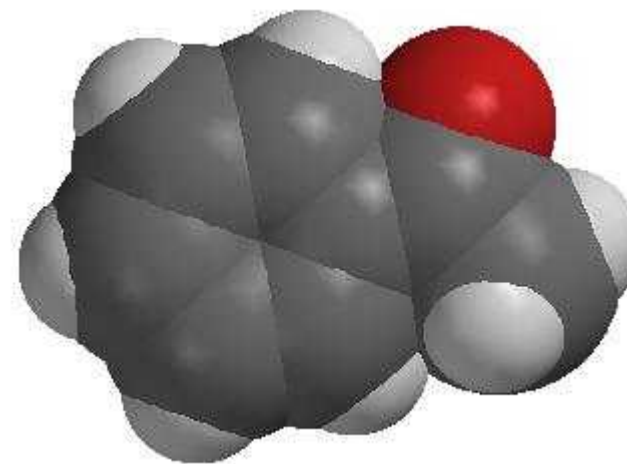


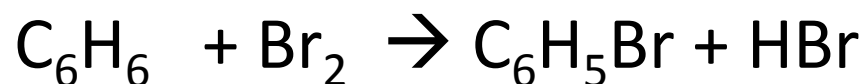
Chapter 4: Aromatic Compounds



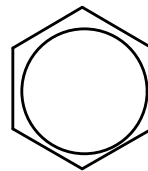
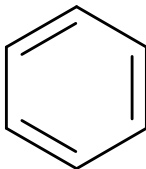
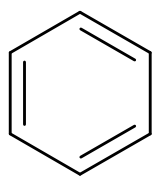
Some facts about Benzene

Benzene:

- formula: C_6H_6
- highly unsaturated
- chemical reactivity: substitution, but only 1 product \therefore all H atoms must be equivalent



- structure: cyclic, planar, sp^2 hybridized



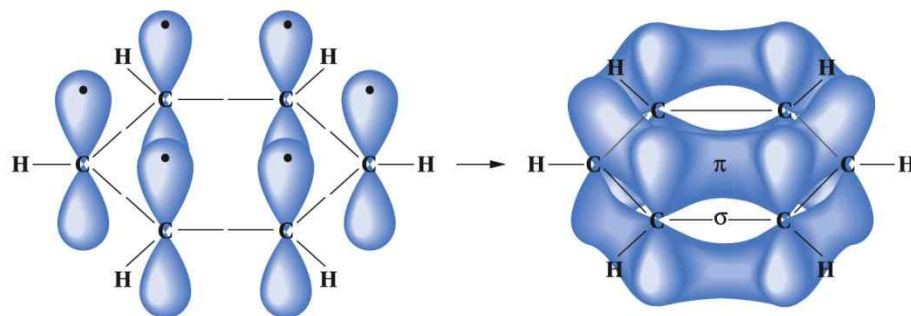
Kekule structure

Robinson structure

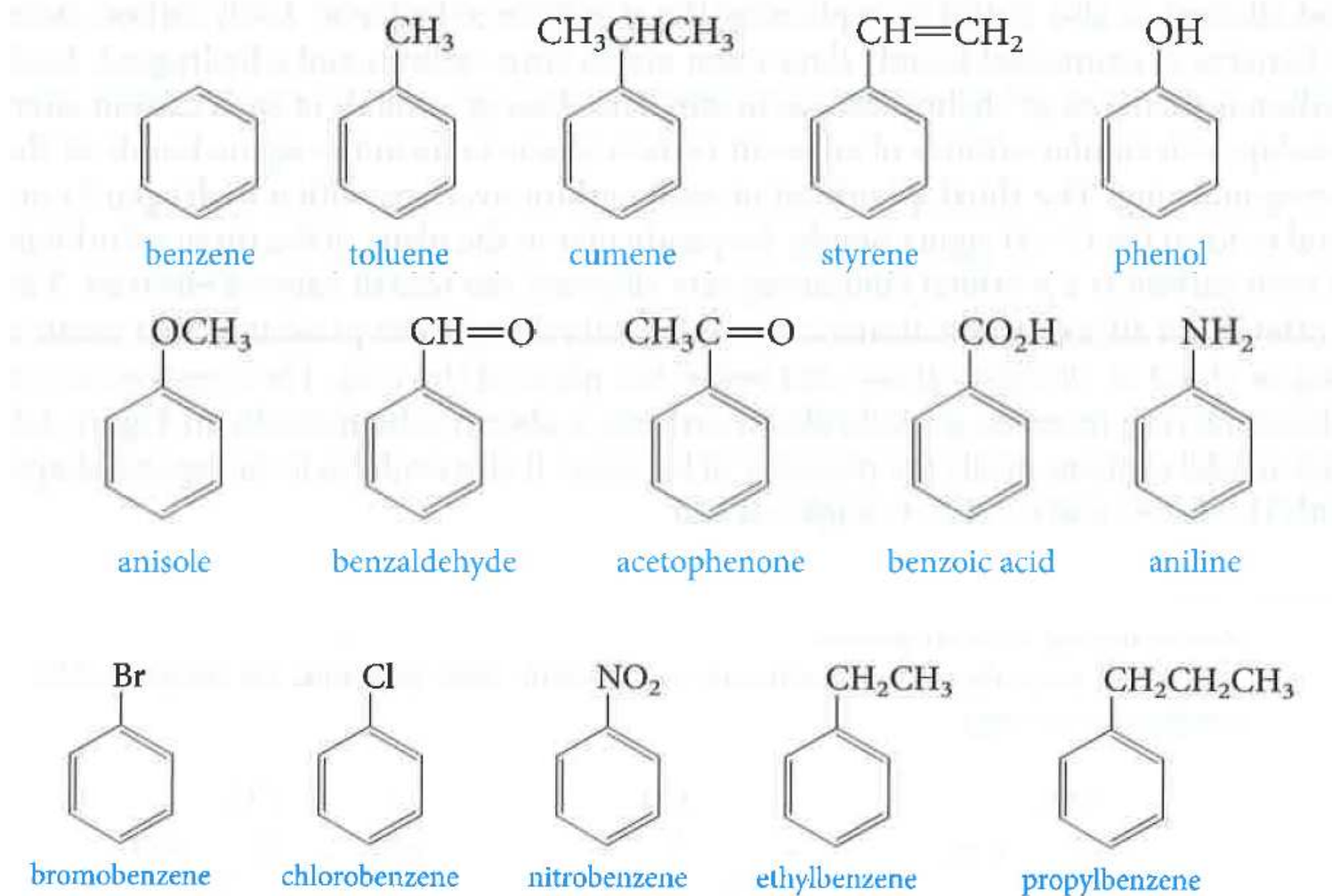
General Properties

Benzene:

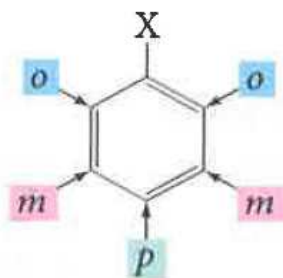
- C-C bond length: 1.39 Å
 - Intermediate to C-C (1.54 Å) and C=C (1.34 Å)
 - All C-C bond lengths are the same → resonance!



Nomenclature



; monosubstituted benzene that do not have common names accepted by IUPAC are named as derivatives of benzene



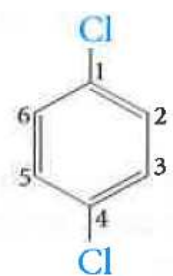
Specific examples are



ortho-dichlorobenzene



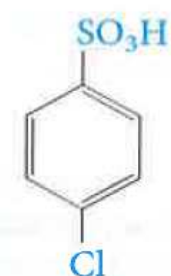
meta-dichlorobenzene



para-dichlorobenzene



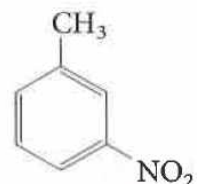
para-xylene**



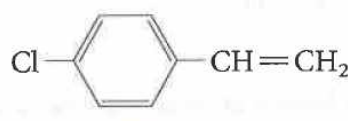
para-chlorobenzenesulfonic acid



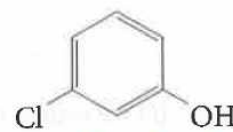
o-bromochlorobenzene
(note alphabetical order)



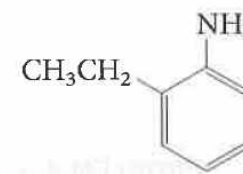
m-nitrotoluene



p-chlorostyrene

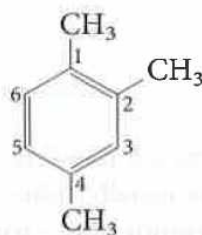


m-chlorophenol

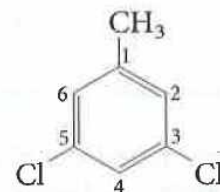


o-ethylaniline

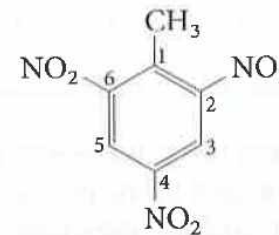
More than two substituent,
present the position



