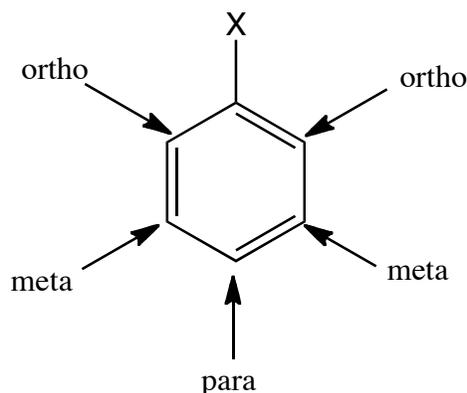


## Nomenclature of substituted benzene rings

When you have two substituents on a benzene ring, *ortho*, *meta*, and *para* are used to tell where the second substitution is relative to the first one.

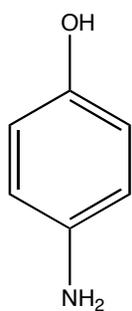


*Ortho* refers to 1,2-substitution and is abbreviated o-

*Meta* refers to 1,3-substitution and is abbreviated m-

*Para* refers to 1,4-substitution and is abbreviated p-

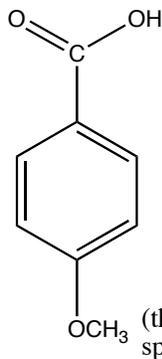
Examples:



p-aminophenol  
(more correct, OH has priority)

or

p-hydroxyaniline

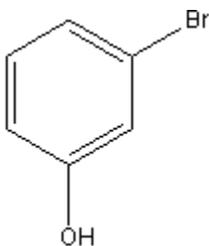


p-methoxybenzoic acid

(this is an ether group,  
specifically methoxy)

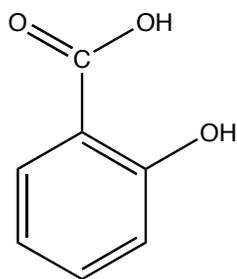
p-Aminophenol:

The amine and hydroxyl group are in the 1 and 4 positions, so they are *para* to each other. The parent structure in this molecule can be either aniline or phenol. For this course, it doesn't matter which parent structure you pick in the nomenclature with these substituents. Usually when naming the substituents, the atomic number takes priority, but there are many exceptions for historical reasons.

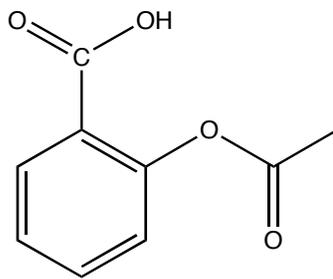


Name: *m*-bromophenol or 3-bromophenol

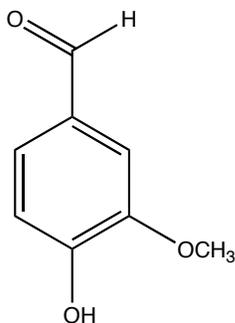
In this compound, the -OH (hydroxy) and -Br are in the 1 and 3 positions, so they are *meta* (or abbreviated *m*) to each other. The parent structure is phenol (phenol is a benzene with a hydroxyl group directly attached, not to be confused with phenyl which means just a benzene ring as a substituent), so we call this meta-bromophenol.



2-hydroxybenzoic acid  
aka salicylic acid

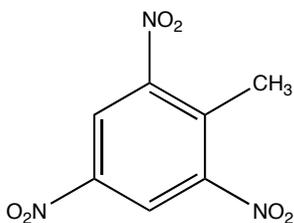


aspirin  
acetylsalicylic acid



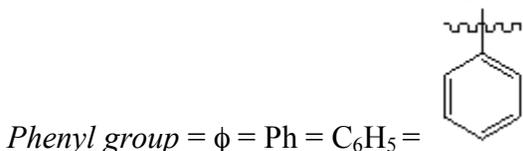
Nomenclature: 4-hydroxy-3-methoxybenzaldehyde (or vanillin from vanilla extract). The carbon substituent (an aldehyde group) gets priority.

Note: we number the ring in a way such that the substituents have the lowest numbers (so it's not 4-hydroxy-5-methoxy-, but 4-hydroxy-3-methoxy-). The substituents are listed in alphabetical order before the parent compound, but this course will not be incredibly picky with the order.

