

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

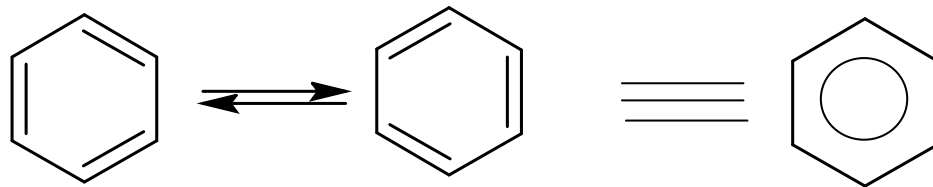
King Saud University

College of Science, Chemistry Department

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**.

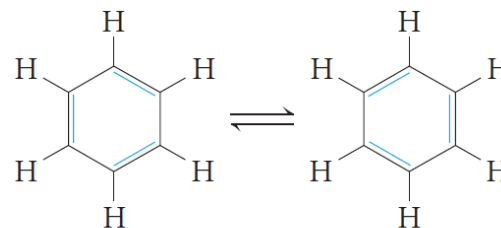


- **Benzene** is the **parent hydrocarbon of aromatic compounds**, because of their special chemical properties.

The Structure of Benzene Ring

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- 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.

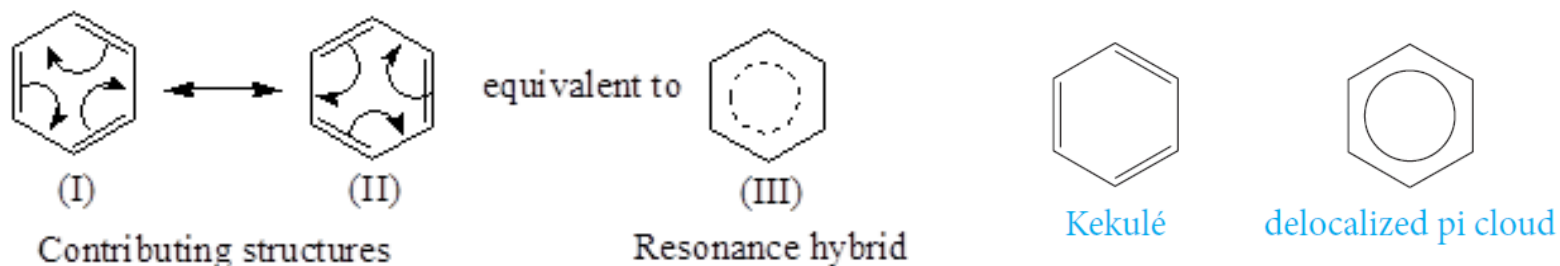


the Kekulé structures for benzene

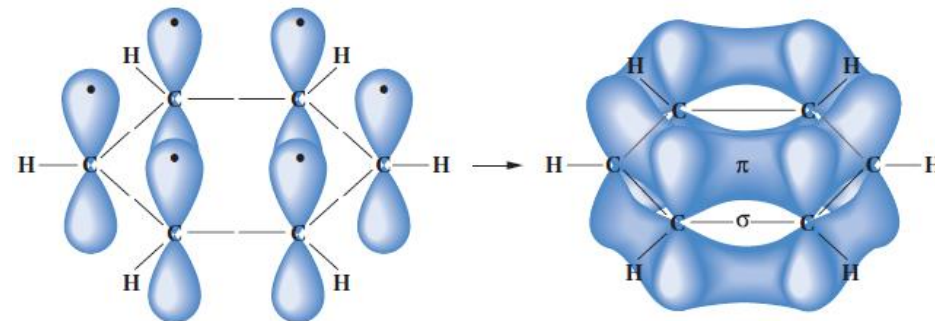
The Structure of Benzene Ring

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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)

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To be classified as aromatic, a compound must have:

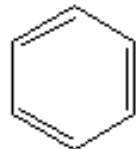
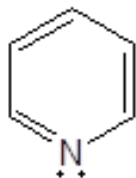
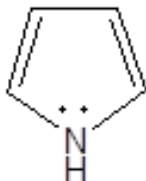
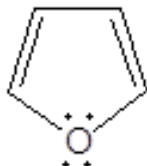
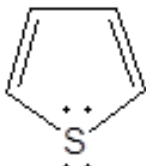
- 1 Cyclic structure
- 2 Cyclic structure contains what looks like a continuous system of alternating double and single bonds
- 3 Aromatic compounds must be planar
- 4 Fulfill Huckel rule

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

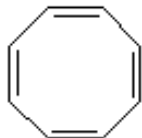
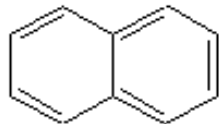





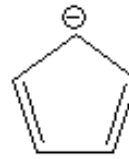

Where $(n = 0, 1, 2, 3, \text{ and so on})$.

Aromatic Character (Aromaticity)

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

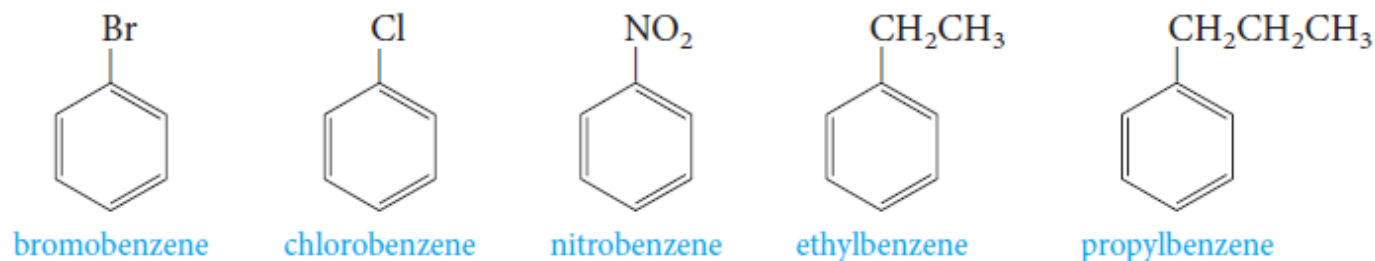
Examples

					
$4n+2 =$	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	

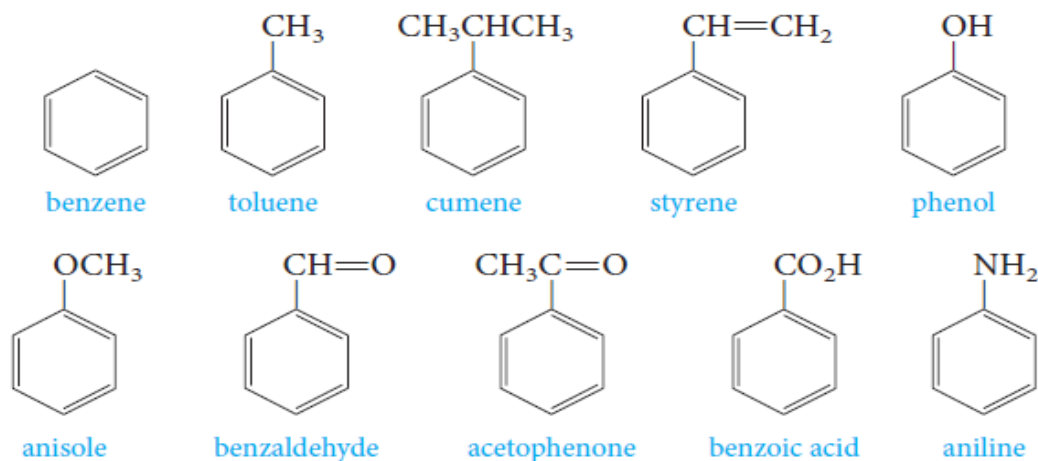
Nomenclature of Aromatic Compounds

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- **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).