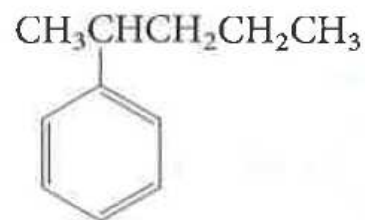
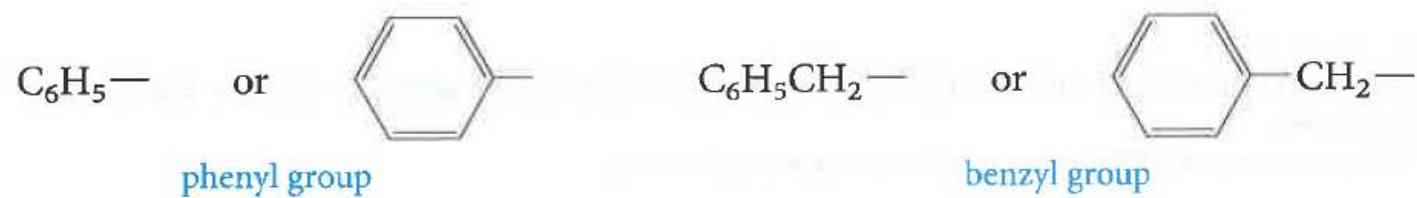
1,2,4-trimethylbenzene



3,5-dichlorotoluene



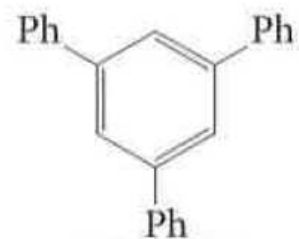
2,4,6-trinitrotoluene
(TNT)



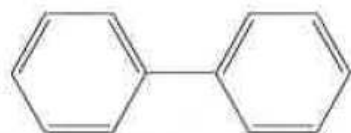
2-phenylpentane
(or 2-pentylbenzene)



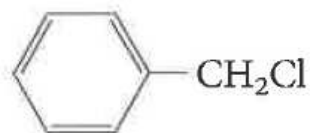
phenylcyclopropane
(or cyclopropylbenzene)



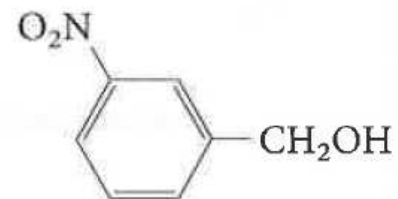
1,3,5-triphenylbenzene



biphenyl



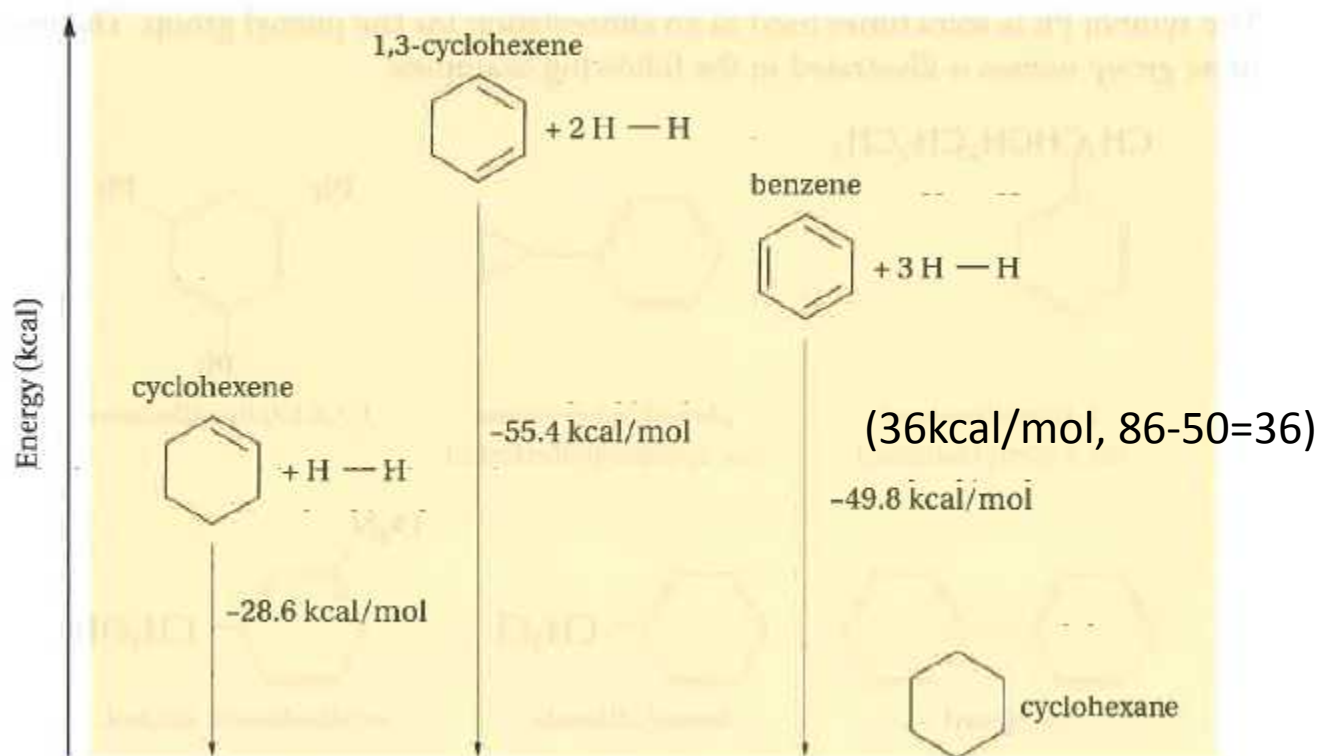
benzyl chloride



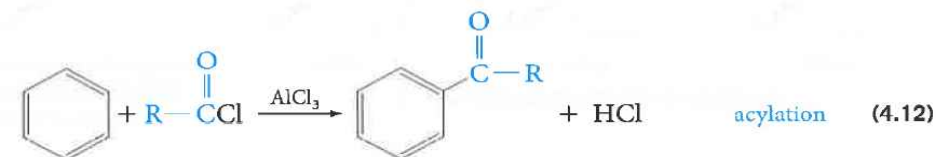
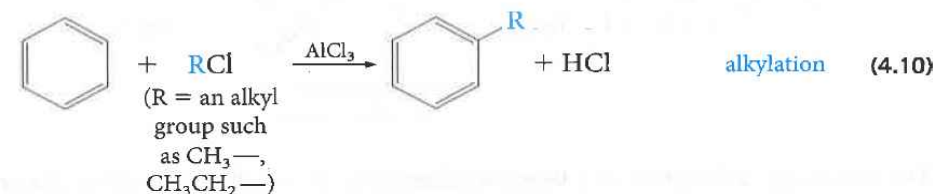
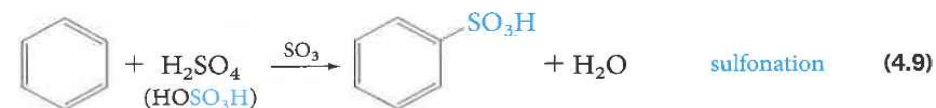
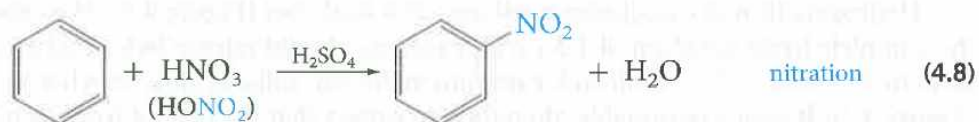
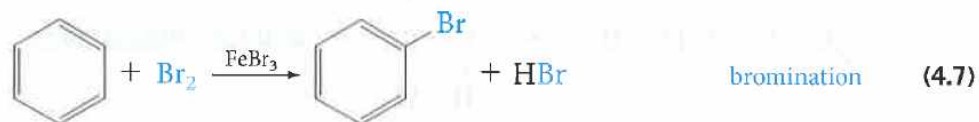
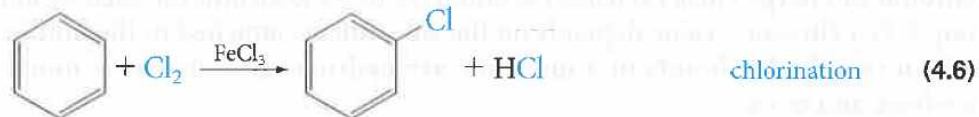
m-nitrobenzyl alcohol

Resonance Energy

The resonance (stabilization) energy is a measure of the extra stability of the cyclic conjugated system compared to the corresponding number of isolated double bonds. The difference between the energy of the real molecule and the calculated energy of the most stable contributing structure.

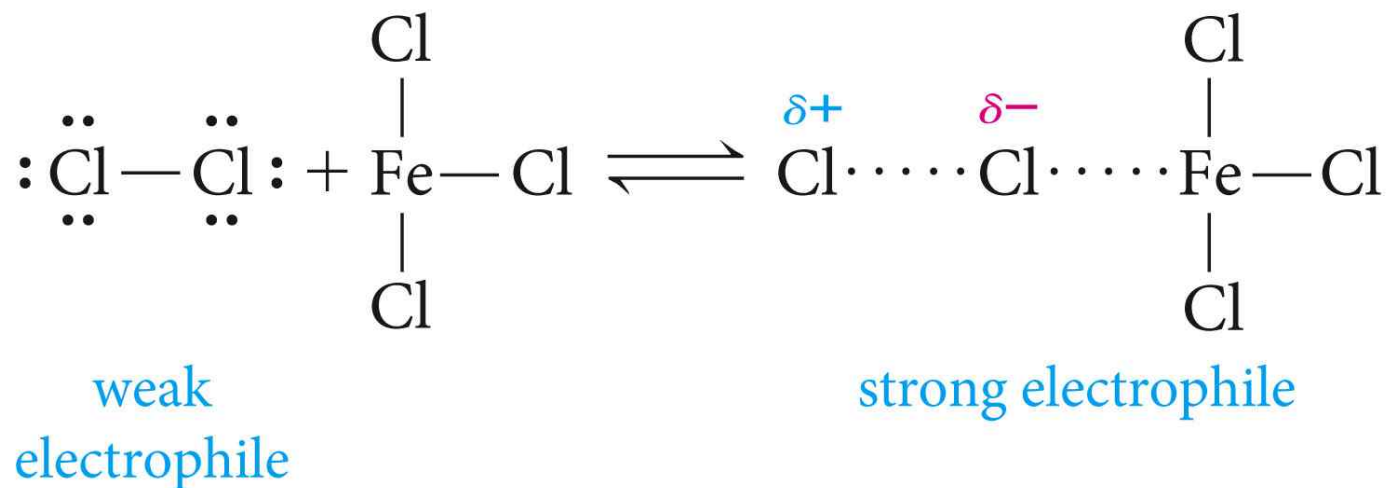


Mechanism of Electrophilic Aromatic Substitution (EArS)

