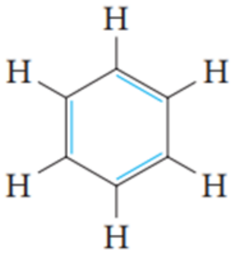
108 Chem

Chapter 3

Aromatic Compounds

- The expressing aromatic compounds came to mean benzene and derivatives.

Structure of Benzene: Resonance Description

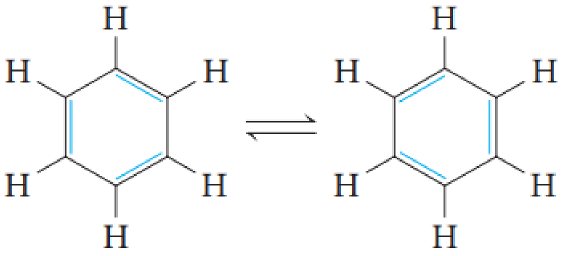


C_6H_6
benzene

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.

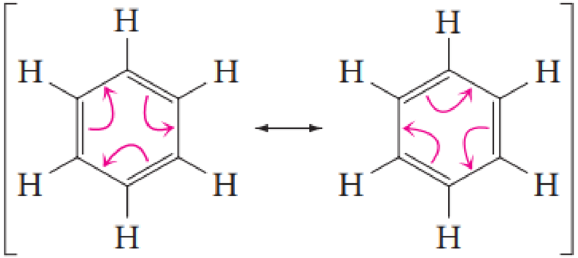
The Kekule Structure for Benzene:

- In 1865, Kekulé proposed a reasonable 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.
- 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).
- Kekulé suggested that the single and double bonds exchange positions around the ring so rapidly that the typical reactions of alkenes cannot take place.



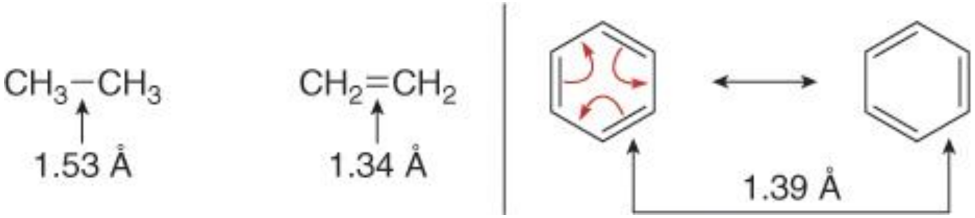
the Kekulé structures for benzene

- Kekulé’s formulas represent two identical contributing structures to a single resonance hybrid structure of benzene.



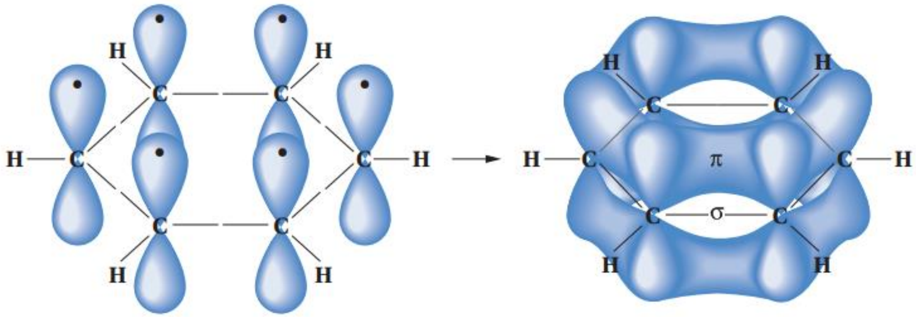
Benzene is a resonance hybrid of these two contributing structures.

- Modern physical measurements support this model for the benzene structure. Benzene is planar, and each carbon atom is at the corner of a regular hexagon. All of the carbon–carbon bond lengths are identical: 1.39 Å, intermediate between typical single (1.54 Å) and double (1.34 Å) carbon–carbon bond lengths.



Orbital Model for Benzene:

- Each carbon atom in benzene is connected to only three other atoms (two carbons and a hydrogen).
- Each carbon is therefore *sp*^{2} -hybridized, as in ethylene.
- It also explains its hexagonal shape, with H-C-C and C-C-C angles of 120°.



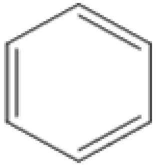
- An orbital representation of the bonding in benzene. Sigma (s) bonds are formed by the end-on overlap of sp2 orbitals. In addition, each carbon contributes one electron to the pi (p) system by lateral overlap of its p orbital with the p orbitals of its two neighbors.

Aromatic Character: The (4n + 2) π Rule

- A molecule must be cyclic.
- A molecule must be planar.
- A molecule must be completely conjugated.
- A molecule must satisfy Hückel’s rule, and contain a particular number of π electrons.

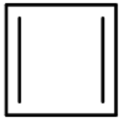
4n+2 π electrons (n= 0, 1, 2, 3, ….= 2, 6, 10, 14, ….)

Examples:



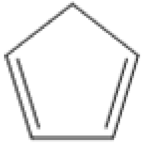
Benzene

Aromatic



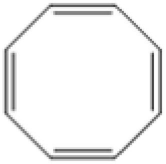
Cyclobutadiene

Not aromatic



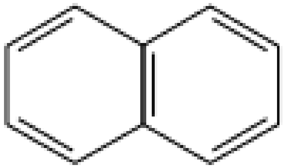
Cyclopentadiene

Not aromatic



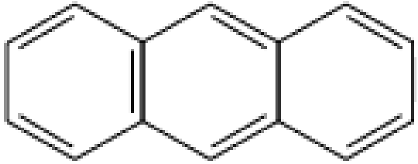
Cyclooctatetraene

Not aromatic



Naphthalene

Aromatic



Anthracene

Aromatic

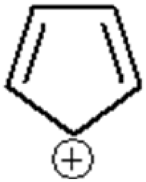
Examples:

Not aromatic

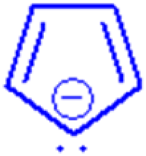
Not aromatic

Aromatic

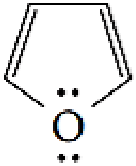
Not aromatic



Not aromatic

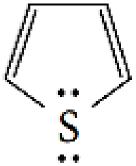


Aromatic



Furan

Aromatic

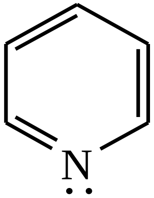


Thiophene

Aromatic

Pyrrole

Aromatic

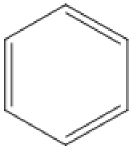


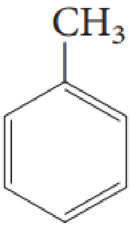
Pyridine

Aromatic

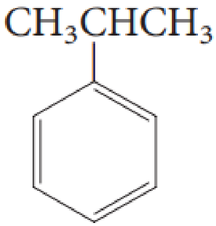
Nomenclature of Aromatic compounds

- Common names have acquired historic respectability and are accepted by IUPAC. Examples include:

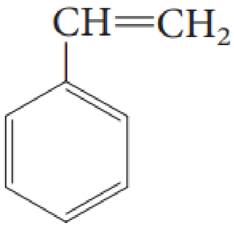

benzene



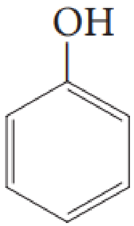
toluene



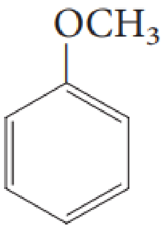
cumene



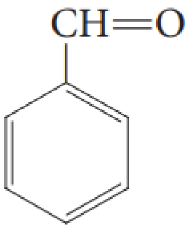
styrene



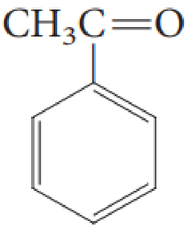
phenol



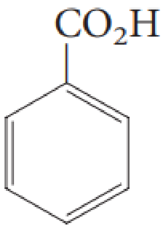
anisole



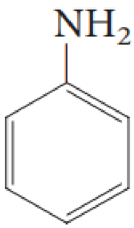
benzaldehyde



acetophenone

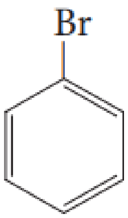


benzoic acid

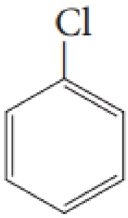


aniline

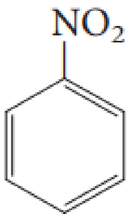
- Monosubstituted benzenes that do not have common names accepted by IUPAC are named as derivatives of benzene.



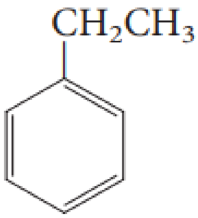
bromobenzene



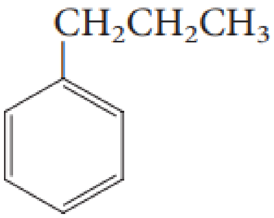
chlorobenzene



nitrobenzene



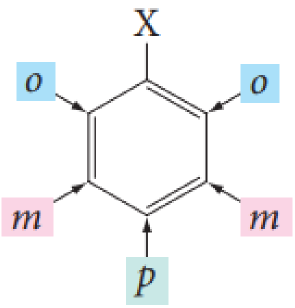
ethylbenzene



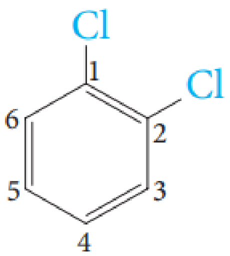
propylbenzene

Nomenclature of Aromatic compounds

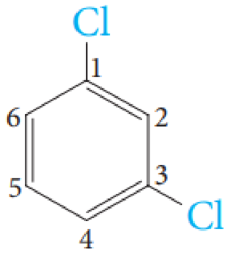
- When two substituents are present, three isomeric structures are possible. They are designated by the prefixes *ortho*-, *meta*-, and *para*- (abbreviated as *o*-, *m*-, and *p*-) or by the use of numbers.



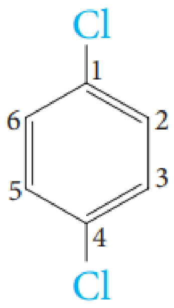
Examples:



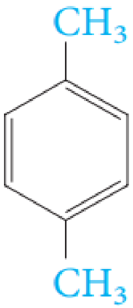
ortho-dichlorobenzene
1,2-Dichlorobenzene



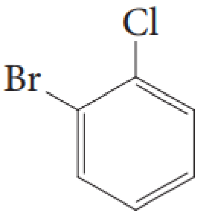
meta-dichlorobenzene
1,3-Dichlorobenzene



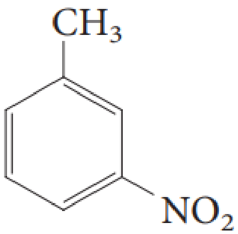
para-dichlorobenzene
1,4-Dichlorobenzene



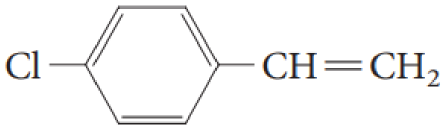
para-xylene
para-dimethylbenzene
1,4-Dimethylbenzene



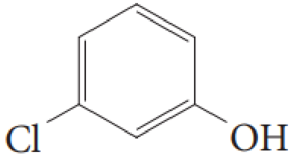
o-bromochlorobenzene
(note alphabetical order)



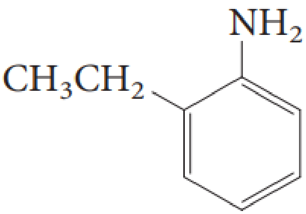
m-nitrotoluene



p-chlorostyrene



m-chlorophenol

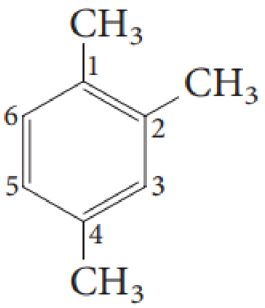


o-ethylaniline

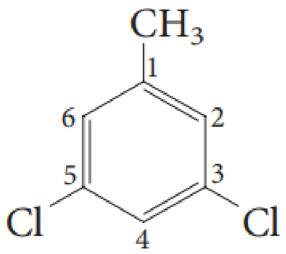
Nomenclature of Aromatic compounds

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

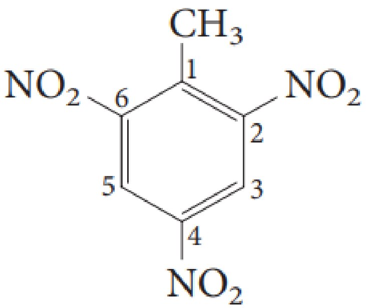
Examples:



1,2,4-trimethylbenzene



3,5-dichlorotoluene



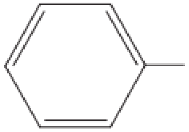
2,4,6-trinitrotoluene
(TNT)

Nomenclature of Aromatic compounds

- Two groups with special names occur frequently in aromatic compounds;

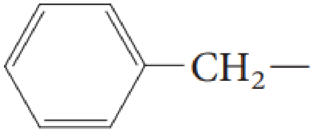
  They are the phenyl group and the benzyl group.

