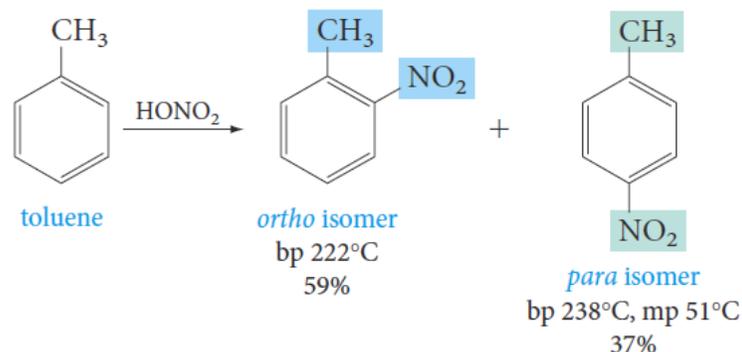
- Substituents that **release electrons** to the ring will **activate the ring** toward electrophilic substitution.
- Substituents that **withdraw electrons** from the ring will **deactivate the ring** toward electrophilic substitution.

	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		

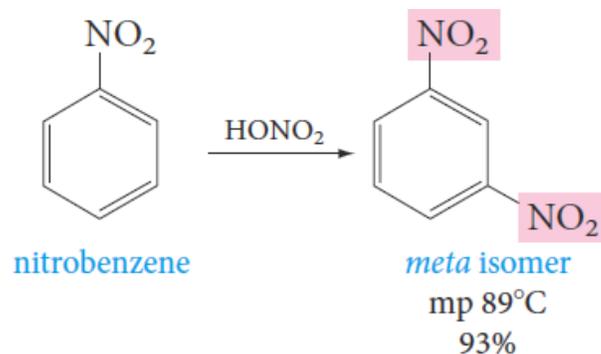
Disubstituted Benzenes: Orientation

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- 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.



Uses of Aromatic compound

- **Aromatic compounds** are important in industry.
- **Aromatic compounds** are extracted from complex mixtures obtained by the refining of oil or by distillation of coal tar, and are used to produce a range of important chemicals and polymers .
- **Styrene** is used to make polymers and plastics.
- **Benzene** used to make some types of rubber, dye, drugs and pesticides.
- **Toluene** used as a fullerene indicator, and it can be used as an octane booster in gasoline fuels used in internal combustion engines.
- **Phenanthrene derivatives** are used as pain medications (morphine, codeine, oxycodone).
- **Naphthalene** acts as a raw material in manufacture of dyes, plasticizers, and insecticides. Also used in production of some pharmaceutical products