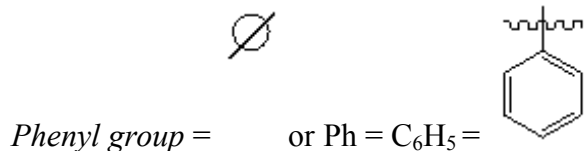
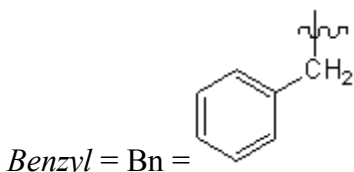


More Nomenclature: Common Names for Selected Aromatic Groups

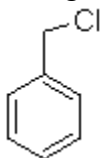


Aryl = Ar = aromatic group. It is a broad term, and includes any aromatic rings.

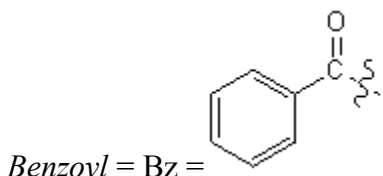


It has a -CH₂- (methylene) group attached to the benzene ring.

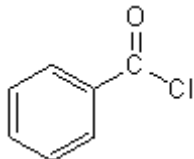
This group can be used to name particular compounds, such as the one shown below.



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



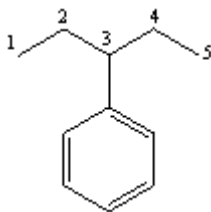
. This is different from benzyl group (there is an extra “o” in the name). It has a carbonyl attached to the benzene ring instead of a methylene group.



For example, is named benzoyl chloride.

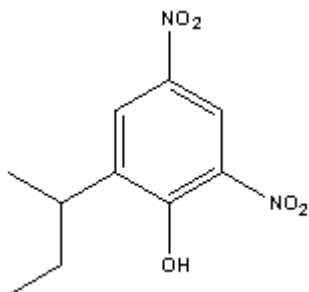
Therefore, it is sometimes helpful to recognize a common structure in order to name a compound.

Example:



Nomenclature: 3-phenylpentane

Example:



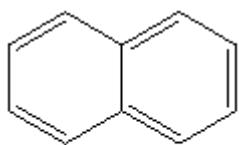
This is Amaize. It is used to enhance the yield of corn production.

The systematic name for this compound is 2,4-dinitro-6-(1-methylpropyl)phenol.

Polynuclear Aromatic Compounds

Aromatic rings can fuse together to form polynuclear aromatic compounds.

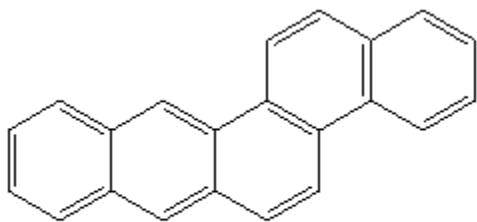
Example:



Naphthalene

It is two benzene rings fused together, and it is aromatic. The electrons are delocalized in both rings (think about all of its resonance form).

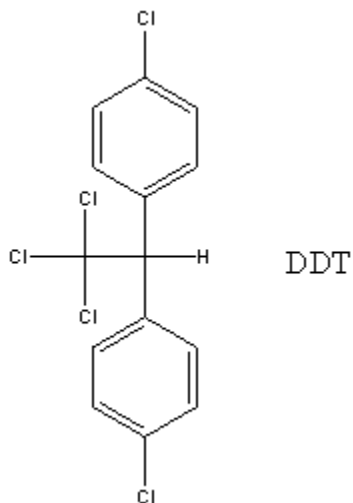
Example:



benzopyrene

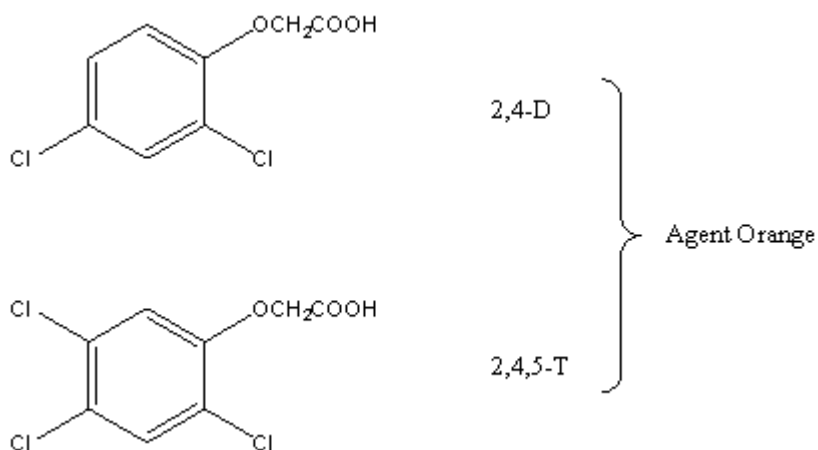
This compound is also aromatic, including the ring in the middle. All carbons are sp^2 hybridized and the electron density is shared across all 5 rings.

Example:



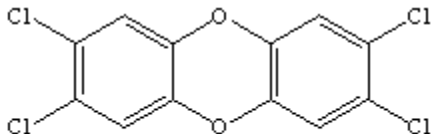
DDT is an insecticide and helped to wipe out malaria in many parts of the world. Consequently, the person who discovered it (Muller) won the Nobel Prize in 1942. The systematic name for this compound is 1,1,1-trichloro-2,2-bis-(4-chlorophenyl)ethane. *Note:* although the two 4-chlorophenyl can also be named using di-, bis is used instead. bis is commonly used for large groups.

Example:



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

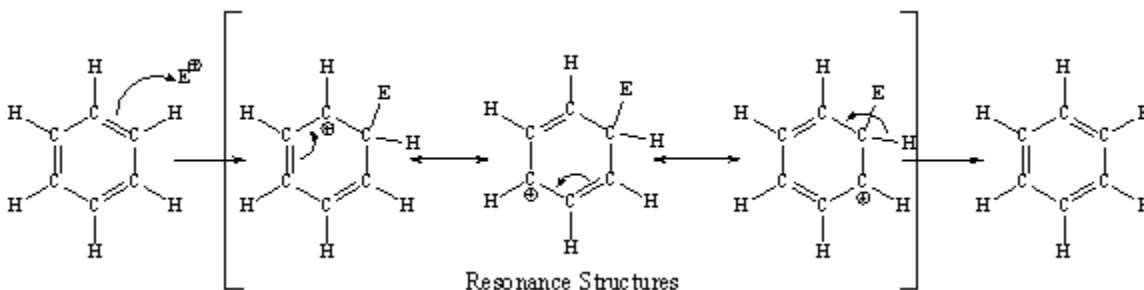
This a potent toxin that can contaminate Agent Orange and can occur in pulp mill waste

Electrophilic Aromatic Substitution

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

Recall from last lecture that 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.

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.

There are 5 main types of electrophilic aromatic substitutions we will consider in this class. (Halogenation, sulfonation, nitration, Friedel Crafts alkylation, and acylation)

Halogenation (addition of halogen)

Recall from last lecture, benzene does not react with Br_2 or Cl_2 like alkenes (e.g. cyclohexene) or alkanes (e.g. cyclohexane). A catalyst is needed to force the reaction.

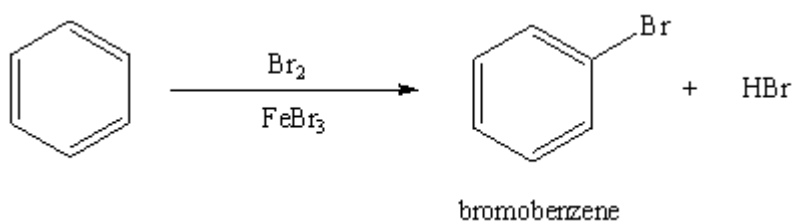


Where X = halogen (Cl, Br, and I)

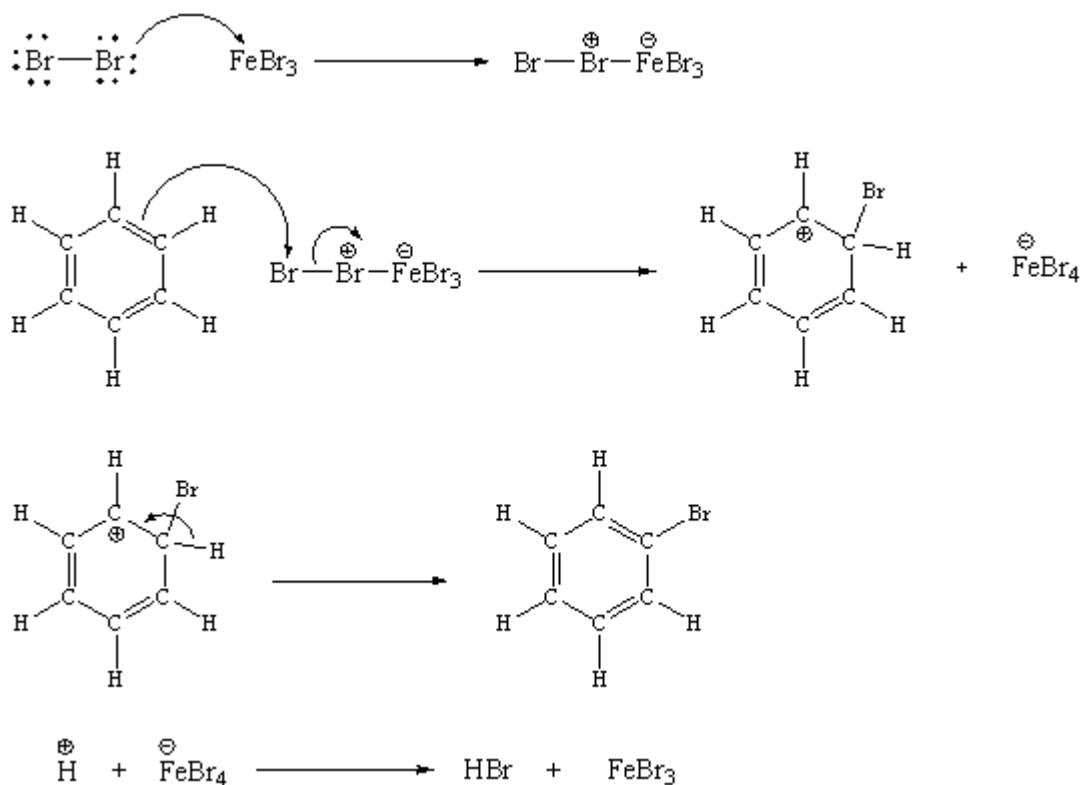
M = metal Fe, B, or Al

In this reaction, MX_3 (i.e., FeBr_3 , AlCl_3) is a Lewis Acid catalyst (a Lewis Acid is a substance that can accept a pair of electrons). MX_3 has an empty orbital to accept a pair of electrons. Chlorine or bromine alone are not strongly enough electrophilic to react with the weakly nucleophilic benzene by themselves. The catalyst converts the halogen into a stronger electrophile, which can react with benzene.

Example:

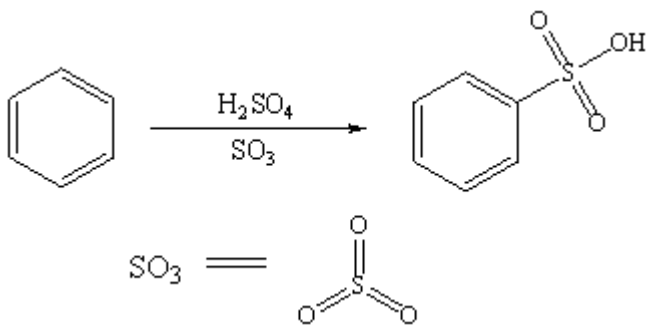


Mechanism:



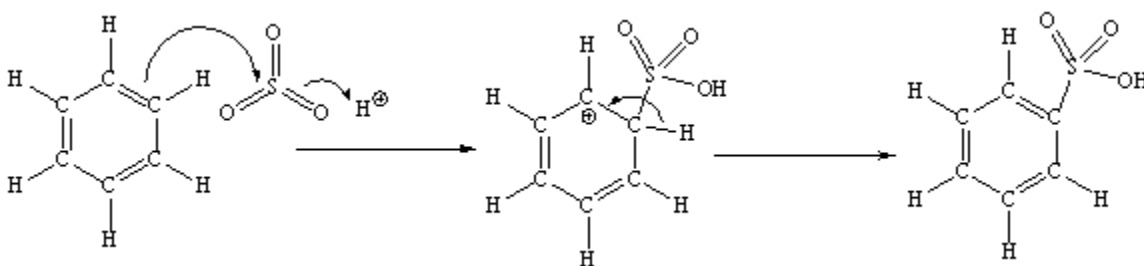
In halogenation, the Lewis Acid catalyst is regenerated at the end of the step.

Sulfonation



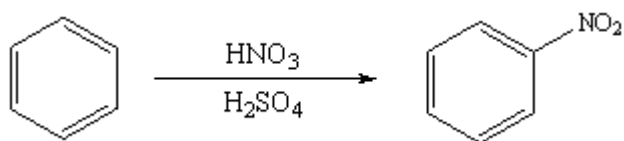
In this reaction, SO_3 is the electrophile.

Mechanism:



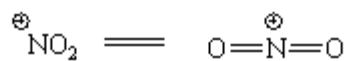
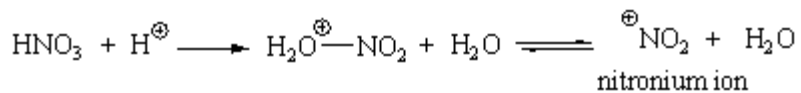
This reaction of SO_3 is followed by loss of proton from the conjugated cation intermediate

Nitration

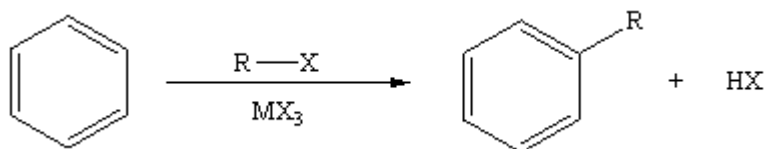


Mechanism:

In strong acid, nitric acid is protonated to give H_2NO_3^+ . Loss of water generates the nitronium ion that acts as electrophile.



Alkylation

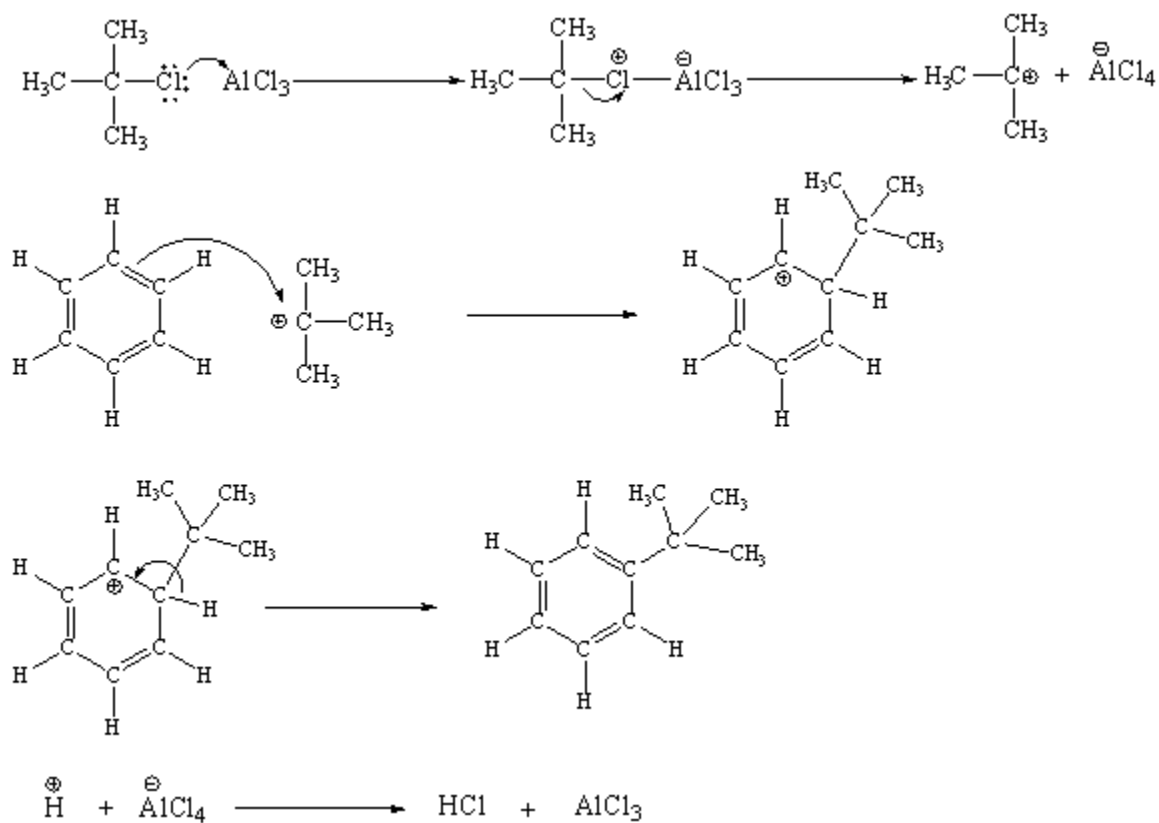


Where R = alkyl (methyl, ethyl, isopropyl, *tert*-butyl, etc)

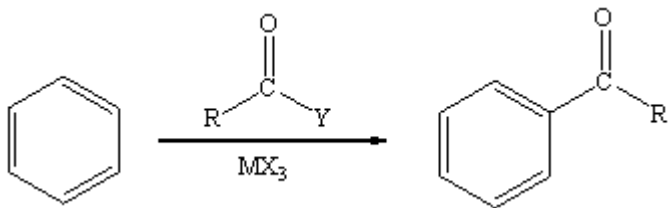
X = halogen (Cl, Br, and I)

M = metal Fe, B, or Al

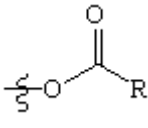
Mechanism:



Acylation (Friedel-Crafts)

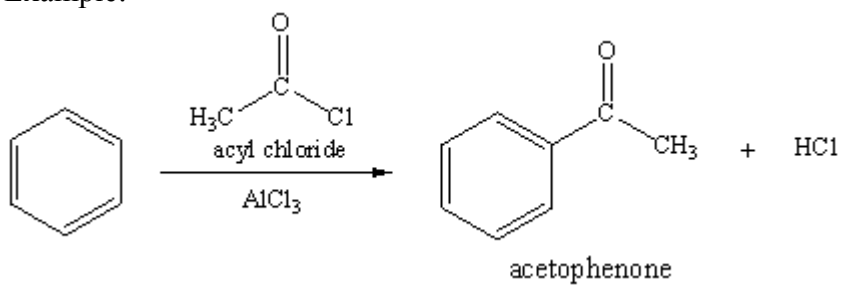


Where R = alkyl (methyl, ethyl, *tert*-butyl, etc)

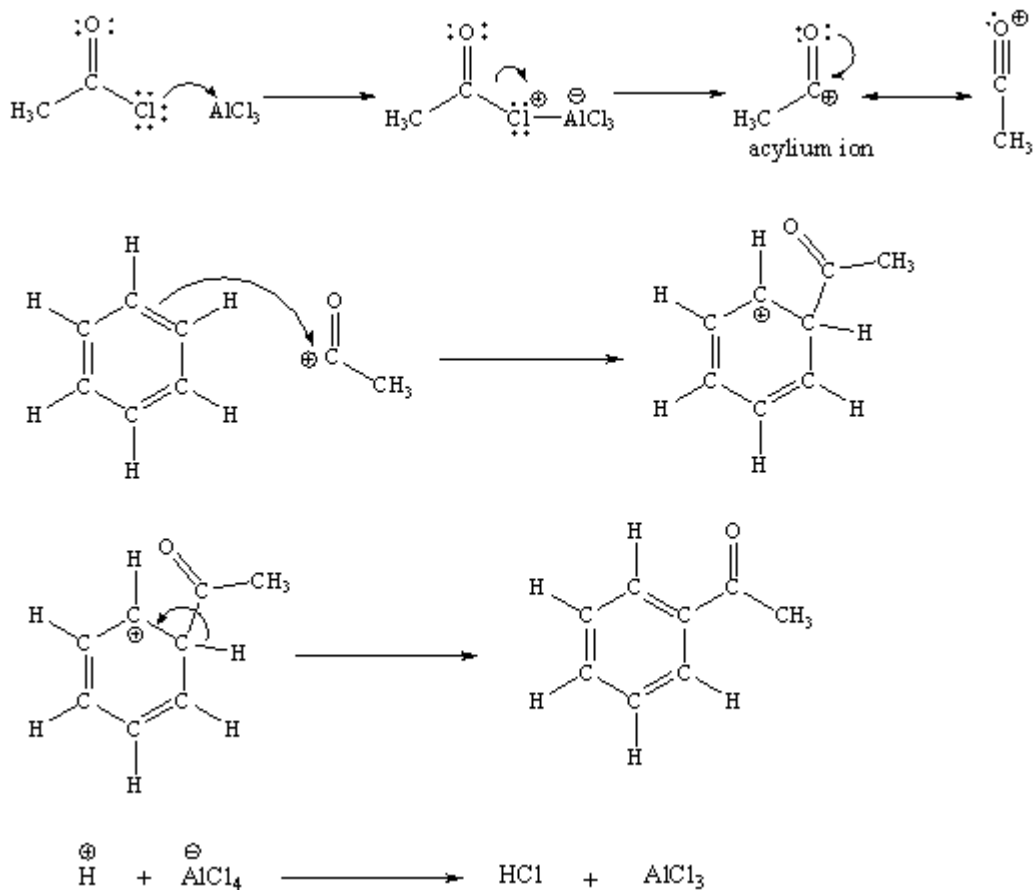
Y = halogen (Cl, Br, and I), or  (an anhydride functionality)
M = metal Fe, B, or Al
X = halogen

An acyl group = $\text{R}-\text{C}(=\text{O})-$. When $\text{R}=\text{CH}_3$, the group is called acetyl ($\text{H}_3\text{C}-\text{C}(=\text{O})-$).

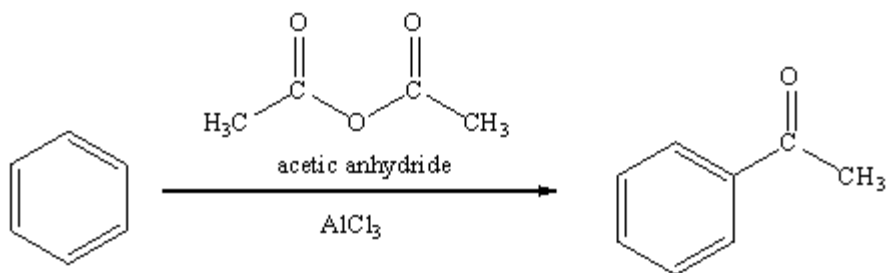
Example:



Mechanism:



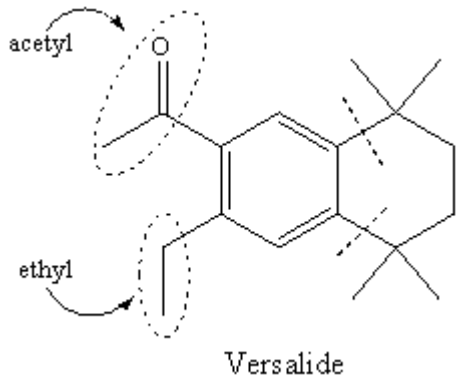
Example:



Similar to the above example, this reaction also proceeds through the acylium ion. However, we need one full equivalent of Lewis acid for this reaction. When the acyloxy group (acyl group with another oxygen) reacts with the Lewis acid, the reaction is essentially irreversible and the Lewis acid cannot be regenerated.

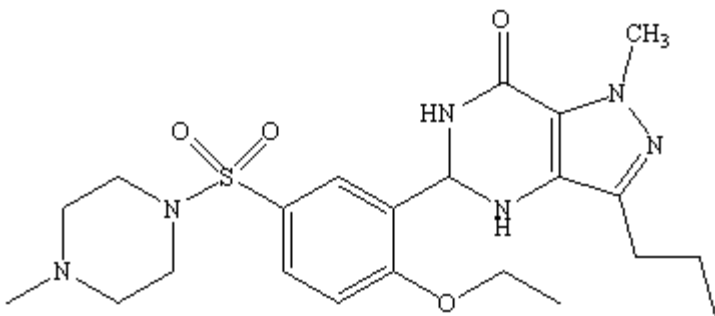
Now, let's look at a couple of molecules and try to analyze how to make them

Example:



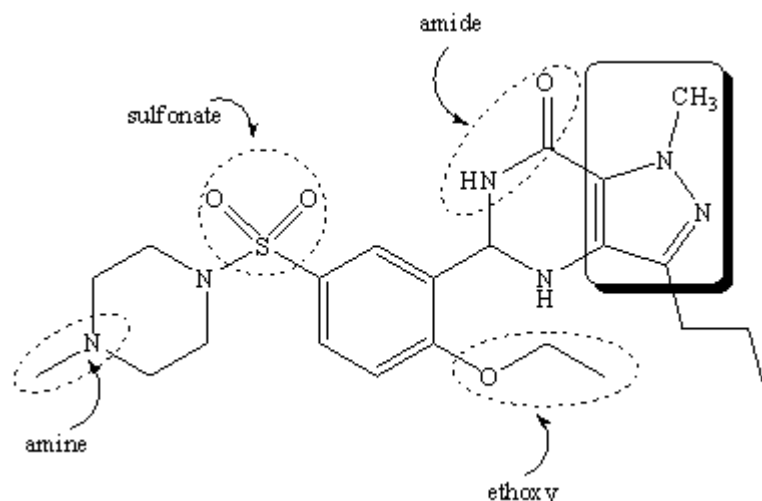
This molecule has an acetyl, ethyl, and an apparent cyclohexyl group attached to the benzene group. From what you had just learned, you should be able to analyze the synthesis of this molecule: the acetyl group can be made through Friedel-Crafts **Acylation**; the ethyl group can be attached through alkylation, and similarly, the cyclohexyl ring can be made by **alkylation** twice.

Example:



The molecule shown is **Viagra**. It generates more than \$ 2.7 billion U.S. per year.

Can you recognize its functional groups?



Is the ring highlighted in rectangle aromatic?

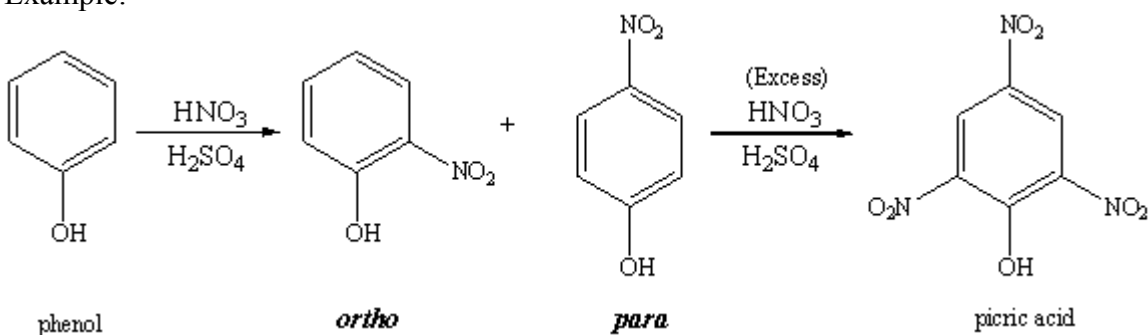
Answer: Yes. It is. Think back to last lecture on heterocycles and criteria for aromaticity. The 5 member ring is cyclic, it has two double bonds (4 pi electrons) that are conjugated, and it is planar. The methyl substituted nitrogen donates its lone pair into the 5 member ring to fit the $4n+2$ rule. The other nitrogen has lone pair in sp^2 orbital perpendicular to the pi (π) system.

If given a molecule, know how to analyze its parts and functional groups on the exam.

Electrophilic Aromatic Substitution for Substituted Benzenes (handout)

Substituents already present on the benzene ring determine the position of reaction and the reactivity of the system.

Example:



In this reaction, phenol already has a hydroxyl (-OH) group attached. When we perform nitration, only *ortho* and *para* substitution occurs. Even when we subject the reaction to excess condition, still only the *ortho* and *para* position reacts. We will see why next lecture.