C_6H_5— or



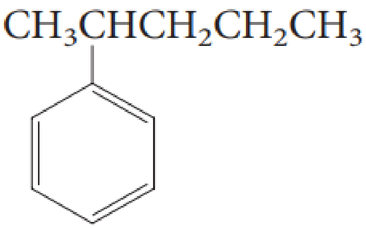
phenyl group

$C_6H_5CH_2$— or

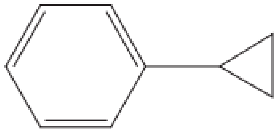


benzyl group

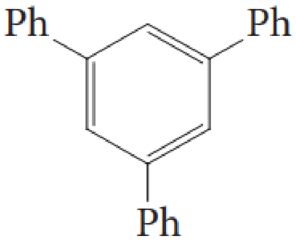
Examples:



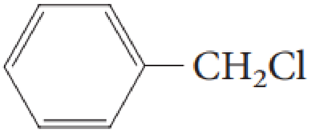
2-phenylpentane
(or 2-pentylbenzene)



phenylcyclopropane
(or cyclopropylbenzene)



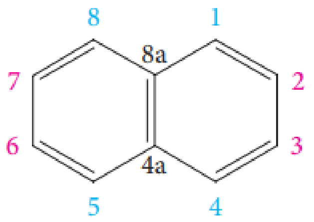
1,3,5-triphenylbenzene



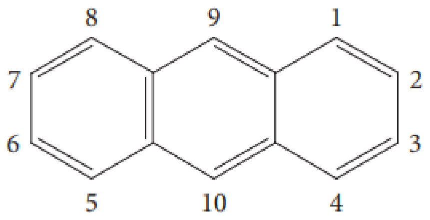
benzyl chloride

Nomenclature of Aromatic compounds

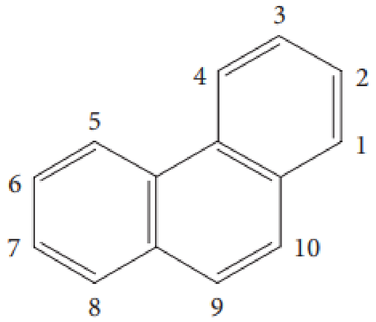
Polycyclic Aromatic Hydrocarbons



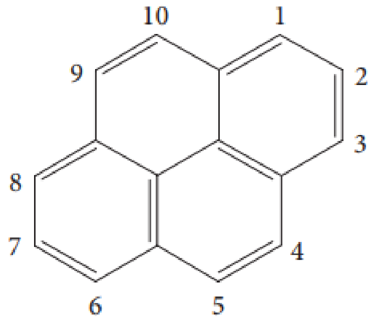
naphthalene



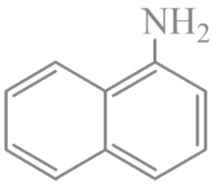
anthracene



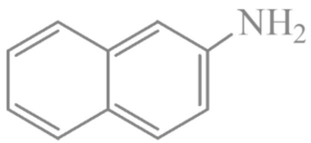
phenanthrene



pyrene



1-Aminonaphthalene

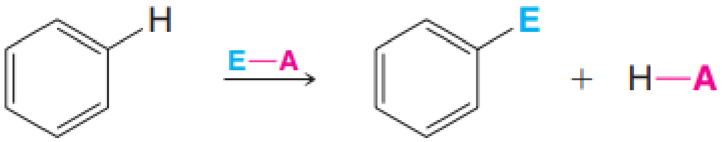


2-Aminonaphthalene

Reaction of Benzene

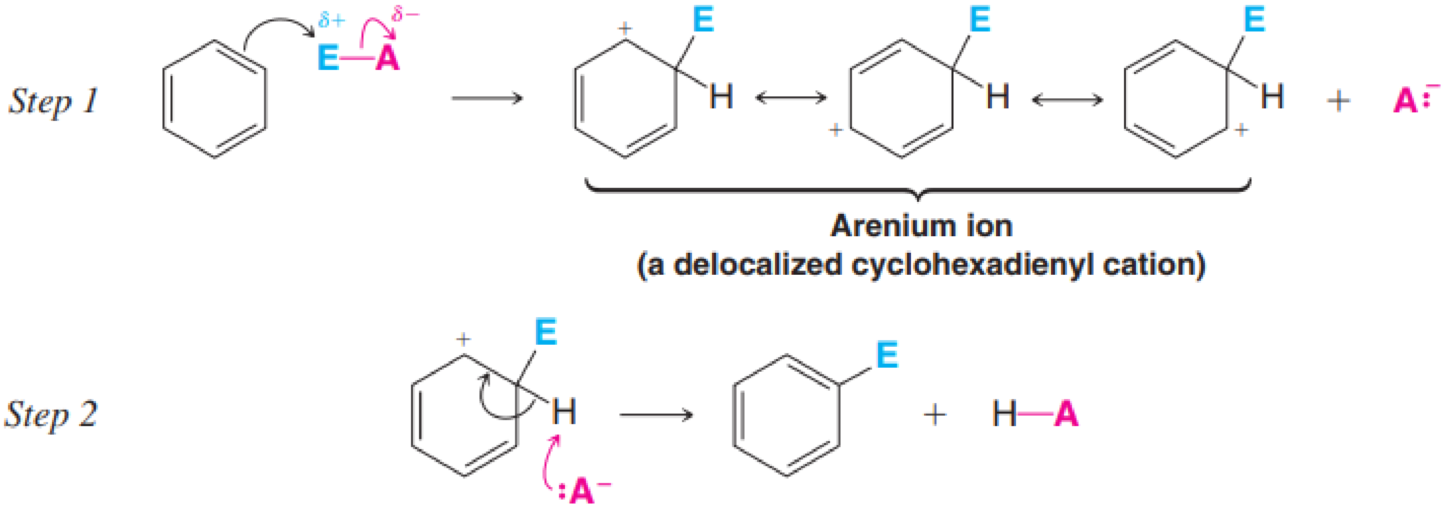
A- Electrophilic Aromatic Substitution

- Some of the most important reactions of aromatic compounds are those in which an electrophile replaces one of the hydrogen atoms of the ring.
- These reactions, called electrophilic aromatic substitutions (EAS).

