Seminar_3

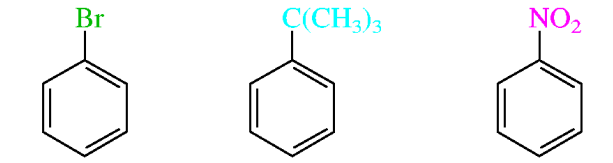
1. Substituded derivatives of benzene and their nomenclature
2. Reactions of arenes. Electrophilic aromatic substitutions
3. Activating substituents. Orientation in the aromatic ring

TEST - Aromatic hydrocarbons. Orientation in the aromatic ring

- Give the names
- Write the structural formula
- Reactions of arenes
- Activating substituents

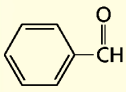
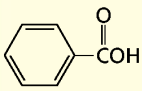
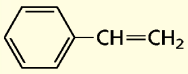
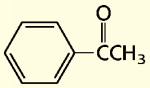
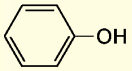
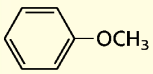
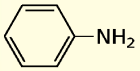
1. Substituded derivatives of benzene and their nomenclature

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.

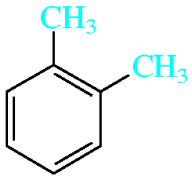


Bromobenzene *tert*-Butylbenzene Nitrobenzene

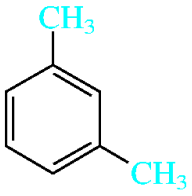
Many simple monosubstituted derivatives of benzene have common names of long standing that have been retained in the IUPAC system. We lists some of the most important ones. Dimethyl derivatives of benzene are called xylenes. There are three xylene isomers, the ortho (o)-, meta (m)-, and para (p)- substituted derivatives.

Structure	Systematic Name	Common Name*
	Benzenecarbaldehyde	Benzaldehyde
	Benzenecarboxylic acid	Benzoic acid
	Vinylbenzene	Styrene
	Methyl phenyl ketone	Acetophenone
	Benzenol	Phenol
	Methoxybenzene	Anisole
	Benzenamine	Aniline

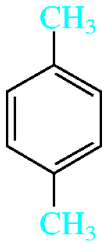
*These common names are acceptable in IUPAC nomenclature and are the names that will be used in this text.



o-Xylene
(1,2-dimethylbenzene)

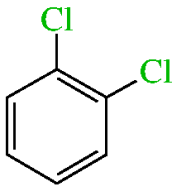


m-Xylene
(1,3-dimethylbenzene)

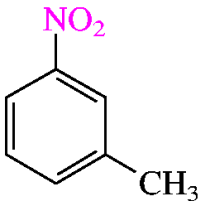


p-Xylene
(1,4-dimethylbenzene)

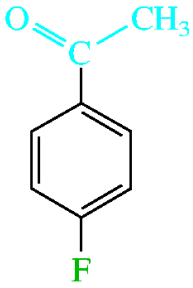
The prefix ortho signifies a 1,2-disubstituted benzene ring, meta signifies 1,3-disubstitution, and para signifies 1,4-disubstitution. The prefixes o, m, and p can be used when a substance is named as a benzene derivative or when a specific base name (such as acetophenone) is used. For example,



o-Dichlorobenzene
(1,2-dichlorobenzene)

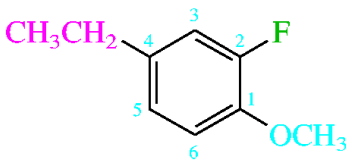


m-Nitrotoluene
(3-nitrotoluene)

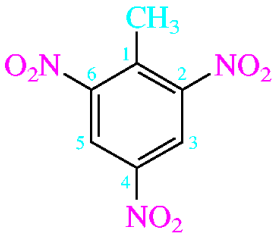


p-Fluoroacetophenone
(4-fluoroacetophenone)

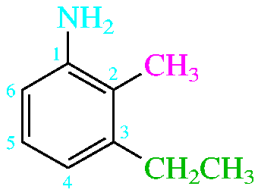
The o, m, and p prefixes are not used when three or more substituents are present on benzene; numerical locants must be used instead.



4-Ethyl-2-fluoroanisole

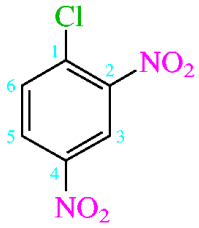


2,4,6-Trinitrotoluene

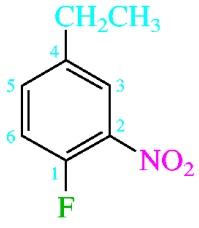


3-Ethyl-2-methylaniline

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:



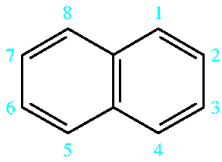
1-Chloro-2,4-dinitrobenzene



4-Ethyl-1-fluoro-2-nitrobenzene

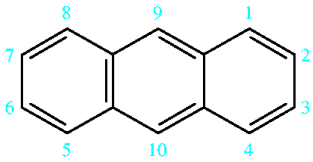
POLYCYCLIC AROMATIC HYDROCARBONS

Members of a class of arenes called polycyclic aromatic hydrocarbons possess substantial resonance energies because each is a collection of benzene rings fused together. Naphthalene, anthracene, and phenanthrene are the three simplest members of this class. They are all present in coal tar, a mixture of organic substances formed when coal is converted to coke by heating at high temperatures (about 1000 C) in the absence of air. Naphthalene is bicyclic (has two rings), and its two benzene rings share a common side. Anthracene and phenanthrene are both tricyclic aromatic hydrocarbons. Anthracene has three rings fused in a "linear" fashion; an "angular" fusion characterizes phenanthrene. The structural formulas of naphthalene, anthracene, and phenanthrene are shown along with the numbering system used to name their substituted derivatives:



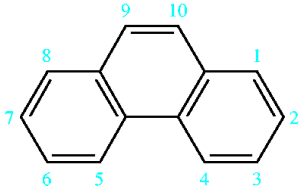
Naphthalene

255 kJ/mol
(61 kcal/mol)



Anthracene

347 kJ/mol
(83 kcal/mol)



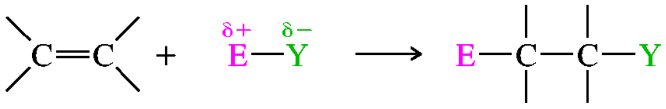
Phenanthrene

381 kJ/mol
(91 kcal/mol)

REACTIONS OF ARENES: ELECTROPHILIC AROMATIC SUBSTITUTION

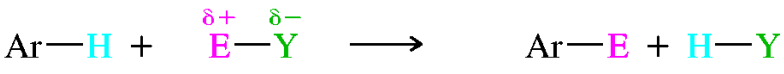
In the preceding chapter the special stability of benzene was described, along with reactions in which an aromatic ring was present as a substituent. Now we'll examine the aromatic ring as a functional group. What kind of reactions are available to benzene and its derivatives? What sort of reagents react with arenes, and what products are formed in those reactions?

Characteristically, the reagents that react with the aromatic ring of benzene and its derivatives are electrophiles. We already have some experience with electrophilic reagents, particularly with respect to how they react with alkenes. Electrophilic reagents add to alkenes.



Alkene | Electrophilic reagent | Product of electrophilic addition

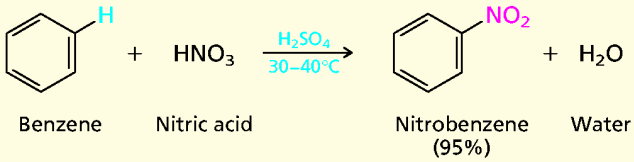
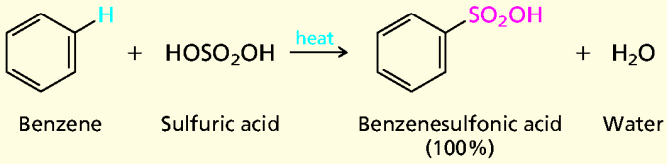
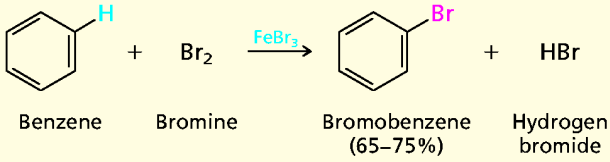
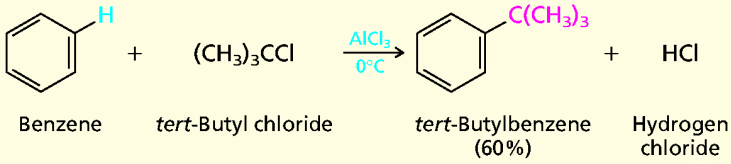
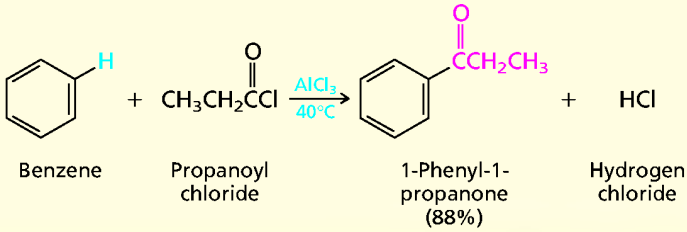
A different reaction takes place when electrophiles react with arenes. Substitution is observed instead of addition. If we represent an arene by the general formula ArH, where Ar stands for an aryl group, the electrophilic portion of the reagent replaces one of the hydrogens on the ring:



Arene | Electrophilic reagent | Product of electrophilic aromatic substitution

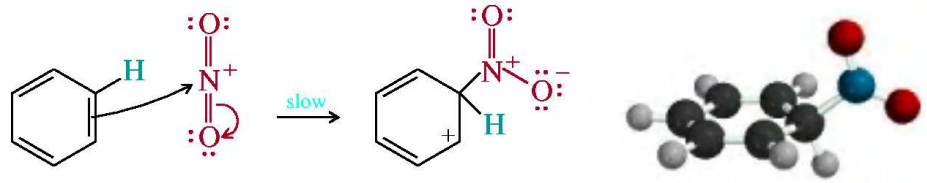
We call this reaction **electrophilic aromatic substitution**; it is one of the fundamental processes of organic chemistry.

REPRESENTATIVE ELECTROPHILIC AROMATIC SUBSTITUTION REACTION OF BENZENE

Reaction and comments	Equation
1. Nitration Warming benzene with a mixture of nitric acid and sulfuric acid gives nitrobenzene. A nitro group ($-NO_2$) replaces one of the ring hydrogens.	 Benzene + HNO_3 (H_2SO_4, 30–40°C) → Nitrobenzene (95%) + H_2O (Water)
2. Sulfonation Treatment of benzene with hot concentrated sulfuric acid gives benzenesulfonic acid. A sulfonic acid group ($-SO_2OH$) replaces one of the ring hydrogens.	 Benzene + $HOSO_2OH$ (heat) → Benzenesulfonic acid (100%) + H_2O (Water)
3. Halogenation Bromine reacts with benzene in the presence of iron(III) bromide as a catalyst to give bromobenzene. Chlorine reacts similarly in the presence of iron(III) chloride to give chlorobenzene.	 Benzene + Br_2 ($FeBr_3$) → Bromobenzene (65–75%) + HBr (Hydrogen bromide)
4. Friedel–Crafts alkylation Alkyl halides react with benzene in the presence of aluminum chloride to yield alkylbenzenes.	 Benzene + $(CH_3)_3CCl$ ($AlCl_3$, 0°C) → *tert*-Butylbenzene (60%) + HCl (Hydrogen chloride)
5. Friedel–Crafts acylation An analogous reaction occurs when acyl halides react with benzene in the presence of aluminum chloride. The products are acylbenzenes.	 Benzene + CH_3CH_2COCl ($AlCl_3$, 40°C) → 1-Phenyl-1-propanone (88%) + HCl (Hydrogen chloride)

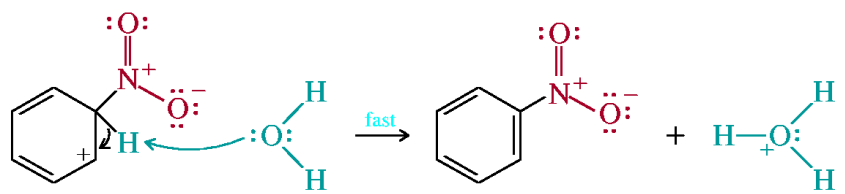
NITRATION OF BENZENE

Step 1: Reaction of nitronium cation with the π system of the aromatic ring



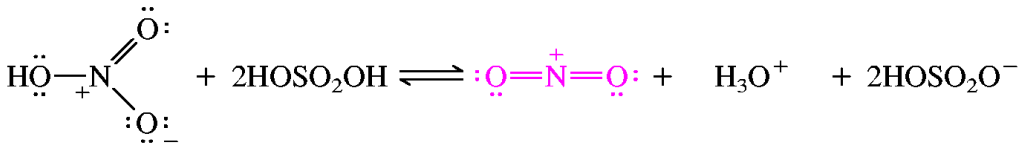
Benzene and nitronium ion — Cyclohexadienyl cation intermediate

Step 2: Loss of a proton from the cyclohexadienyl cation



Cyclohexadienyl cation intermediate — Water — Nitrobenzene — Hydronium ion

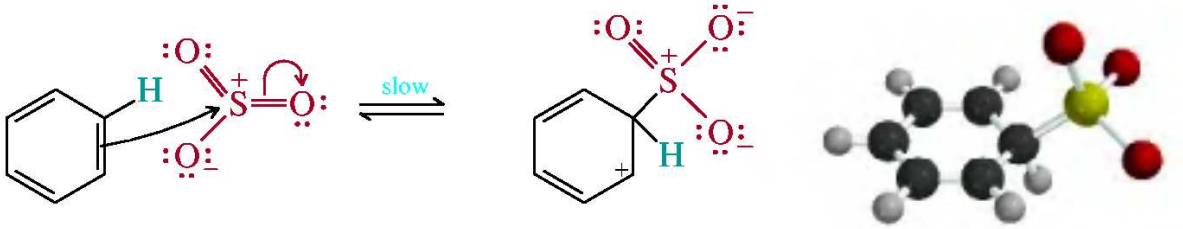
The purpose of sulfuric acid in the reaction is to increase the concentration of nitronium ion. Nitric acid alone does not furnish a high enough concentration of nitronium ion for the reaction to proceed at a convenient rate. Nitric acid reacts with sulfuric acid to give nitronium ion according to the equation:



Nitric acid | Sulfuric acid | Nitronium ion | Hydronium ion | Hydrogen sulfate ion

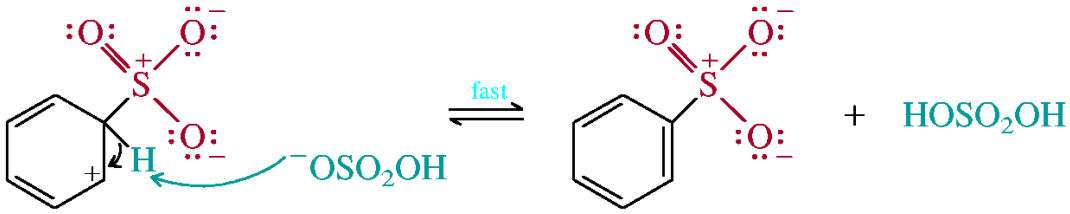
SULFONATION OF BENZENE

Step 1: Sulfur trioxide attacks benzene in the rate-determining step



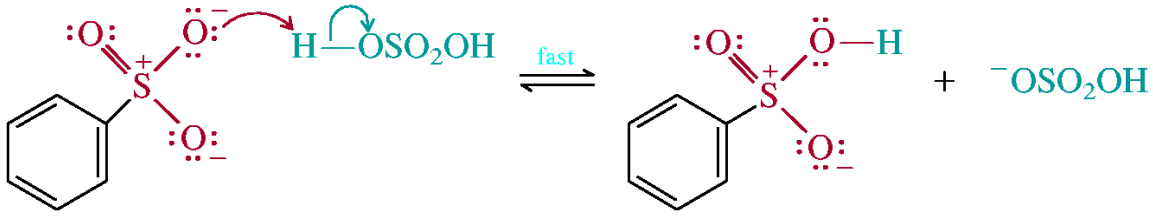
Benzene and sulfur trioxide | Cyclohexadienyl cation intermediate

Step 2: A proton is lost from the sp^3-hybridized carbon of the intermediate to restore the aromaticity of the ring. The species shown that abstracts the proton is a hydrogen sulfate ion formed by ionization of sulfuric acid.



Cyclohexadienyl cation intermediate | Hydrogen sulfate ion | Benzenesulfonate ion | Sulfuric acid

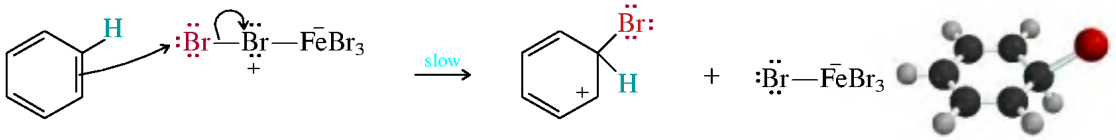
Step 3: A rapid proton transfer from the oxygen of sulfuric acid to the oxygen of benzenesulfonate completes the process.



Benzenesulfonate ion | Sulfuric acid | Benzenesulfonic acid | Hydrogen sulfate ion

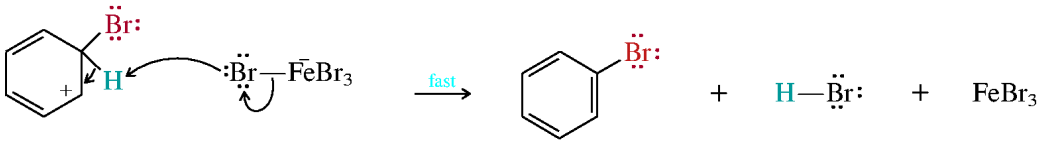
HALOGENATION OF BENZENE

Step 1: The bromine–iron(III) bromide complex is the active electrophile that attacks benzene. Two of the π electrons of benzene are used to form a bond to bromine and give a cyclohexadienyl cation intermediate.



Benzene and bromine–iron(III) bromide complex | Cyclohexadienyl cation intermediate | Tetrabromoferrate ion

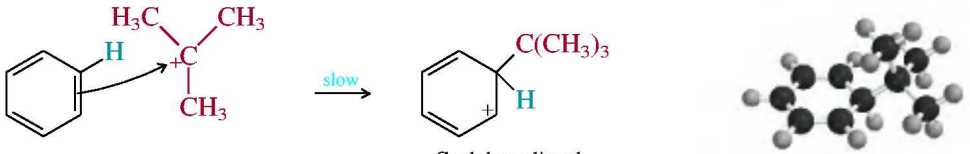
Step 2: Loss of a proton from the cyclohexadienyl cation yields bromobenzene.



Cyclohexadienyl cation intermediate | Tetrabromoferrate ion | Bromobenzene | Hydrogen bromide | Iron(III) bromide

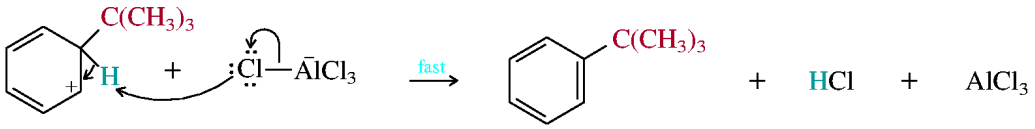
FRIEDEL-CRAFTS ALKYLATION OF BENZENE

Step 1: Once generated by the reaction of *tert*-butyl chloride and aluminum chloride, *tert*-butyl cation attacks the π electrons of benzene, and a carbon–carbon bond is formed.



Benzene and *tert*-butyl cation | Cyclohexadienyl cation intermediate

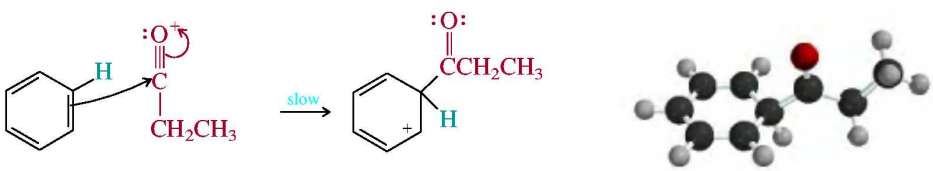
Step 2: Loss of a proton from the cyclohexadienyl cation intermediate yields *tert*-butylbenzene.



Cyclohexadienyl cation intermediate | Tetrachloroaluminate ion | *tert*-Butylbenzene | Hydrogen chloride | Aluminum chloride

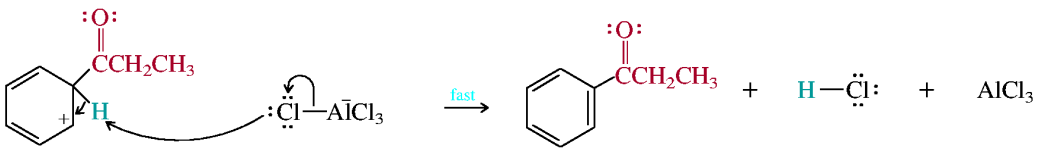
FRIEDEL-CRAFTS ACYLATION OF BENZENE

Step 1: The acyl cation attacks benzene. A pair of π electrons of benzene is used to form a covalent bond to the carbon of the acyl cation.



Benzene and propanoyl cation | Cyclohexadienyl cation intermediate

Step 2: Aromaticity of the ring is restored when it loses a proton to give the aryl ketone.

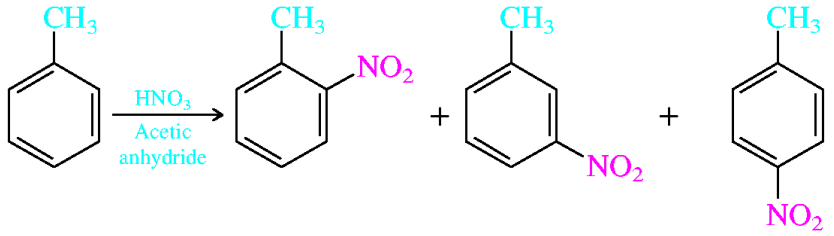


Cyclohexadienyl cation intermediate | Tetrachloroaluminate ion | 1-Phenyl-1-propanone | Hydrogen chloride | Aluminum chloride

3. SUBSTITUENT EFFECTS IN ELECTROPHILIC AROMATIC SUBSTITUTION: ACTIVATING SUBSTITUENTS

We've been concerned only with electrophilic substitution of benzene. Two important questions arise when we turn to substitution on rings that already bear at least one substituent:
1. What is the effect of a substituent on the rate of electrophilic aromatic substitution?
2. What is the effect of a substituent on the regioselectivity of electrophilic aromatic substitution?

