Fundamentals of Organic Chemistry

CHEM 108

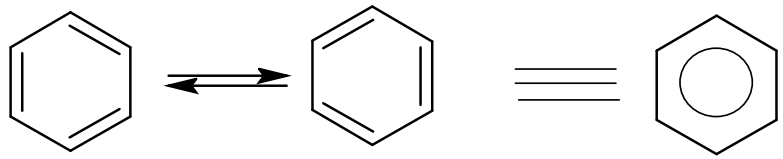
King Saud University

College of Science, Chemistry Department

CHAPTER 3. AROMATIC HYDROCARBONS

Aromatic Hydrocarbons

- Originally called **aromatic** due to fragrant odors, although this definition seems inaccurate as many products posses 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

- **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

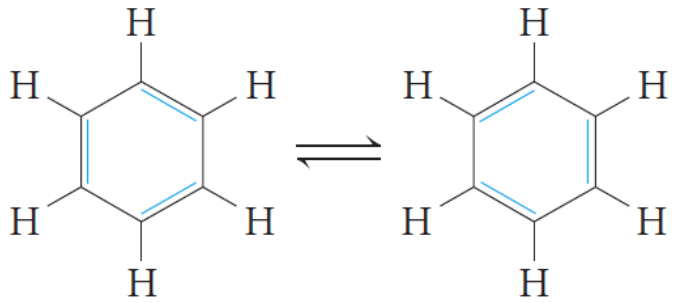
  The carbon-to-hydrogen ratio in benzene, suggests a ***highly unsaturated structure.***

- *Benzene reacts mainly by* ***substitution***.

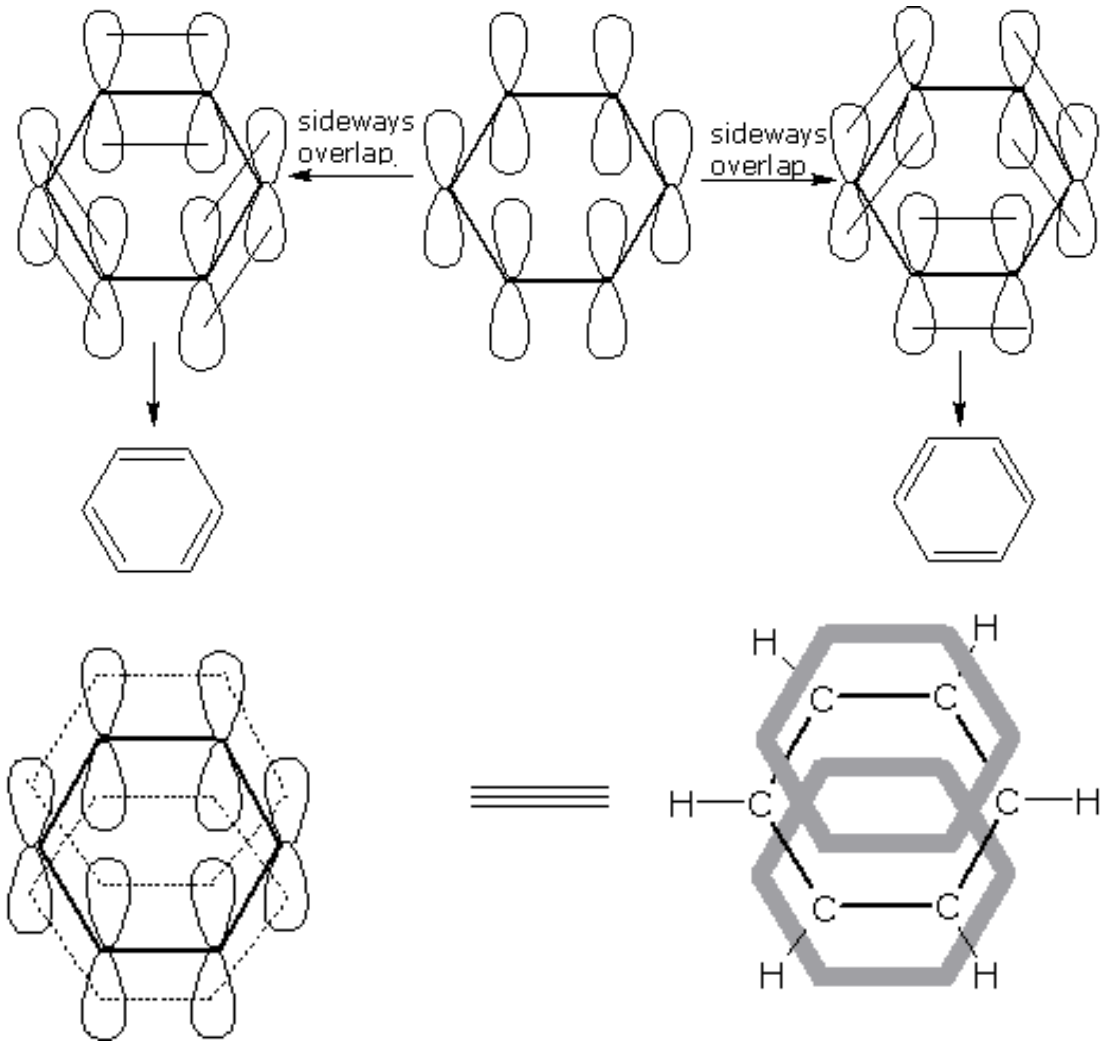
  It does not undergo the typical addition reactions of alkenes or alkynes.

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.*

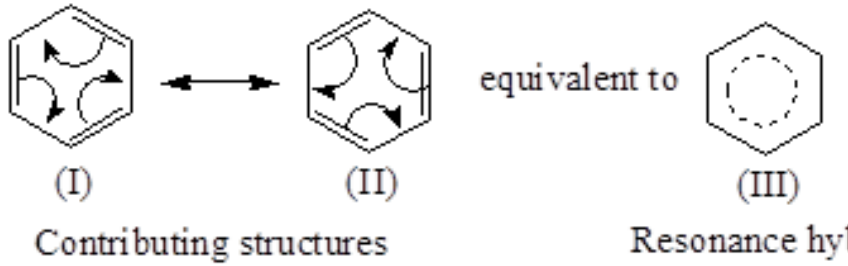


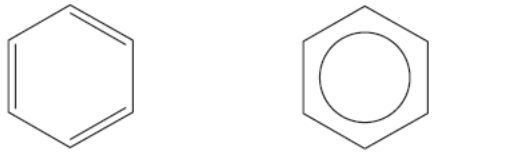
the Kekulé structures for benzene


sideways
overlap
sideways
overlap
H
H
C
C
H
C
C
H
C
C
H
H

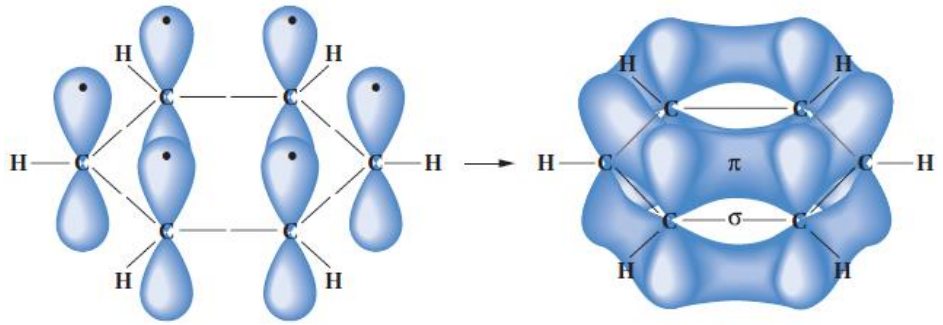
The Structure of Benzene Ring

- ***Resonance Model for Benzene.***





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



Aromatic Character (Aromaticity)

