Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

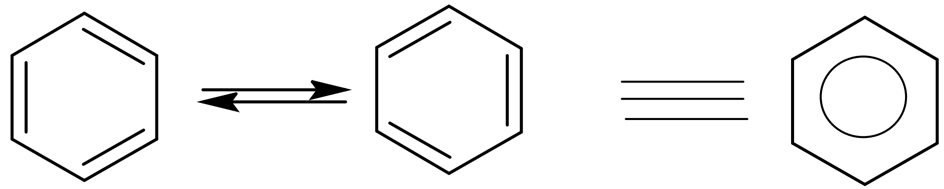
King Saud University

College of Science, Chemistry Department

CHAPTER 3. AROMATIC HYDROCARBONS

Aromatic Hydrocarbons

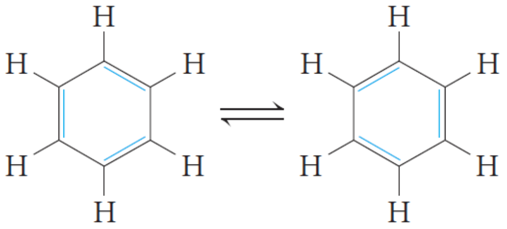
- Originally called **aromatic** due to fragrant odors, although this definition seems inaccurate as many products posses distinctly non-fragrant smells!
- Currently a compound is said to be aromatic if it has ***benzene-like in its properties***.



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

The Structure of Benzene Ring

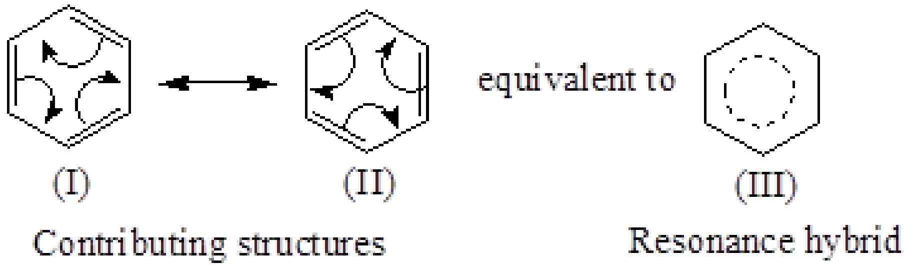
- Molecular formula = C_6H_6
  The carbon-to-hydrogen ratio in benzene, suggests a highly unsaturated structure.
- *Benzene reacts mainly by substitution.*
  It does not undergo the typical addition reactions of alkenes or alkynes.
- **Kekulé Structure for Benzene**
  - *He suggested that*
    - *six 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.*



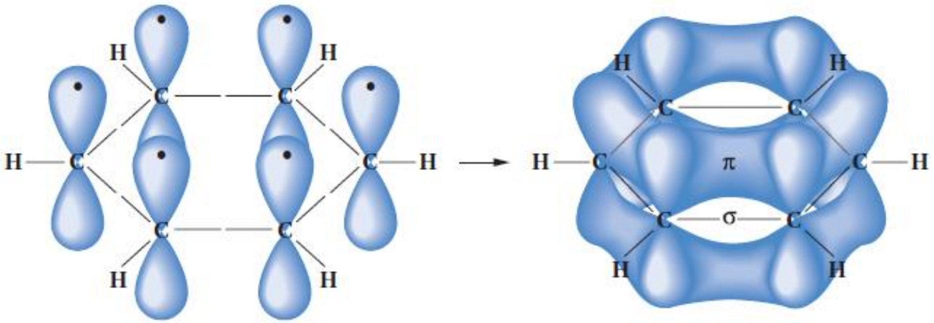
the Kekulé structures for benzene

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:

❶ Cyclic structure

❷ Cyclic structure contains what looks like a continuous system of alternating double and single bonds.