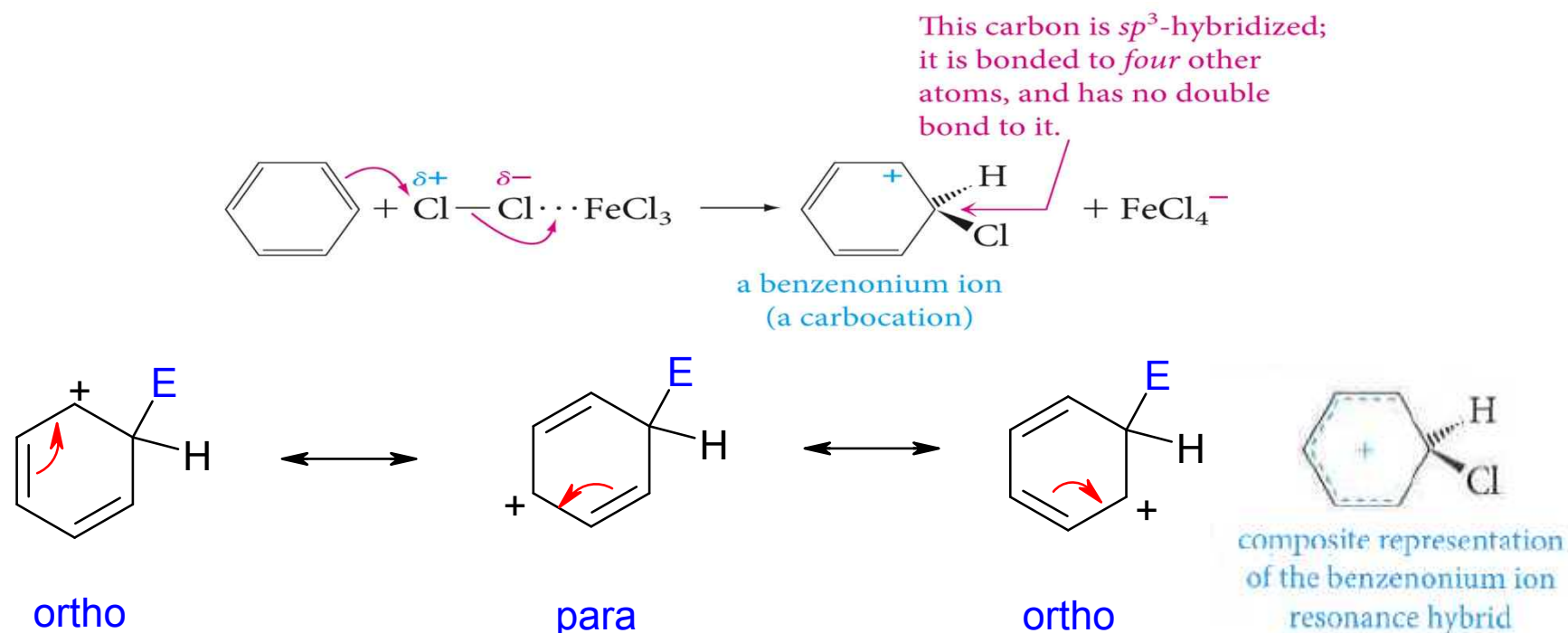


The mechanism of Electrophilic aromatic substitution

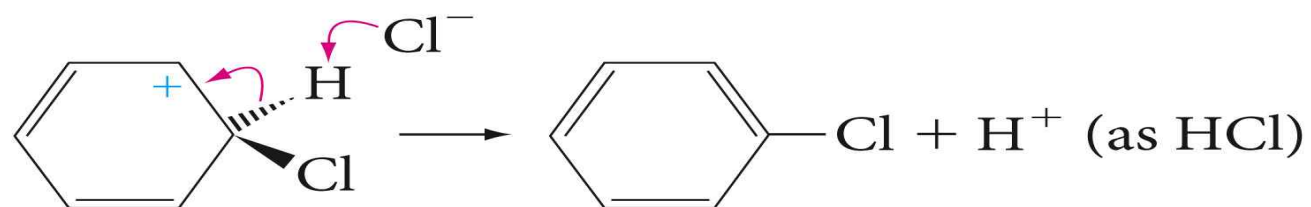
- Cl_2 and Br_2 are weak electrophiles on their own so need to be “activated” by using a Lewis acid catalyst.
- Commonly the corresponding iron trihalide is used, FeCl_3 or FeBr_3

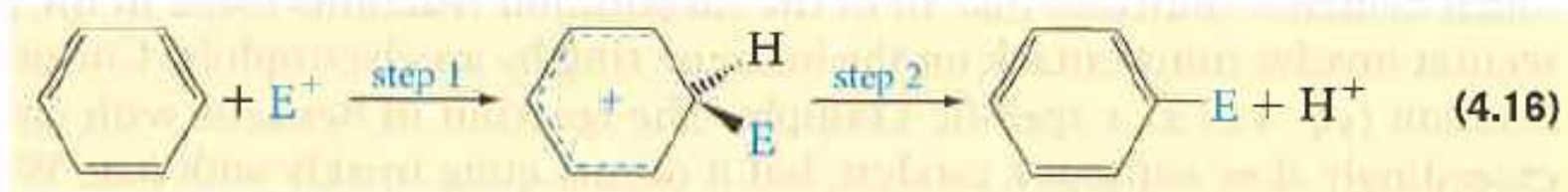


The rate determining step is:



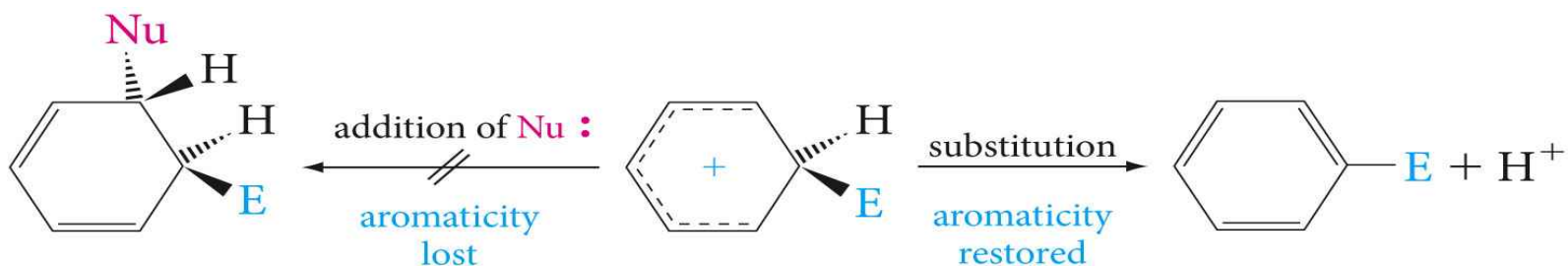
The base in this case is the chloride ion:





Step 1 ; slow or rate determining step (high activation energy)

Step 2 ; fast, low activation energy

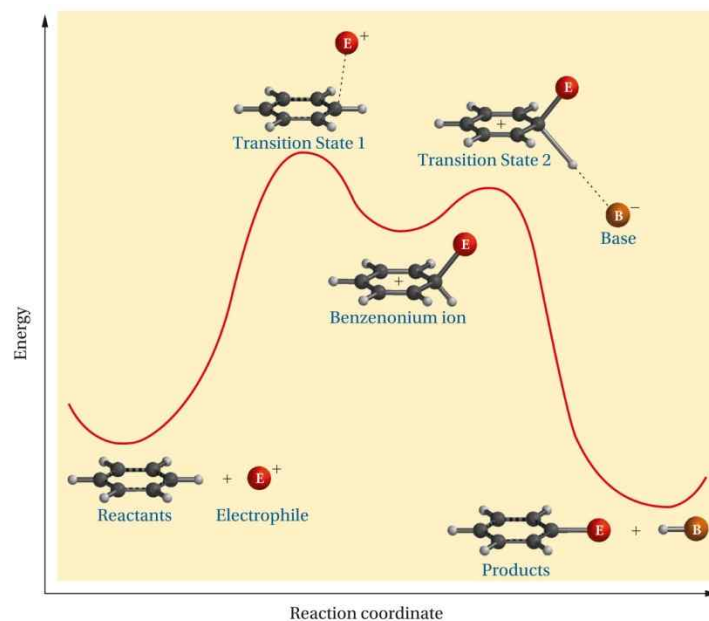


Halogenation

; Chlorine or Bromine is introduced into an aromatic ring by using the halogen together with the corresponding iron halide as a catalyst ($\text{Cl}_2 + \text{FeCl}_3$, $\text{Br}_2 + \text{FeBr}_3$)

Mechanism of Electrophilic Aromatic Substitution (EArS)