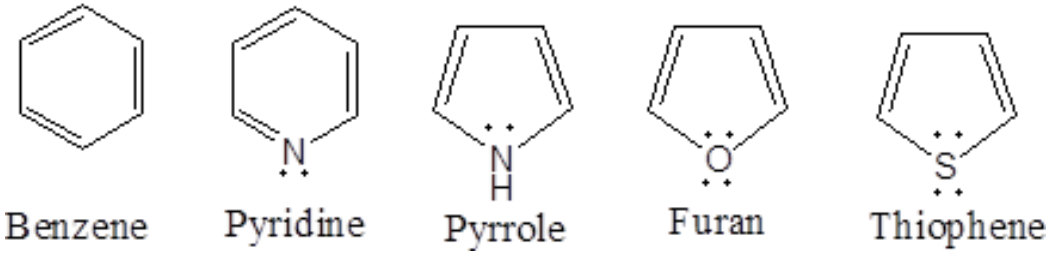
To be classified as aromatic, a compound must have:

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 Hückel's rule

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

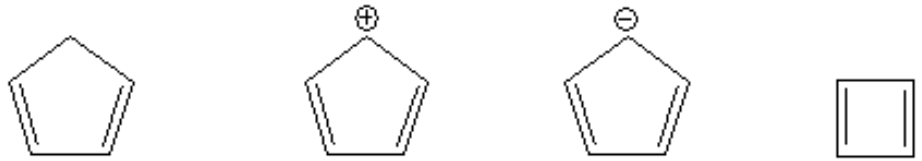
Where (n = 0,1, 2, 3, and so on).

Aromatic Character (Aromaticity)

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

Examples

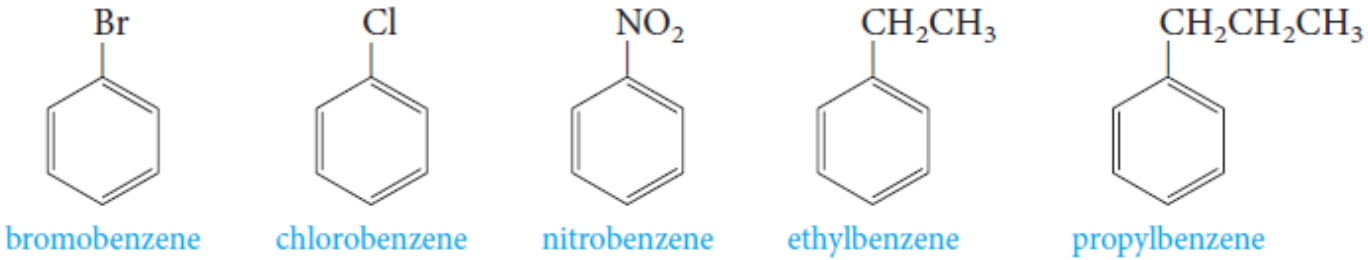
4n+2 =	8	10	2	2	4
n=	1.5	2	0	0	0.5



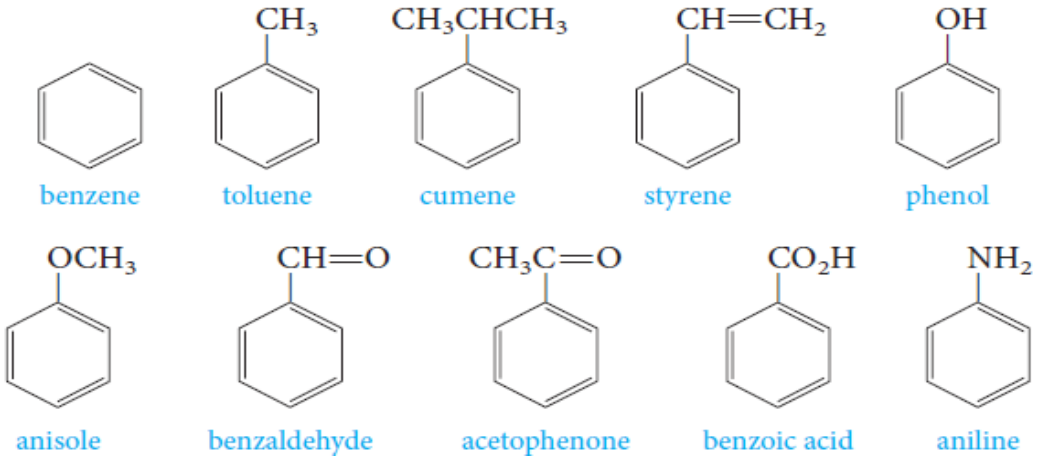
4n+2 =	4	4	6	4
n=	0.5	0.5	1	0.5

Nomenclature of Aromatic Compounds

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

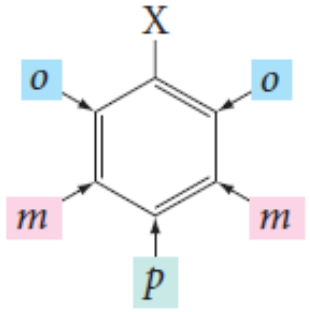


Common names are accepted by IUPAC (parent compounds).

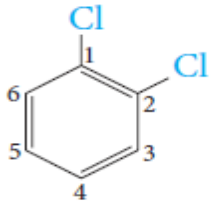


Nomenclature of Aromatic Compounds

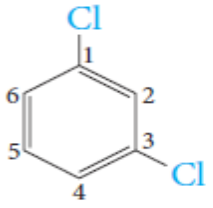
- When **two substituents** are present, *three isomeric structures are possible.*
  - They are designated by the prefixes; *ortho-* (o-), *meta-* (*m*-) and *para-* (*p*-).
  - If substituent X is attached to carbon 1; o- groups are on carbons 2 and 6, *m*- groups are on carbons 3 and 5, and *p*- groups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



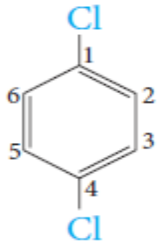
- **Examples;**



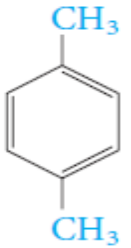
ortho-dichloro-benzene



meta-dichloro-benzene



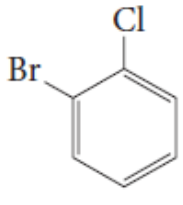
para-dichloro-benzene



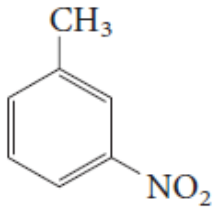
para-xylene*

Nomenclature of Aromatic Compounds

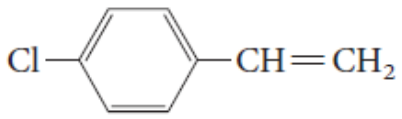
- The prefixes; *ortho-* (o-), *meta-* (*m*-) and *para-* (*p*-) are used when the two substituents are not identical.