❸ Aromatic compounds must be planar

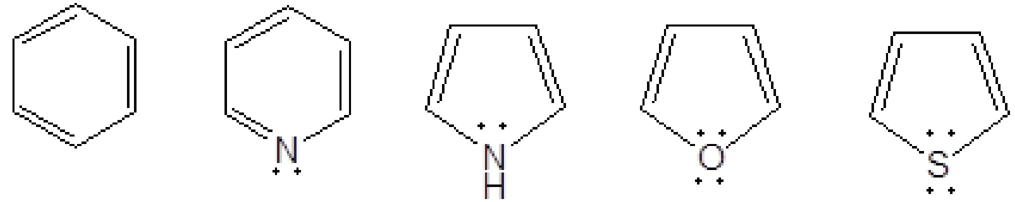
❹ Fulfill Huckel rule

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

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

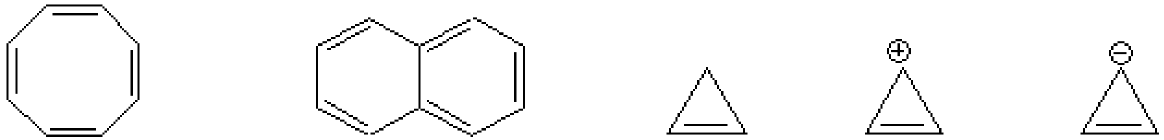
Aromatic Character (Aromaticity)