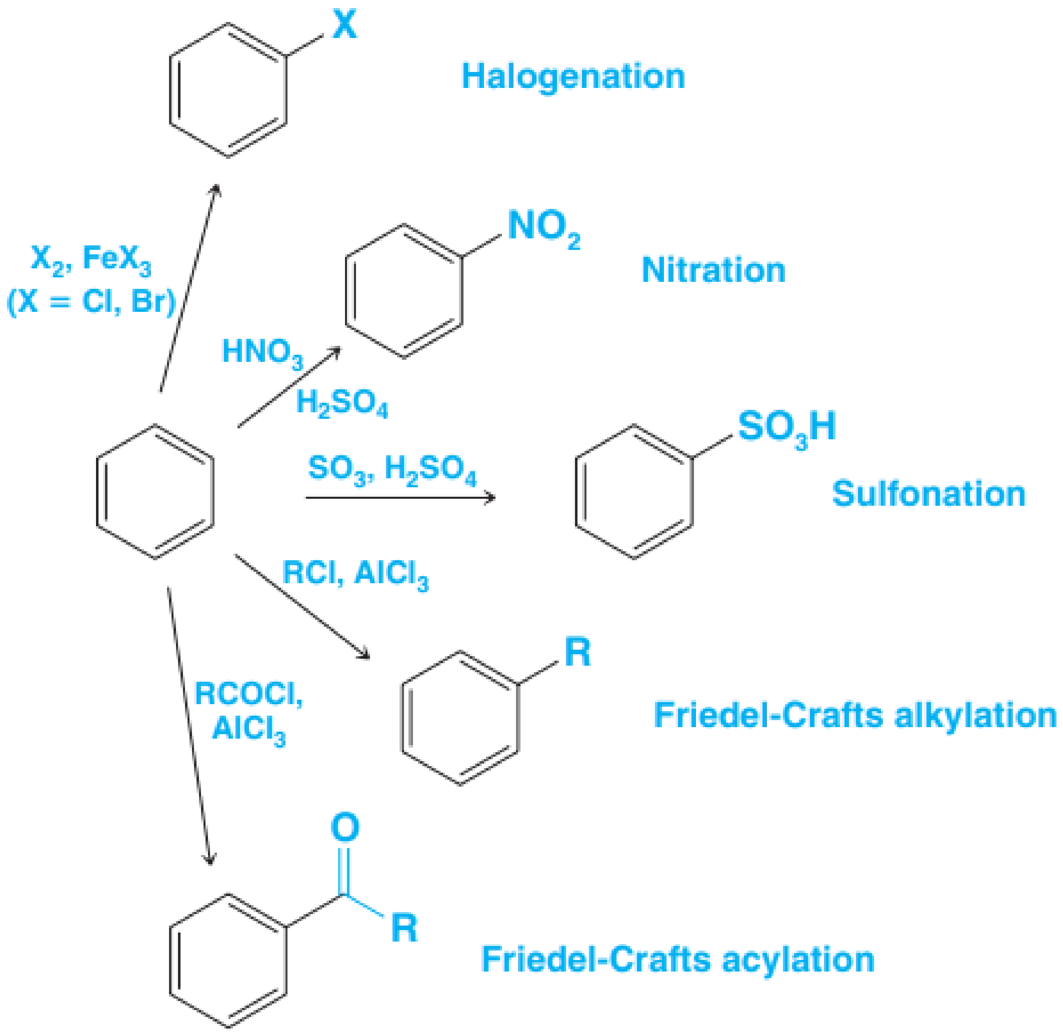


(E—A is an electrophilic reactant)

The Mechanism of Electrophilic Aromatic Substitution

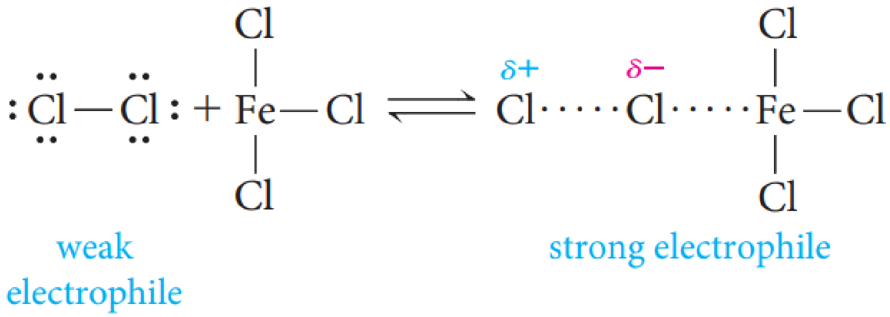


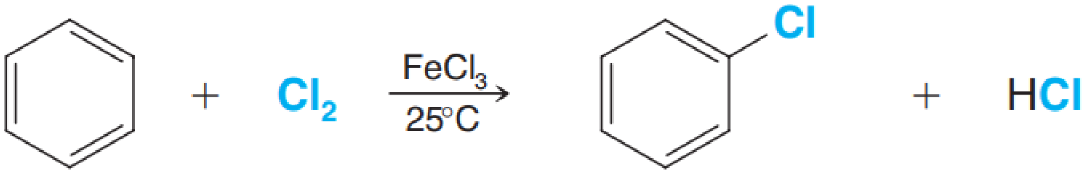
Electrophilic Aromatic Substitution



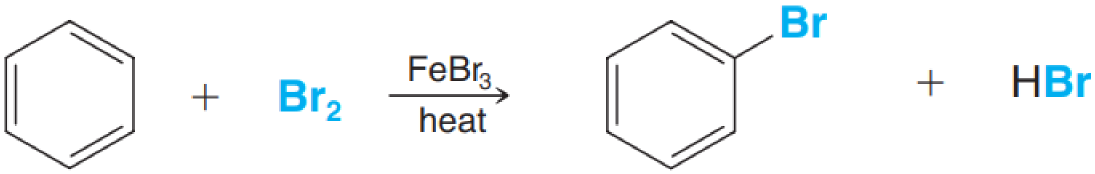
Halogenation of Benzene

- Benzene reacts with bromine and chlorine in the presence of Lewis acids (iron chloride ($FeCl_3$) for chlorination, and iron bromide ($FeBr_3$) for bromination).





