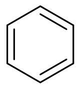
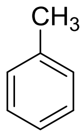
Aromatic compounds

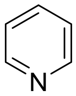
Aromatic compounds

Aromatic compounds, also known as arenes or aromatics, are chemical compounds that contain conjugated planar ring systems with delocalized π-electrons clouds instead of discrete alternating single and double bonds. Typical aromatic compounds are benzene and toluene. They should satisfy Hückel's rule.

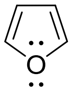

benzene



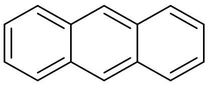
toluene

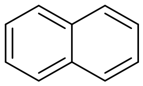


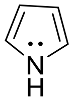
pyridine



furan


anthracene


naphthalene

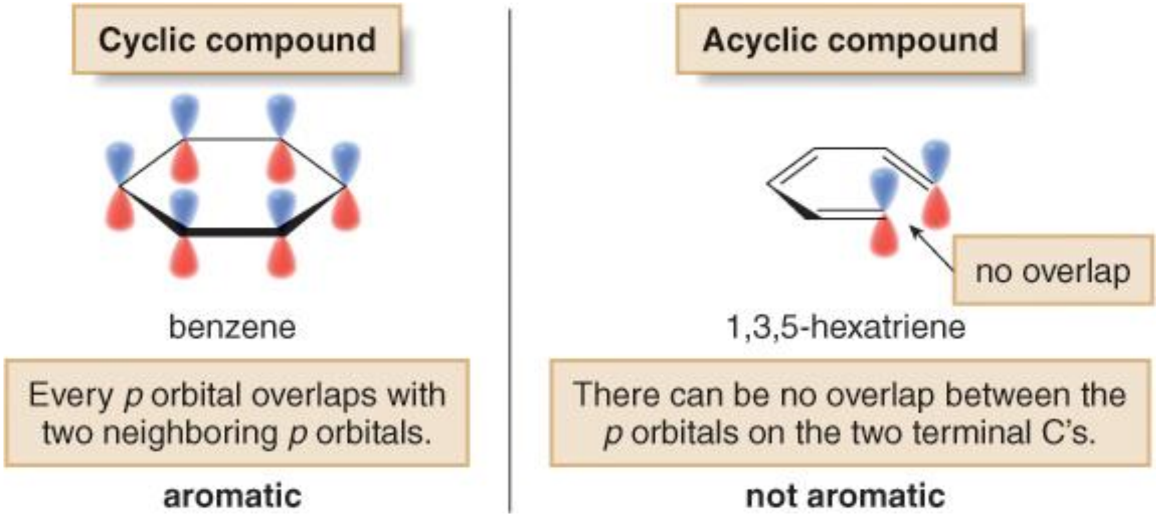


pyrrole

The Criteria for Aromaticity — Hückel's Rule

Four structural criteria must be satisfied for a compound to be aromatic.

1-Amolecule must be cyclic.



Every *p* orbital overlaps with two neighboring *p* orbitals.

There can be no overlap between the *p* orbitals on the two terminal C's.

To be aromatic, each p orbital must overlap with p orbitals on adjacent atoms.

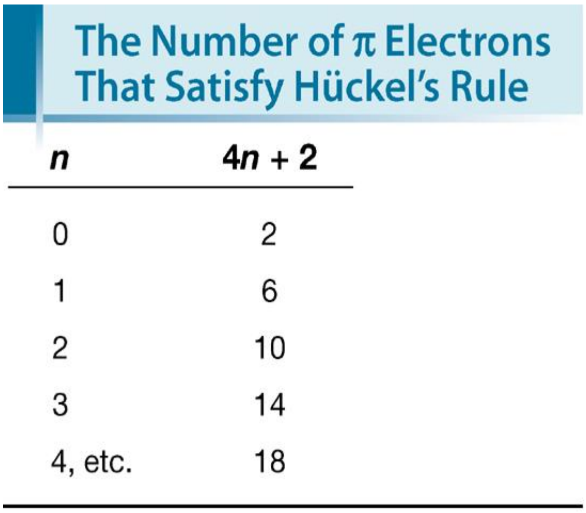
2-Amolecule must be planar (all atoms in the molecule lie in the same plane)

3- Amolecule must be completely conjugated .

4- The molecule has 4n+2π electrons (Hückel's rule)

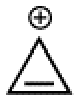
Hückel’s rule

A cyclic ring molecule follows Hückel's rule when the number of its π-electrons equals 4*n*+2 where *n* is zero or any positive integer , The most common case in six π electrons (n=1) which is found for example in benzene ,pyrrole ,furan ,and pyridine .



The Number of π Electrons That Satisfy Hückel’s Rule

n	4*n* + 2
0	2
1	6
2	10
3	14
4, etc.	18

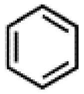


2 π electrons

Aromatic

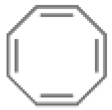
4 π electrons

Not Aromatic



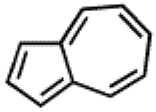
6 π electrons

Aromatic



8 π electrons

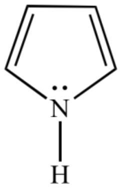
Not Aromatic



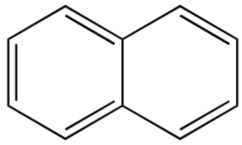
10 π electrons

Aromatic

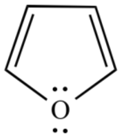
Aromatic Molecules



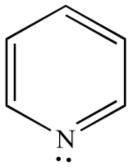
Pyrrole
6π electrons
n = 1



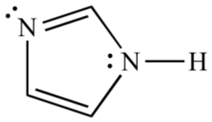
Naphthalene
10 πelectrons
n = 2



Furan
6 πelectrons
n = 1

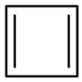


Pyridine
6 π electrons
n = 1

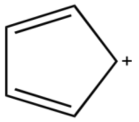


Imidazole
6 π electrons
n = 1

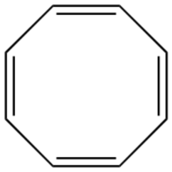
Non aromatic Molecules



Cyclobutadiene
4 π electrons



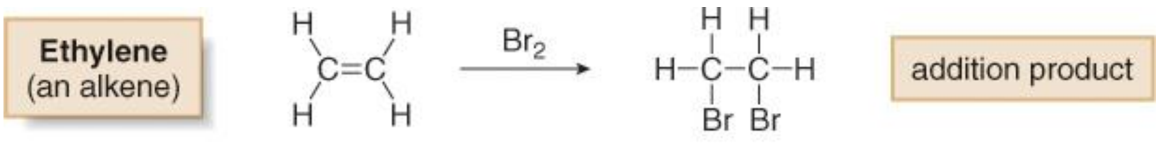
Cyclopentadienyl cation
4 πelectrons



Cyclooctatetraene
8 π electrons

Benzene

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not.



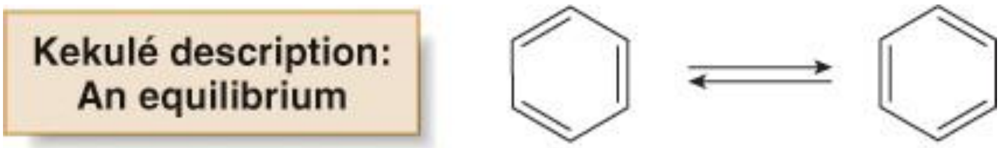
Benzene (an arene) $C_6H_6 \xrightarrow{Br_2}$ **No reaction**

- Benzene does react with bromine, but only in the presence of $FeBr_3$ (Lewis acid), and the reaction is a substitution, not an addition.

$$C_6H_6 \xrightarrow[FeBr_3]{Br_2} C_6H_5Br$$

substitution
Br replaces H

- Proposed structures of benzene must account for its high degree of unsaturation and its lack of reactivity towards electrophilic addition.
- August Kekulé proposed that benzene was a rapidly equilibrating mixture of two compounds, each containing a six-membered ring with three alternating π bonds.
- In the Kekulé description, the bond between any two carbon atoms is sometimes a single bond and sometimes a double bond.
- These structures are known as Kekulé structures.

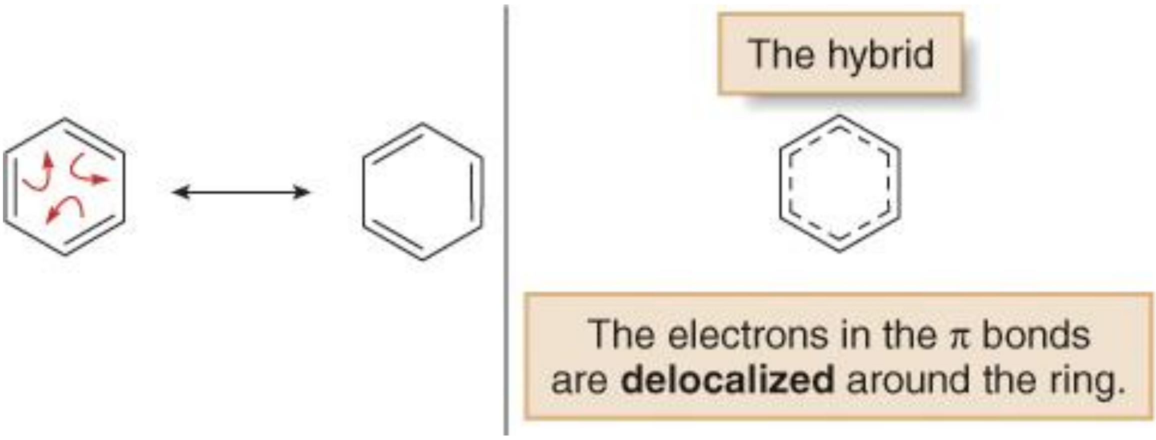


- Although benzene is still drawn as a six-membered ring with alternating π bonds, in reality there is no equilibrium between the two different kinds of benzene molecules.
- Current descriptions of benzene are based on resonance and electron delocalization due to orbital overlap.
- In the nineteenth century, many other compounds having properties similar to those of benzene were isolated from natural sources. Since these compounds possessed strong and characteristic odors, they were called aromatic compounds. It should be noted, however, that it is their chemical properties, and not their odor, that make them special.

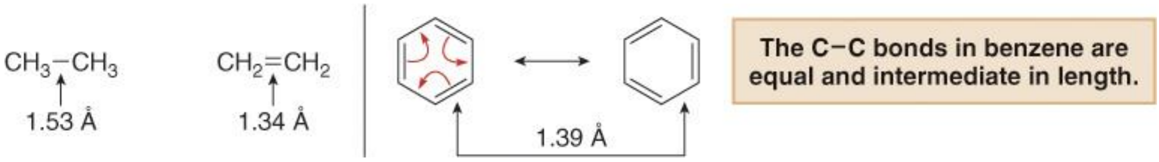
Any structure for benzene must account for the following facts:

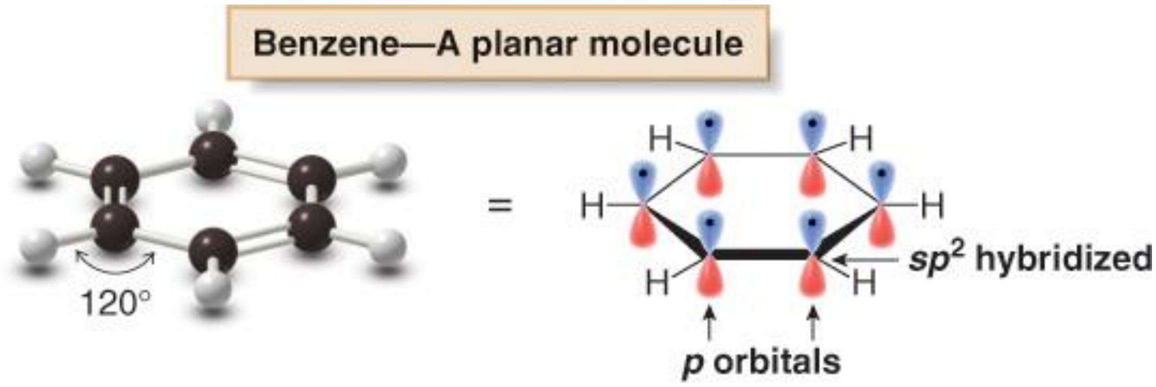
1. It contains a six-membered ring and three additional degrees of unsaturation.
2. It is planar.
3. All C—C bond lengths are equal.

- The resonance description of benzene consists of two equivalent Lewis structures, each with three double bonds that alternate with three single bonds.
- The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds.
- We will use one of the two Lewis structures and not the hybrid in drawing benzene. This will make it easier to keep track of the electron pairs in the π bonds (the π electrons).



- In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon single bond (1.53 Å) and the carbon—carbon double bond (1.34 Å).

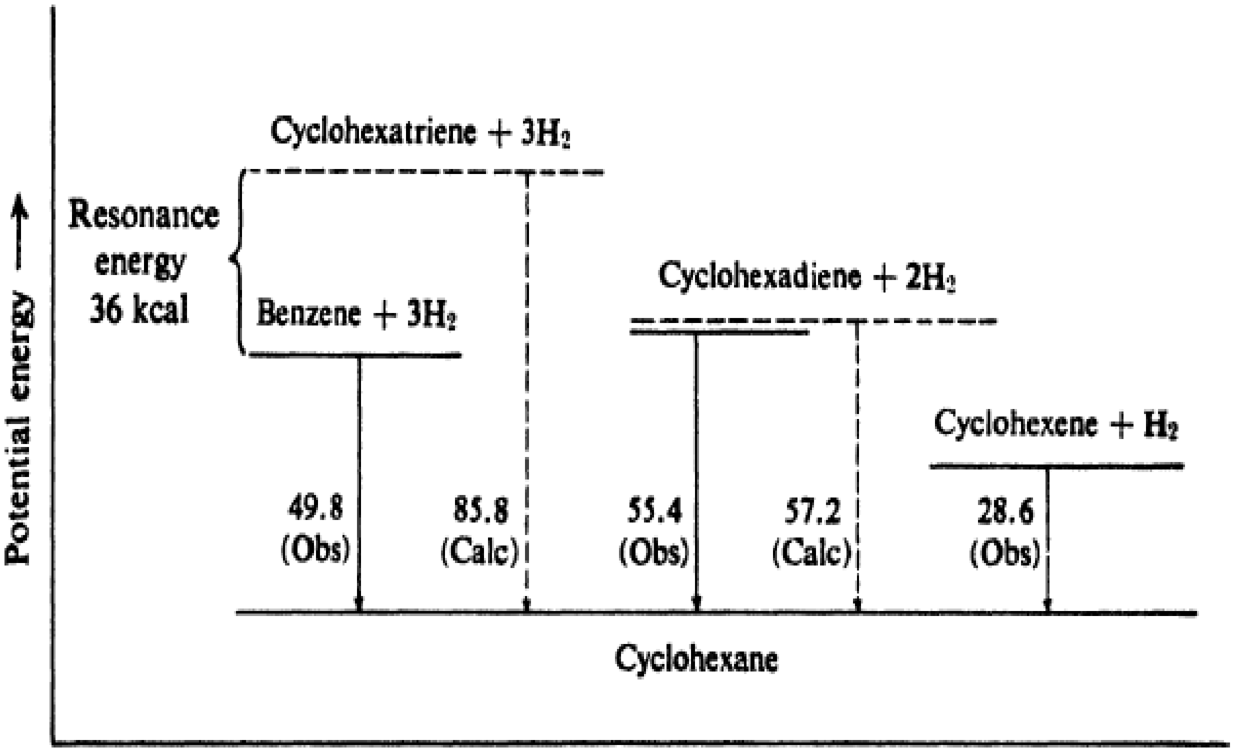




Stability of the benzene ring. Heats of hydrogenation and combustion:

Heats of hydrogenation and combustion of benzene are lower than expected,

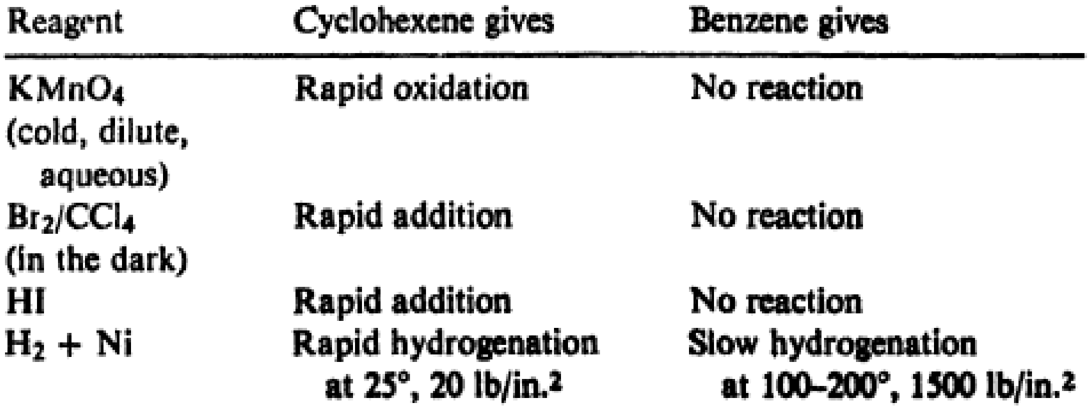
Heat of hydrogenation is the quantity of heat evolved when one mole of an unsaturated compound is hydrogenated. In most cases the value is about 28-30 kcal for each double bond the compound contains. It is not surprising, then, that cyclohexene has a heat of hydrogenation of 28.6 kcal and cyclohexadiene has one about twice that (55.4 kcal.)We might reasonably expect cyclohexatriene to have a heat of hydrogenation about three times as large as cyclohexene, that is, about 85.8 kcal. Actually, the value for benzene (49.8 kcal) is 36 kcal less than this expected amount. This can be more easily visualized, perhaps, by means of an energy diagram, in which the height of a horizontal line represents the potential energy content of a molecule. The broken lines represent the expected values, based upon three equal steps of 28.6 kcal. The final product, cyclohexane, is the same in all three cases.



The fact that benzene evolves 36 kcal less energy than predicted can only mean that benzene contains 36 kcal less energy than predicted; in other words, benzene is more stable by 36 kcal than we would have expected cyclohexatriene to be. The heat of combustion of benzene is also lower than that expected, and by about the same amount.

Reactions of benzene

Benzene undergoes substitution rather than addition. Kekule's structure of benzene is one that we would call "cyclohexatriene." We would expect this cyclohexatriene, like the very similar compounds, cyclohexadiene and cyclohexene, to undergo readily the addition reactions characteristic of the alkene structure. As the examples in the following table show, this is not the case; under conditions that cause an alkene to undergo rapid addition, benzene reacts either not at all or very slowly.

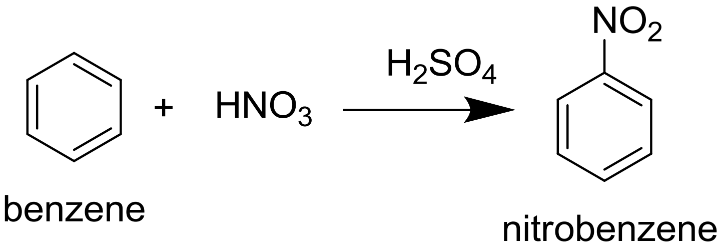


Reagent	Cyclohexene gives	Benzene gives
$KMnO_4$ (cold, dilute, aqueous)	Rapid oxidation	No reaction
Br_2/CCl_4 (in the dark)	Rapid addition	No reaction
HI	Rapid addition	No reaction
H_2 + Ni	Rapid hydrogenation at 25°, 20 lb/in.^{2}	Slow hydrogenation at 100–200°, 1500 lb/in.^{2}

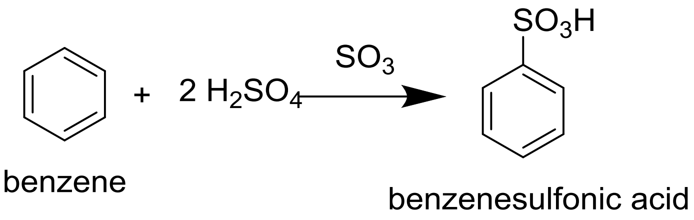
In place of addition reactions, benzene readily undergoes a new set of reactions, all involving substitution. The most important are shown below

<u>Electrophilic Aromatic Substitution</u>

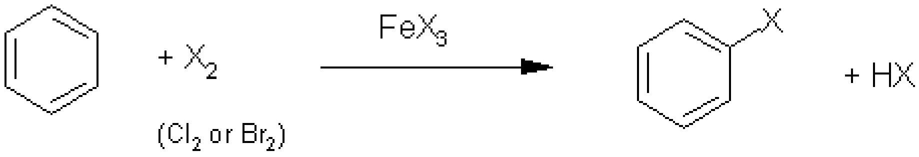
1. Nitration:



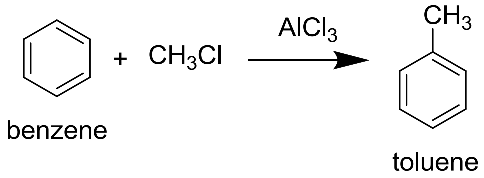
2. Sulfonation:



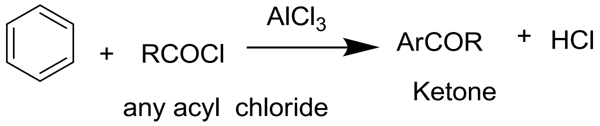
3. Halogenation:

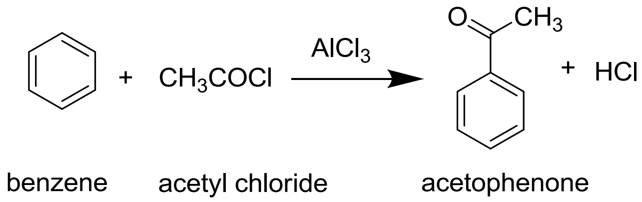


4. Friedel-Crafts alkylation:



5. Friedel-Crafts acylation:

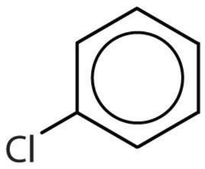




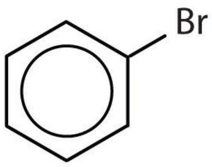
In each of these reactions an atom or group has been substituted for one of the hydrogen atoms of benzene. The product can itself undergo further substitution of the same kind; the fact that it has retained the characteristic properties of benzene indicates that it has retained the characteristic structure of benzene. It would appear that benzene resists addition, in which the benzene ring system would be destroyed, whereas it readily undergoes substitution, in which the ring system is preserved.

Nomenclature of benzene derivatives

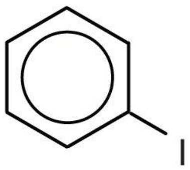
All compounds that contain a benzene ring are aromatic, and substituted derivatives of benzene make up the largest class of aromatic compounds. Many such compounds are named by attaching the name of the substituent as a prefix to benzene.



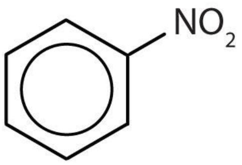
Chlorobenzene



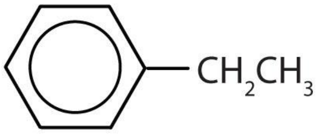
Bromobenzene



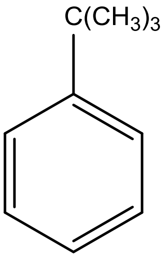
Iodobenzene



Nitrobenzene



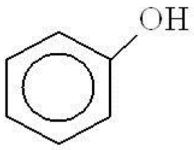
Ethylbenzene



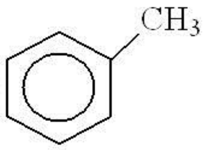
tert-butylbenzene

Many simple monosubstituted derivatives of benzene have common names of long standing that have been retained in the IUPAC system.

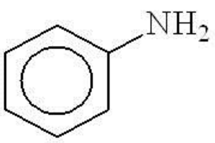
Common Names of Benzene Derivatives



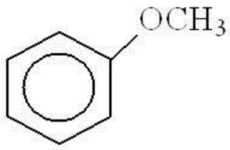
phenol



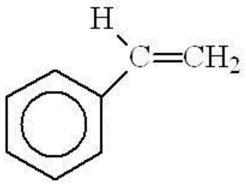
toluene



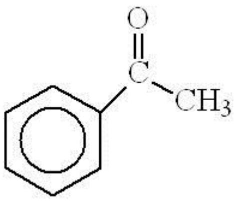
aniline



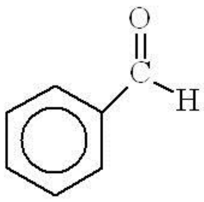
anisole



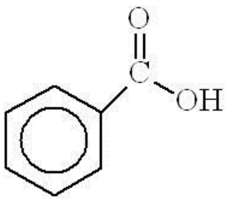
styrene



acetophenone

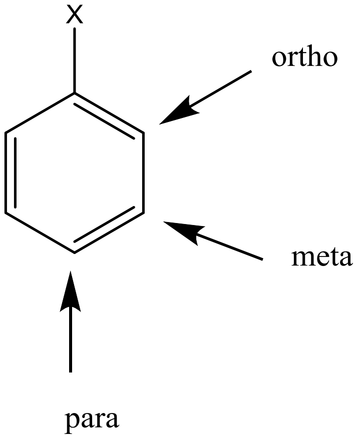


benzaldehyde



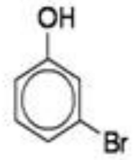
benzoic acid

The prefix ortho signifies a 1,2-disubstituted benzene ring, meta signifies 1,3-disubstitution, and para signifies 1,4-disubstitution.

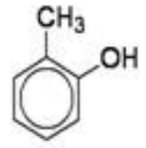


X= any group

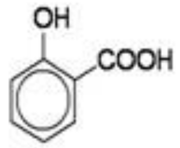
phenol



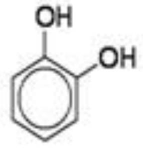
m-bromophenol



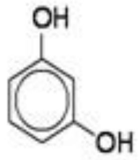
o-cresol



salicylic acid

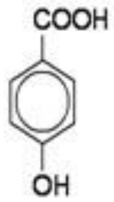


catechol

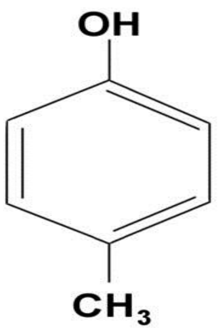


resorcinol

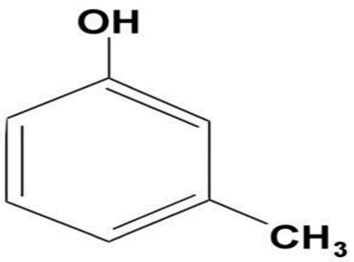
hydroquinone



p-hydroxybenzoic acid

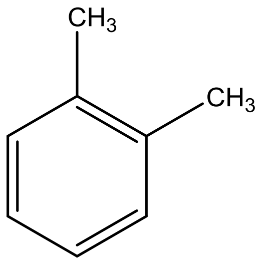


p-cresol



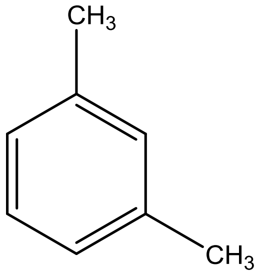
m-cresol

Dimethyl derivatives of benzene are called xylenes. There are three xylene isomers, the ortho (o)-, Meta (m)-, and para (p) - substituted derivatives.



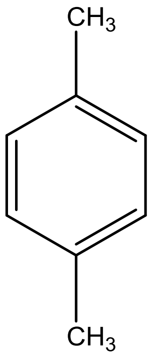
o-xylene

(1,2-dimethylbenzene)



m-xylene

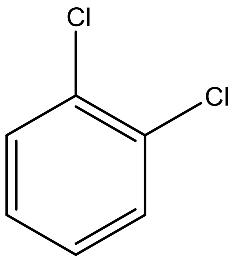
(1,3-dimethylbenzene)



p-xylene

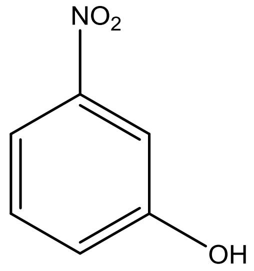
(1,4-dimethylbenzene)

The prefixes o , m, and p can be used when a substance is named as a benzene derivative or when a specific base name such as



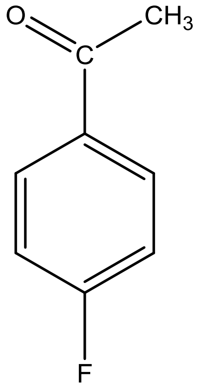
o-dichlorobenzene

(1,2-dichlorobenzene)



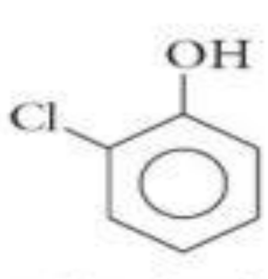
m-nitrophenol

(3-nitrophenol)

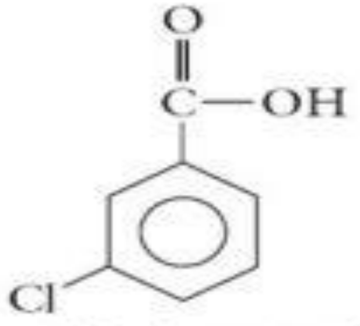


p-fluroacetophenone

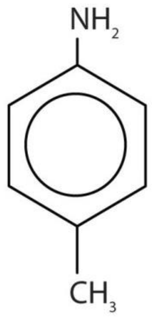
(4-fluroacetophenone)



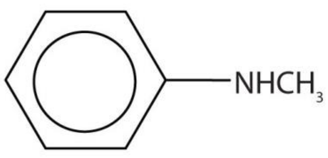
o-Clorophenol



m-Chlorobenzoic acid

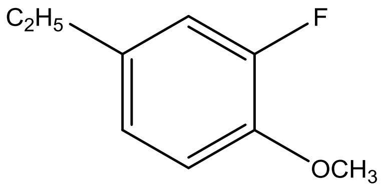


p-Methylaniline (1°)

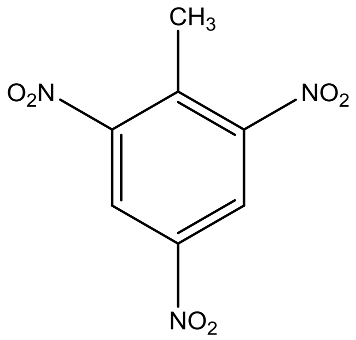


Methylphenylamine (2°)

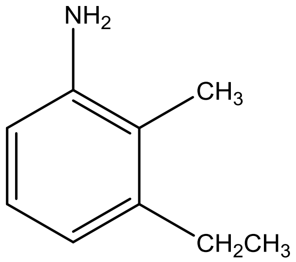
The o, m, and p prefixes are not used when three or more substituents are present on benzene; numerical locants must be used instead.



4-ethyl-2-fluoroanisole
or
4-ethyl-2-fluoro-1-methoxybenzene

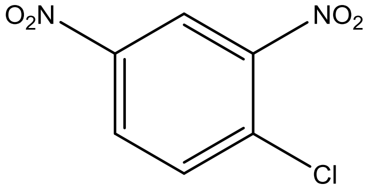


2,4,6-Trinitrotoluene

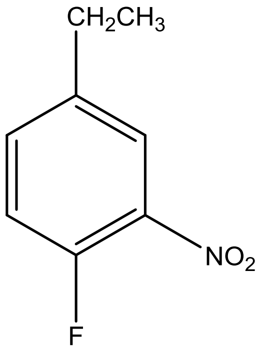


3-ethyl-2-methylaniline

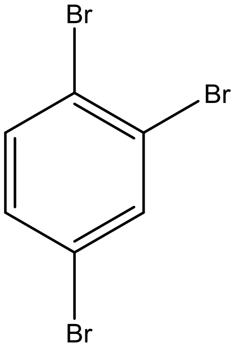
In these examples the base name of the benzene derivative determines the carbon at which numbering begins: anisole has its methoxy group at C-l, toluene its methyl group at C-l, and aniline its amino group at C-1. The direction of numbering is chosen to give the next substituted position the lowest number irrespective of what substituent it bears. The order of appearance of substituents in the name is alphabetical. When no simple base name other than benzene is appropriate, positions are numbered so as to give the lowest locant at the first point of difference. Thus, each of the following examples is named as a 1, 2, 4-trisubstituted derivative of benzene rather than as a 1, 3, 4-derivative:



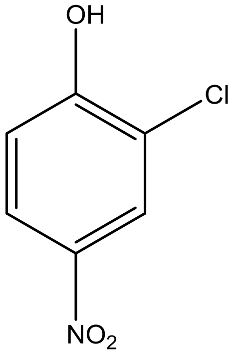
1-Chloro-2,4-dinitrobenzene



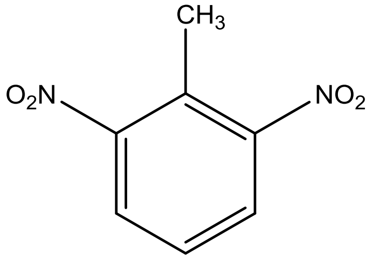
4-ethyl-1-fluoro-2-nitrobenzene



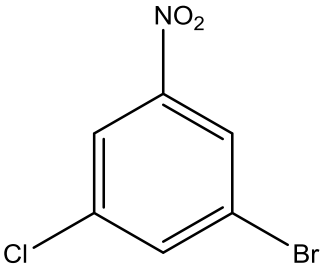
1,2,4-tribromobenzene

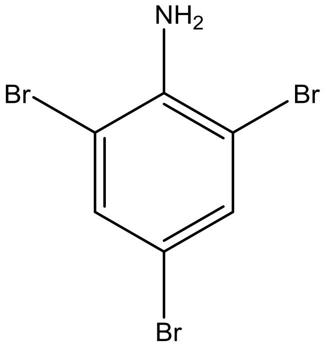


2-chloro-4-nitrophenol

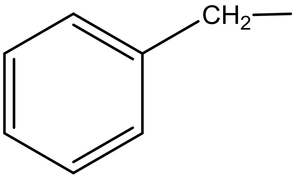


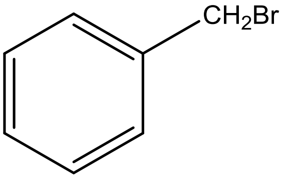
2,6-dinitrotoluene

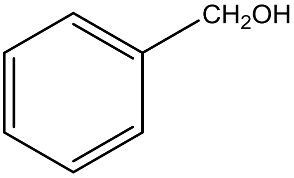

3-bromo-5-chloronitrobenzene

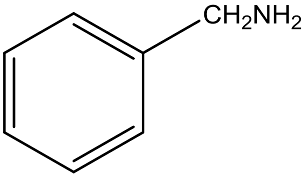

2,4,6-tribromoaniline

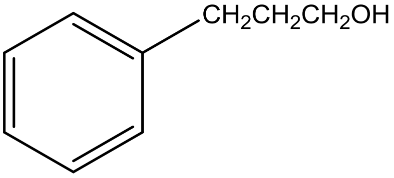
When the benzene ring is named as a substituent, the word phenyl stands for C_6H_5–. Similarly, an arene named as a substituent is called an aryl group. A benzyl group is $C_6H_5CH_2$- .

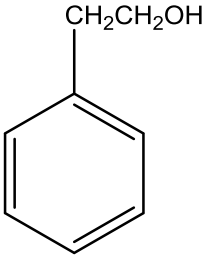

Benzyl group


Benzyl bromide

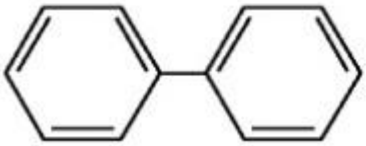

Benzyl alcohol


Benzyl amine

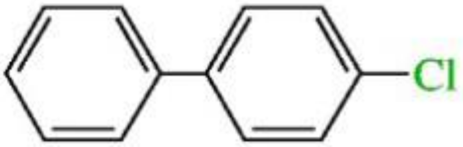

3-phenyl-1-propanol


2-phenylethanol

Biphenyl is the accepted IUPAC name for the compound in which two benzene rings are connected by a single bond.



Biphenyl



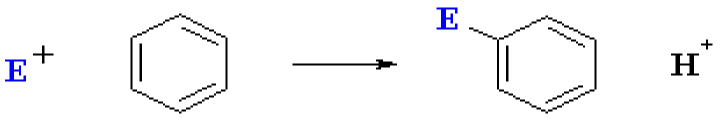
p-Chlorobiphenyl

Electrophilic Aromatic Substitution

It is not surprising that in its typical reactions the benzene ring serves as a source of electrons, that is, as a base. The compounds with which it reacts are deficient in electrons, that is, are electrophilic reagents or acids. Just as the typical reactions of the alkenes are electrophilic addition reactions, so the typical reactions of the benzene ring are **electrophilic substitution reactions.** Electrophilic aromatic substitution includes a wide variety of reactions: nitration, halogenation, sulfonation, and Friedel-Crafts reactions, undergone by nearly all aromatic rings; reactions like nitrosation and diazo coupling, undergone only by rings of high reactivity.

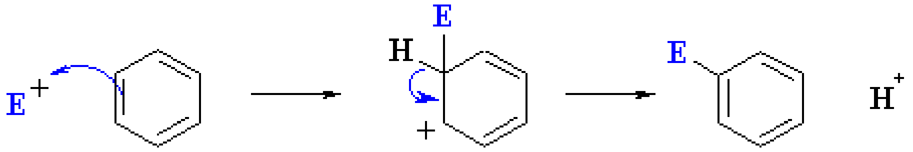
Electrophilic Aromatic Substitution (EAS) is a substitution reaction usually involving the benzene ring; more specifically it is “a reaction in which the hydrogen atom of an aromatic ring is replaced as a consequence of electrophilic attack on the aromatic ring.”

- An **electrophile, E$^+$**, is an electron poor species that will react with an electron rich species.



There are three fundamental components to an electrophilic substitution reaction:

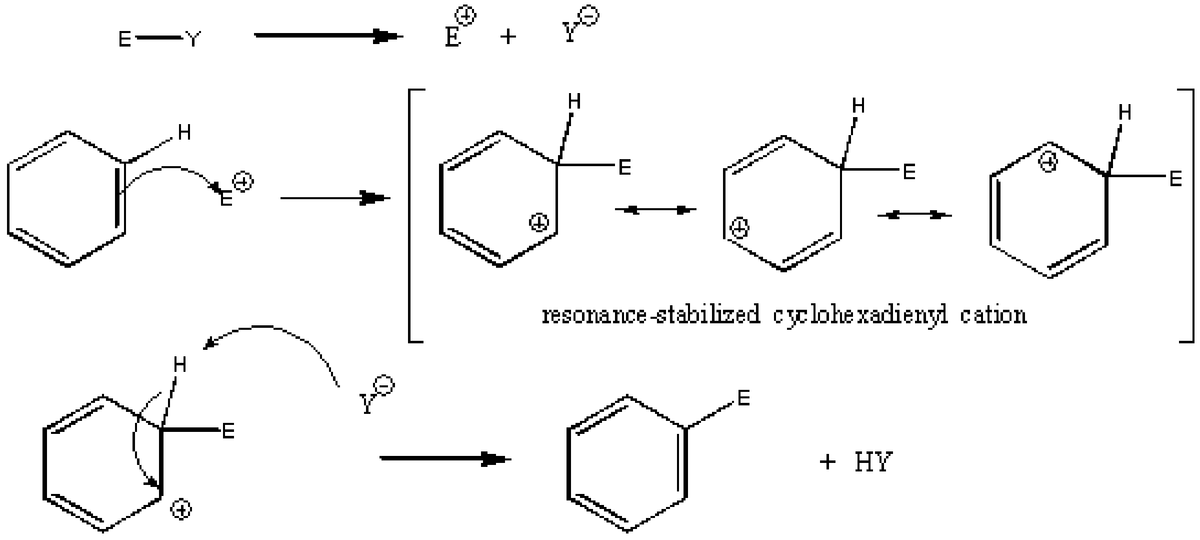
1. formation of the new □ bond from a C=C in the arene nucleophile
2. removal of the proton by breaking the C-H □ bond
3. reform the C=C and restore aromaticity



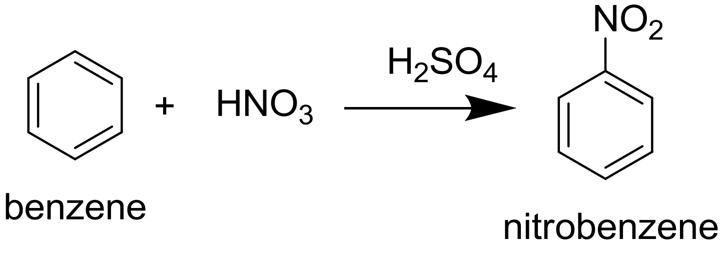
The mechanism is represented by the following series of events:

- Formation of the reactive electrophile, $\mathbf{E}^+$
- Slow reaction of the arene **C=C** with the $\mathbf{E}^+$ to give a resonance stabilized carbocation (see below)
- Loss of $\mathbf{H}^+$ from the carbocation to restore the **C=C** and the aromatic system

The reaction of the electrophile $\mathbf{E}^+$ with the arene is the slow step since it results in the loss of aromaticity even though the resulting cation is still resonance stabilized.

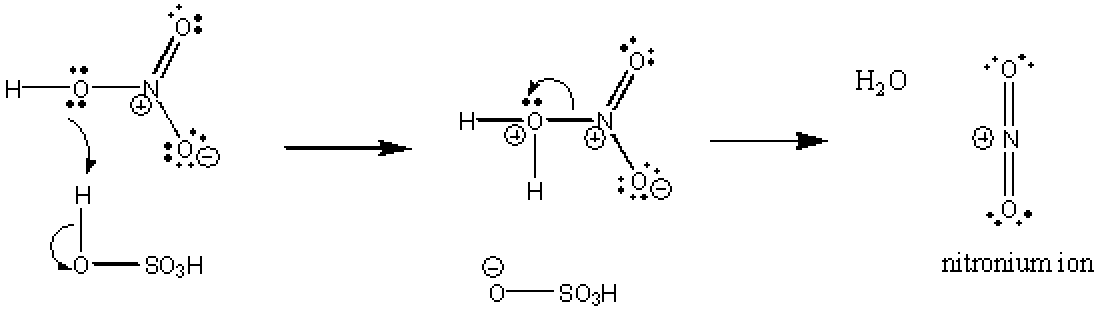


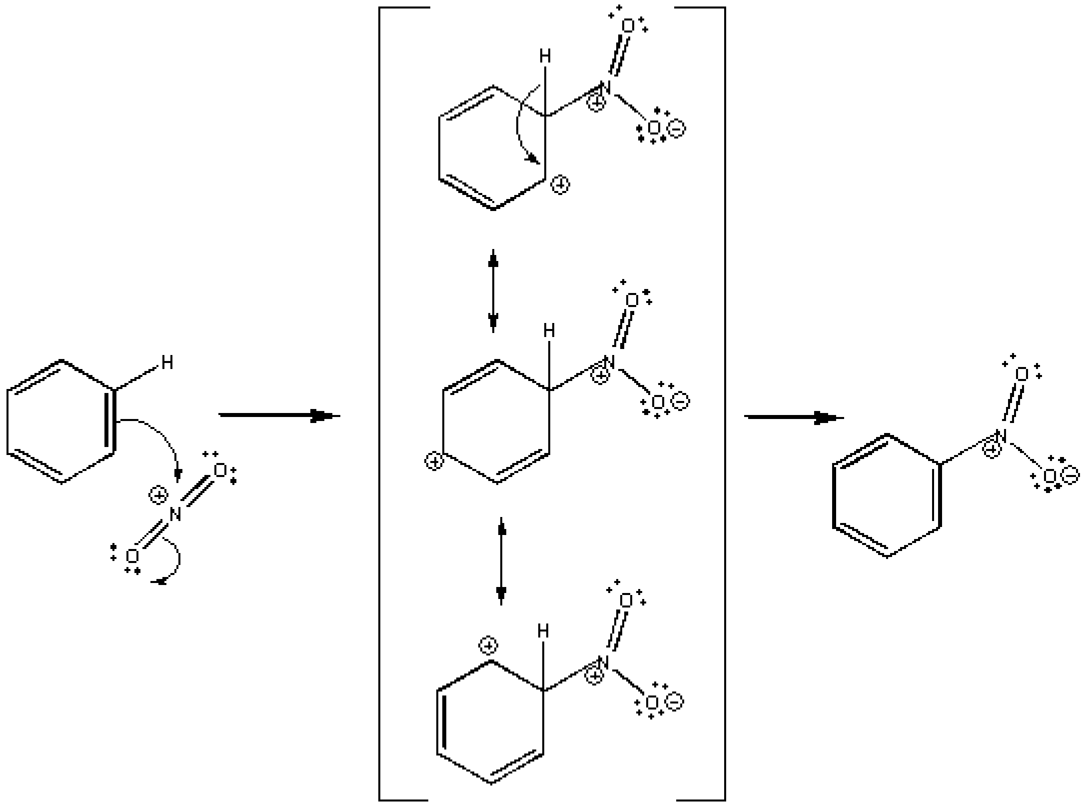
1. **Nitration:**



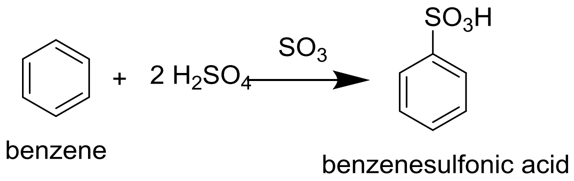
Mechanism of nitration

1) Nitration of an aromatic is accomplished by first obtaining a reactive electrophile NO_2^+ and then combining it with an aromatic :



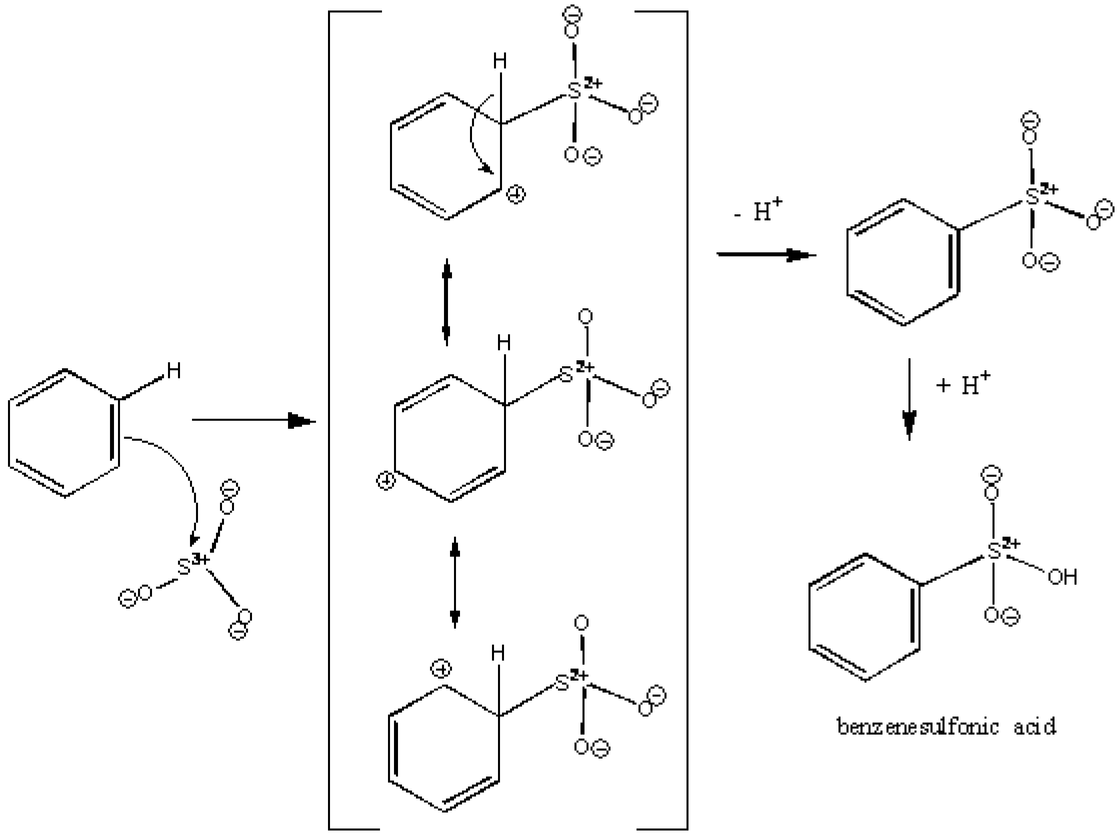


2 .Sulfonation:

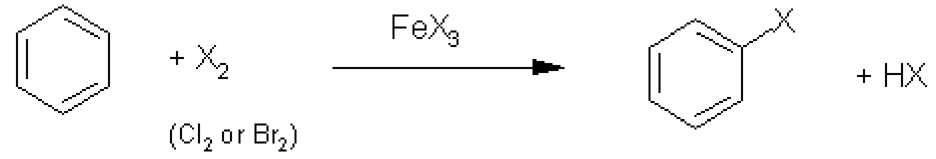


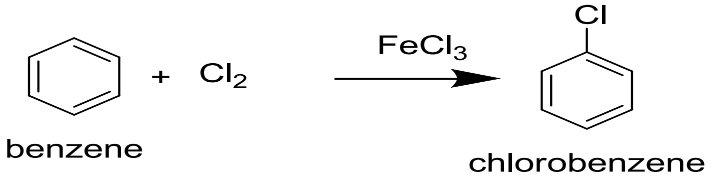
Mechanism of reaction

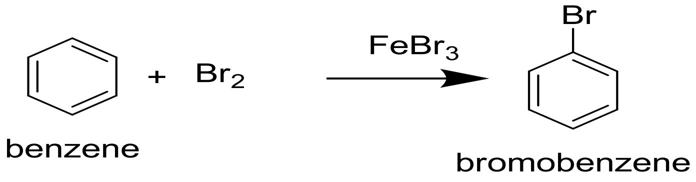
$$2\,H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$$



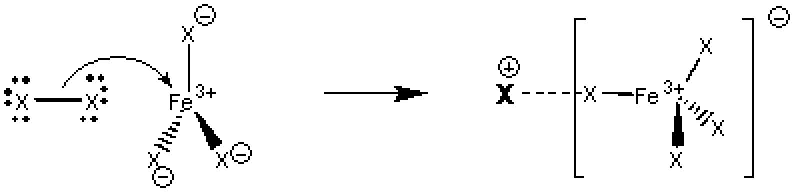
2) halogenation



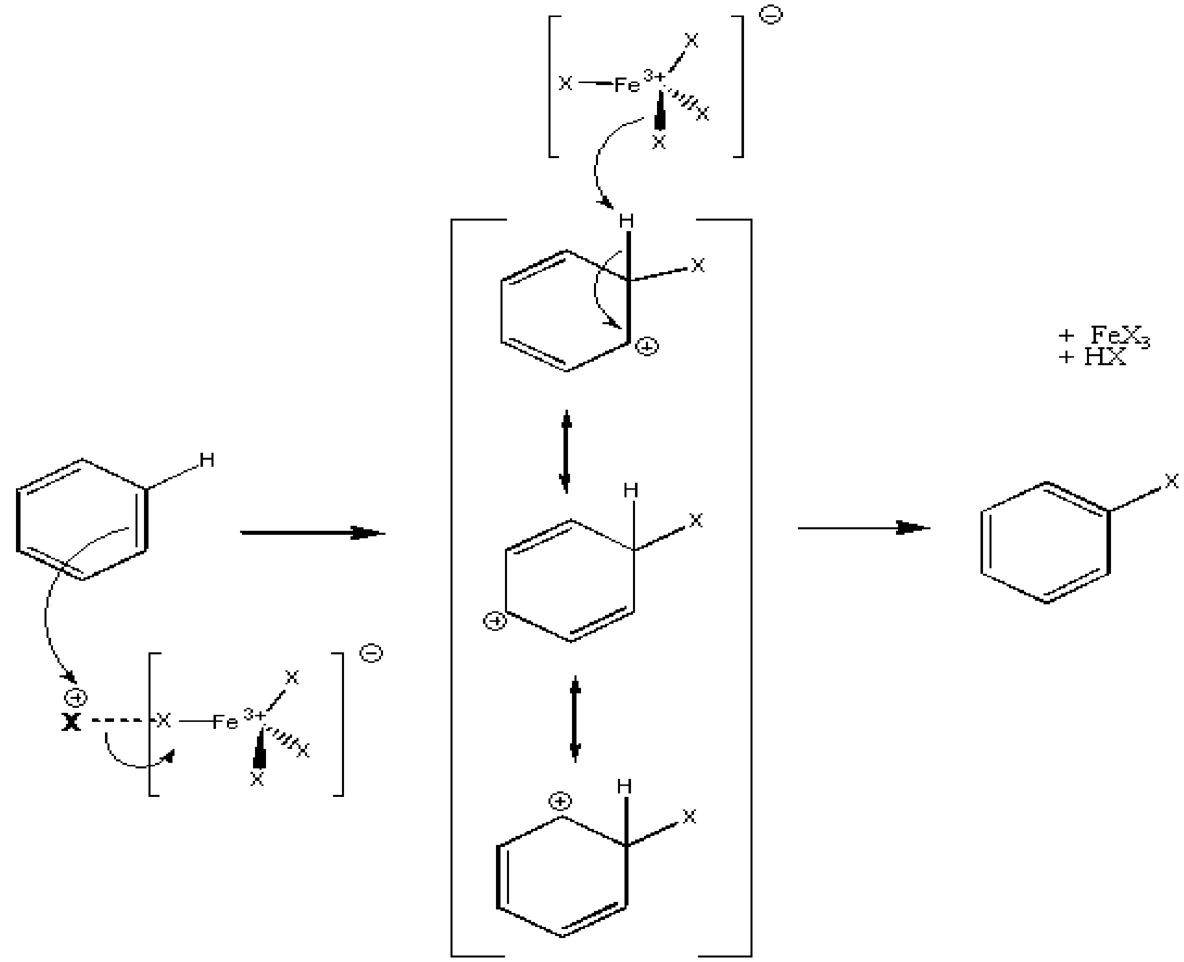




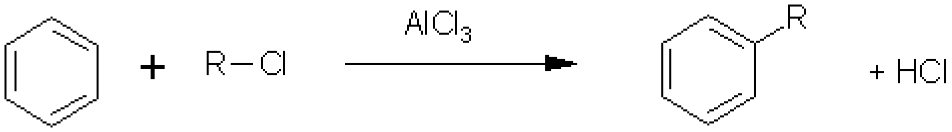
Mechanism Of halogenation



$X = Cl, Br$

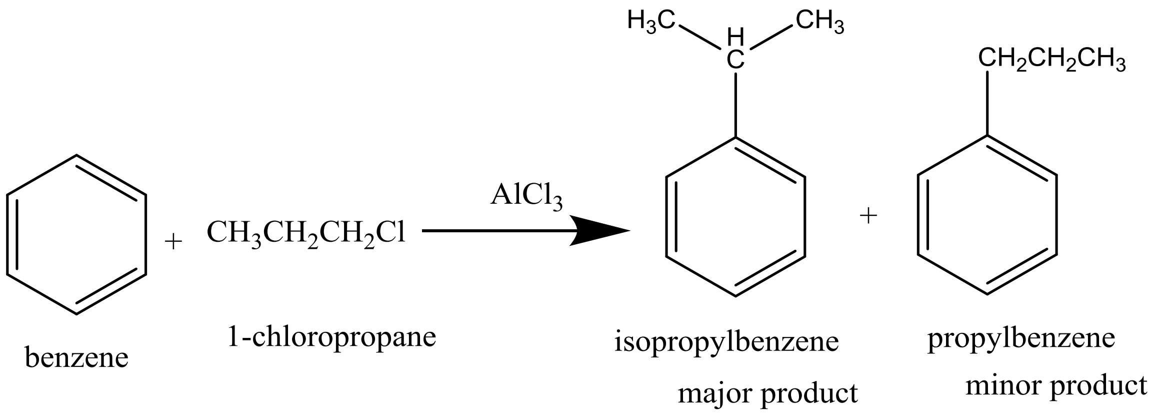


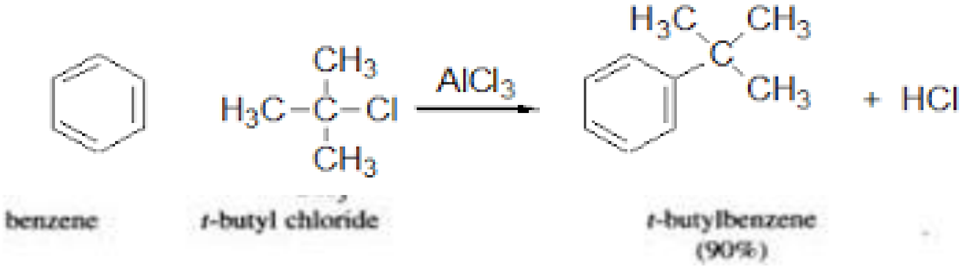
3) Friedel-Crafts Alkylation



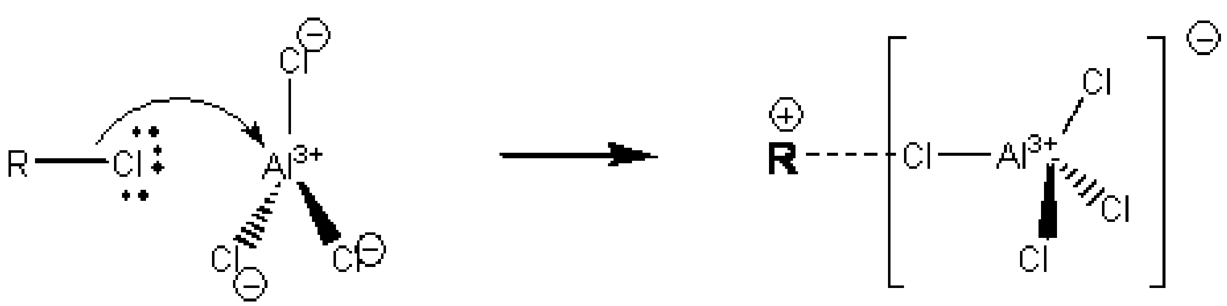
$R = 2^o, 3^o, -CH_3, -CH_2CH_3$

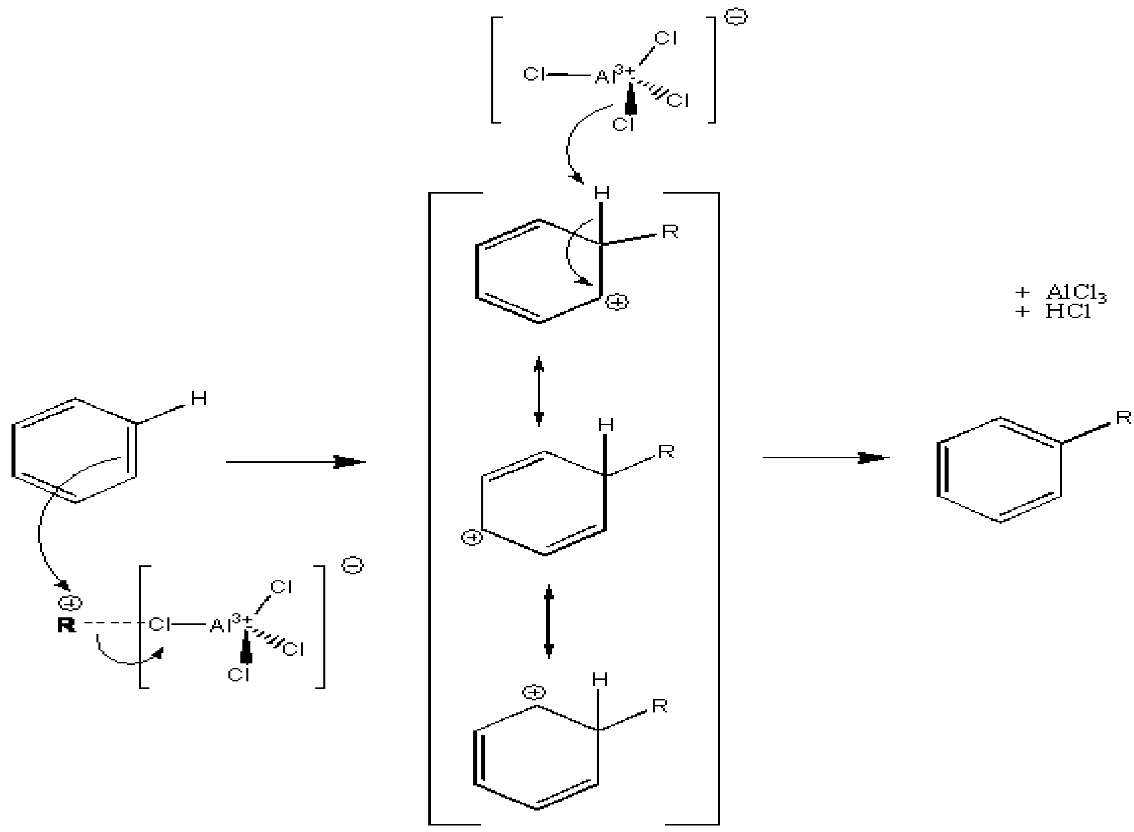
Primary alkyl groups other than Me or Et rearrange.