n	4*n* + 2	Structure and name of aromatic compound
1	6	

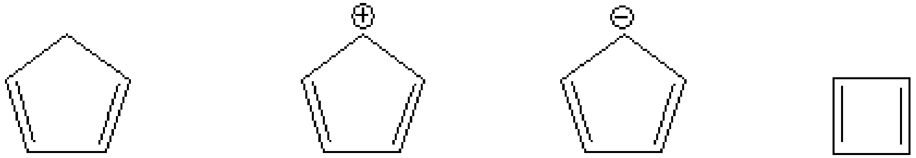


Benzene Pyridine Pyrrole Furan Thiophene

Examples



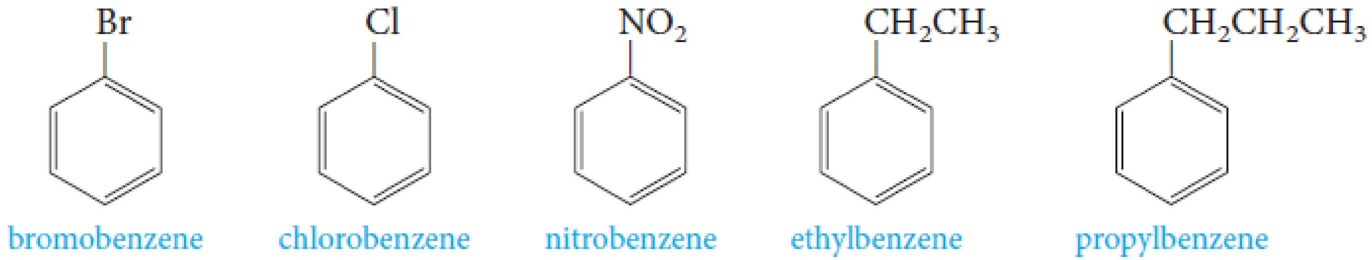
4n+2 =	8	10	2	2	4
n=	1.5	2	0	0	0.5



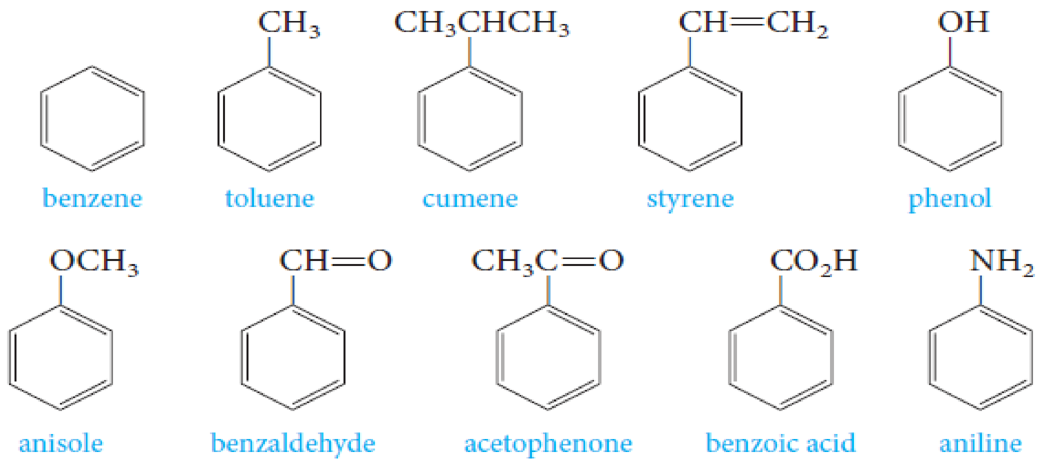
4n+2 =	4	4	6	4
n=	0.5	0.5	1	0.5

Nomenclature of Aromatic Compounds

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

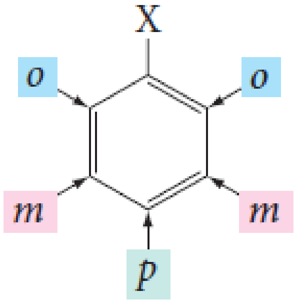


Common names are accepted by IUPAC (parent compounds).

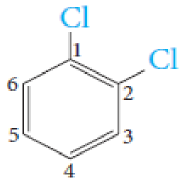


Disubstituted Benzenes

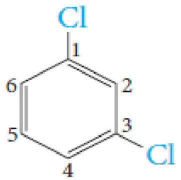
- When **two substituents** are present, *three isomeric structures are possible.*
  - They are designated by the prefixes; ***ortho-* (*o*-), *meta-* (*m*-)** and ***para-* (*p*-).**
  - If substituent X is attached to carbon 1;
    - *o*- groups are on carbons 2 and 6,
    - *m*- groups are on carbons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



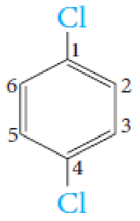
- **Examples;**



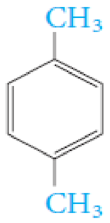
ortho-dichloro-benzene



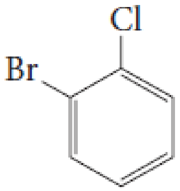
meta-dichloro-benzene



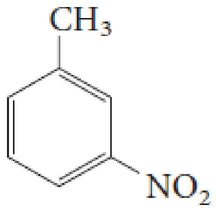
para-dichloro-benzene



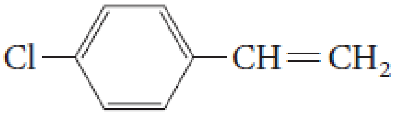
para-xylene*



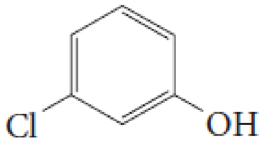
o-bromochlorobenzene (note alphabetical order)



m-nitrotoluene



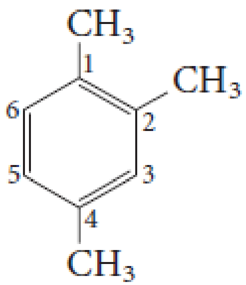
p-chlorostyrene



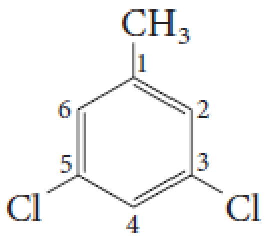
m-chlorophenol

Polysubstituted Benzenes

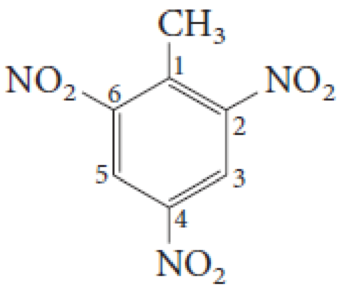
- When **more than two substituents** are present, their positions are designated by numbering the ring.



1,2,4-tri-methylbenzene



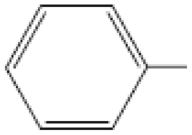
3,5-dichlorotoluene



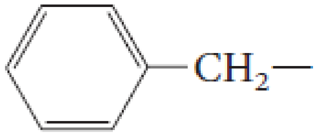
2,4,6-trinitrotoluene (TNT)