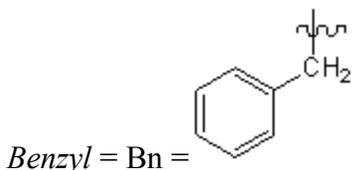


Nomenclature: 2,4,6-trinitrotoluene (TNT)  
An explosive

### Nomenclature of some Aromatic Groups:

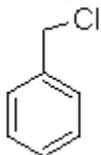


Aryl = Ar = aromatic group. It is a broad term, and includes any aromatic rings.

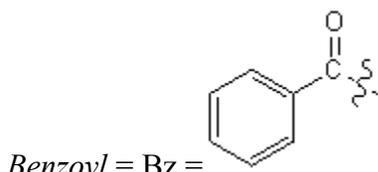


It has a -CH<sub>2</sub>- (methylene) group attached to the benzene ring.

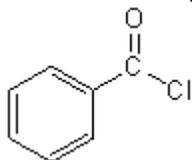
This group can be used to name particular compounds, such as the one shown below.

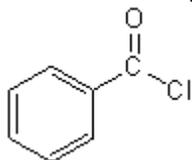


This compound has chlorine attached to a benzyl group, therefore it is called benzyl chloride.



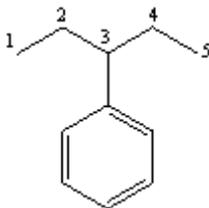
. This is different from benzyl group (there is an extra “o” in the name). It has a carbonyl attached to the benzene ring instead of a methylene group.



For example,  is named benzoyl chloride.

Therefore, it is sometimes useful to name a compound with the aromatic part as a substituent rather than it forming a part of the parent name.

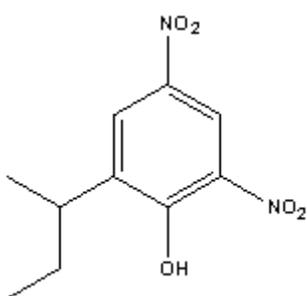
Example:



Nomenclature: 3-phenylpentane (pentan-3-ylbenzene is also an acceptable name, but it is more complicated and isn't the best name).

(Note that this molecule is achiral: it has a plane of symmetry)

Example:



Naming this compound is a little complicated, and for the purposes of this course, there are a few names that would be accepted:

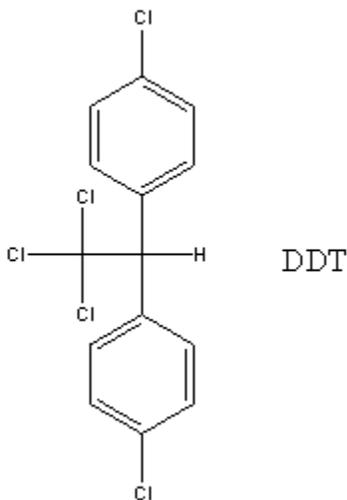
6-(but-2-yl)-2,4-dinitrophenol

6-(1-methylpropyl)-2,4-dinitrophenol

This is Amax. It is used to enhance the yield of corn production.

The systematic name for this compound is 2-*sec*-butyl-4,6-dinitrophenol.

Example:



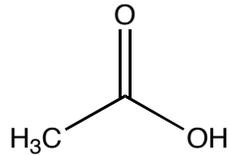
DDT

1,1,1-trichloro-2,2-bis-(4-chlorophenyl)ethane

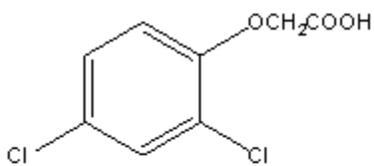
*Note:* although the two 4-chlorophenyl can also be named using di-, bis is used instead. bis is commonly used for large groups. The 4-chlorophenyl could also be called p-chlorophenyl

DDT is an insecticide and helped to wipe out malaria in many parts of the world. Consequently, the person who discovered its properties (Paul Müller) won the Nobel Prize in Medicine in 1948.

Example:

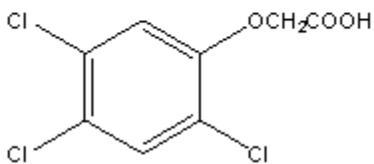


Note: Acetic acid is the parent structure



2,4-dichlorophenoxyacetic acid

2,4-D



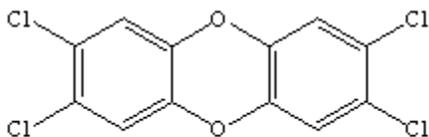
2,4,5-trichlorophenoxyacetic acid

2,4,5-T

Agent Orange

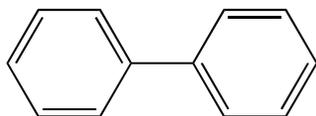
Agent Orange, a broad leaf herbicide, was used in the Vietnam War to defoliate large areas. It was used in Edmonton on lawns as Weed and Feed to get rid of weeds.