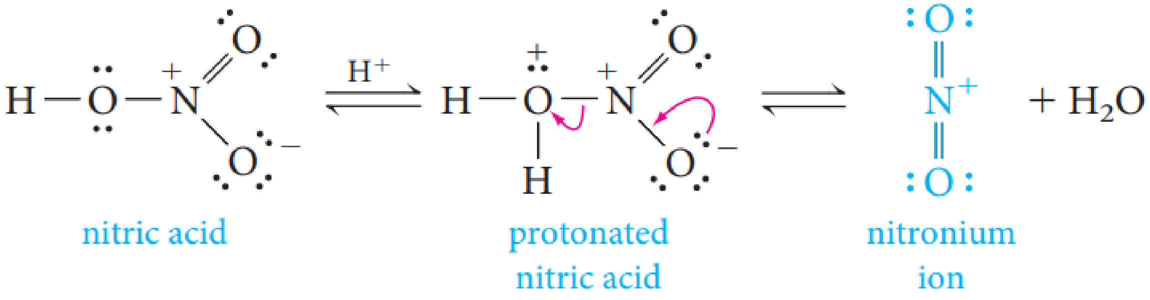
Chlorobenzene (90%)

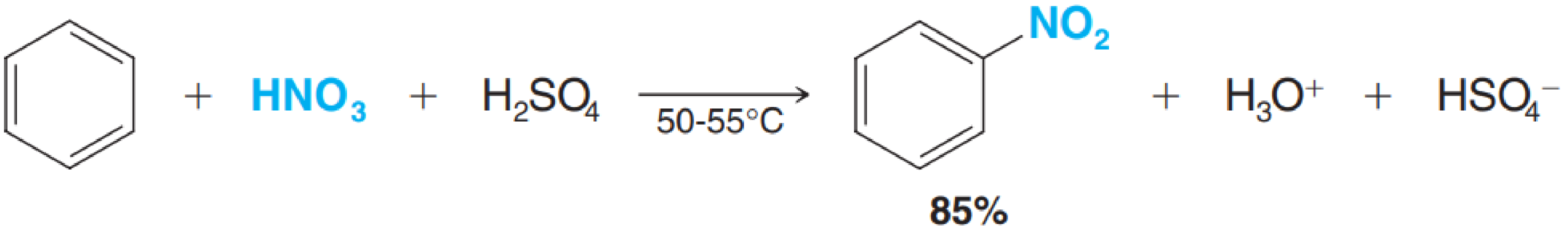


Bromobenzene (75%)

Nitration of Benzene

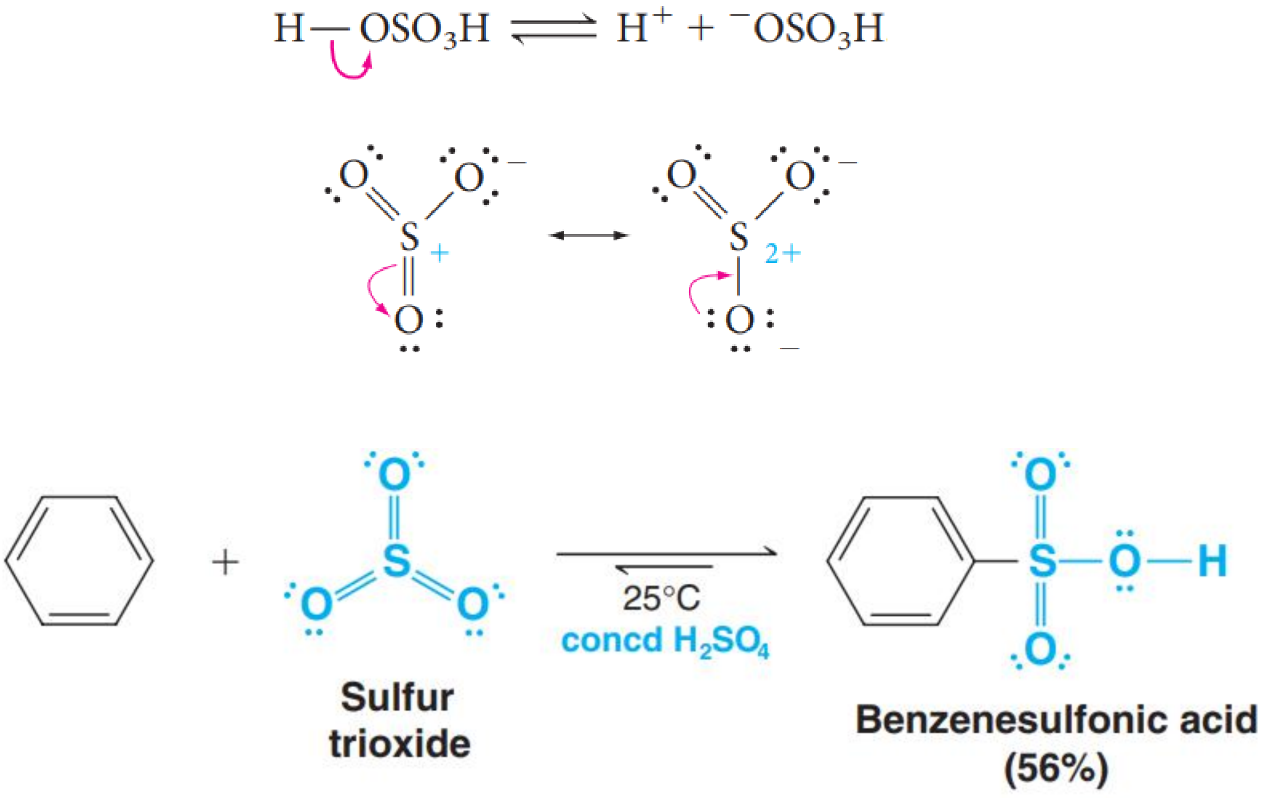
- Benzene undergoes nitration on reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid.