Nomenclature of Aromatic Compounds

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

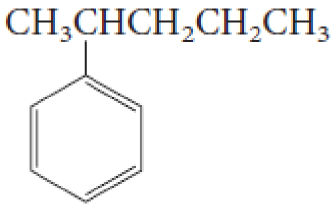
C_6H_5— or 

phenyl group

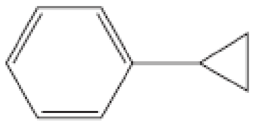
$C_6H_5CH_2$— or 

benzyl group

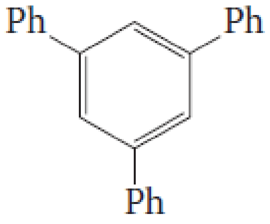
- **Examples;**



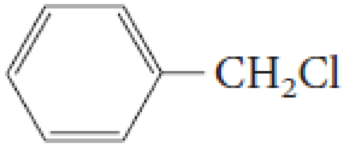
2-phenylpentane
(or 2-pentylbenzene)



phenylcyclopropane
(or cyclopropylbenzene)



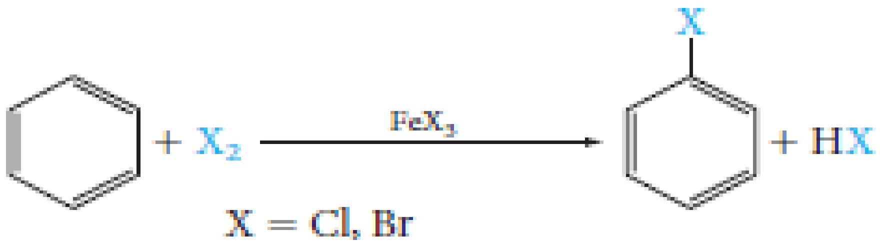
1,3,5-triphenylbenzene



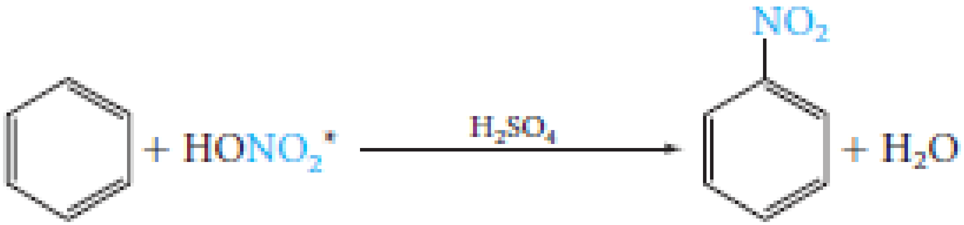
benzyl chloride

Electrophilic Substitution Reactions   Reactions of Benzene

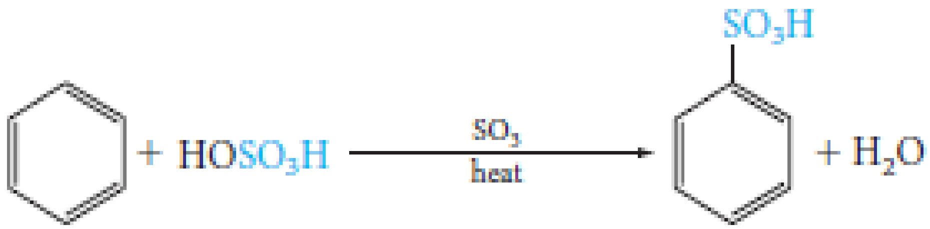
1) Halogenation



2) Nitration

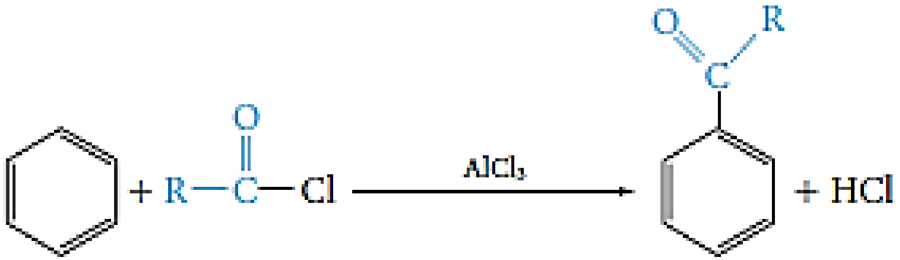


3) Sulfonation



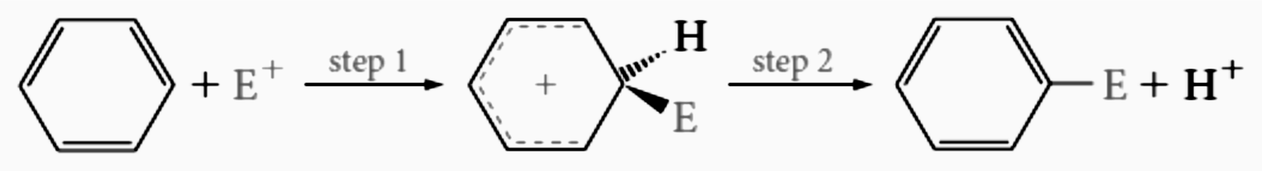
4) Alkylation (Friedel-Crafts)

5) Acylation (Friedel-Crafts)