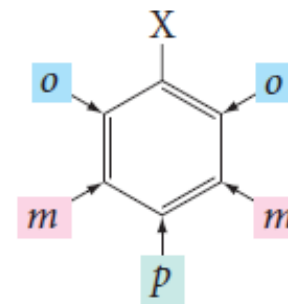


Disubstituted Benzenes

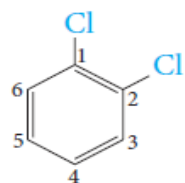
Nomenclature of Aromatic Compounds

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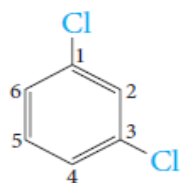
- When **two substituents** are present, *three isomeric structures are possible*.
 - They are designated by the prefixes; **ortho- (o-)**, **meta- (m-)** and **para- (p-)**.
 - If substituent X is attached to carbon 1;
 - **o- groups** are on **carbons 2 and 6**,
 - **m- groups** are on **carbons 3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



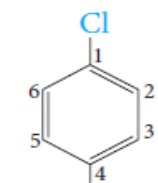
○ Examples;



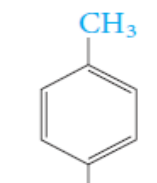
ortho-dichlorobenzene



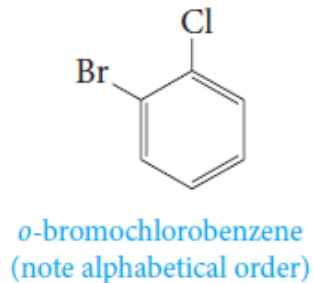
meta-dichlorobenzene



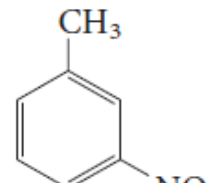
para-dichlorobenzene



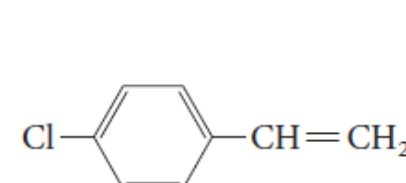
para-xylene*



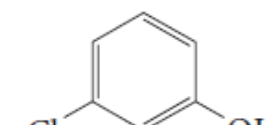
o-bromochlorobenzene
(note alphabetical order)



m-nitrotoluene



p-chlorostyrene



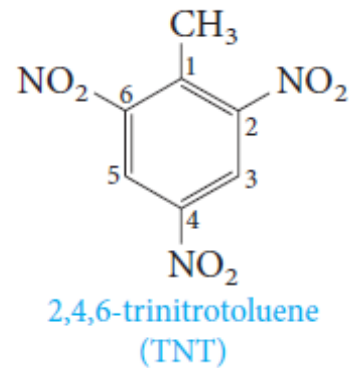
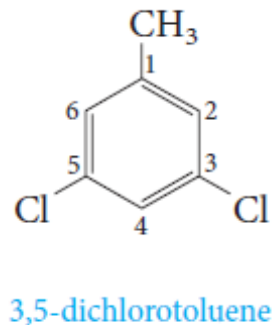
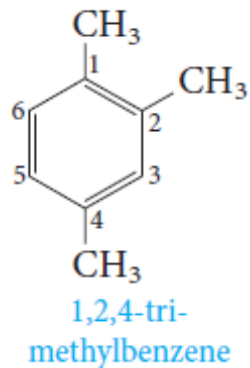
m-chlorophenol

Polysubstituted Benzenes

Nomenclature of Aromatic Compounds

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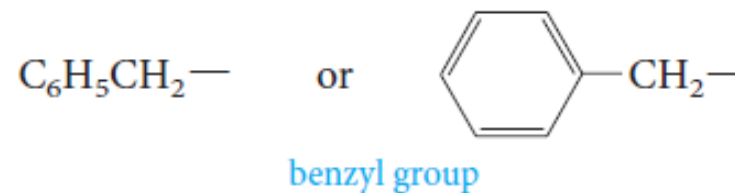
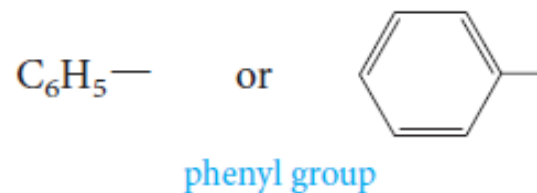
- When **more than two substituents** are present, their positions are designated by **numbering the ring**.