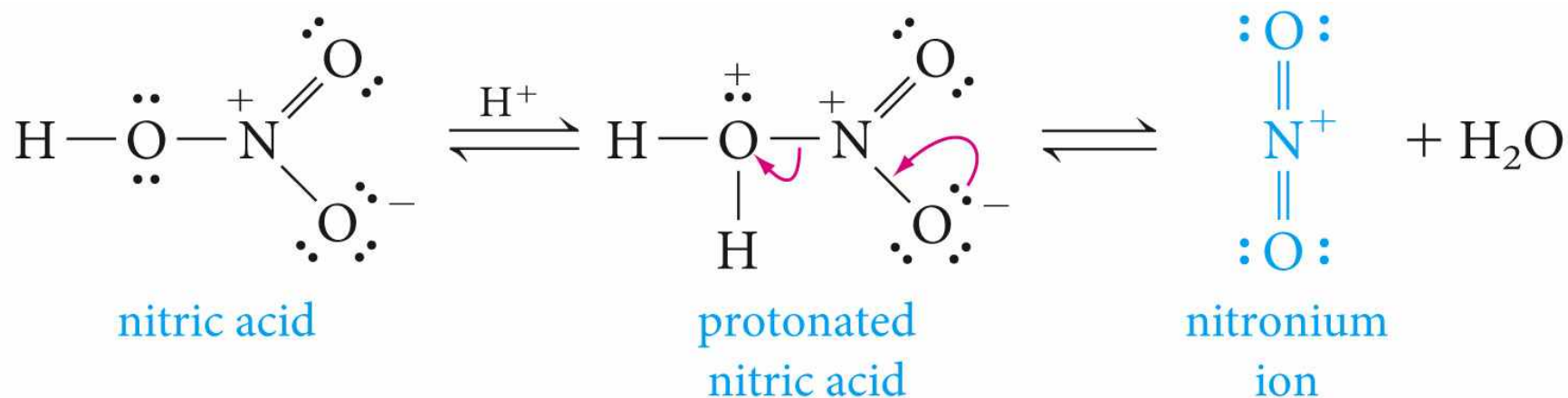
As with allenes and alkynes, the carbocation generated by the addition of the electrophile is a stable intermediate, i.e.



The formation of the carbocation is the rate determining step as it takes energy to break the aromaticity.

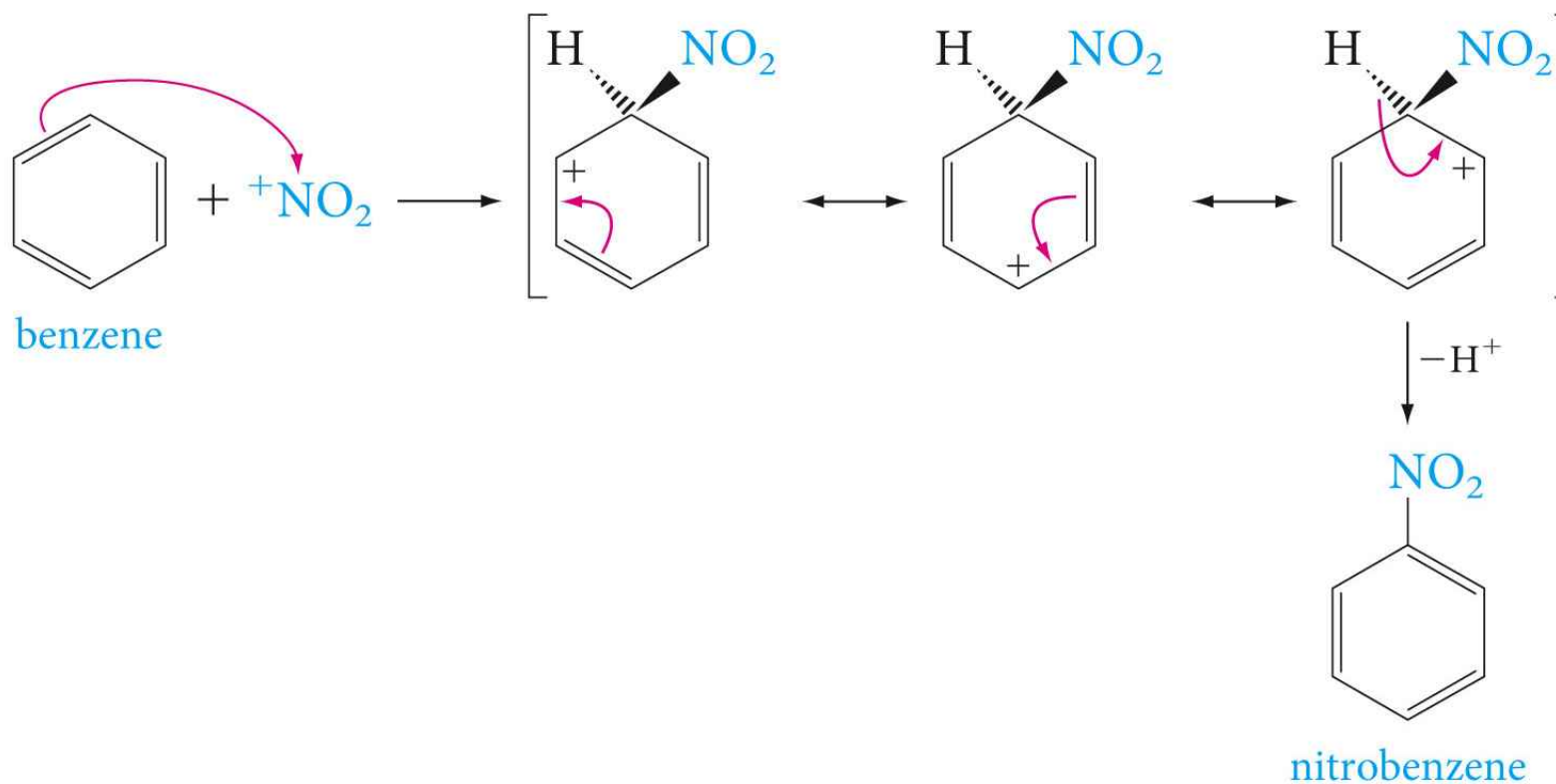
EArS - Nitration

In the case of nitration, sulfuric acid is used to generate a more reactivity electrophile, a nitronium ion(NO_2^+).



Example 4.2

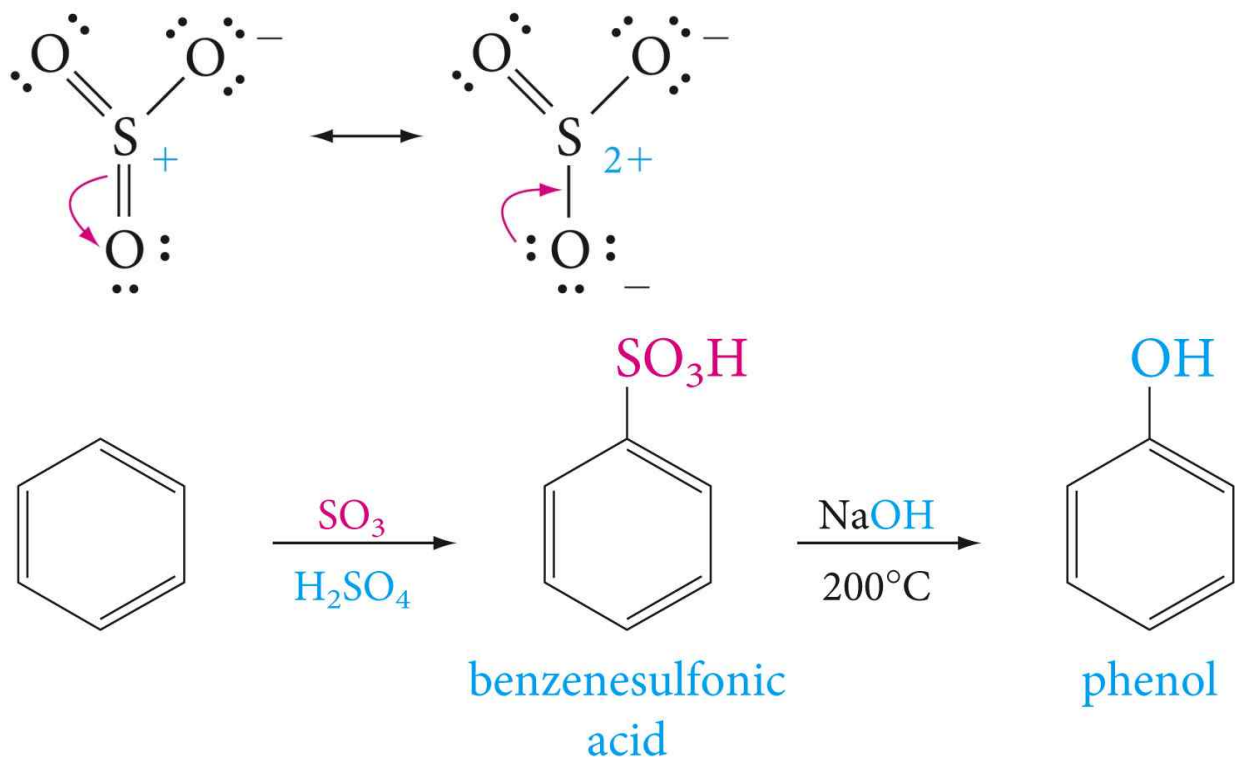
The product of the reaction is nitrobenzene, i.e.



EArS - Sulfonation

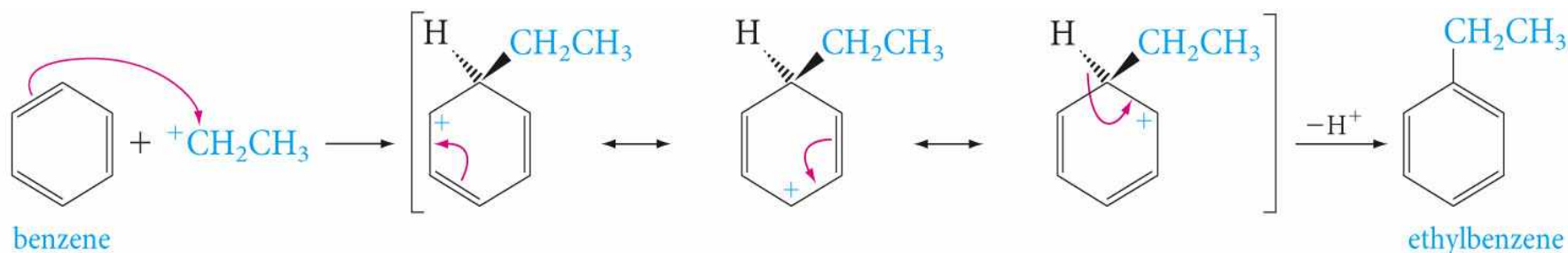
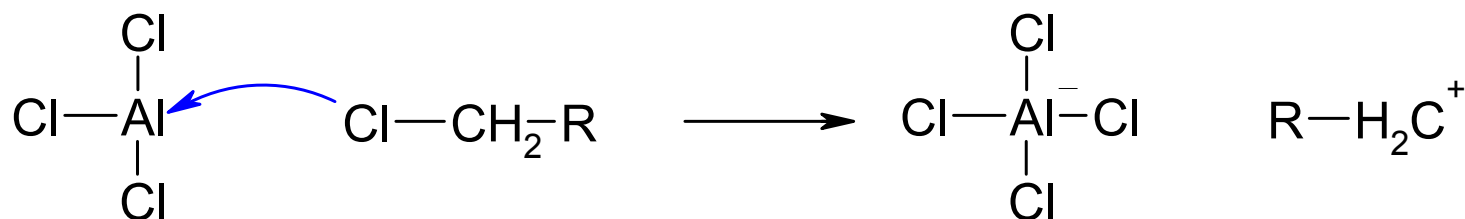
Sulfonation will generate a benzenesulfonic acid.

The electrophile used is sulfur trioxide, which is a strong electrophile, i.e.



Alkylation and Acylation (Friedel-Crafts reaction)

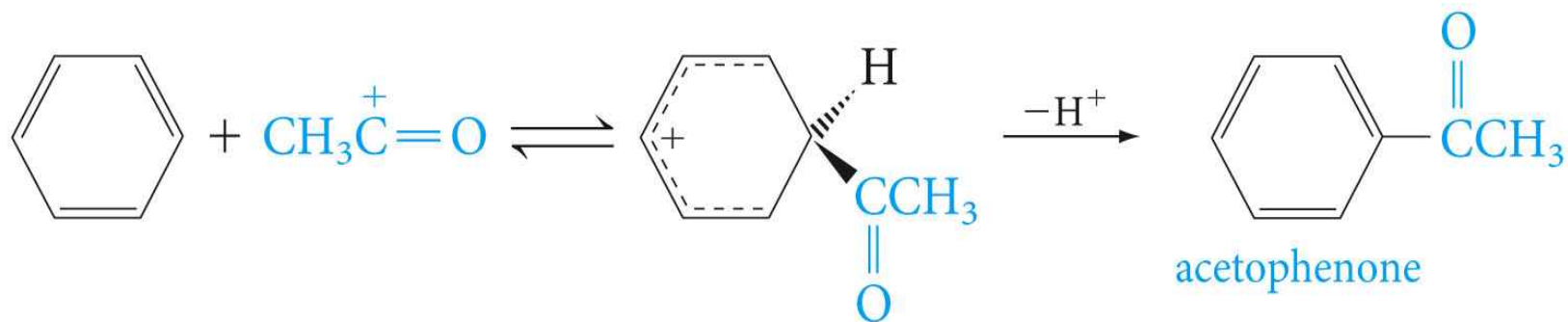
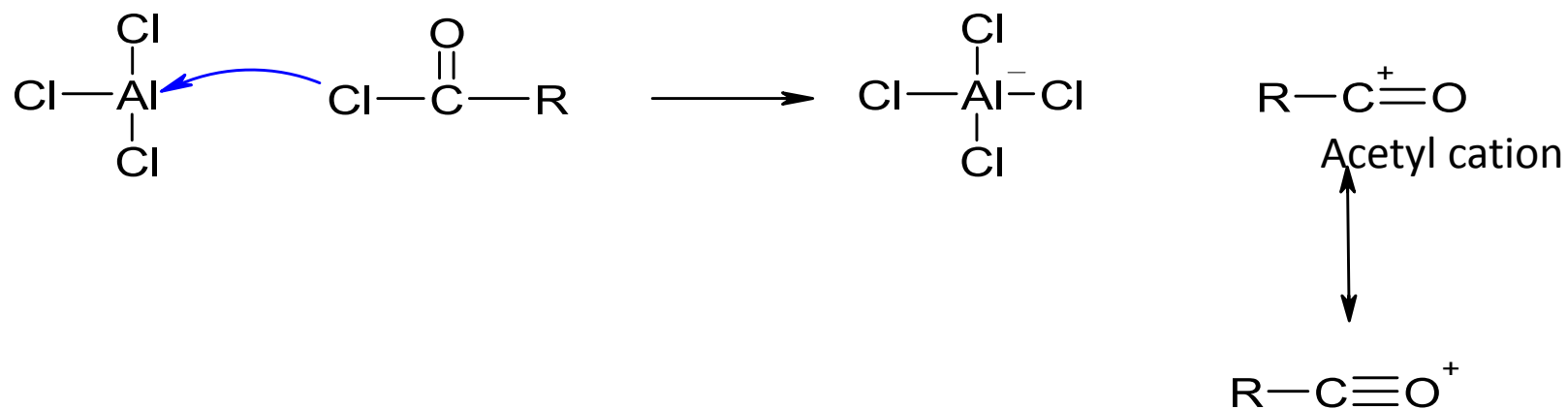
This process uses an alkyl halide (Cl or Br usually) and a Lewis acid catalyst similar to a halogenation reaction. In this case we use the corresponding aluminum trihalide as the Lewis acid catalyst.



Note: there are limitations to Friedel-Crafts reactions, they **can not be done on a nitrobenzene or benzenesulfonic acid** as these group complex with the aluminum chloride catalyst deactivation it.

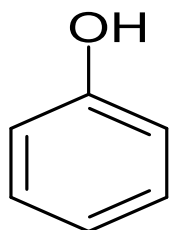
Friedel-Crafts Acylation

This process is identical to an alkylation except we use an acyl chloride, i.e.

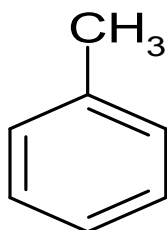


Ring activating and ring-deactivating substituent

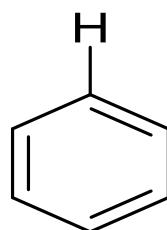
Experimentally you can observe the following relative nitration rates of reaction:



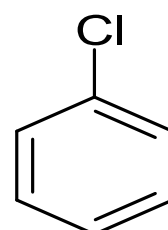
phenol
1000



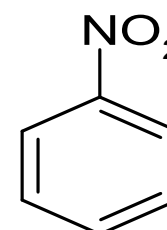
toluene
24.5



benzene
1



chlorobenzene
0.033



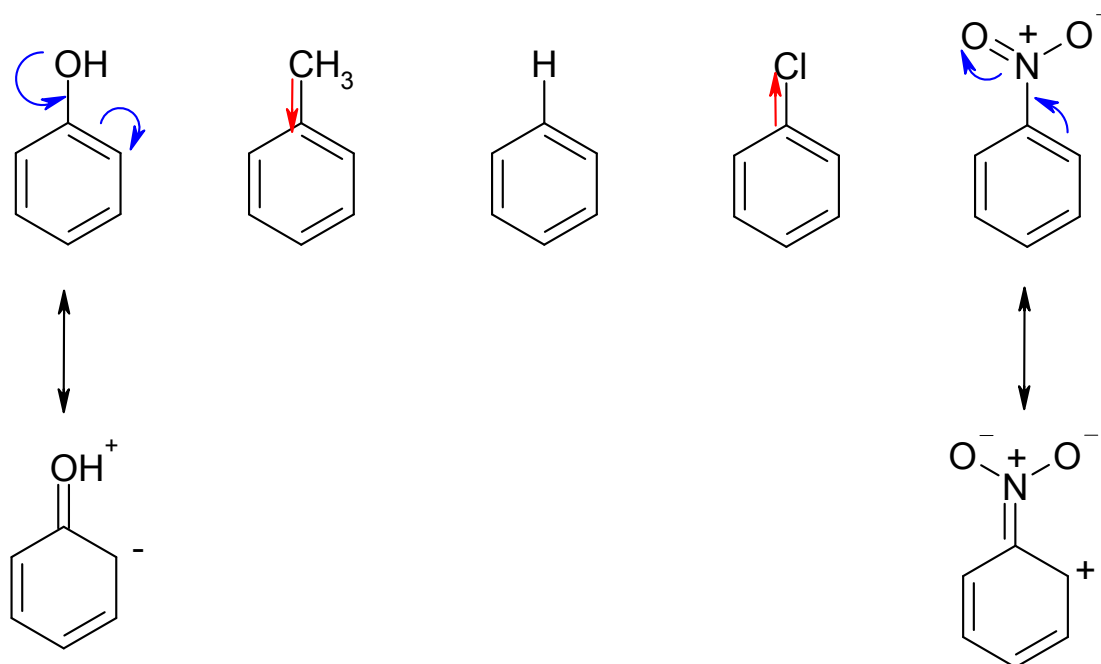
nitrobenzene
0.0000001

What is causing these differences?

Substituent that donate electrons to the ring will increase it's electron density and speed up the reaction

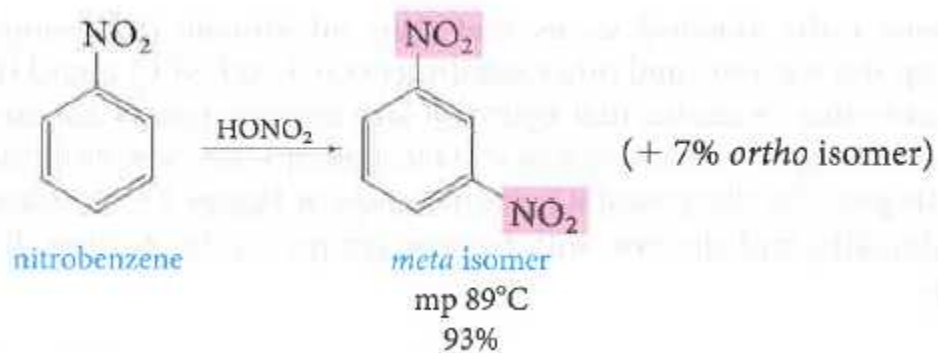
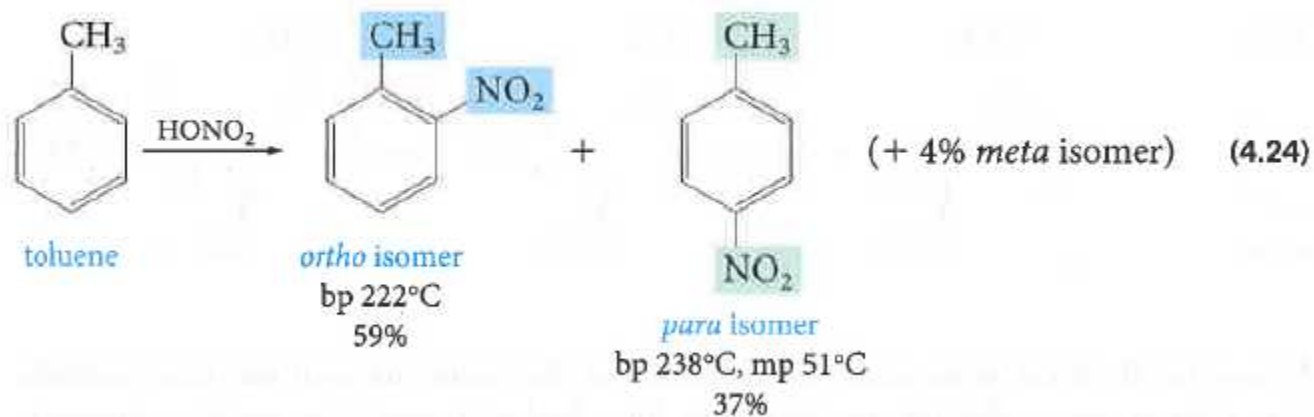
Reaction Rates

The reaction depends on the attack of an electrophile on the benzene ring, this means the charge density in the ring will be very important. Groups that increase the charge density will speed up the reaction while those that decrease charge density slow it down.



Ortho, Para-Directing and Meta-Directing Groups

A second experimental observation is:



Directing Effects

The directing effects are caused by the same processes that control the rate of the reaction. The table right groups substituents as o,p-directing or m-directing.

These are relative to an H atom.

Electron donating groups (EDG) activate the ring and are o,p-directing.

Electron withdrawing groups (EWG) deactivate the ring and are m-directing.

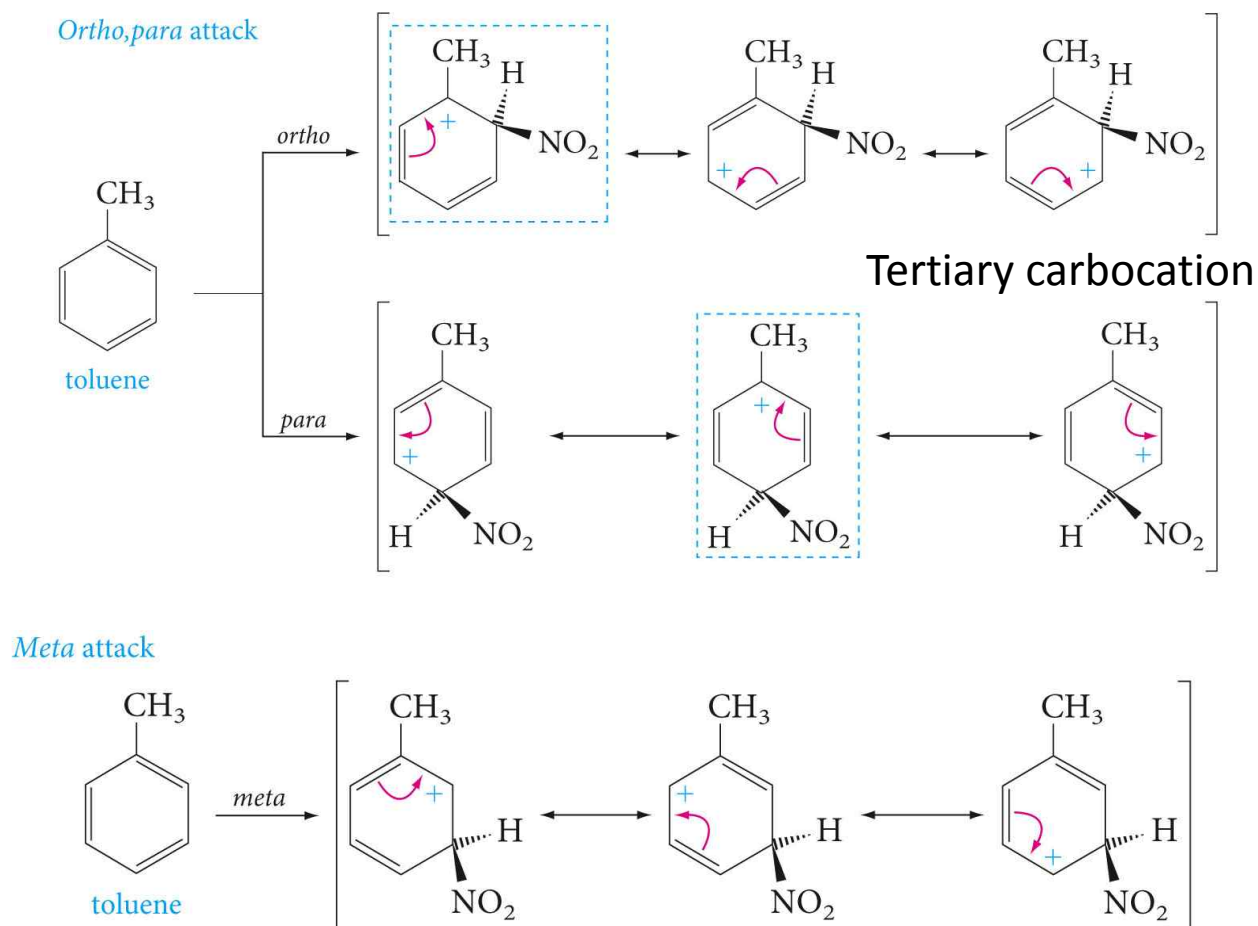
Why?

	<i>Substituent group</i>	<i>Name of group</i>	
<i>Ortho, Para-Directing</i>	$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{HR}, -\ddot{\text{N}}\text{R}_2$	amino	<i>Activating</i>
	$-\ddot{\text{O}}\text{H}, -\ddot{\text{O}}\text{CH}_3, -\ddot{\text{O}}\text{R}$	hydroxy, alkoxy	
	$\begin{array}{c} \text{O} \\ \\ \ddot{\text{N}}\text{HC}-\text{R} \end{array}$	acylamino	
	$-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$	alkyl	
	$-\ddot{\text{F}}:, -\ddot{\text{Cl}}:, -\ddot{\text{Br}}:, -\ddot{\text{I}}:$	halo	
<i>Meta-Directing</i>	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\text{R} \end{array}$	acyl, carboxy	<i>Deactivating</i>
	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{O}}\text{H} \end{array}$		
	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$	carboxamido, carboalkoxy	
	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{O}}\text{R} \end{array}$		
	$\begin{array}{c} \text{:O:} \\ \\ -\text{S}-\ddot{\text{O}}\text{H} \\ \\ \text{:O:} \end{array}$	sulfonic acid	
	$-\text{C}\equiv\text{N:}$	cyano	
$\begin{array}{c} \text{:O:} \\ \\ -\text{N}^+ \\ \\ \text{:O:}^- \end{array}$	nitro		

Ortho, Para-directing Groups

So how does this effect a reaction?

Activating o,p-directing group, i.e. CH₃ (alkyl groups),

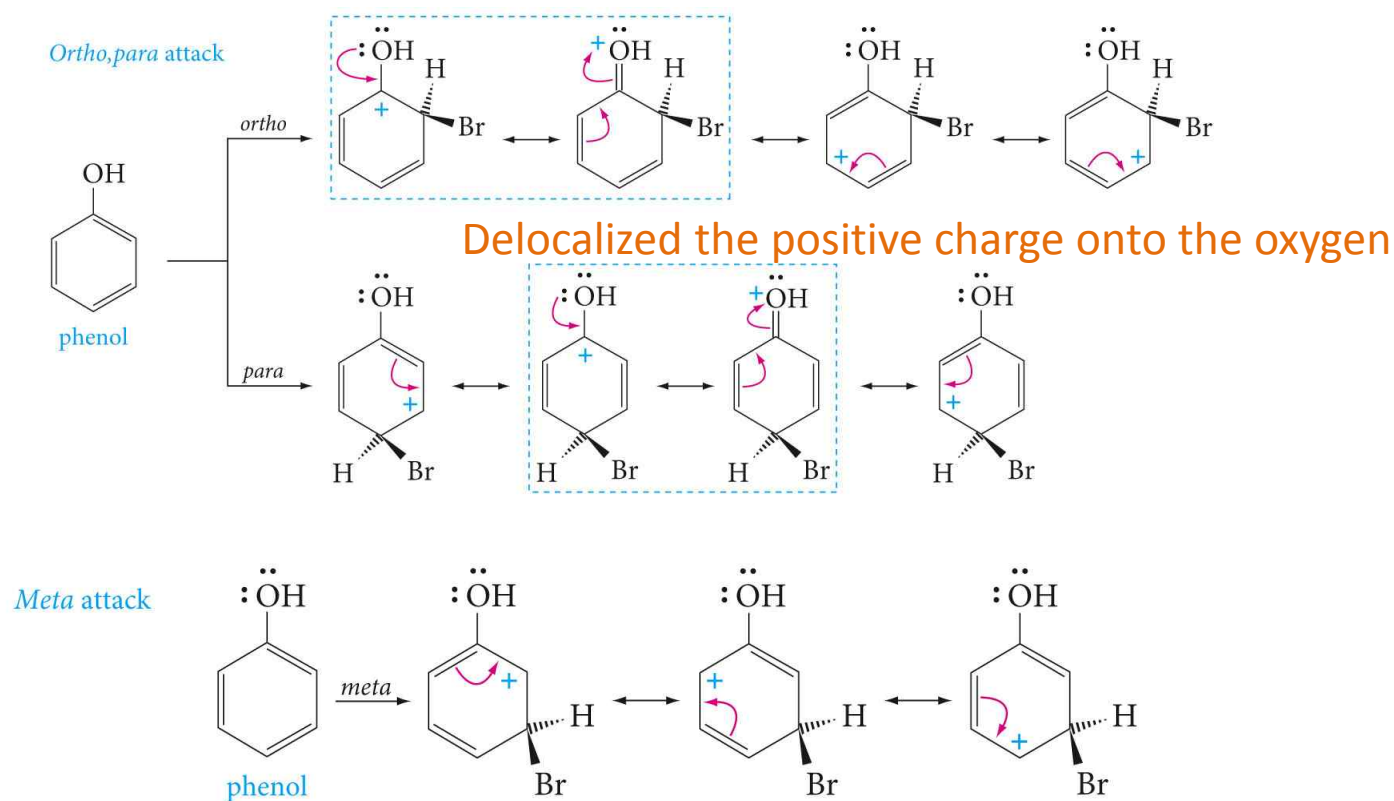


Ortho, Para-directing Groups

So how does this effect a reaction?

Activating o,p-directing group, i.e. OH,

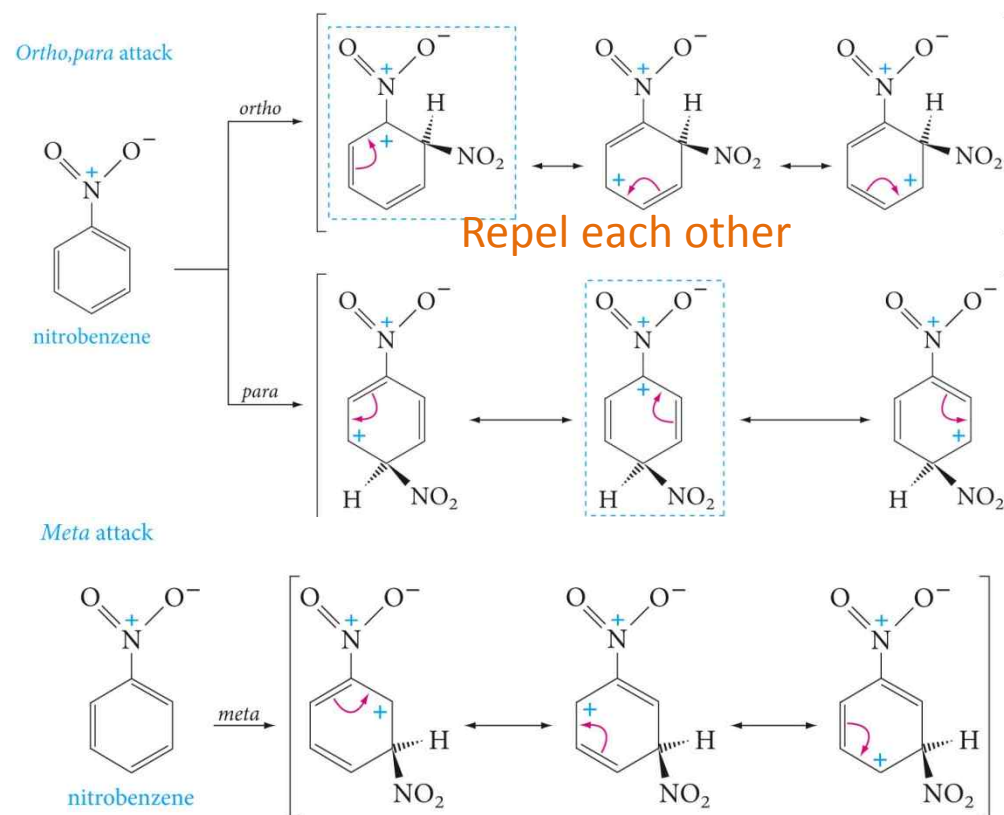
(all groups with unshared electrons on the atom attached to the ring)



Meta-Directing groups

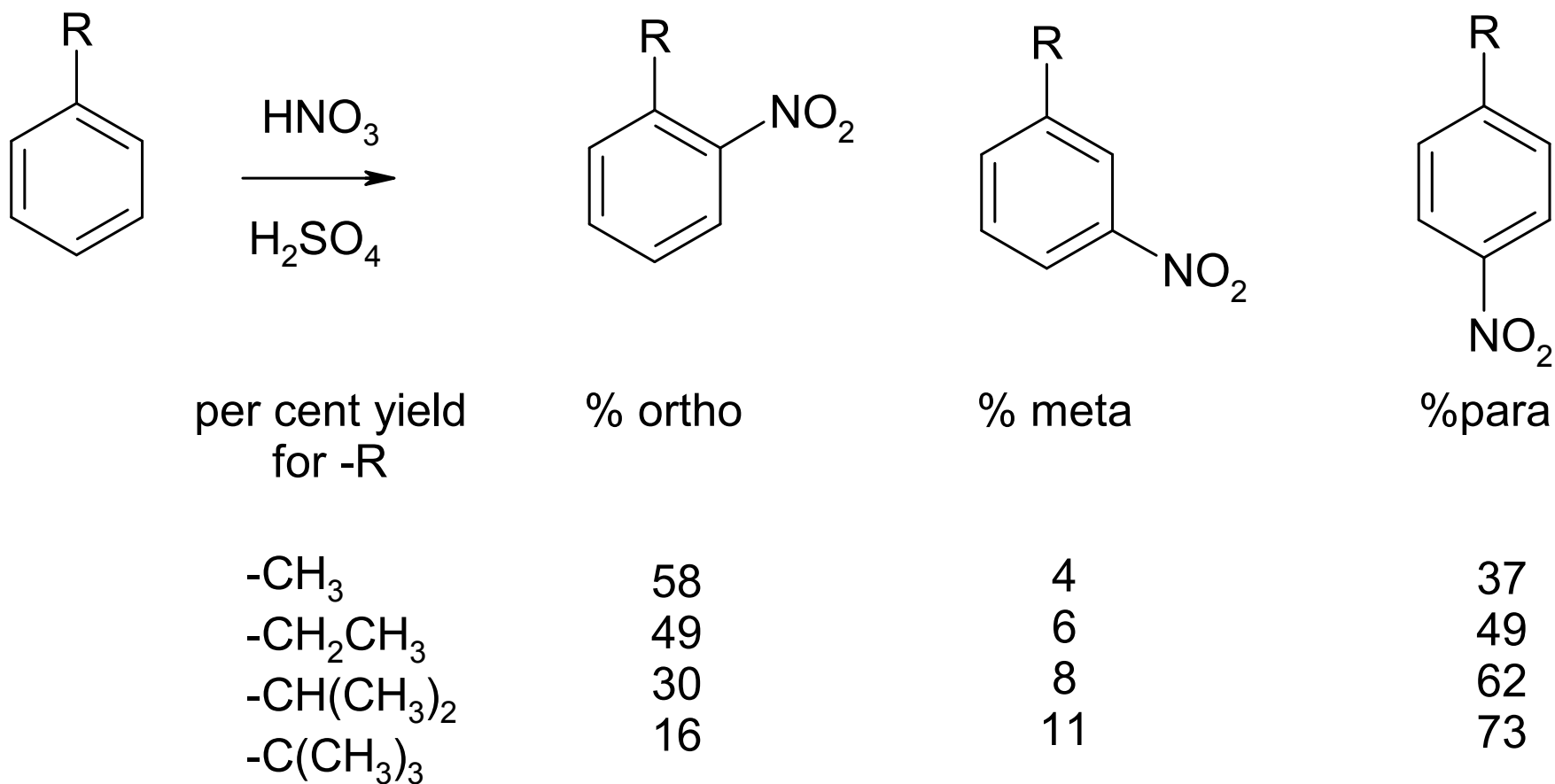
So how does this effect a reaction?

Deactivating m-directing group, i.e. NO_2 (groups in which the atom directly attached to the aromatic ring is positively charged or is part of multiple bond to a more electronegative element)



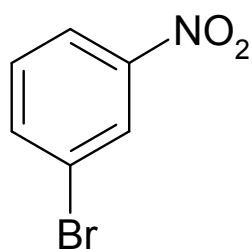
Directing Effects

Besides electronic effects the size of the substituent can effect the location of a subsequent reaction. These are *steric effects*, i.e.

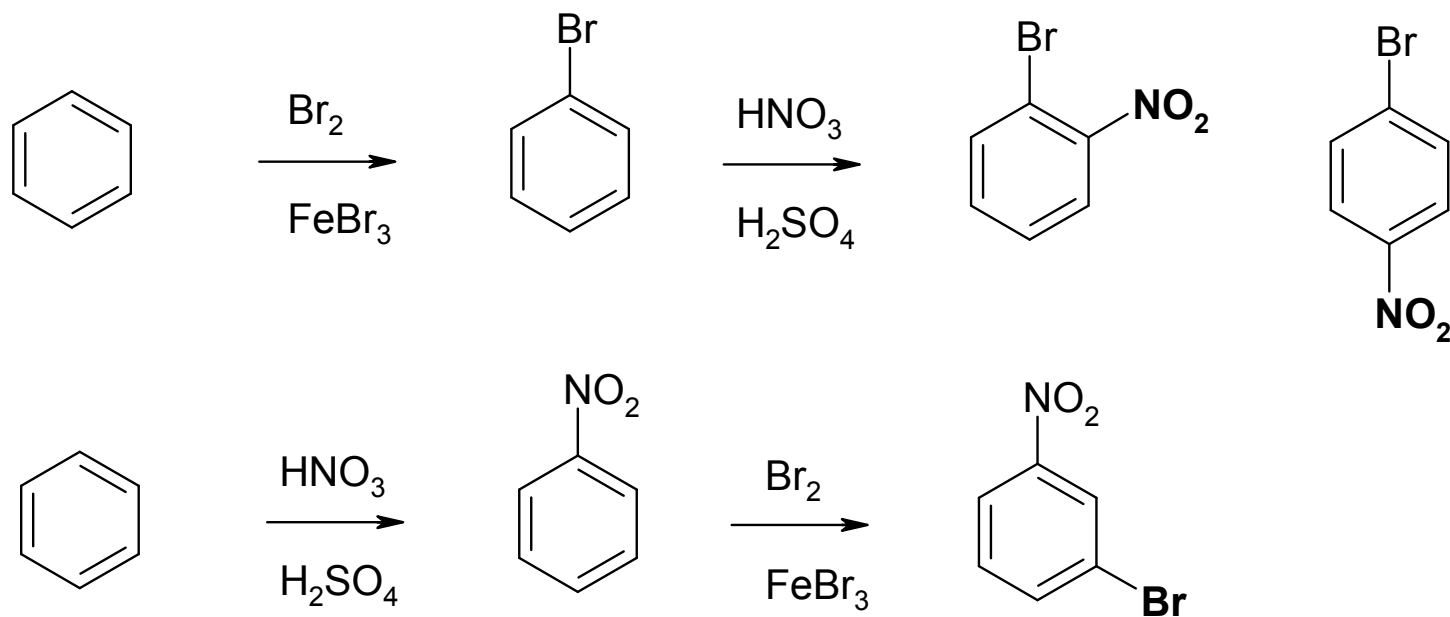


Synthesis of Aromatic Compounds

“Direct” introduction of groups:

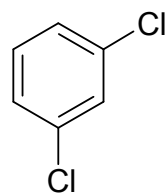


desired product

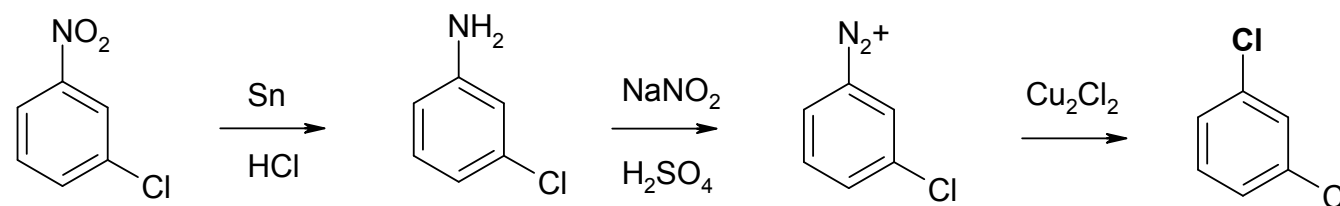
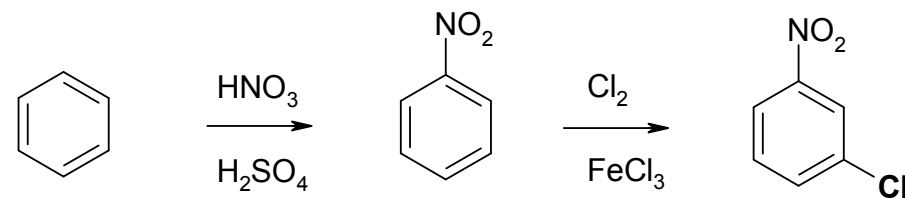
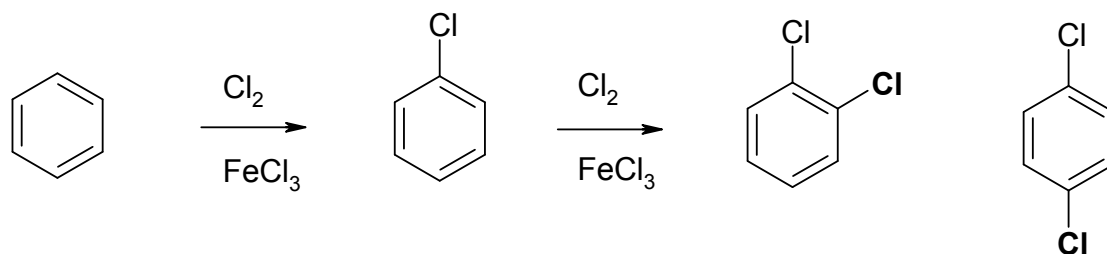


Synthesis of Aromatic Compounds

“Indirect” introduction of groups:

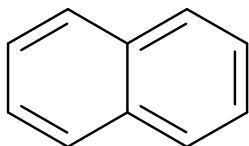


desired product

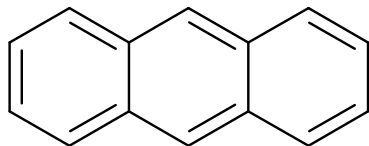


Polycyclic Aromatic Hydrocarbons

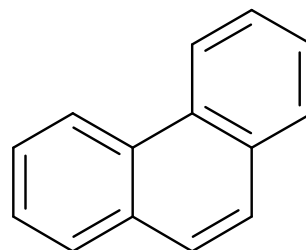
A number of polycyclic (multiple fused rings) hydrocarbons exist. They still obey Huckel's rule, alternating single & double bonds etc. They also exhibit a reduced reactivity to addition / substitutions and react by EArS.



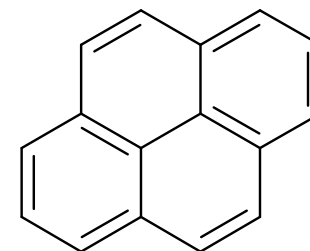
naphthalene



anthracene



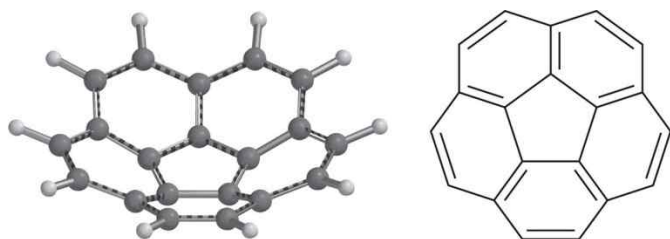
phenanthrene



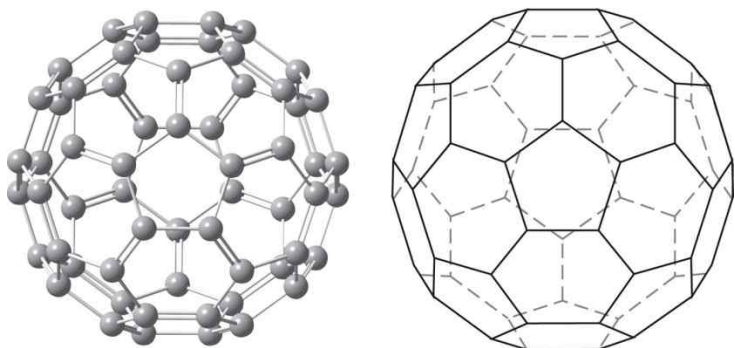
pyrene

Polycyclic Aromatic Hydrocarbons

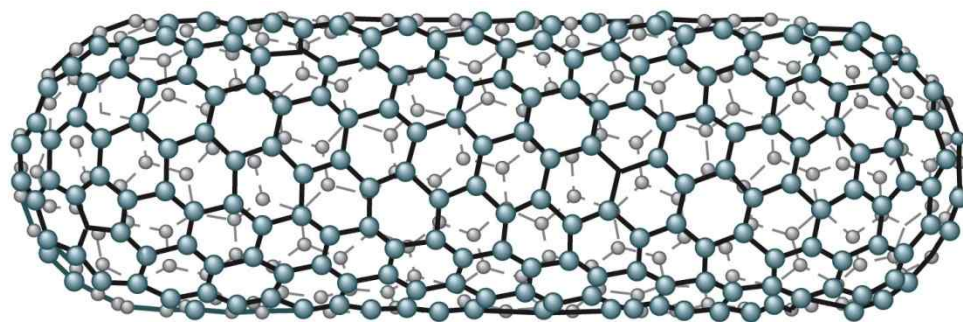
Two other cases of polycyclic hydrocarbons exist, fullerenes and carbon nanotubes. These compounds have interesting properties of electrical conductance and very high strength.



corannulene



C₆₀ (the pi bonds are not shown)



Carbon nanotube¹