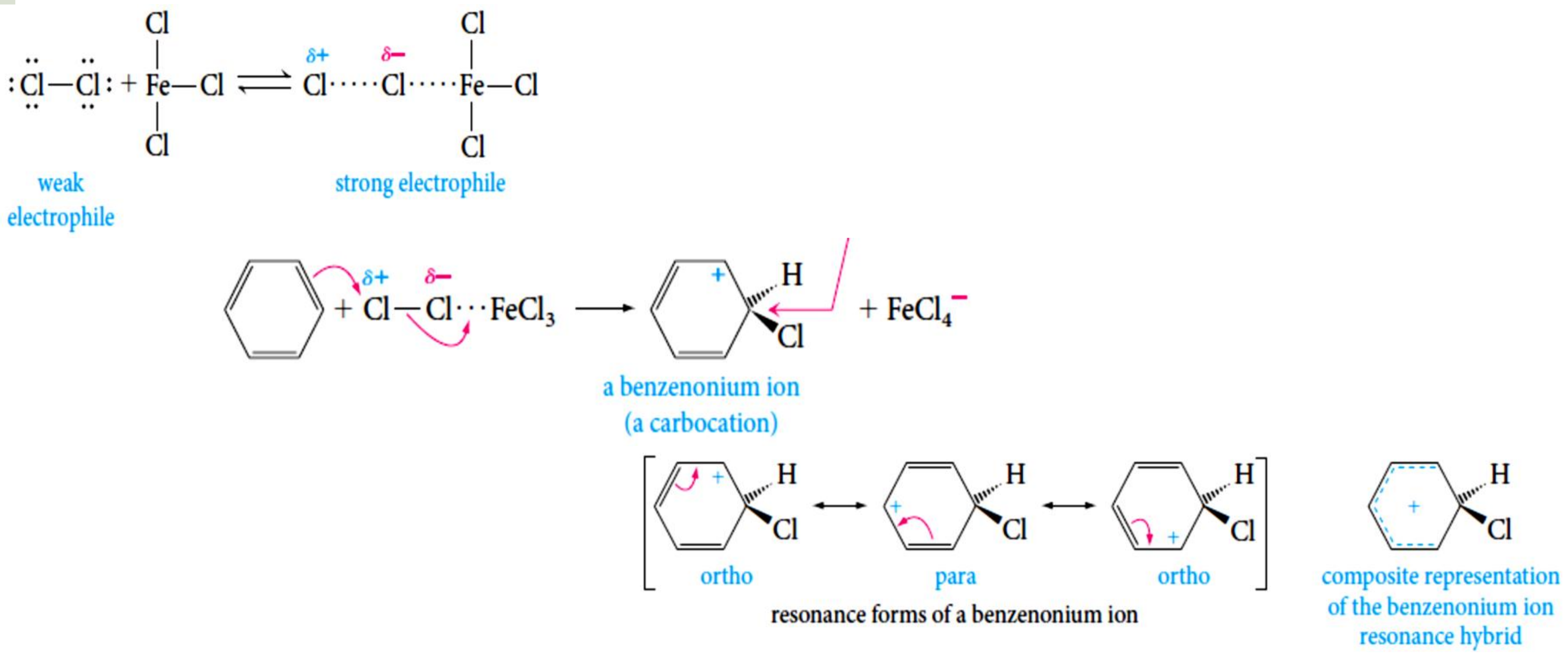


The Mechanism of Electrophilic Substitution Reactions

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



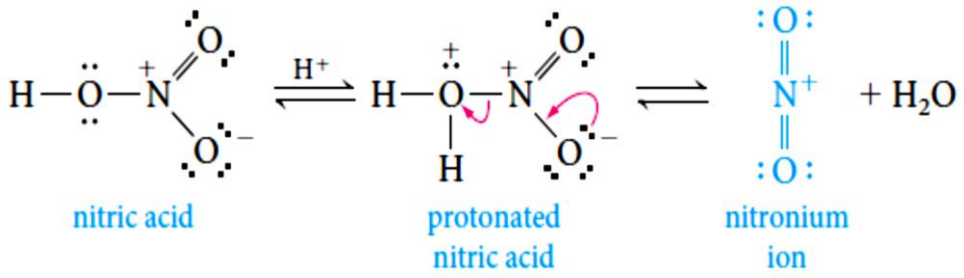
1) Halogenation



The Mechanism of Electrophilic Substitution Reactions

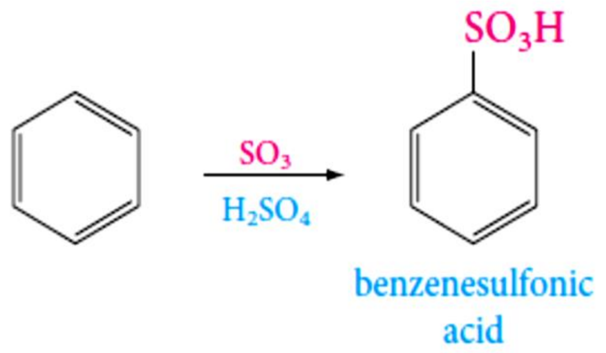
2) Nitration

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

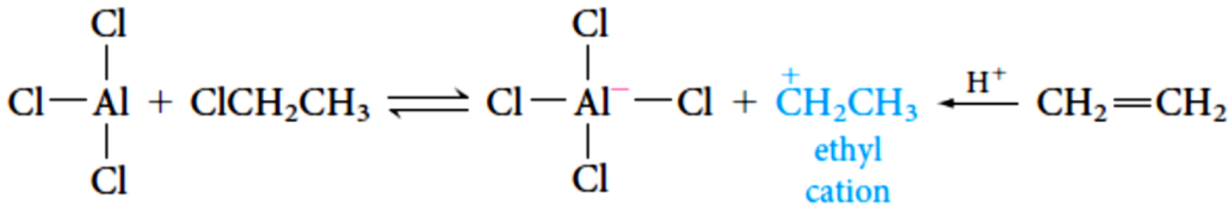
We use either concentrated or fuming sulfuric acid, and the electrophile may be sulfur trioxide, SO_3, or protonated sulfur trioxide, $^+SO_3H$.



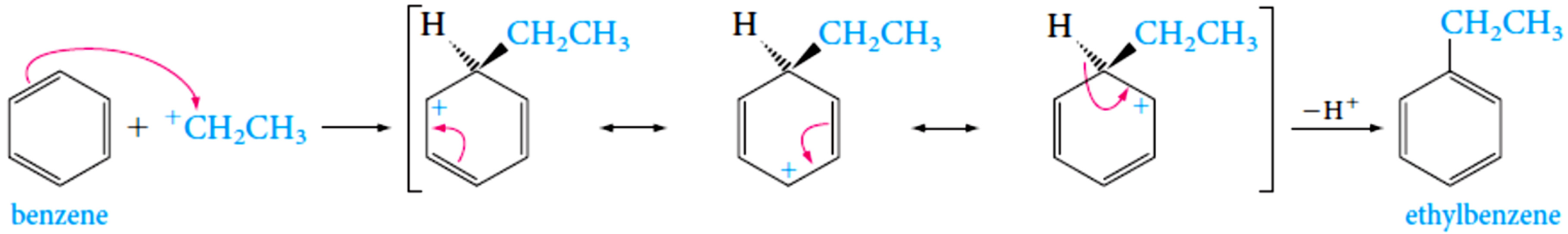
Electrophilic Aromatic Substitution Reactions

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, $AlCl_3$) .