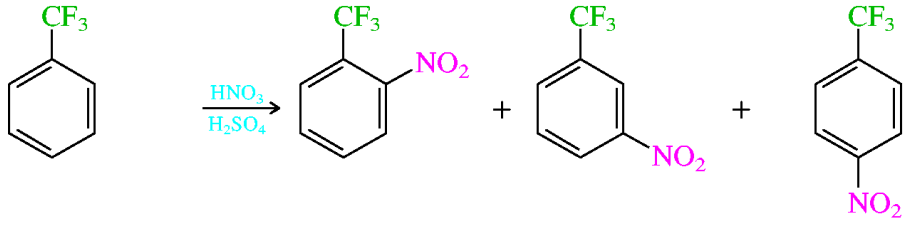
Three products are possible from nitration of toluene: o-nitrotoluene, m-nitrotoluene, and p-nitrotoluene. All are formed, but not in equal amounts. Together, the ortho- and para-substituted isomers make up 97% of the product mixture; the meta only 3%.



Toluene | *o*-Nitrotoluene (63%) | *m*-Nitrotoluene (3%) | *p*-Nitrotoluene (34%)

Because substitution in toluene occurs primarily at positions ortho and para to methyl, we say that a **methyl substituent is an ortho, para director.**

Nitration of (trifluoromethyl)benzene, on the other hand, yields almost exclusively m-nitro(trifluoromethyl)benzene (91%). The ortho- and para-substituted isomers are minor components of the reaction mixture.



(Trifluoromethyl)benzene | *o*-Nitro(trifluoromethyl)benzene (6%) | *m*-Nitro(trifluoromethyl)benzene (91%) | *p*-Nitro(trifluoromethyl)benzene (3%)

Because substitution in (trifluoromethyl)benzene occurs primarily at positions meta to the substituent, we say that **a trifiuoromethyl group is a meta director.**

Our analysis of substituent effects has so far centered on two groups: methyl and trifluoromethyl. We have seen that a methyl substituent is activating and ortho, para-directing. A trifluoromethyl group is strongly deactivating and meta-directing. What about other substituents? We summarizes orientation and rate effects in electrophilic aromatic substitution reactions for a variety of frequently encountered substituents. It is arranged in order of decreasing activating power: the most strongly activating substituents are at the top, the most strongly deactivating substituents are at the bottom. The main features of the table can be summarized as follows:
1. All activating substituents are ortho, para directors.
2. Halogen substituents are slightly deactivating but are ortho, para-directing.
3. Strongly deactivating substituents are meta directors.

Some of the most powerful activating substituents are those in which an oxygen atom is attached directly to the ring. These substituents include the hydroxyl group as well as alkoxy and acyloxy groups. All are ortho, para directors.

Classification of substituents in electrophilic aromatic substitution reaction

Effect on rate	Substituent		Effect on orientation
Very strongly activating	$-\ddot{N}H_2$	(amino)	Ortho, para-directing
	$-\ddot{N}HR$	(alkylamino)	
	$-\ddot{N}R_2$	(dialkylamino)	
	$-\ddot{O}H$	(hydroxyl)	
Strongly activating	$-\ddot{N}HC(=O)R$	(acylamino)	Ortho, para-directing
	$-\ddot{O}R$	(alkoxy)	
	$-\ddot{O}C(=O)R$	(acyloxy)	
Activating	$-R$	(alkyl)	Ortho, para-directing
	$-Ar$	(aryl)	
	$-CH{=}CR_2$	(alkenyl)	
Standard of comparison	$-H$	(hydrogen)	
Deactivating	$-X$ (X = F, Cl, Br, I)	(halogen)	Ortho, para-directing
	$-CH_2X$	(halomethyl)	
Strongly deactivating	$-C(=O)H$	(formyl)	Meta-directing
	$-C(=O)R$	(acyl)	
	$-C(=O)OH$	(carboxylic acid)	
	$-C(=O)OR$	(ester)	
	$-C(=O)Cl$	(acyl chloride)	
	$-C{\equiv}N$	(cyano)	
	$-SO_3H$	(sulfonic acid)	
Very strongly deactivating	$-CF_3$	(trifluoromethyl)	Meta-directing
	$-NO_2$	(nitro)	