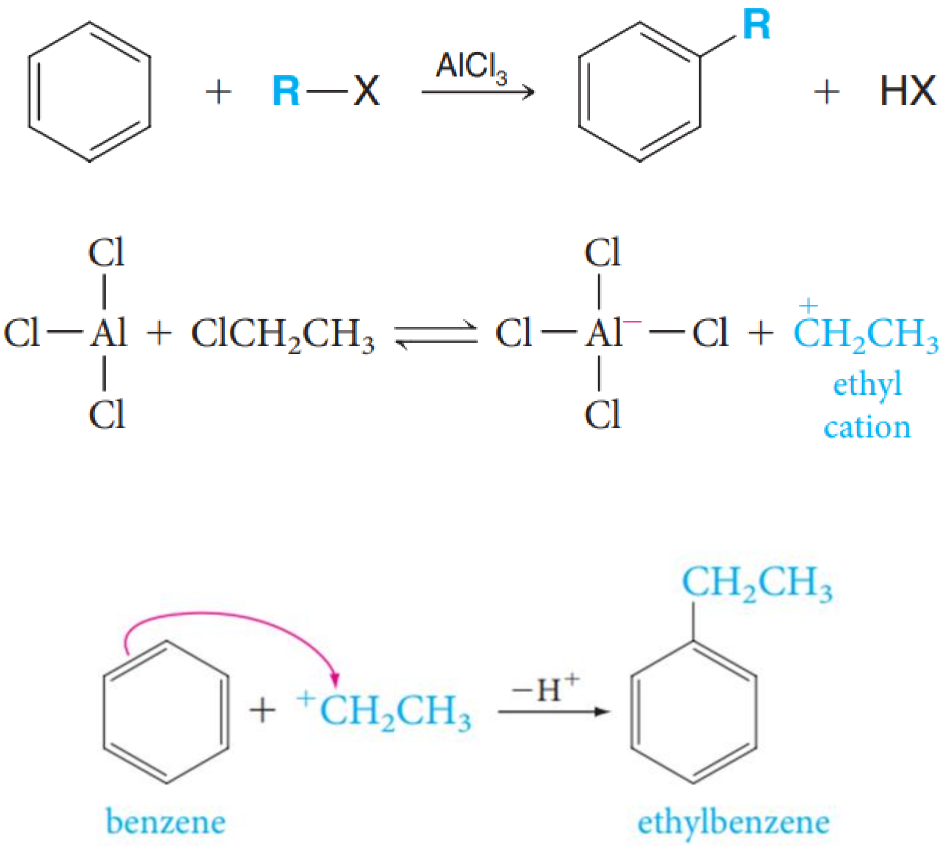
Sulfonation of Benzene

Benzene reacts with concentrated or fuming sulfuric acid, and the electrophile may be sulfur trioxide (SO_3), or protonated sulfur trioxide ($^+SO_3H$).



Friedel-Crafts Alkylation

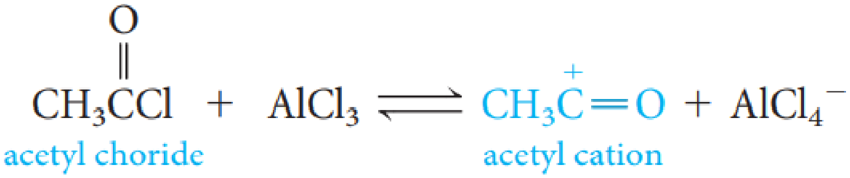
- The Electrophile is a carbocation, which can be formed either by removing a halide ion from an alkyl halide with a Lewis acid catalyst (for example, $AlCl_3$).



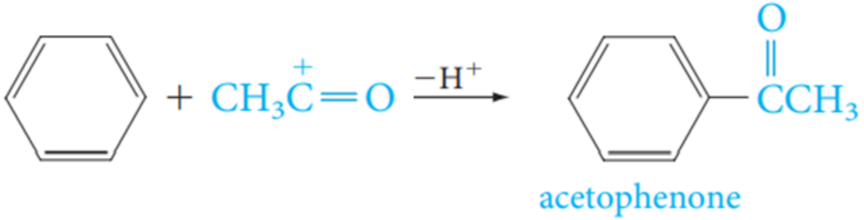
$$AlCl_3 + ClCH_2CH_3 \rightleftharpoons AlCl_4^- + \overset{+}{C}H_2CH_3$$

Friedel-Crafts Acylation

- The Electrophile is an acyl cation generated from an acyl halide, the reaction requires the addition of at least one equivalent of a Lewis acid (such as $AlCl_3$). The product of the reaction is an aryl ketone.



$$CH_3\overset{\overset{O}{\|}}{C}Cl + AlCl_3 \rightleftharpoons CH_3\overset{+}{C}{=}O + AlCl_4^-$$

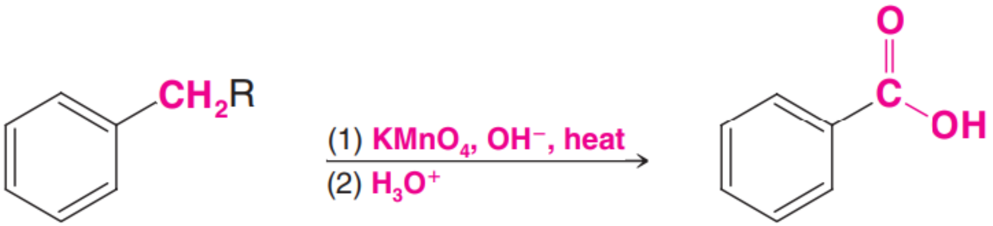


Reaction of Benzene

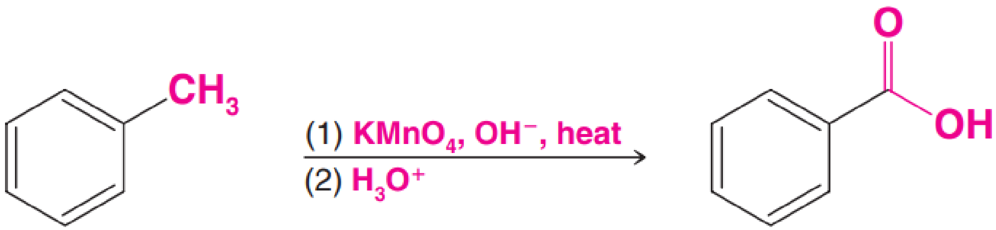
B- Reactions of the Side Chain of Alkylbenzene

1- Oxidation of the Side Chain

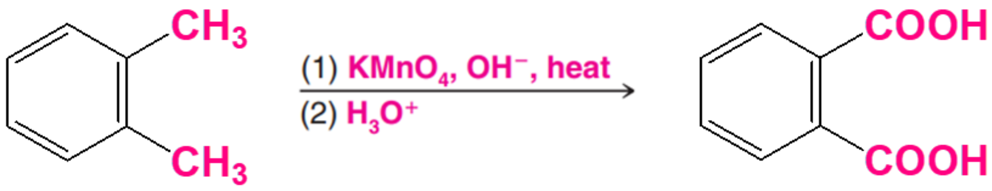
- Alkylbenzenes with alkyl groups longer than methyl are ultimately degraded to benzoic acids.



An alkylbenzene **Benzoic acid**

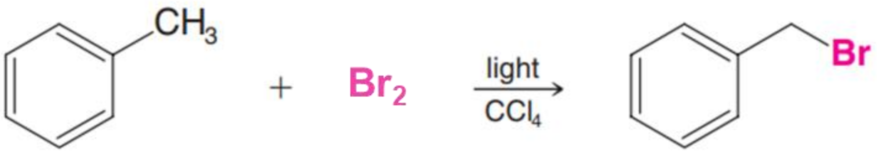


Benzoic acid

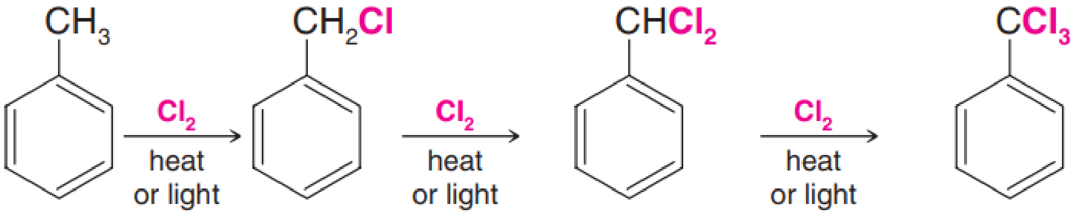


2- Halogenation of the Side Chain

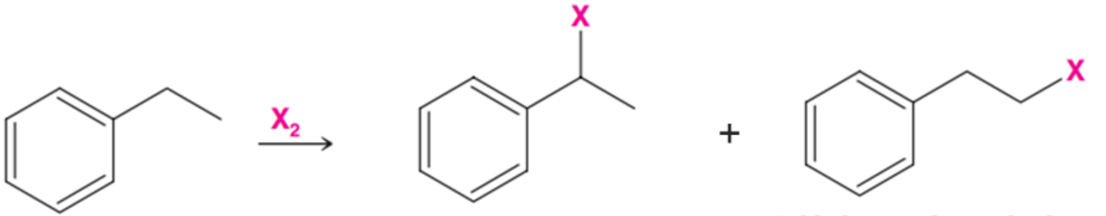
- Chlorine and bromine can be made to replace hydrogen atoms that are on a benzylic carbon, such as the methyl group of toluene.
- Benzylic halogenation is carried out in the absence of Lewis acids and under conditions that favor the formation of radicals.



Benzyl bromide



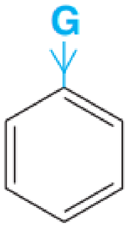
Benzyl chloride **Dichloromethylbenzene** **Trichloromethylbenzene**



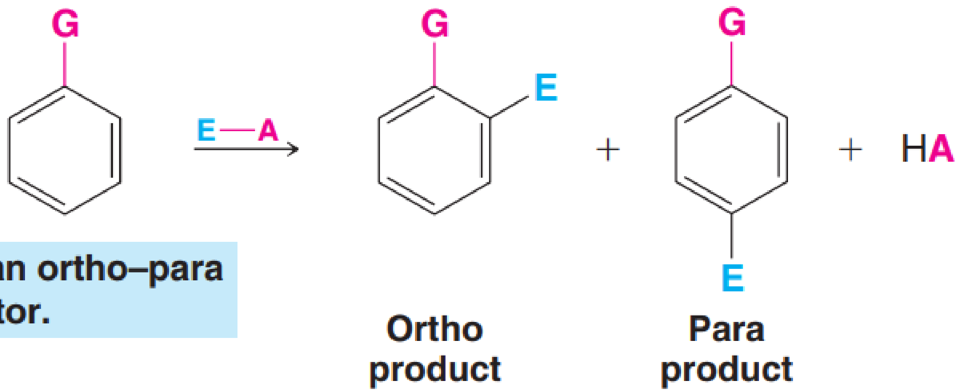
1-Halo-1-phenylethane (major product) **1-Halo-2-phenylethane (minor product)**

Substituents Can Affect Both the Reactivity of the Ring and the Orientation of the Incoming Group

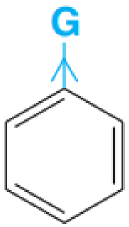
- A substituent group already present on a benzene ring can affect both the reactivity of the ring toward electrophilic substitution and the orientation that the incoming group takes on the ring.



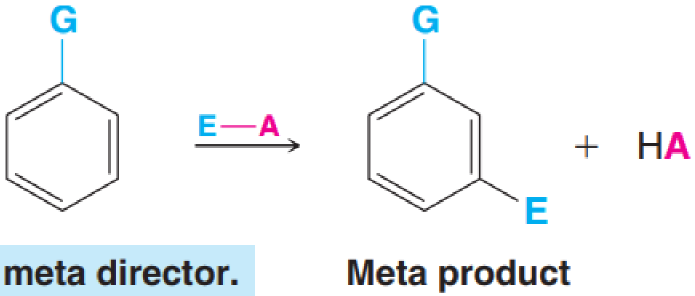
If G donates electrons the ring is activated; it reacts faster, and at an ortho or para position.



