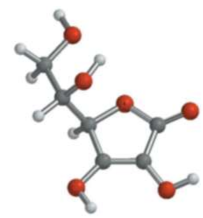
CHEM 240

PRINCIPLES OF ORGANIC CHEMISTRY I

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 2 (2+0)



Prof. Mohamed El-Newehy

Chemistry Department, College of Science, King Saud University

http://fac.ksu.edu.sa/melnewehy/home

CHAPTER 4

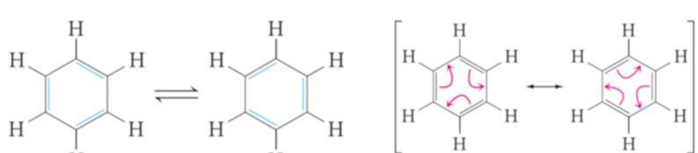
AROMATIC COMPOUNDS

THE STRUCTURE OF BENZENE RING

- *Benzene*, C_6H_6, is the parent hydrocarbon of the especially stable compounds known as aromatic compounds.
- The carbon-to-hydrogen ratio in *benzene*, C_6H_6, suggests a highly unsaturated structure.
- It does not undergo the typical addition reactions of alkenes or alkynes.
- Instead, *benzene reacts mainly by substitution* reactions*.*

THE KEKULÉ STRUCTURE OF 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.
- To give each carbon atom a valence of 4, he suggested that single and double bonds alternate around the ring (what we now call a *conjugated* system of double bonds).
- *All of thebcarbon–carbon bond lengths are identical*: 1.39 Å, intermediate between typical single (1.54 Å) and double (1.34 Å) carbon–carbon bond lengths.



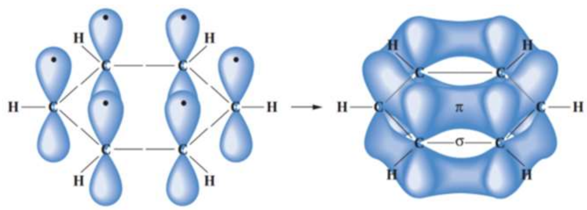
the Kekulé structures for benzene

Benzene is a resonance hybrid of these two contributing structures.

THE STRUCTURE OF BENZENE RING

ORBITAL MODEL FOR BENZENE

- Each carbon is therefore sp^2-hybridized,
- It also explains its hexagonal shape, with H – C - C and C – C - C angles of 120°.



An orbital representation of the bonding in benzene. Sigma (s) bonds are formed by the end-on overlap of sp^2 orbitals.
In addition, each carbon contributes one electron to the pi (p) system by lateral overlap of its *p* orbital with the *p* orbitals of its two neighbors.

SYMBOLS FOR BENZENE

- Two symbols are used to represent benzene.
  - One is the Kekulé structure, and
  - The other is a hexagon with an inscribed circle, to represent the idea of a delocalized pi electron cloud.

AROMATIC CHARACTER (ARMATICITY)

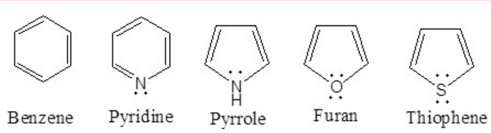
- Aromatic character (Aromaticity) is associated with several structural requirements.

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) Aromaticity is possible only if it obeys Hückel's rule.

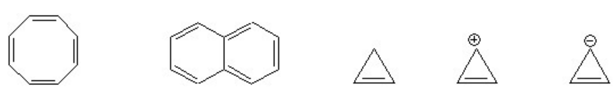
The number of π electrons in the compound = (4n + 2)

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

AROMATIC CHARACTER (ARMATICITY)

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

Examples

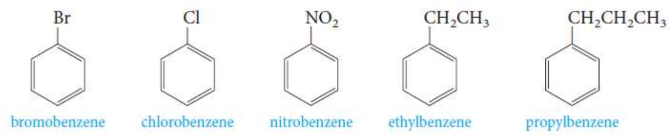


4n+2 =	8	10	2	2	4
n=	1.5	2	0	0	0.5

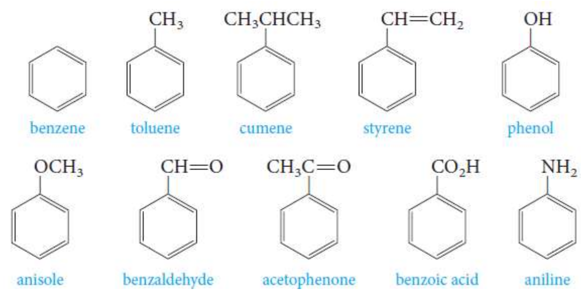
4n+2 =	4	4	6	4
n=	0.5	0.5	1	0.5

NOMENCLATURE OF AROMATIC COMPOUNDS

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

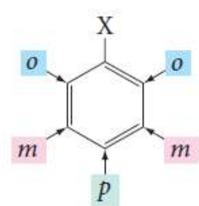


- Monosubstituted benzenes that have common names are accepted by IUPAC (parent compounds).



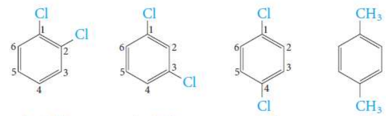
NOMENCLATURE OF AROMATIC COMPOUNDS

- 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.



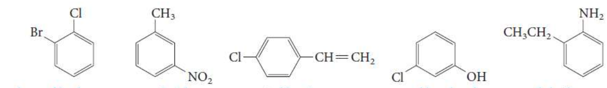
NOMENCLATURE OF AROMATIC COMPOUNDS

- Examples;



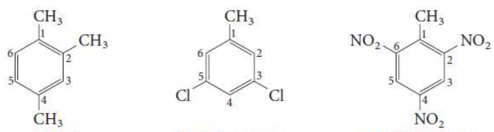
ortho-dichlorobenzene, *meta*-dichlorobenzene, *para*-dichlorobenzene, *para*-xylene*

- 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

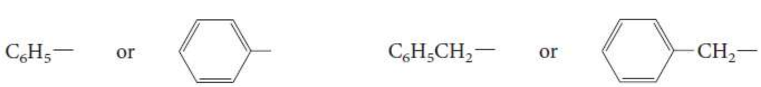
- When more than two substituents are present, their positions are designated by numbering the ring.



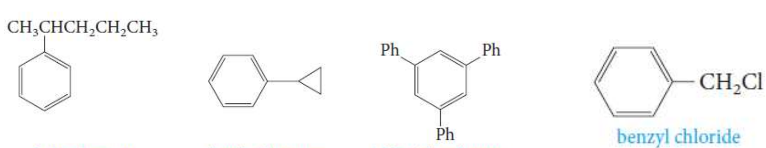
1,2,4-trimethylbenzene, 3,5-dichlorotoluene, 2,4,6-trinitrotoluene (TNT)

NOMENCLATURE OF AROMATIC COMPOUNDS

- Aromatic hydrocarbons, as a class, are called arenes.
- The symbol Ar is used for an aryl group, (symbol R is used for an alkyl group).
- Therefore, the formula Ar - R would represent any arylalkane.
- Two groups with special names occur frequently in aromatic compounds; the phenyl group and the benzyl group.



phenyl group, benzyl group

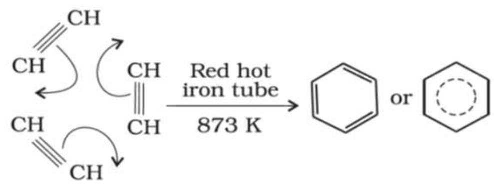


2-phenylpentane (or 2-pentylbenzene), phenylcyclopropane (or cyclopropylbenzene), 1,3,5-triphenylbenzene, benzyl chloride

PREPARATION OF BENZENE

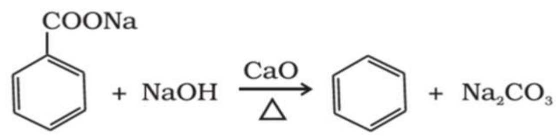
- Benzene may be prepared in the laboratory by the following methods.

1) Cyclic polymerisation of ethyne:



2) Decarboxylation of aromatic acids:

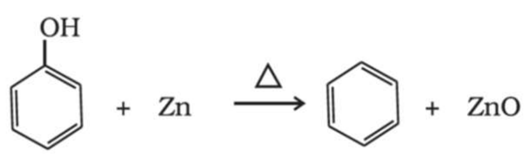
- Sodium salt of benzoic acid on heating with sodalime gives benzene.



PREPARATION OF BENZENE

3) Reduction of phenol:

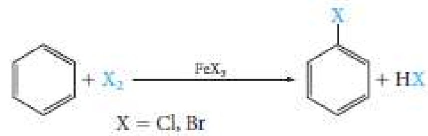
- Phenol is reduced to benzene by passing its vapors over heated zinc dust.



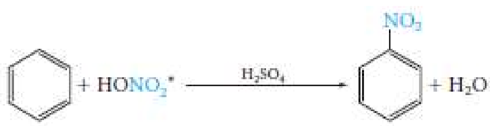
REACTIONS OF BENZENE

A) ELECTROPHILIC AROMATIC SUBSTITUTION

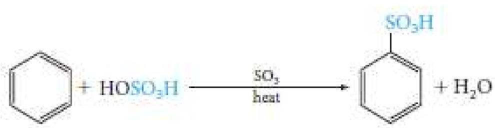
1) Halogenation



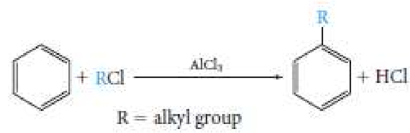
2) Nitration



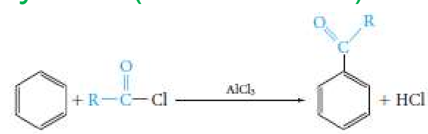
3) Sulfonation



4) Alkylation (Friedel-Crafts)



5) Acylation (Friedel-Crafts)

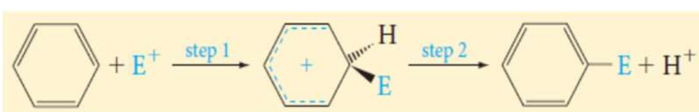


REACTIONS OF BENZENE

A) ELECTROPHILIC AROMATIC SUBSTITUTION

The Mechanism of Electrophilic Aromatic Substitution

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

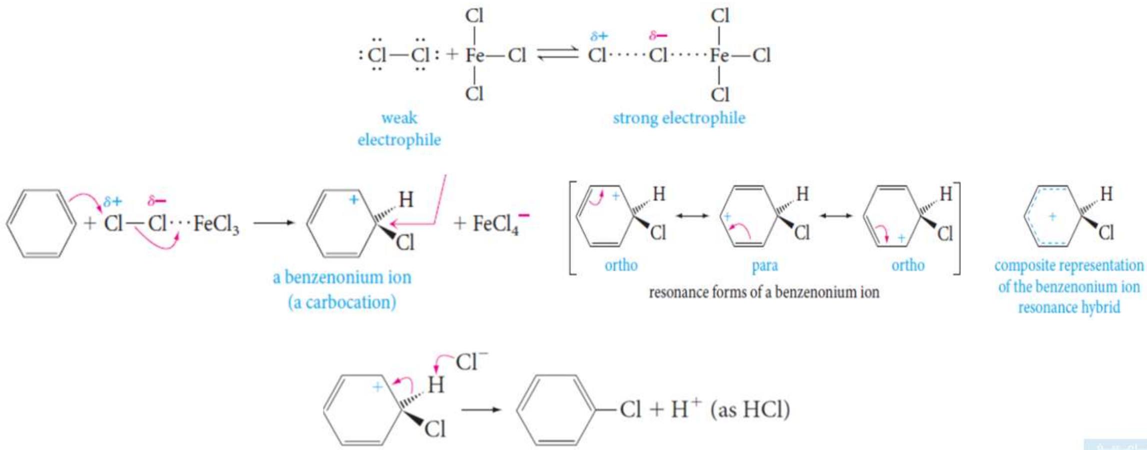


REACTIONS OF BENZENE

A) ELECTROPHILIC AROMATIC SUBSTITUTION

The Mechanism of Electrophilic Aromatic Substitution

1) Halogenation



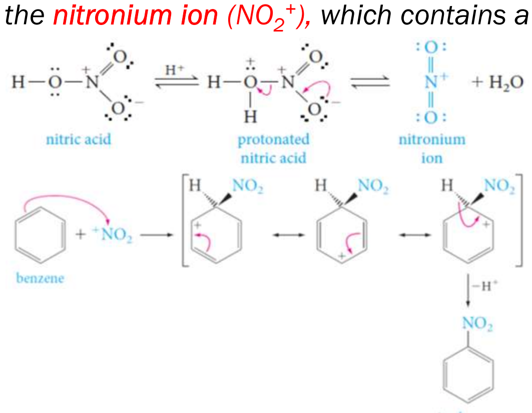
REACTIONS OF BENZENE

A) ELECTROPHILIC AROMATIC SUBSTITUTION

The Mechanism of Electrophilic Aromatic Substitution

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.



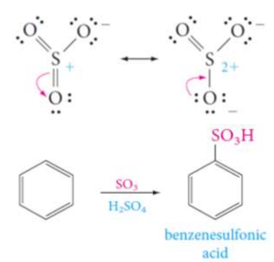
A) ELECTROPHILIC AROMATIC SUBSTITUTION

The Mechanism of Electrophilic Aromatic Substitution

3) Sulfonation

- *We use either concentrated or fuming sulfuric acid, and the electrophile may be sulfur trioxide, SO_3, or protonated sulfur trioxide, $^{+}SO_3H$.*
- *Sulfuric acid provides catalyst as following:*

$$H{-}OSO_3H \rightleftharpoons H^+ + {}^-OSO_3H.$$

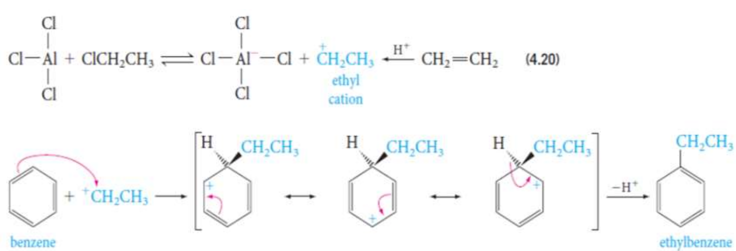


A) ELECTROPHILIC AROMATIC SUBSTITUTION

The Mechanism of Electrophilic Aromatic Substitution

4) Alkylation (Friedel-Crafts)

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, $AlCl_3$) .



REACTIONS OF BENZENE

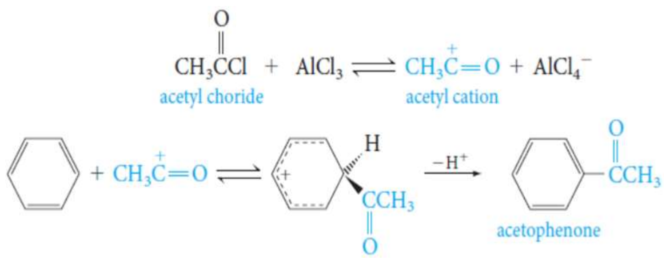
A) ELECTROPHILIC AROMATIC SUBSTITUTION

The Mechanism of Electrophilic Aromatic Substitution

5) Acylation (Friedel-Crafts)

The electrophile is an acyl cation generated from an acid derivative, usually an acyl halide.

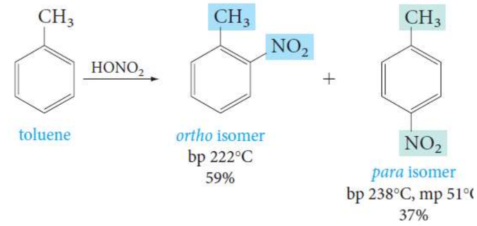
The reaction provides a useful general route to aromatic ketones.



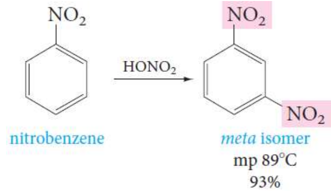
DISUBSTITUTED BENZENES: ORIENTATION

Substituents present on an aromatic ring determine the position taken by a new substituent.