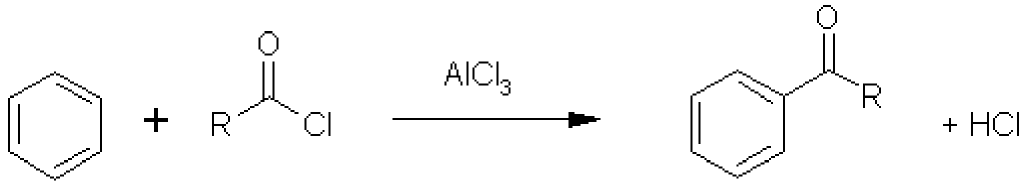


Mechanism of alkylation



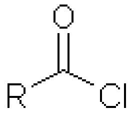
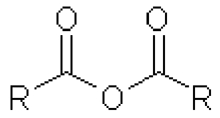


4) **Friedel-Crafts Acylation**



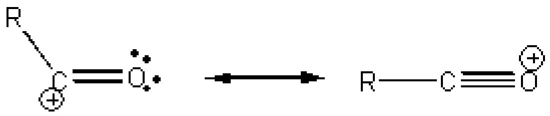
R = alkyl or aryl group.

This reaction works with acid chlorides (or acyl) or acid anhydrides.

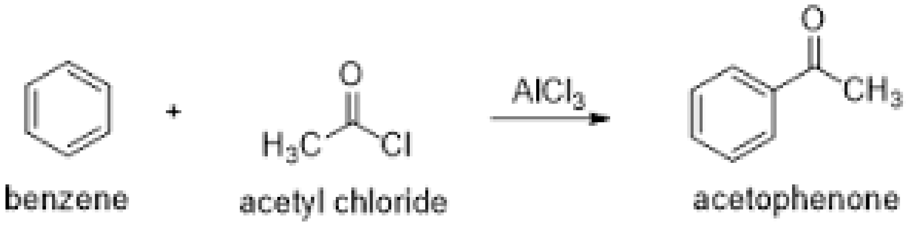



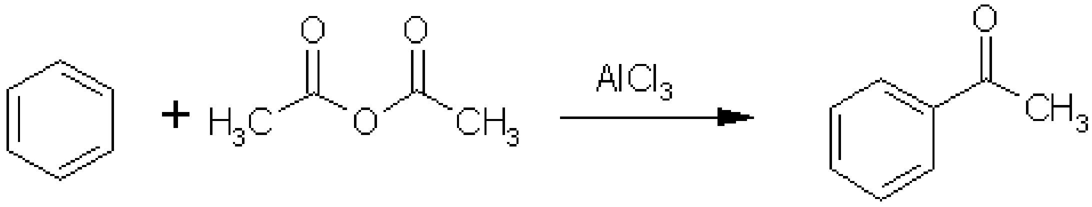
Acid chloride acid anhydride

An important feature of this reaction: **no rearrangements occur**. The mechanism involves the formation of the acylium ion (acyl cation).the stability of this ion (due to resonance stabilization) avoids rearrangement.

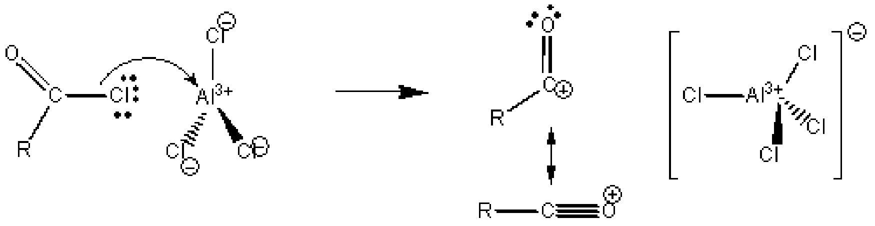


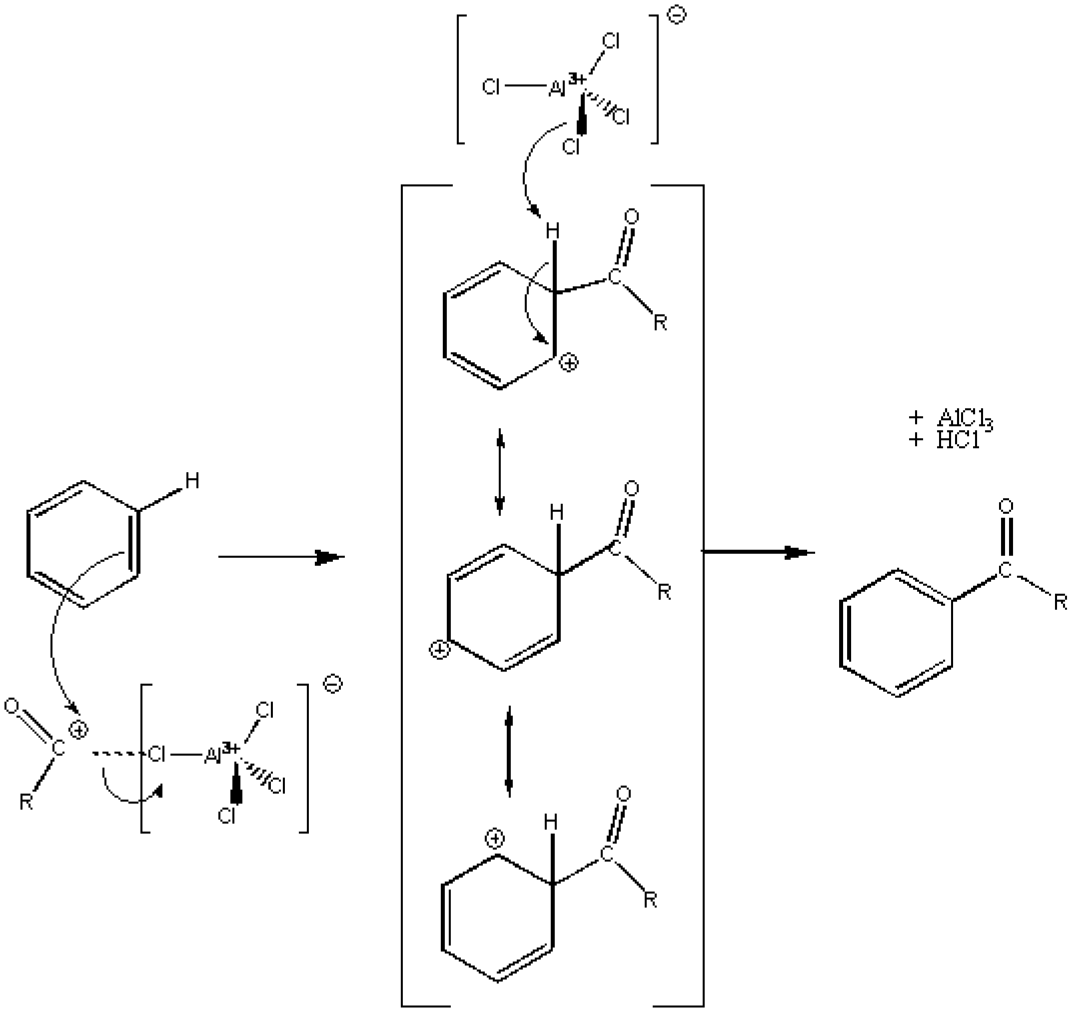
Acylium ion (acyl cation)



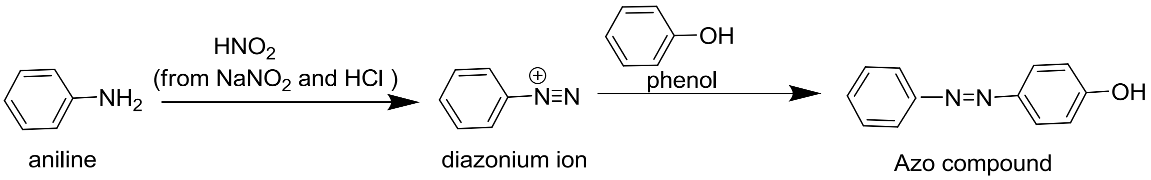


Mechanism of acylation:-



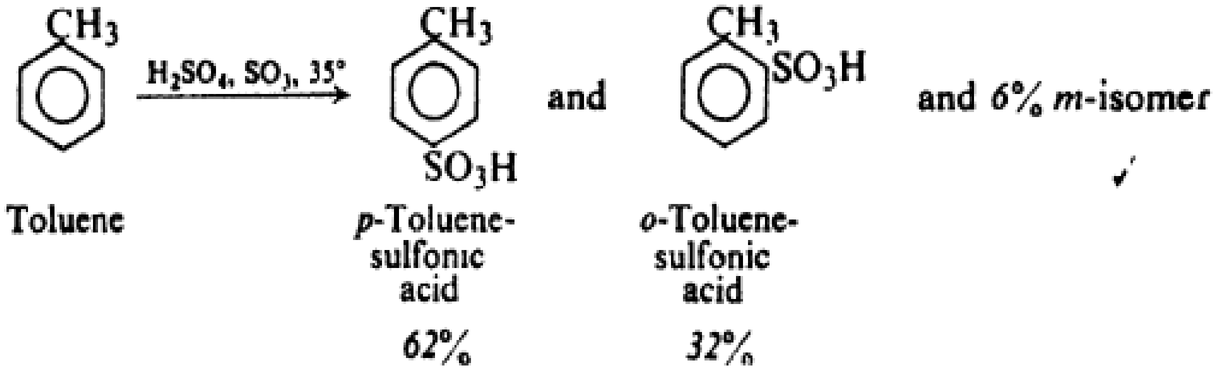


5). Diazo coupling:



Effect of substituent groups

Like benzene, toluene undergoes electrophilic aromatic substitution: sulfonation, for example. Although there are three possible mono sulfonation products, this reaction actually yields appreciable amounts of only two of them: the *o*- and *p*- isomers.



On the other hand, nitrobenzene, to take a different example, has been found to undergo substitution more slowly than benzene, and to yield chiefly the meta isomer. Like methyl or nitro, any group attached to a benzene ring affects the reactivity of the ring and determines the orientation of substitution. When an electrophilic reagent attacks an aromatic ring, it is the group already attached to the ring that determines how readily the attack occurs and where it occurs.

A group that makes the ring more reactive than benzene is called an **activating group**.

A group that makes the ring less reactive than benzene is called a **deactivating group**.