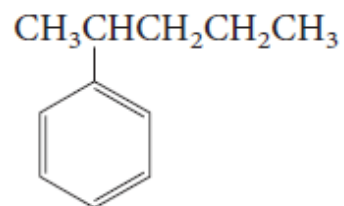
Nomenclature of Aromatic Compounds

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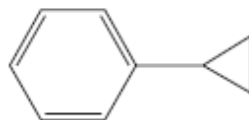
- Two groups with special names occur frequently in aromatic compounds; the **phenyl group** and the **benzyl group**.



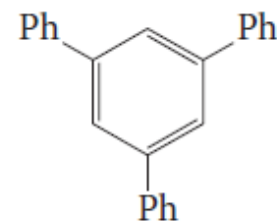
- **Examples;**



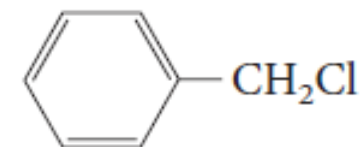
2-phenylpentane
(or 2-pentylbenzene)



phenylcyclopropane
(or cyclopropylbenzene)



1,3,5-triphenylbenzene



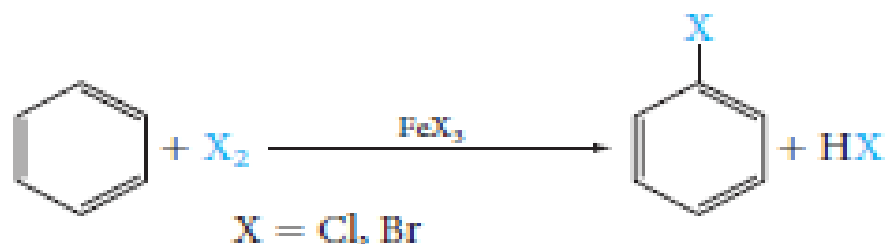
benzyl chloride

Electrophilic Substitution Reactions

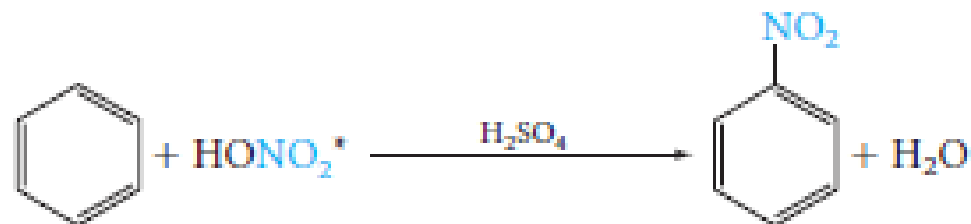
Reactions of Benzene

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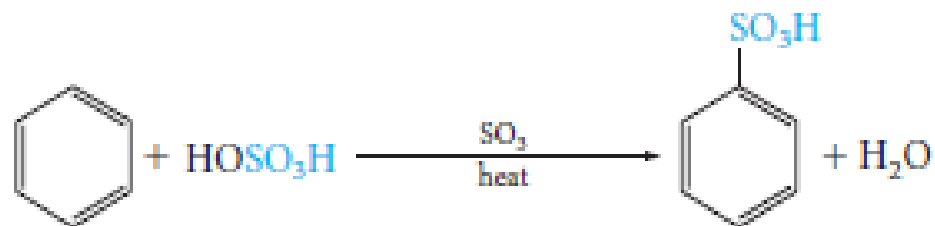
1) Halogenation