- 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

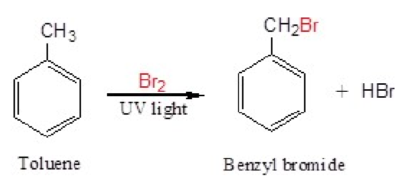
Directing and Activating Effects of Common Functional Groups

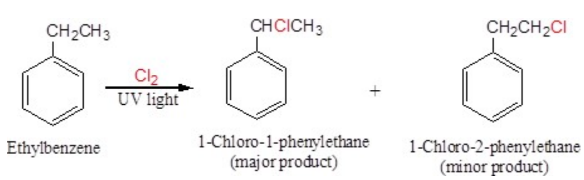
	Substituent group	Name of group	
Ortho,Para-Directing	$-NH_2$, $-NHR$, $-NR_2$	amino	Activating
Ortho,Para-Directing	$-OH$, $-OCH_3$, $-OR$	hydroxy, alkoxy	Activating
Ortho,Para-Directing	$-NHC(=O)-R$	acylamino	Activating
Ortho,Para-Directing	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	Activating
Ortho,Para-Directing	$-F$, $-Cl$, $-Br$, $-I$	halo	Deactivating
Meta-Directing	$-C(=O)-R$, $-C(=O)-OH$	acyl, carboxy	Deactivating
Meta-Directing	$-C(=O)-NH_2$, $-C(=O)-OR$	carboxamido, carboalkoxy	Deactivating
Meta-Directing	$-S(=O)_2-OH$	sulfonic acid	Deactivating
Meta-Directing	$-C\equiv N$	cyano	Deactivating
Meta-Directing	$-N^+(=O)-O^-$	nitro	Deactivating

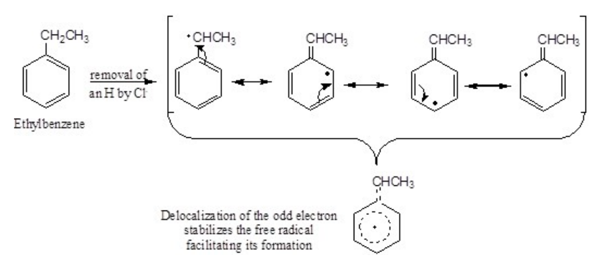
- *Substituents that release electrons to the ring will activate the ring toward electrophilic substitution.*
- *Substituents that withdraw electrons from the ring will deactivate the ring toward electrophilic substitution.*

SIDE-CHAIN REACTIONS OF BENZENE-DERIVATIVES

1. Halogenation of an Alkyl Side Chain



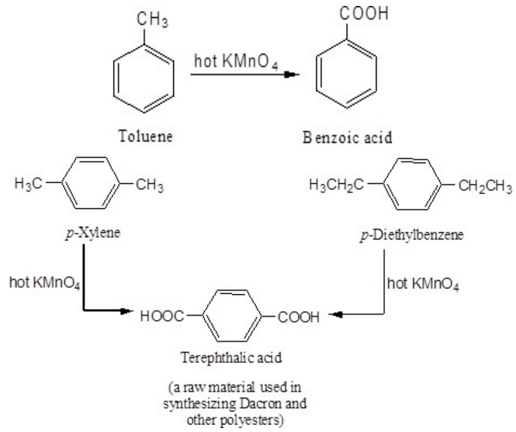




SIDE-CHAIN REACTIONS OF BENZENE-DERIVATIVES

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.



GENERAL QUESTIONS

PROBLEM 4.7 Draw the structure of

a. *o*-dinitrobenzene
b. *m*-nitrotoluene
c. *p*-bromophenol
d. 4-chloroaniline
e. *p*-vinylbenzaldehyde
f. 1,4-dichlorobenzene
g. 1,3,5-trimethylphenol
h. 4-ethyl-2,6-difluorotoluene

EXAMPLE 4.2

Write out the steps in the mechanism for the nitration of benzene.

PROBLEM 4.12 Write out the steps in the mechanism for the sulfonation of benzene.