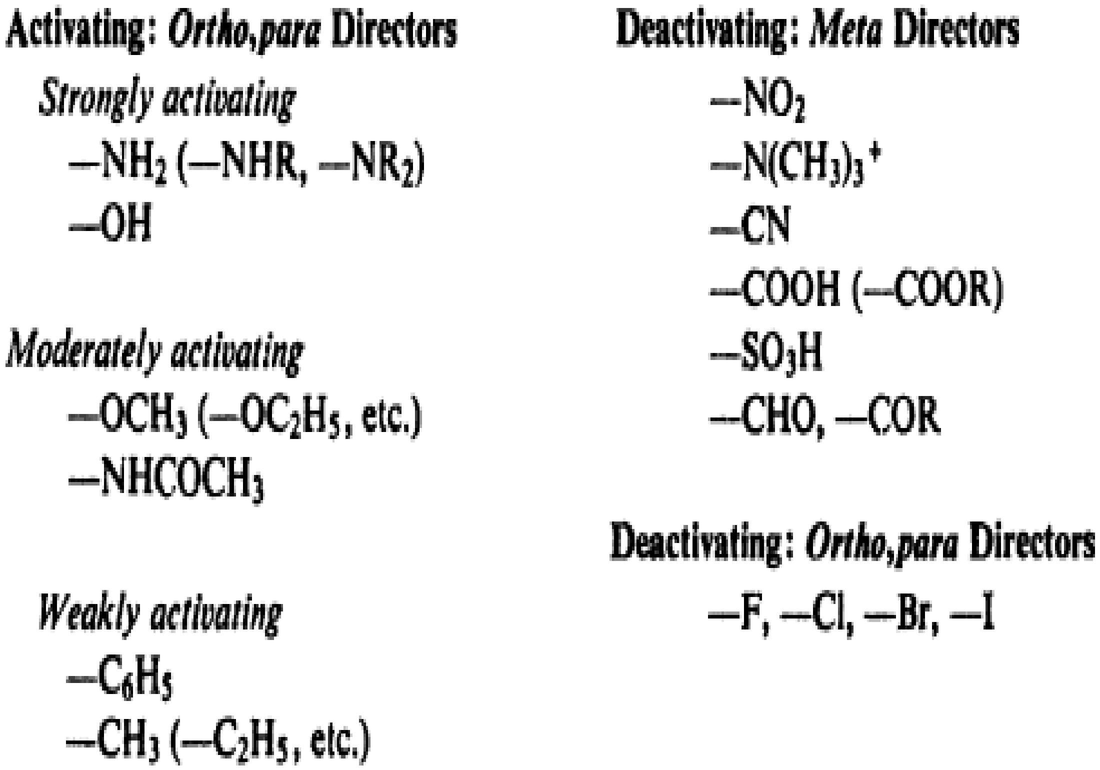
A group that causes attack to occur chiefly at positions ortho and para to it is called an **ortho , para director**.

A group that causes attack to occur chiefly at positions Meta to it is called A **Meta director.**

Classification of substituent groups

Nearly all groups fall into one of two glasses: activating and ortho, para-directing, or deactivating and meta-directing. The halogens are in a class by themselves, being deactivating but ortho-, para- directing.

Effect of groups on electrophilic aromatic substitution



Activating: *Ortho,para* Directors

Strongly activating

$-NH_2$ $(-NHR, -NR_2)$

$-OH$

Moderately activating

$-OCH_3$ $(-OC_2H_5$, etc.)

$-NHCOCH_3$

Weakly activating

$-C_6H_5$

$-CH_3$ $(-C_2H_5$, etc.)

Deactivating: *Meta* Directors

$-NO_2$

$-N(CH_3)_3^+$

$-CN$

$-COOH$ $(-COOR)$

$-SO_3H$

$-CHO$, $-COR$

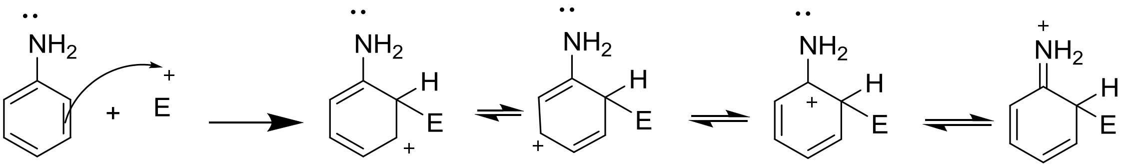
Deactivating: *Ortho,para* Directors

$-F$, $-Cl$, $-Br$, $-I$

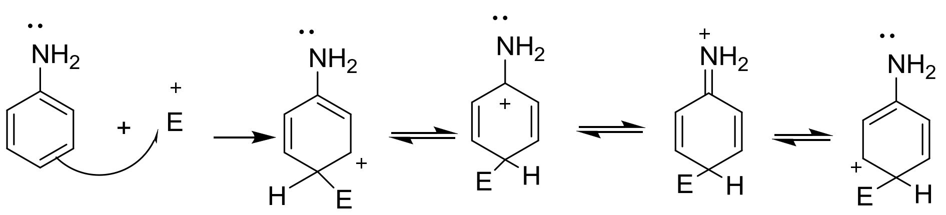
***Ortho/para* directors**

Groups with unshared pairs of electrons, such as the amino group of aniline, are strongly *activating* and *ortho/para*-directing. Such activating groups donate those unshared electrons to the *pi* system. When the electrophile attacks the ortho and para positions of aniline, the nitrogen atom can donate electron density to the *pi* system (forming an iminium ion), giving four resonance structures This substantially enhances the stability of the cationic intermediate.

ortho

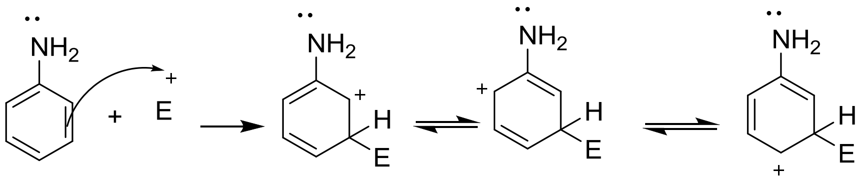


Para



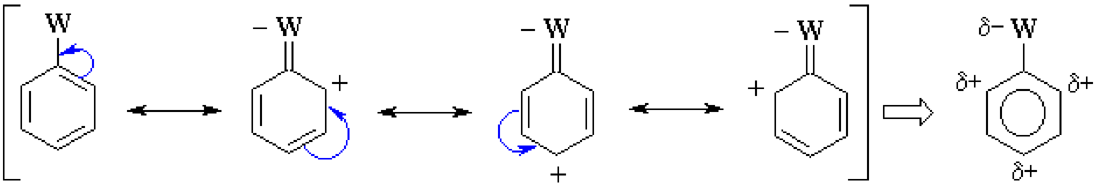
Compare this with the case when the electrophile attacks the *Meta* position. In that case, the nitrogen atom cannot donate electron density to the *pi* system, giving only three resonance contributors. For this reason, the *meta*-substituted product is produced in much smaller proportion to the *ortho* and *para* products.

Meta



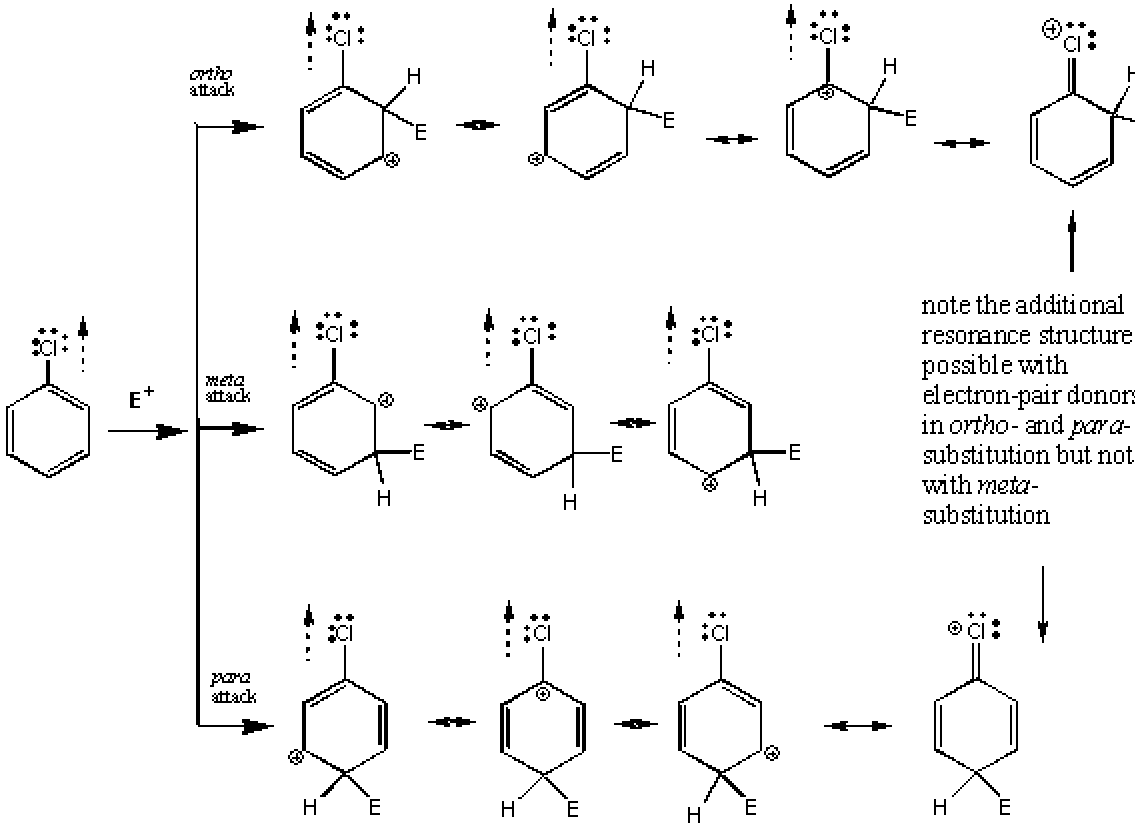
***Meta* directors**

Electron withdrawing groups (EWG) with pi bonds to **electronegative atoms** (*e.g.* -C=O, $-NO_2$) adjacent to the pi system **deactivate** the aromatic ring by decreasing the electron density on the ring through a **resonance withdrawing effect**. The resonance only decreases the electron density at the ortho- and para- positions. Hence these sites are **less** nucleophilic, and so the system tends to react with electrophiles at the **meta** sites.



Halogens: - Are a special case since they are deactivating groups yet are *ortho /para* directors**.**

1) They are deactivating due to their high electronegativities (inductive effects).
2) They are *ortho/para* directors since they can, via their lone pairs, donate electrons into the pi system of the ring when substitution is o/p (resonance effect)
3) The high electronegativity of halogen atoms leads to overall ring deactivating by their electron-withdrawing inductive effect .However ,their electro-donating resonance effect causes substitution to be more favorable ortho and para positions than at meta positions



note the additional resonance structure possible with electron-pair donor in *ortho*- and *para*-substitution but not with *meta*-substitution