Example:

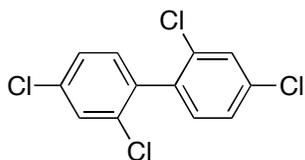


Dioxin

This potent toxin and carcinogen that can contaminate Agent Orange and can occur in pulp mill waste. While this is only an example of one dioxin, typically the term dioxin refers to this particular molecule.



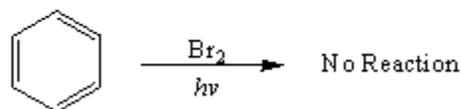
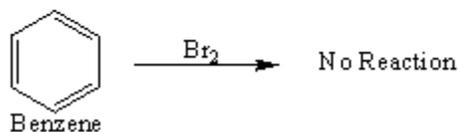
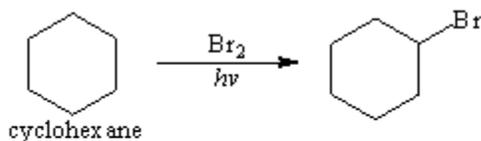
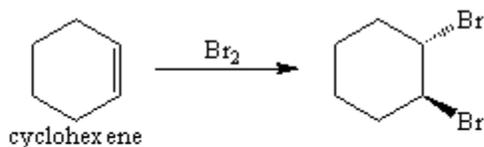
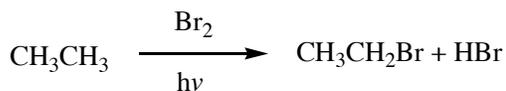
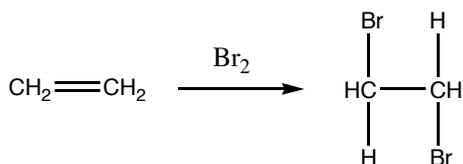
biphenyl



A polychlorinated biphenyl (PCB)  
If the Cl's were Br's this would be a  
polybrominated biphenyl (PBB)

## Electrophilic Aromatic Substitution

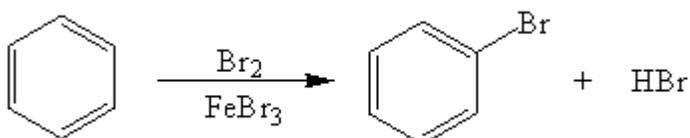
Benzene appears to be a remarkably stable and unreactive compared to alkenes, such as cyclohexene or ethylene, or even alkanes, such as cyclohexane or ethane.



When ethylene or cyclohexene is allowed to react with bromine (an addition reaction), a dibrominated product is formed. However, when benzene is allowed to react with bromine in the absence of catalyst, nothing occurs. It is much less reactive.

In the case of alkanes such as ethane or cyclohexane, light ( $h\nu$ ) or heat are required for the bromination to occur (this is a substitution). For benzene, there is still no reaction under these conditions.

However, this is not to say that benzene is completely unreactive. Under certain conditions, benzene can be forced to react.

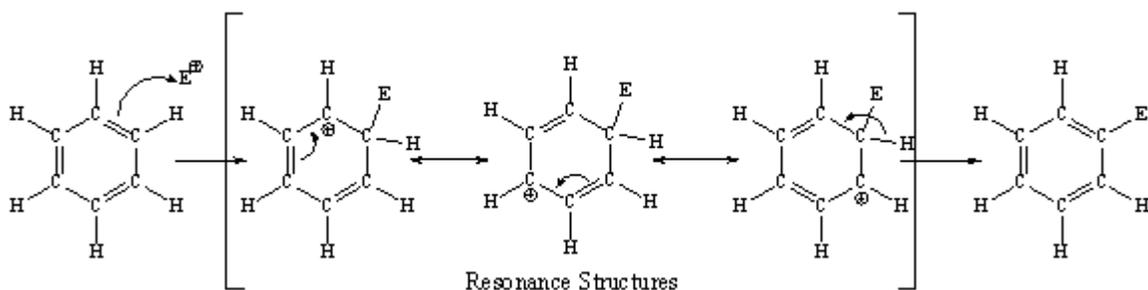


This is an Aromatic Electrophilic Substitution.

In electrophilic aromatic substitution, an electrophile ( $E^+$ ) is substituted for a hydrogen on the aromatic (e.g. benzene) ring.

Aromatic compounds are very stable and un-reactive. In this type of reaction, the electrophile must be especially reactive (electron deficient).