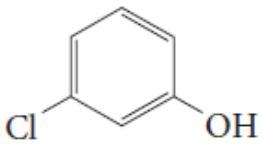
o-bromochlorobenzene
(note alphabetical order)



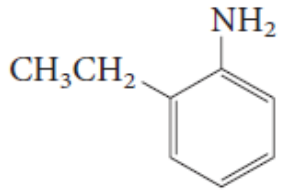
m-nitrotoluene



p-chlorostyrene

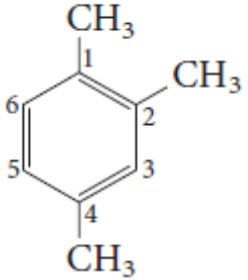


m-chlorophenol

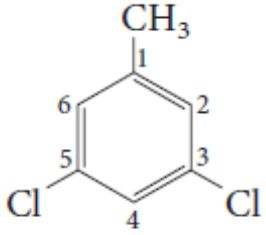


o-ethylaniline

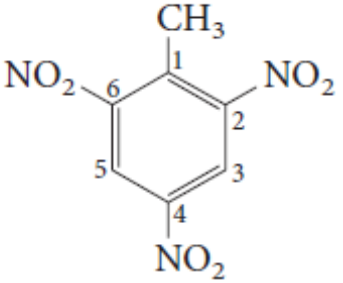
- When **more than two substituents** are present, their positions are designated by numbering the ring.



1,2,4-tri-
methylbenzene



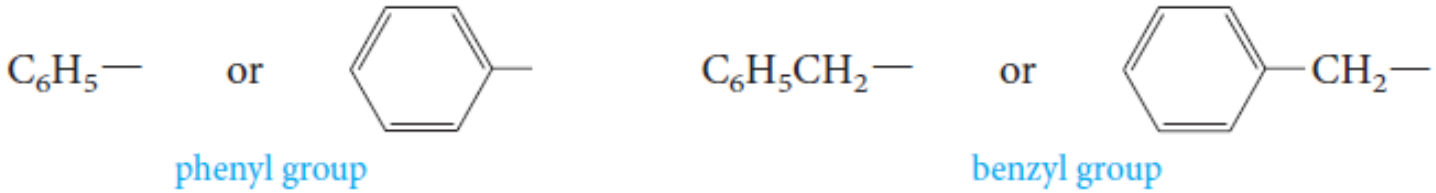
3,5-dichlorotoluene



2,4,6-trinitrotoluene
(TNT)

Nomenclature of Aromatic Compounds

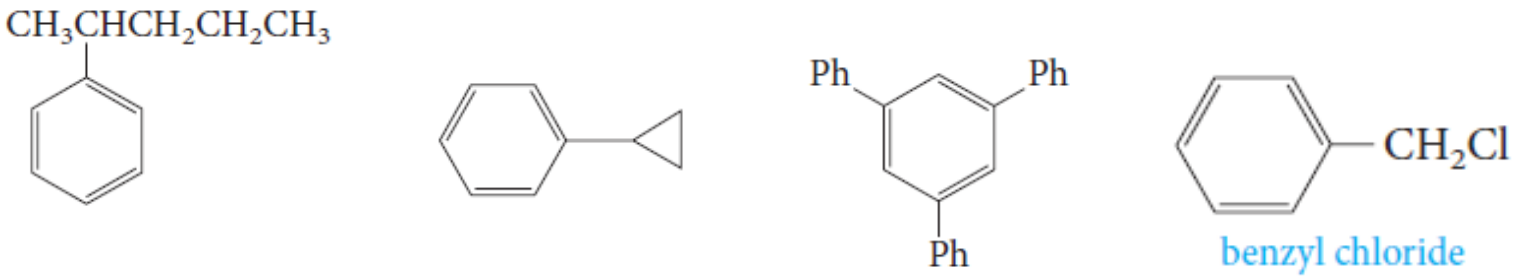
- Two groups with special names occur frequently in aromatic compounds; the **phenyl group** and the **benzyl group**.



phenyl group

benzyl group

- **Examples;**



2-phenylpentane (or 2-pentylbenzene)

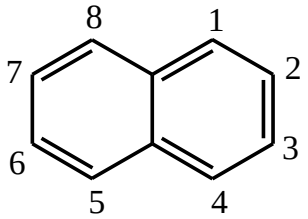
phenylcyclopropane (or cyclopropylbenzene)

1,3,5-triphenylbenzene

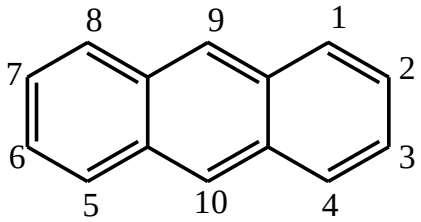
benzyl chloride

Nomenclature of Aromatic Compounds

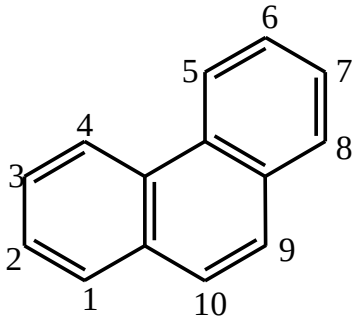
Polynuclear aromatic hydrocarbons containing two, three & four rings are :



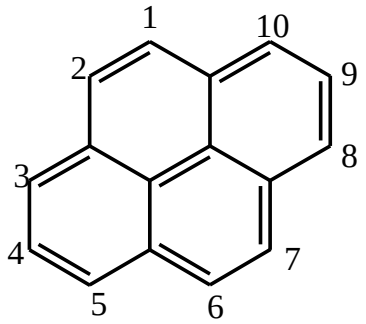
Naphthalene



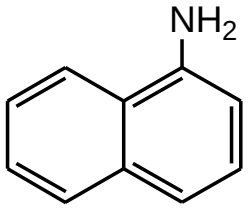
Anthracene



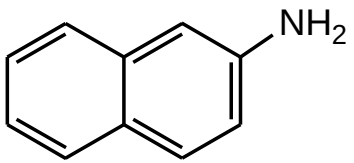
Phenancrene



Pyrene



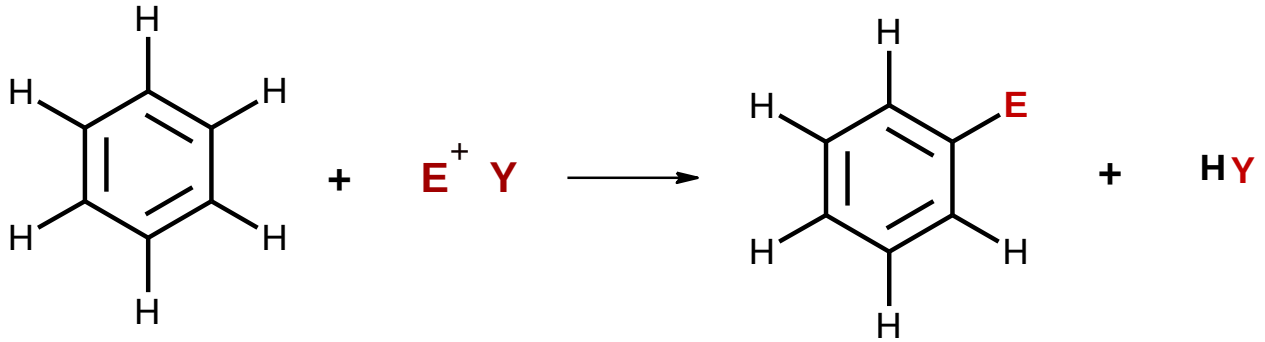
IUPAC name: 1-Aminonaphthalene
Common name: a-Naphthaylamine
(a weak carcinogen)



2-Aminonaphthalene
B-Naphthaylamine
(a strong carcinogen)

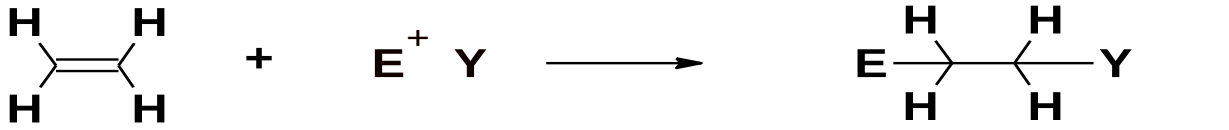
Electrophilic Aromatic Substitution Reactions

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



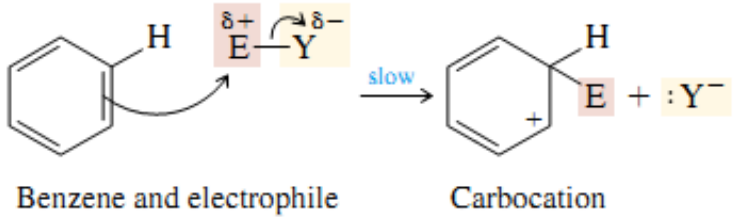
Arene | **Electrophilic reagent** | **Product of electrophilic aromatic substitution**

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

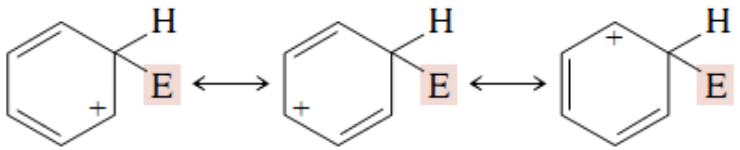


Alkene | **Electrophilic reagent** | **Product of electrophilic addition**

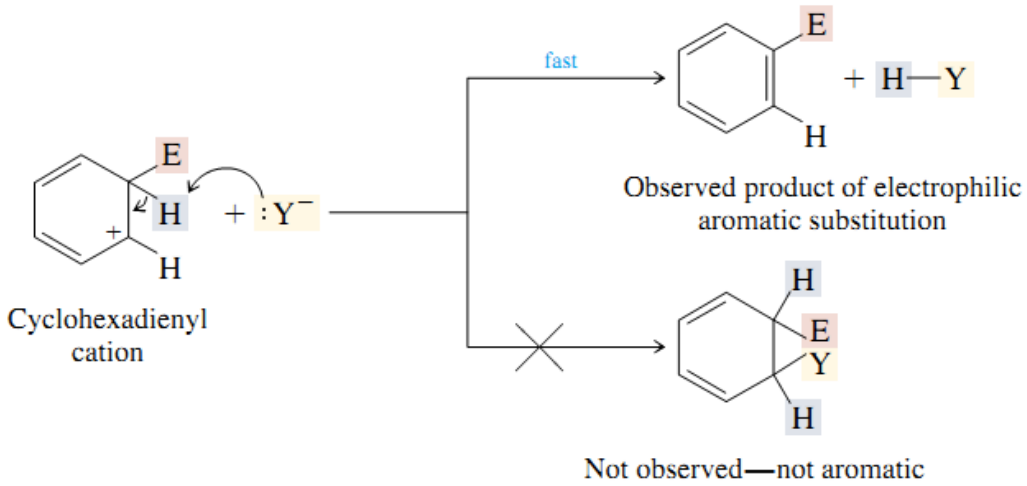
Electrophilic Aromatic Substitution Reactions



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



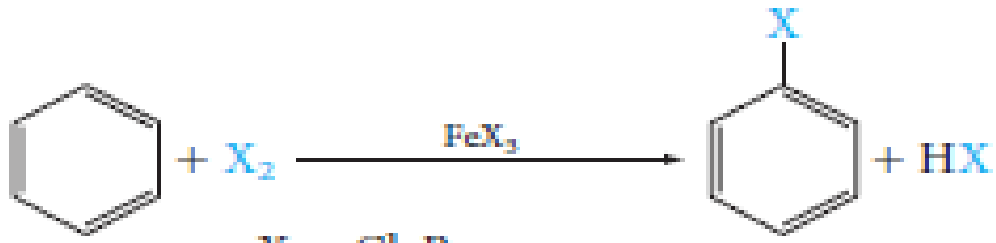
The removal of the proton by the nucleophile Y^-, which leads to the restoration of the aromatic ring



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

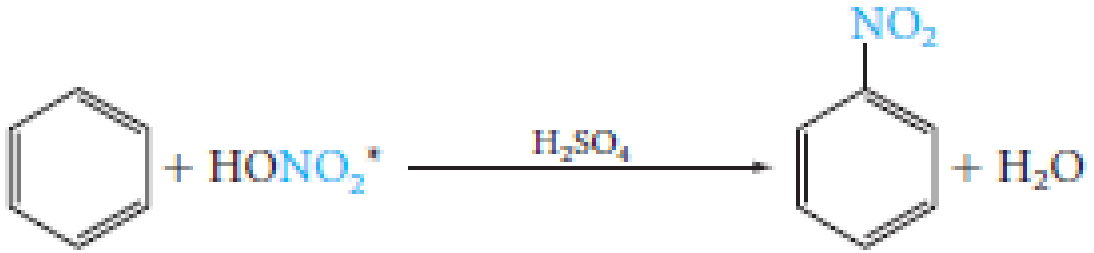
Electrophilic Aromatic Substitution Reactions

1) Halogenation

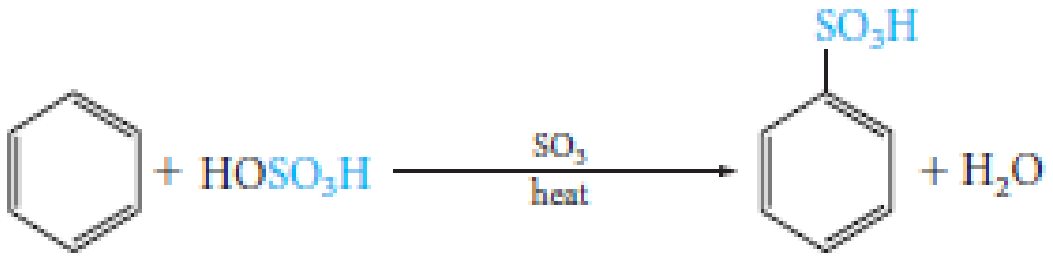


X = Cl, Br

2) Nitration



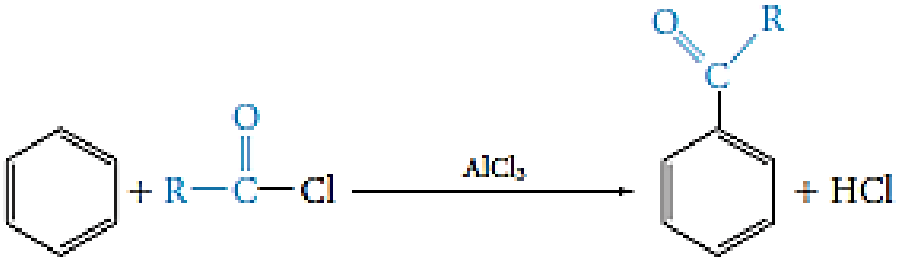
3) Sulfonation



Electrophilic Aromatic Substitution Reactions

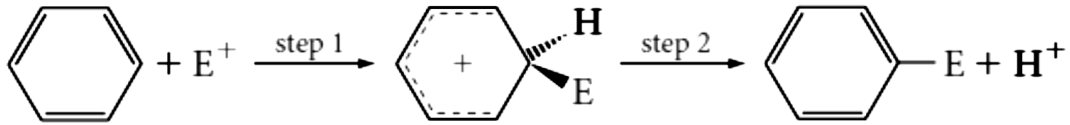
4) Alkylation (Friedel-Crafts)

5) Acylation (Friedel-Crafts)



The Mechanism of Electrophilic Aromatic Substitution

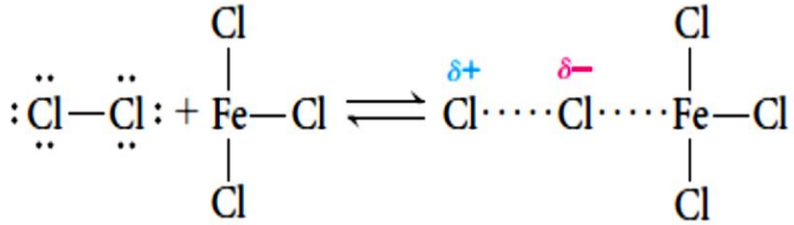
We can generalize this two-step mechanism for all the electrophilic aromatic substitutions.



Electrophilic Aromatic Substitution Reactions

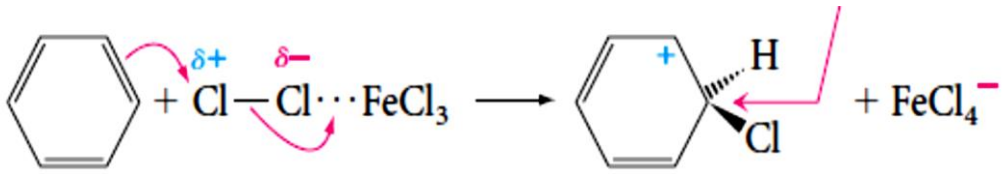
The Mechanism of Electrophilic Aromatic Substitution

- **Halogenation**

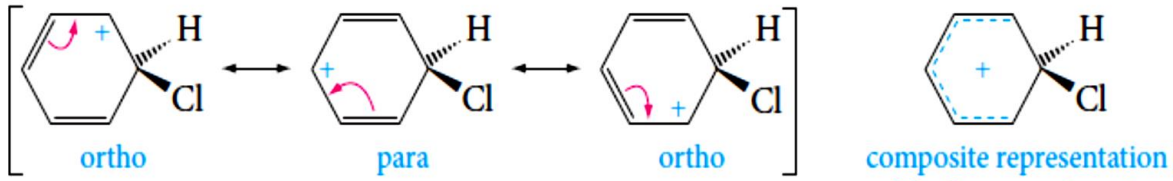


weak electrophile

strong electrophile



a benzenonium ion
(a carbocation)



resonance forms of a benzenonium ion

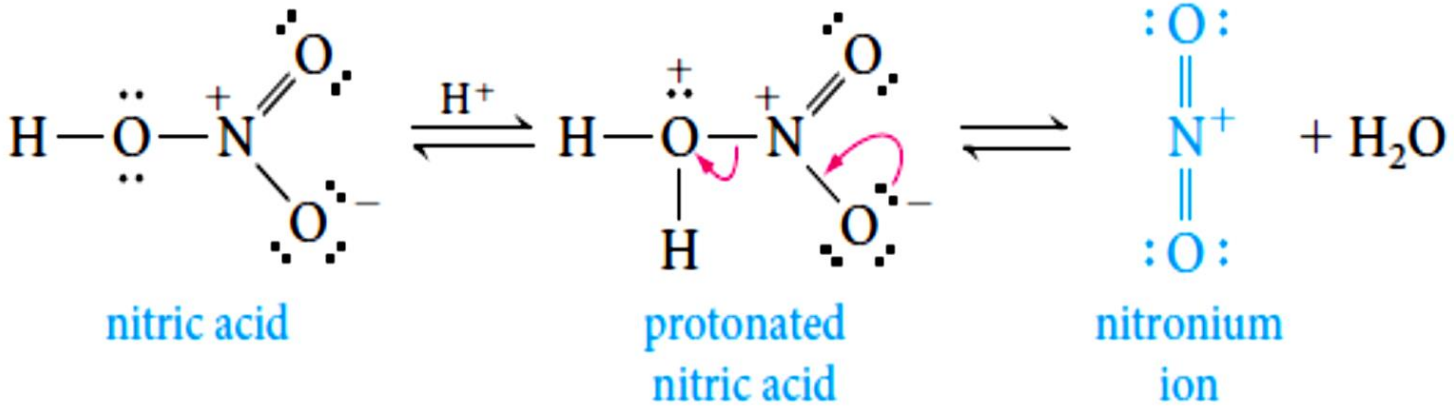
composite representation of the benzenonium ion resonance hybrid

Electrophilic Aromatic Substitution Reactions

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.

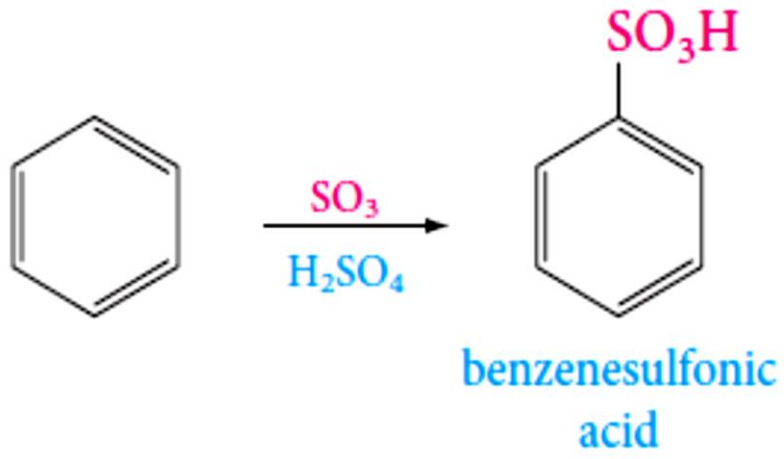


Electrophilic Aromatic Substitution Reactions

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, $^{+}SO_3H$.



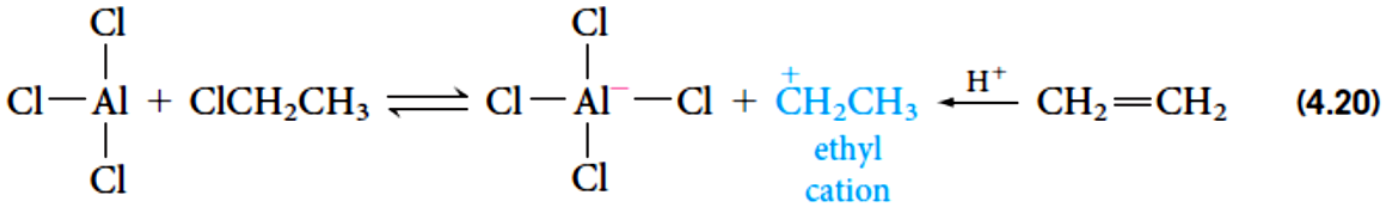
benzenesulfonic acid

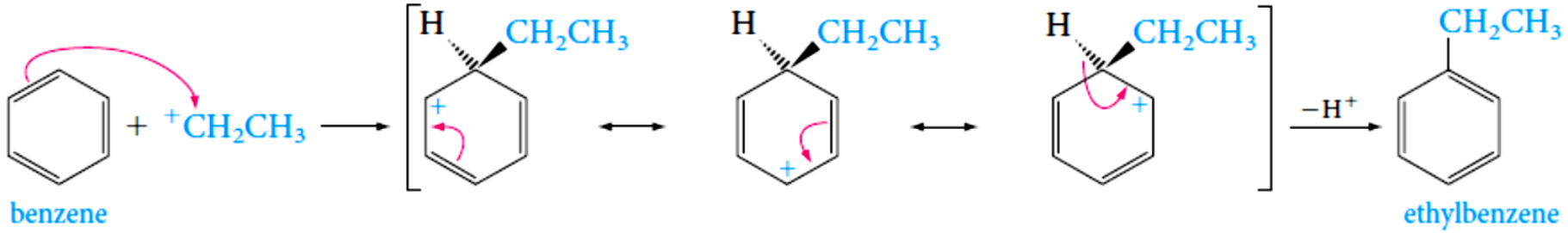
Electrophilic Aromatic Substitution Reactions

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, $AlCl_3$) .



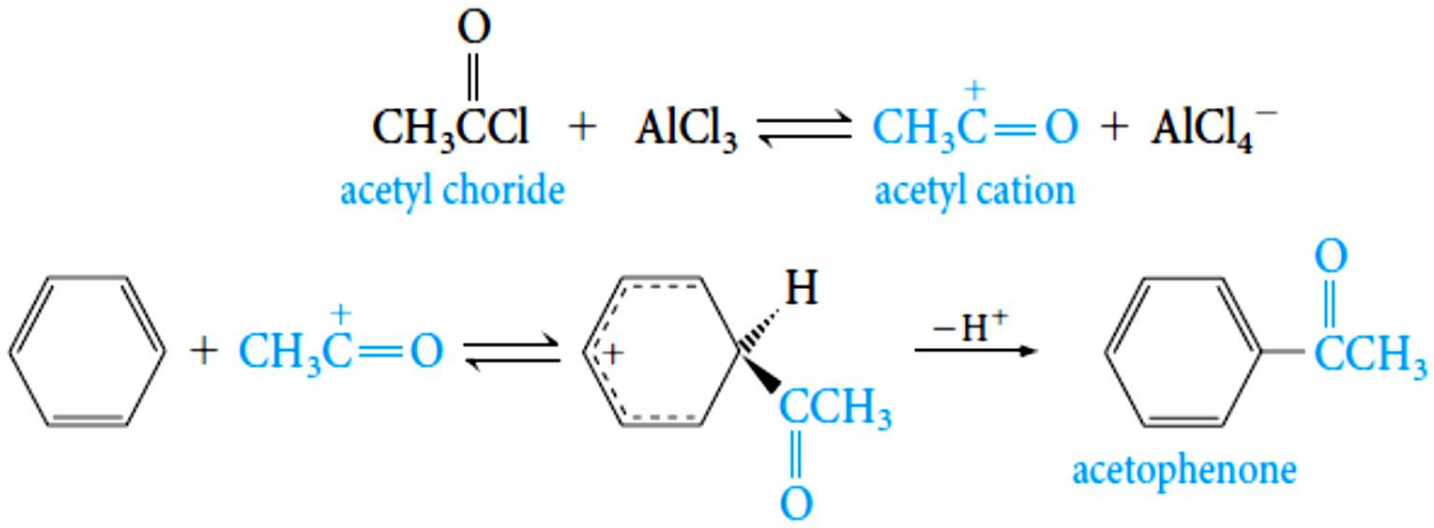


Electrophilic Aromatic Substitution Reactions

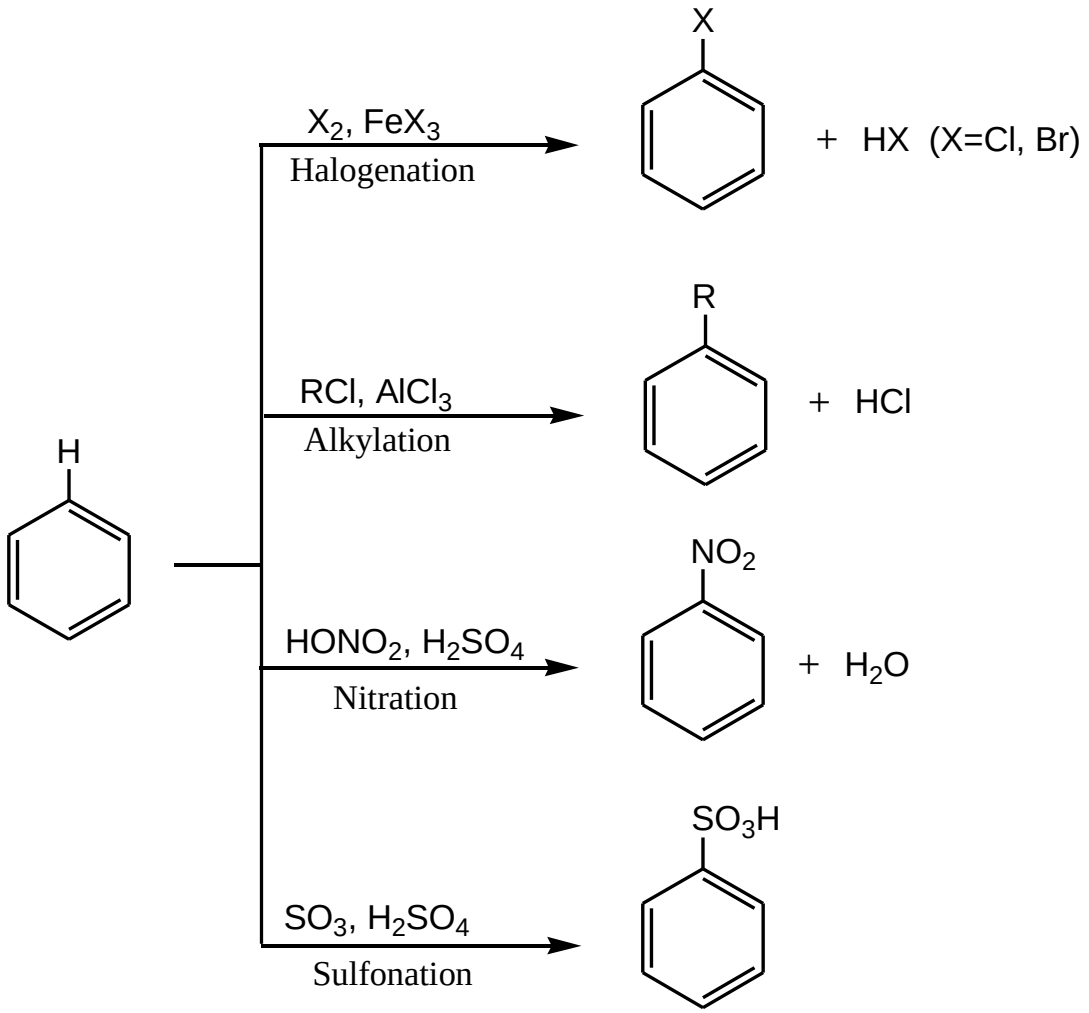
The Mechanism of Electrophilic Aromatic Substitution

➢ 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.

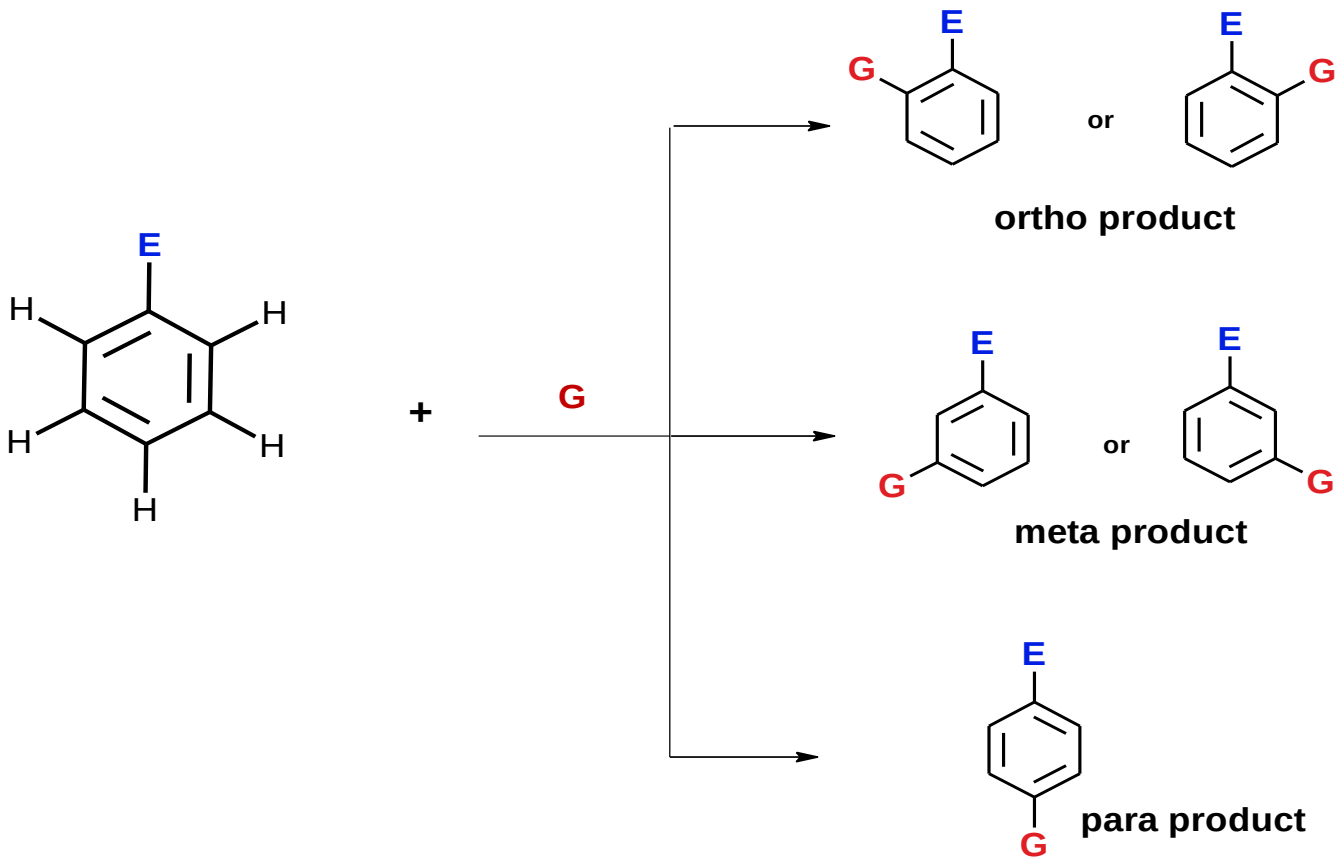


Electrophilic Aromatic Substitution Reactions



Disubstituted Benzenes: Orientation

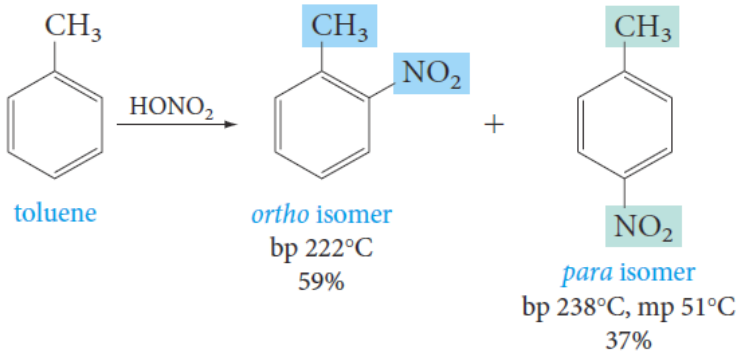
Introduction of a second group, G, into a monosubstituted benzene, $C_6H_5 - E$



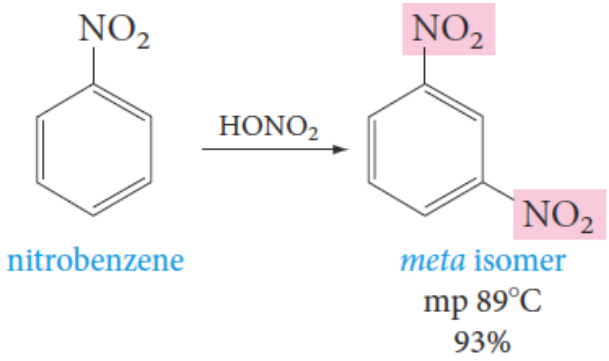
Three possible products for second substitution

Disubstituted Benzenes: Orientation

- 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

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.*

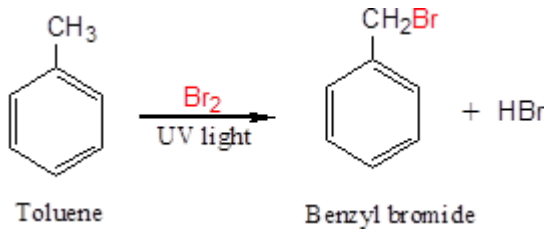
	Substituent group	Name of group	
Ortho,Para-Directing	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	Activating
	$-\ddot{O}H$, $-\ddot{O}CH_3$, $-\ddot{O}R$	hydroxy, alkoxy	
	$-\ddot{N}HC(=O)-R$	acylamino	
	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	
	$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$	halo	Deactivating
Meta-Directing	$-C(=O)-R$ $-C(=O)-\ddot{O}H$	acyl, carboxy	
	$-C(=O)-\ddot{N}H_2$ $-C(=O)-\ddot{O}R$	carboxamido, carboalkoxy	
	$-S(=O)(=O)-\ddot{O}H$	sulfonic acid	
	$-C\equiv N:$	cyano	
	$-N^{+}(=O)\ddot{O}:^{-}$	nitro	

Disubstituted Benzenes: Orientation

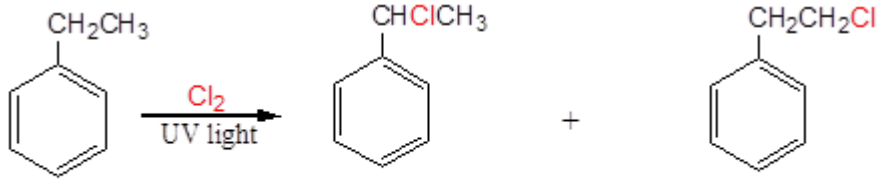
Substituent	Effect on reactivity
o,p- director	
$-NH_2$, $-NHR$, $-NR_2$, -OH,	Very strongly activating
-NHCOR , OR	Strongly activating
$-C_6H_5$, $-CH_3$, -R (Alkyl), CH_2=CHR	Moderately activating
H	**Standard for comparison**
-F, -Cl, -Br, -I	Deactivating
***m*- director**	
$-SO_3H$, -COOH, -COOR	Strongly deactivating
, -CHO, -COR, -CN	
$-NO_2$, $-CF_3$	Very strongly deactivating

Side-Chain Reactions of Benzene-Derivatives

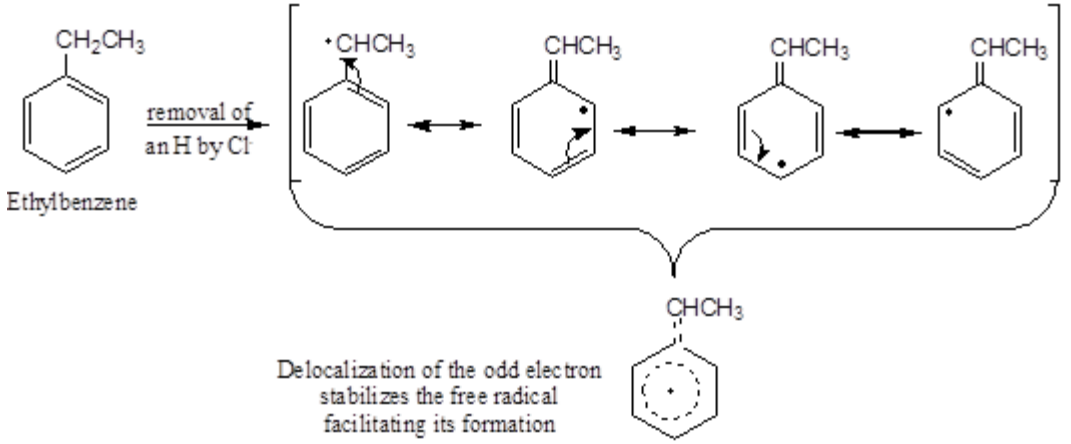
1. Halogenation of an Alkyl Side Chain



Toluene — Benzyl bromide



Ethylbenzene — 1-Chloro-1-phenylethane (major product) + 1-Chloro-2-phenylethane (minor product)



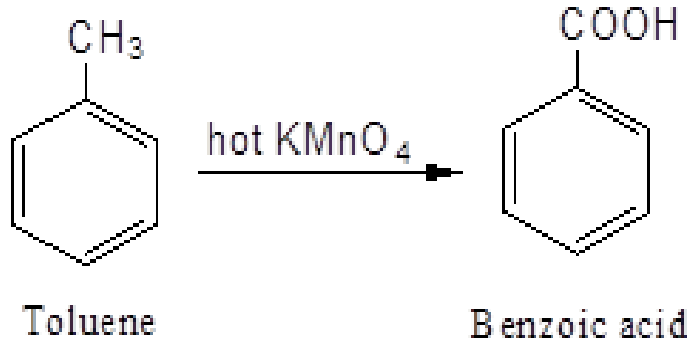
Ethylbenzene

Delocalization of the odd electron stabilizes the free radical facilitating its formation

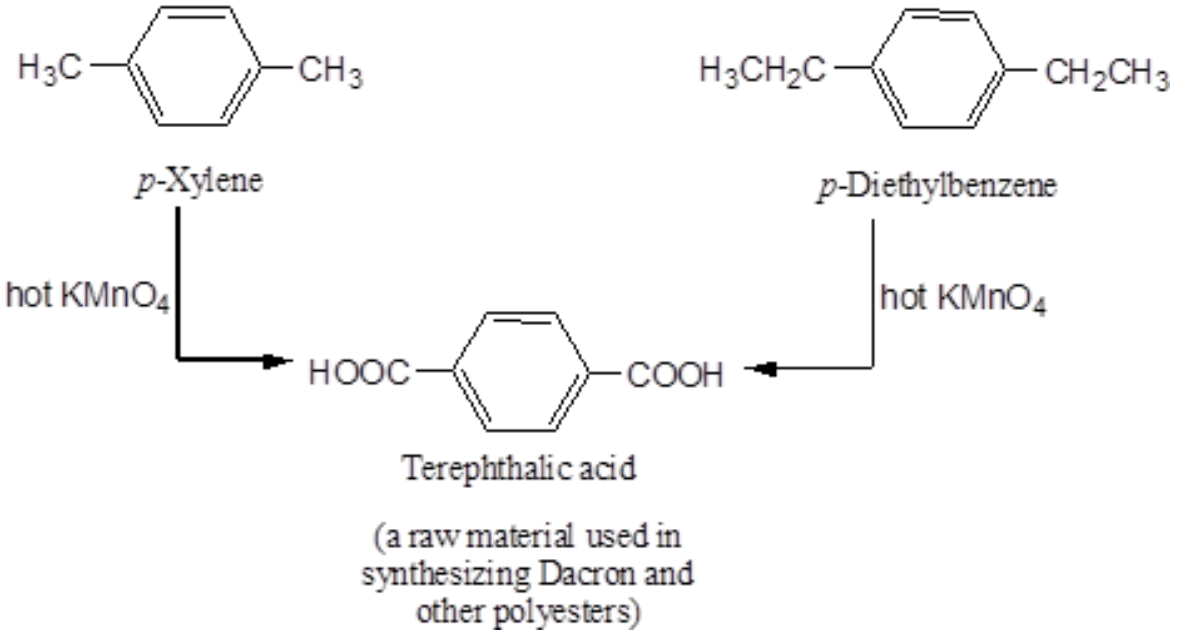
Side-Chain Reactions of Benzene-Derivatives

2. Oxidation of an Alkyl Side Chain

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



Toluene → Benzoic acid



Terephthalic acid

(a raw material used in synthesizing Dacron and other polyesters)