G is an ortho–para director.

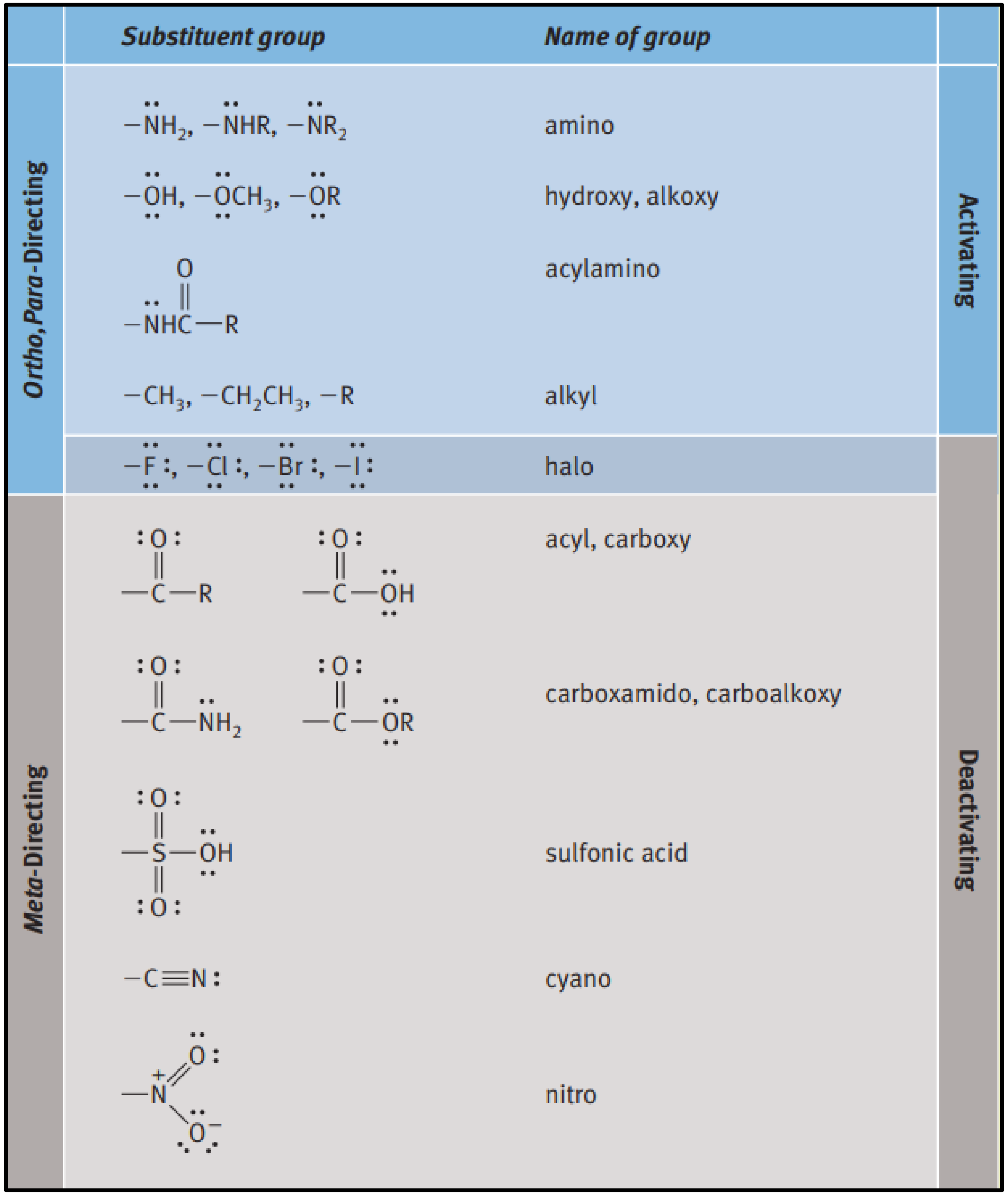


If G withdraws electrons the ring is deactivated; it reacts more slowly, and at a meta position (except when G is a halogen).



G is a meta director.

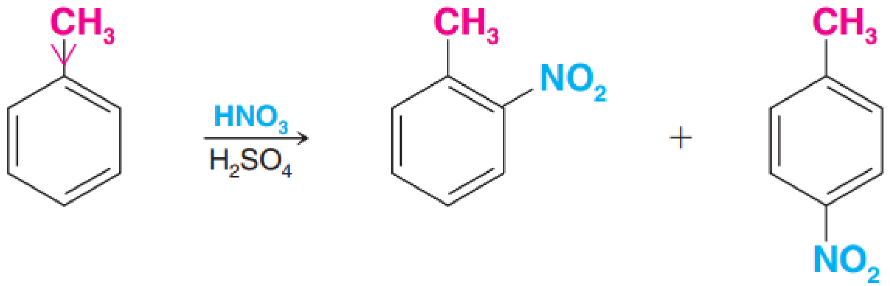
Directing and Activating Effects of Common Functional Groups
(Groups are Listed in Decreasing Order of Activation)



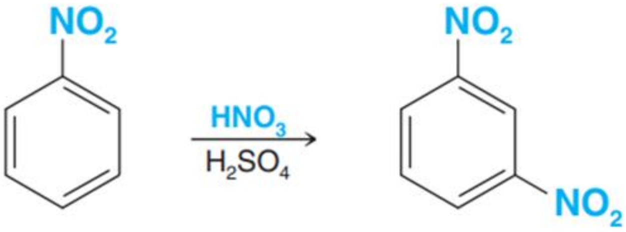
	Substituent group	Name of group	
Ortho, Para-Directing	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	Activating
	$-\ddot{O}H$, $-\ddot{O}CH_3$, $-\ddot{O}R$	hydroxy, alkoxy	
	$-\ddot{N}H\overset{O}{\overset{\|}{C}}-R$	acylamino	
	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	
	$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$,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

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

Examples:



o-Nitrotoluene *p*-Nitrotoluene



m-Dinitrobenzene