The General Mechanism:

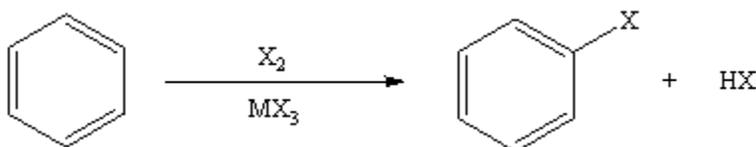


The pi system of the benzene ring acts as the nucleophile.

The cation formed in the reaction is resonance stabilized (conjugated with the two double bonds). However, it is not aromatic. Note that the positive charge is ortho and para to the electrophile.

Once the aromatic stabilization is lost, it is easily regained (remember that by staying aromatic, the compound becomes more stable). Hence the last step (loss of proton) is fast to regenerate the aromatic system.

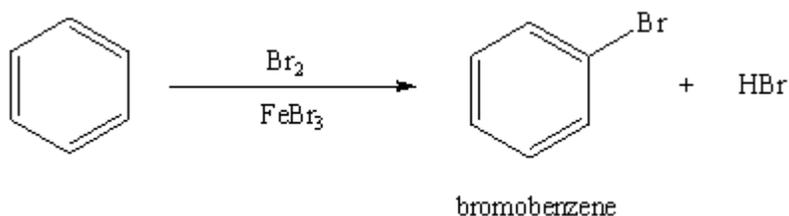
**Halogenation (addition of halogen)**



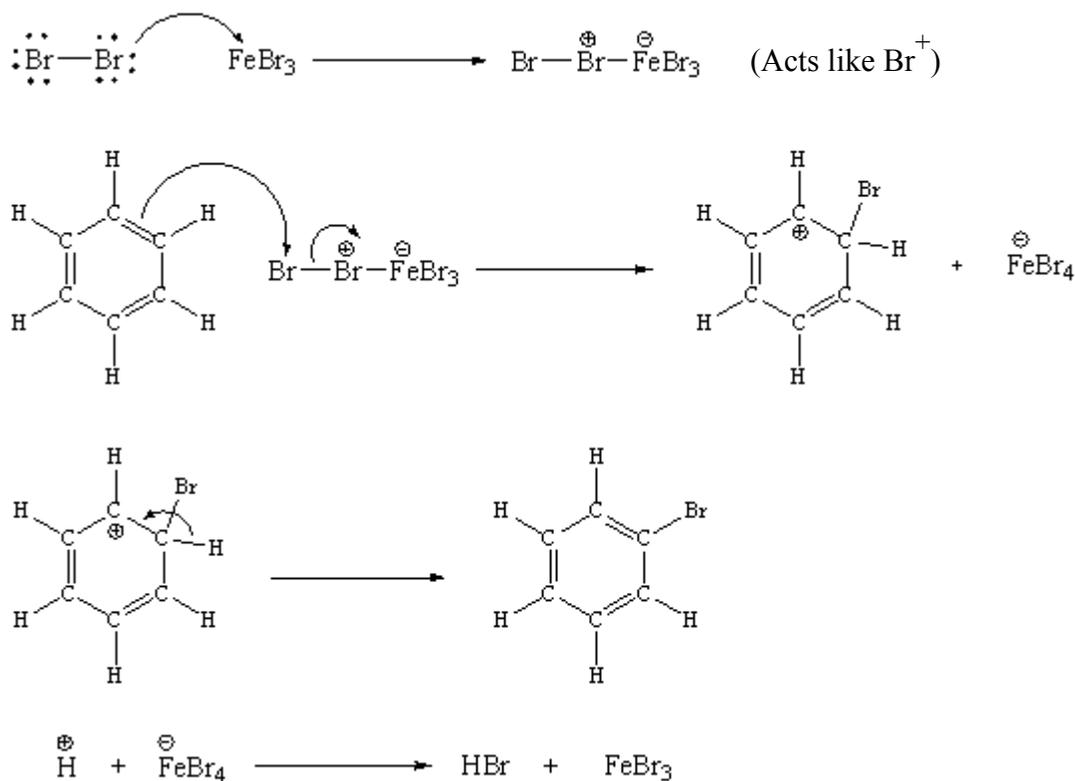
Where X = halogen (Cl, Br, and I)

M = metal Fe, B, or Al

In this reaction,  $\text{MX}_3$  ( $\text{FeBr}_3$ ,  $\text{AlCl}_3$ ) is a Lewis Acid catalyst (a Lewis Acid is a substance that can accept a pair of electrons).  $\text{MX}_3$  has an empty orbital to accept a pair of electrons. Chlorine or bromine alone are not strong enough electrophiles to react with the weakly nucleophilic benzene by themselves. The catalyst converts the halogen into a stronger electrophile, which can react with benzene.