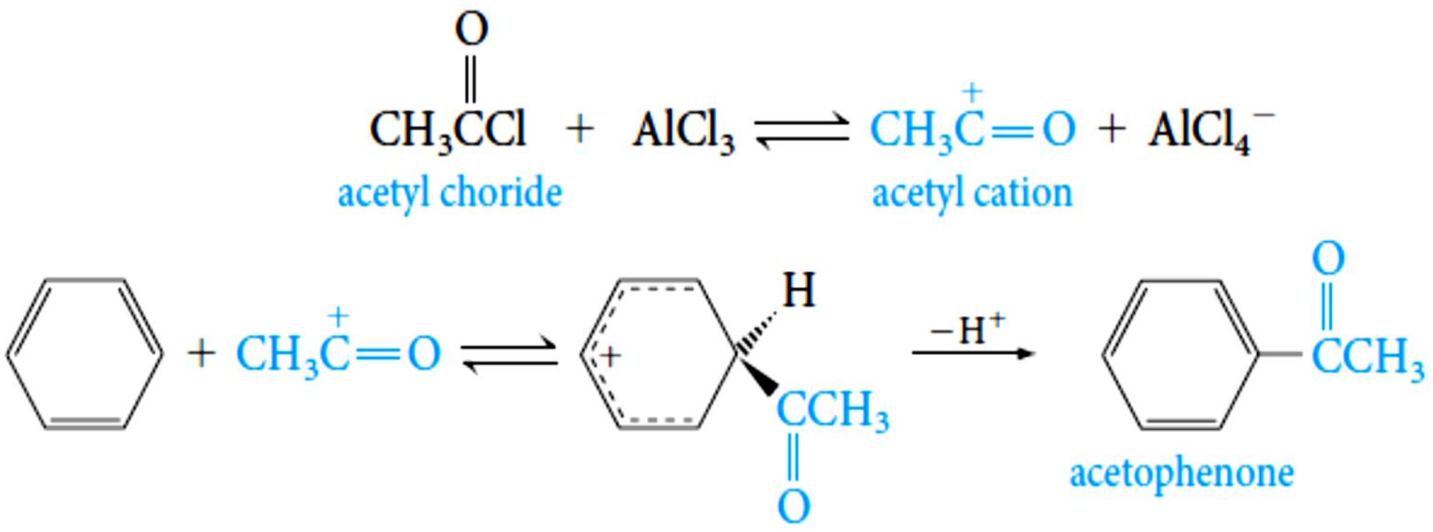


(4.20)



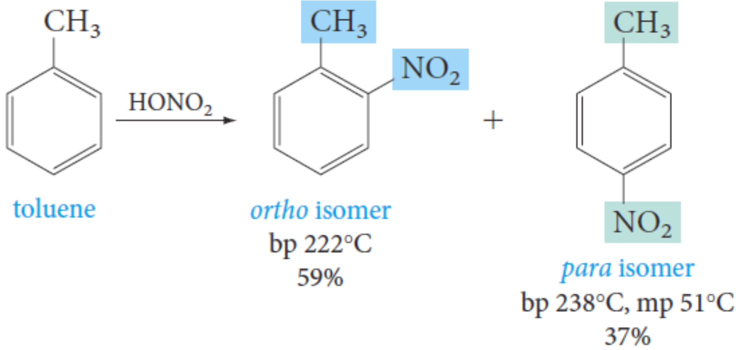
5) Friedel–Crafts Acylation

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.

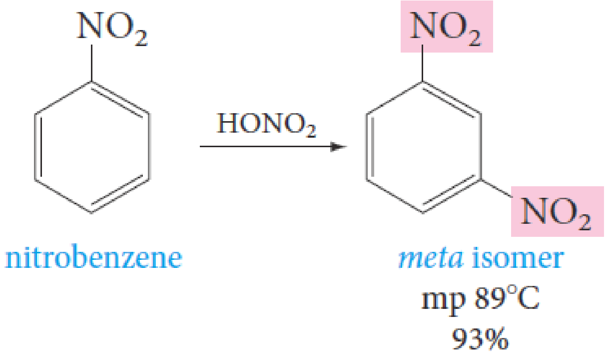


Disubstituted Benzenes: Orientation

- 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

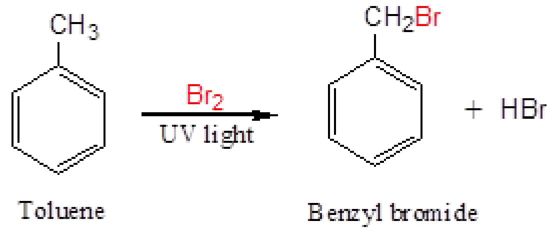
Directing and Activating Effects of Common Functional Groups

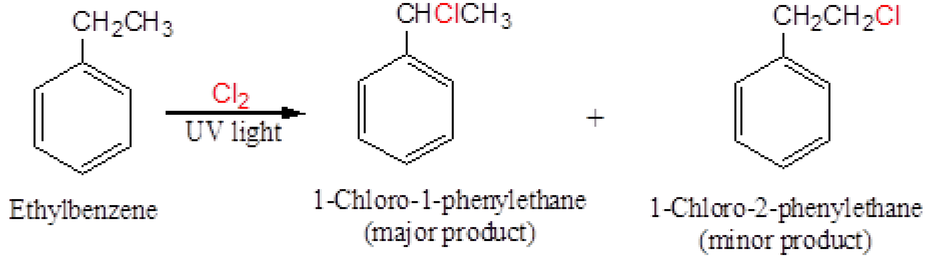
- *Substituents that release electrons to the ring will activate the ring toward electrophilic substitution.*
- *Substituents that withdraw electrons from the ring will deactivate the ring toward electrophilic substitution.*

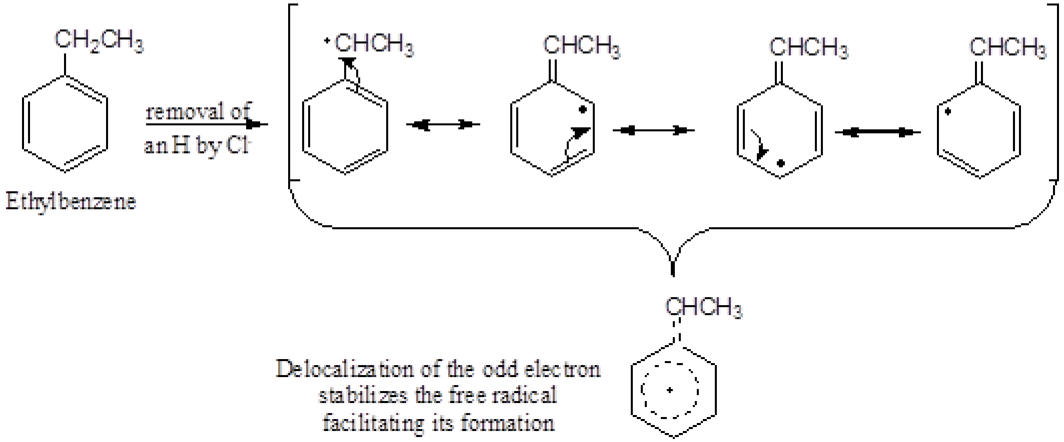
	Substituent group	*Name of group*	
Ortho,Para-Directing	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	Activating
Ortho,Para-Directing	$-\ddot{O}H$, $-\ddot{O}CH_3$, $-\ddot{O}R$	hydroxy, alkoxy	Activating
Ortho,Para-Directing	$-\ddot{N}HC(=O)-R$	acylamino	Activating
Ortho,Para-Directing	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	Activating
Ortho,Para-Directing	$-F:$, $-Cl:$, $-Br:$, $-I:$	halo	Deactivating
Meta-Directing	$-C(=O)-R$, $-C(=O)-\ddot{O}H$	acyl, carboxy	Deactivating
Meta-Directing	$-C(=O)-\ddot{N}H_2$, $-C(=O)-\ddot{O}R$	carboxamido, carboalkoxy	Deactivating
Meta-Directing	$-S(=O)_2-\ddot{O}H$	sulfonic acid	Deactivating
Meta-Directing	$-C\equiv N:$	cyano	Deactivating
Meta-Directing	$-\overset{+}{N}(=O)-O^-$	nitro	Deactivating

Side-Chain Reactions of Benzene-Derivatives

1. Halogenation of an Alkyl Side Chain







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.