2) Nitration



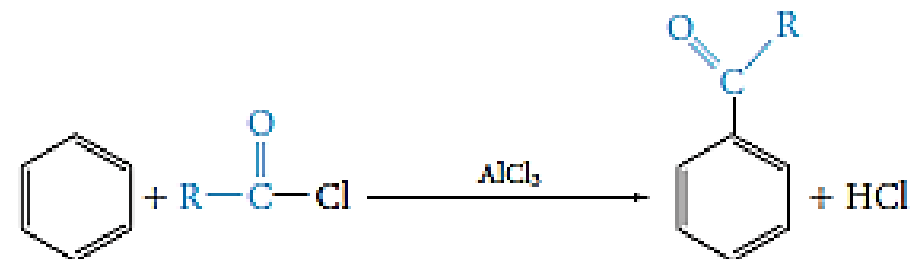
3) Sulfonation



4) Alkylation (Friedel-Crafts)



5) Acylation (Friedel-Crafts)

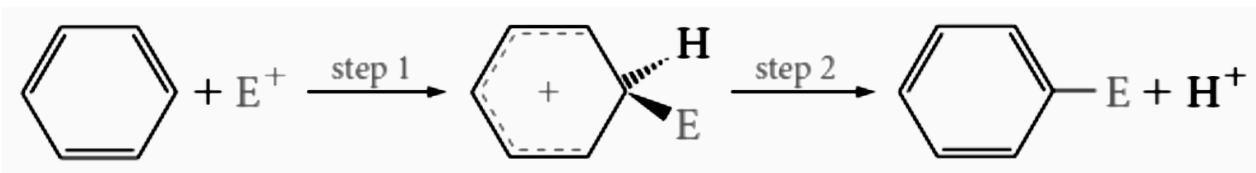


The Mechanism of Electrophilic Substitution Reactions

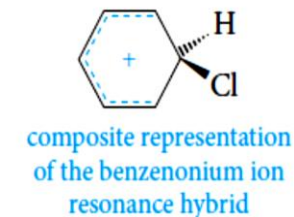
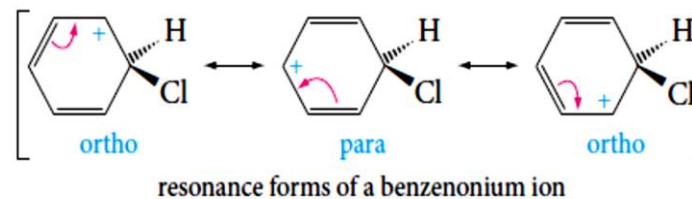
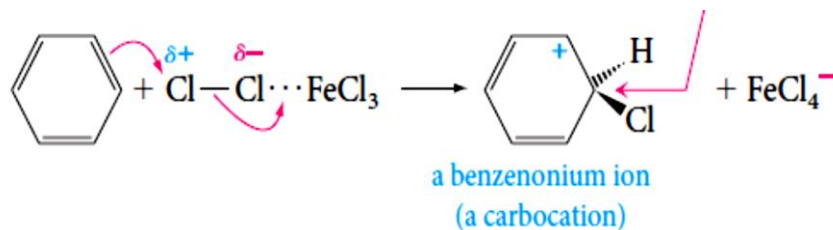
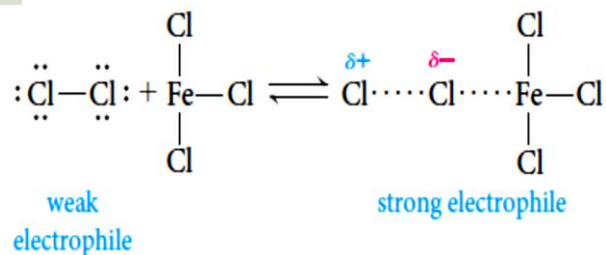
Reactions of Benzene

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



1) Halogenation



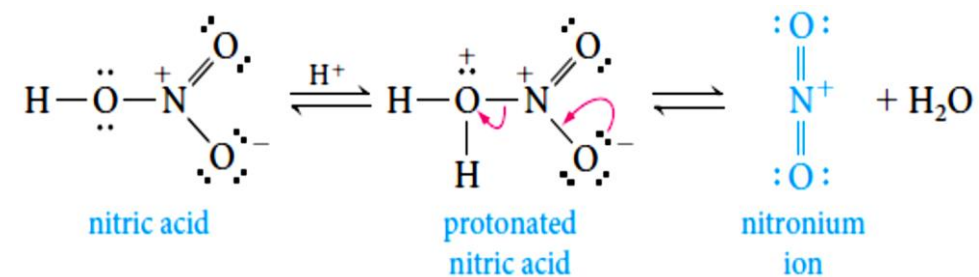
The Mechanism of Electrophilic Substitution Reactions

Reactions of Benzene

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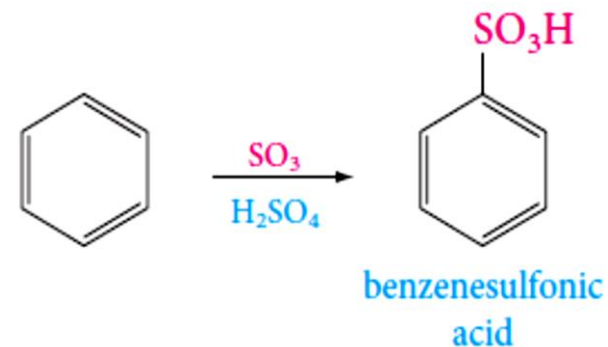
2) Nitration

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.



3) Sulfonation

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

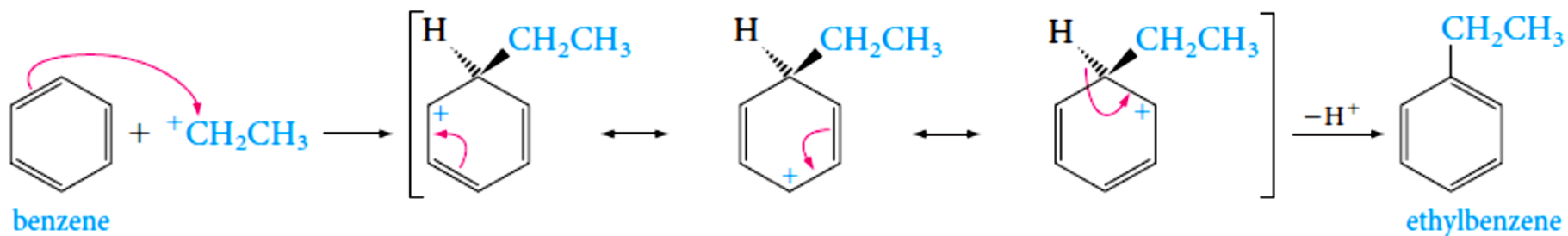
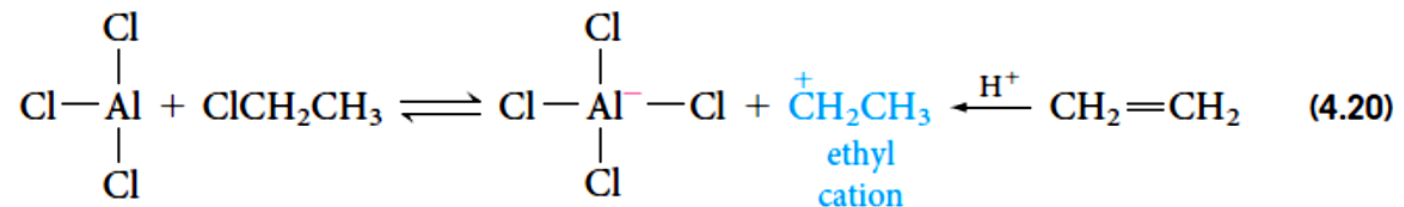


Electrophilic Aromatic Substitution Reactions

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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, $AlCl_3$).

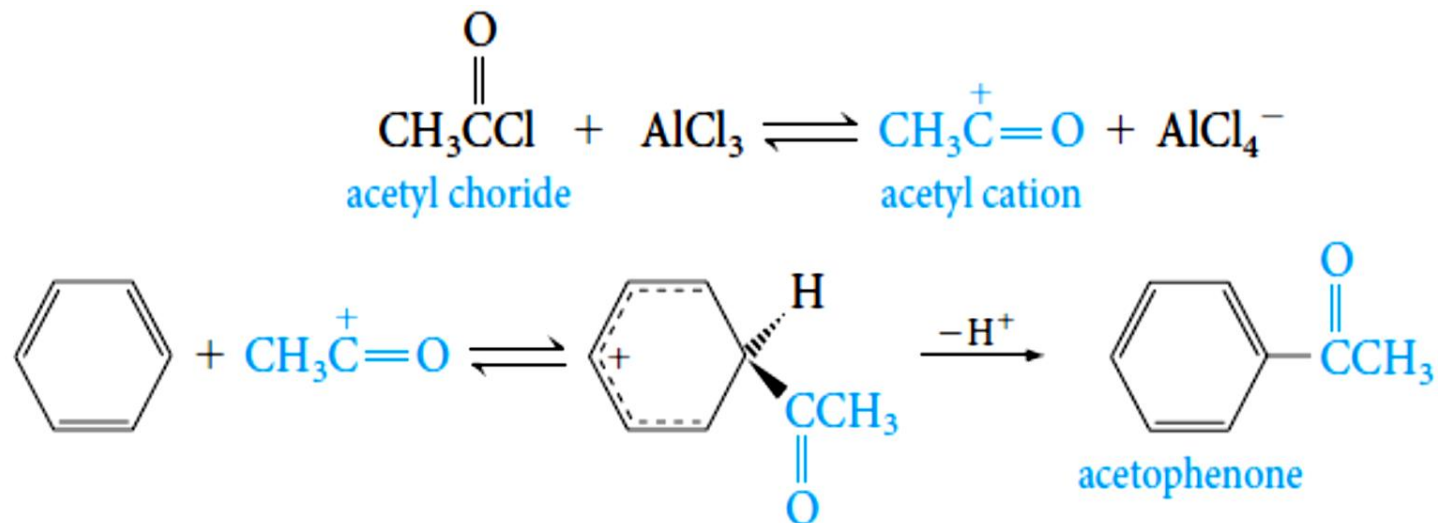


Electrophilic Aromatic Substitution Reactions

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5) Friedel–Crafts Acylation

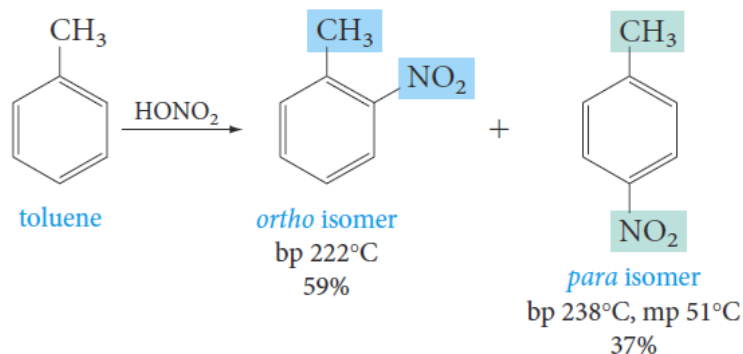
The *electrophile is an acyl cation* generated from an acid derivative, usually an *acyl halide*. The reaction provides a useful general route to aromatic ketones.



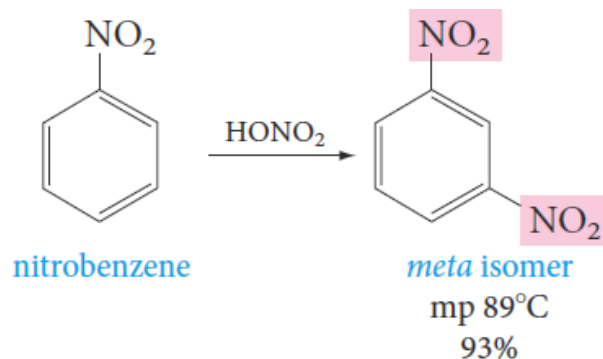
Disubstituted Benzenes: Orientation

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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.



Disubstituted Benzenes: Orientation & Reactivity

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Directing and Activating Effects of Common Functional Groups

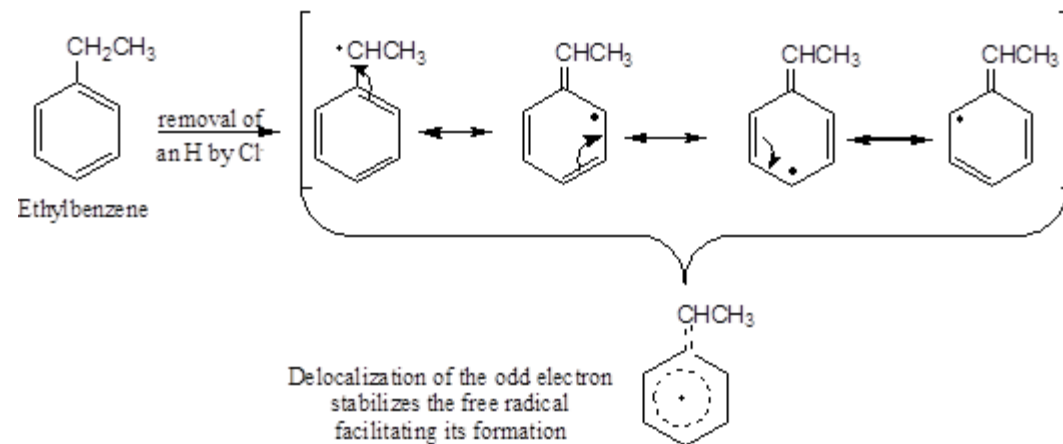
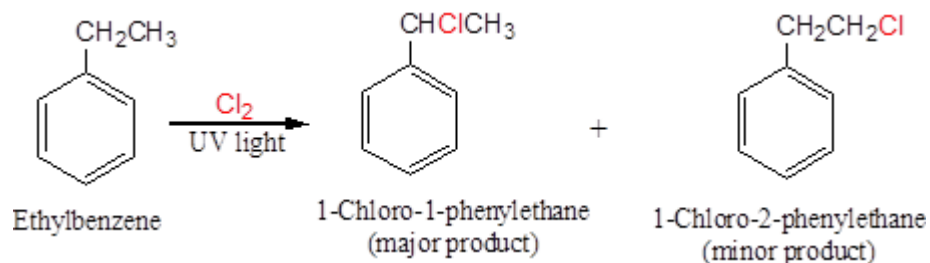
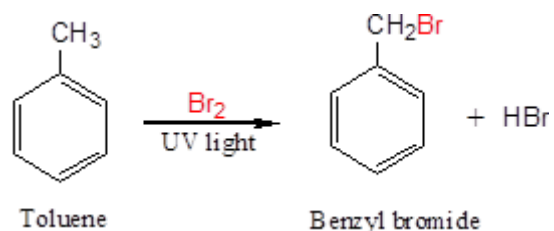
- Substituents that **release electrons** to the ring will **activate the ring** toward electrophilic substitution.
- Substituents that **withdraw electrons** from the ring will **deactivate the ring** toward electrophilic substitution.

	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	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{O}}\text{H} \end{array}$	acyl, carboxy	Deactivating
	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{O}}\text{R} \end{array}$	carboxamido, carboalkoxy	
	$\begin{array}{c} \text{:O:} \\ \\ -\text{S}-\ddot{\text{O}}\text{H} \\ \\ \text{:O:} \end{array}$		sulfonic acid	
	$-\text{C}\equiv\text{N:}$		cyano	
	$\begin{array}{c} \text{:O:} \\ \\ -\text{N}^+ \\ \\ \text{:O:}^- \end{array}$		nitro	

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.