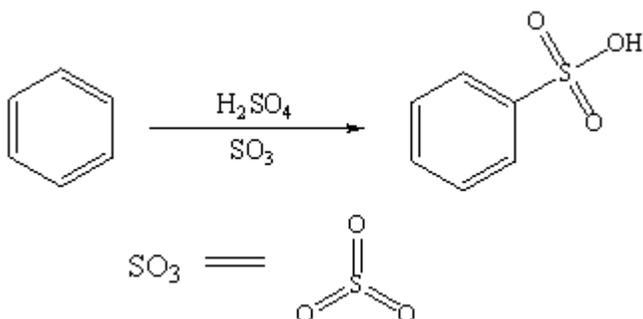


Mechanism:



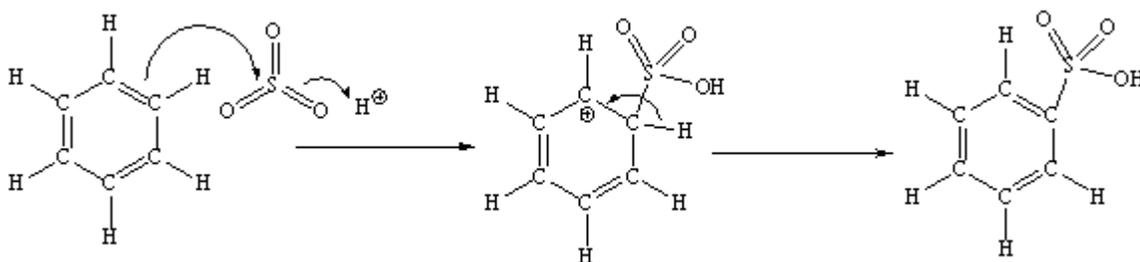
In halogenation, the Lewis Acid catalyst is regenerated at the end of the step.

## Sulfonation



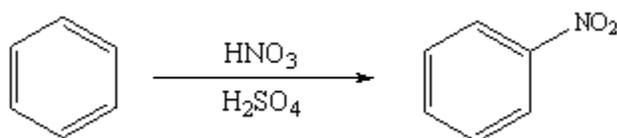
In this reaction,  $\text{SO}_3$  is the electrophile.

Mechanism:



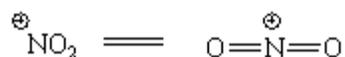
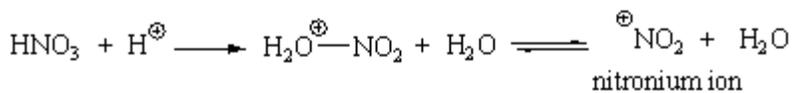
This reaction of  $\text{SO}_3$  is followed by loss of proton from the conjugated cation intermediate (similar to the one we saw in halogenation).

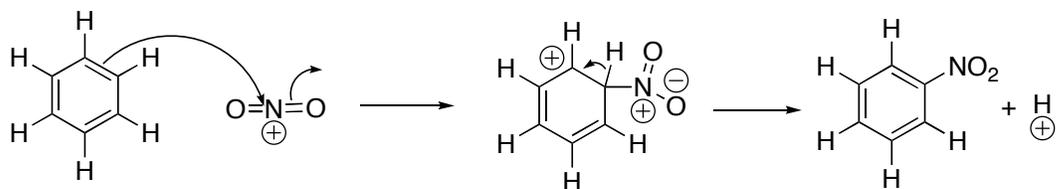
## Nitration



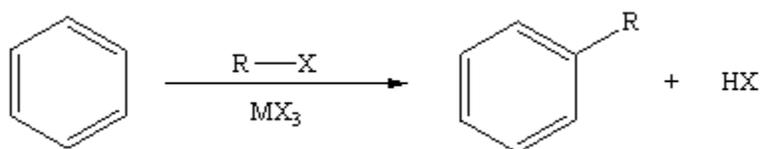
Mechanism:

In strong acid, nitric acid is protonated to give  $\text{H}_2\text{NO}_3^+$ . Loss of water generates the nitronium ion that acts as an electrophile.





### Alkylation (Friedel-Crafts)



Where R = alkyl (methyl, ethyl, isopropyl, *tert*-butyl, etc)

X = halogen (Cl, Br, and I)

M = metal Fe, B, or Al

Mechanism:

