UNIT I	Benzene and its derivatives	10 Hours
A.	Analytical, synthetic and other evidences in the derivation of structure of benzene, Orbital picture, resonance in benzene, aromatic characters, Huckel's rule	
B.	Reactions of benzene - nitration, sulphonation, halogenationreactivity, Friedelcrafts alkylation- reactivity, limitations, Friedelcrafts acylation.	
C.	Substituents, effect of substituents on reactivity and orientation of mono substituted benzene compounds towards electrophilic substitution reaction	
D.	Structure and uses of DDT, Saccharin, BHC and Chloramine	

Aromatic Compounds: Benzene and its derivatives

Chemists have found it useful to divide all organic compounds into two broad classes: aliphatic compounds and aromatic compounds. The original meanings of the words "aliphatic" (fatty) and "aromatic" (fragrant/ pleasant smell).

Aromatic compounds are benzene and compounds that resemble benzene in chemical behavior. Aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons.

Benzene:

- A liquid that smells like gasoline
- Boils at 80°C & Freezes at 5.5°C
- It was formerly used to decaffeinate coffee and component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers.
- A precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes.
- It is used as a solvent in cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes.
- Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.
- In 1970s it was associated with leukemia deaths.

Structure of benzene

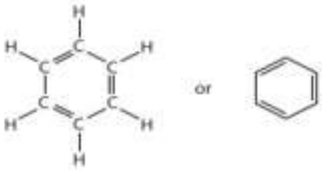
History, Analytical, Synthetic and other evidences in the derivation of structure of benzene:

(a) History of benzene:

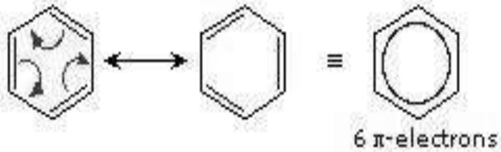
- Isolated in 1825 by Michael Faraday who determined C:H ratio to be 1:1.
- Synthesized in 1834 by Eilhard Mitscherlich who determined molecular formula to be C6H6. He named it benzin later known as benzene.

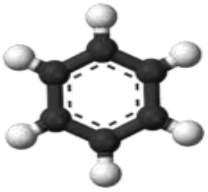
(b) Benzene has the molecular formula C_6H_6. The question was: how are these atoms arranged? In 1858, August Kekule (of the University of Bonn) had proposed that carbon atoms can join to one another to form chains. Then, in 1865, he offered an answer to the question of benzene: these carbon chains can. Sometimes be closed, to form rings.

Kekule's structure of benzene was one that we would represent today as

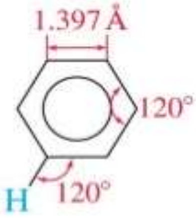


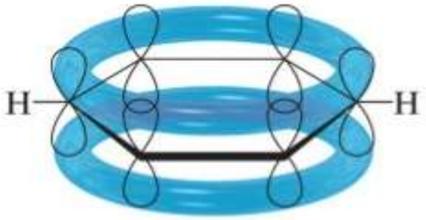
- All the carbon-to-carbon bonds in benzene are equivalent
- The molecule is unusually stable
- Chemists often represent benzene as a hexagon with an inscribed circle





- The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized, or spread out, over all the carbon atoms).
- Each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it.
- Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon.
- The six bond lengths are identical and they are one-and-a half bonds and their length, 1.39 A or 139 picometer (pm), is intermediate between the lengths of single and double bonds (is shorter than typical single-bond lengths, yet longer than typical double-bond lengths).

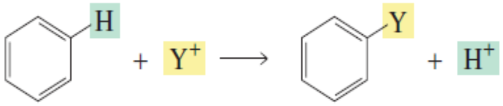




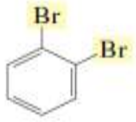
- Benzene is a flat molecule, with every carbon and hydrogen lying in the same plane these bonds are designated as a sigma (σ) bonds.

- Each sp^2 hybridized C in the ring has an unhybridized *p* orbital perpendicular to the ring which overlaps around the ring.
- The six pi (π) electrons are delocalized over the six carbons.

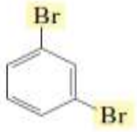
(c) Benzene yields only one monosubstitution product, C_6H_5Y. Only one bromobenzene, C_6H_5Br, is obtained when one hydrogen atom is replaced by bromine; similarly, only one chlorobenzene, C_6H_5C1, or one nitrobenzene, $C_6H_5NO_2$, etc., has ever been made. This fact places a severe limitation on the structure of benzene: each hydrogen must be exactly equivalent to every other hydrogen, since the replacement of any one of them yields the same product.



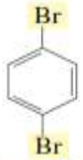
(d) Benzene yields three isomeric disubstitution products, $C_6H_4Y_2$ or C_6H_4YZ. e.g. like only three isomeric dibromobenzenes, $C_6H_4Br_2$, three chloronitrobenzenes, $C_6H_4ClNO_2$, etc. This fact further limits our choice of a structure to Kekule's structure of benzene compare to any other structures with the molecular formula C_6H_6.



1,2-dibromobenzene
ortho-dibromobenzene
o-dibromobenzene



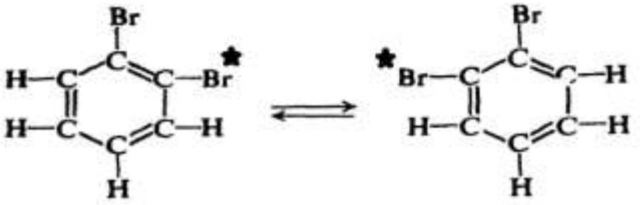
1,3-dibromobenzene
meta-dibromobenzene
m-dibromobenzene



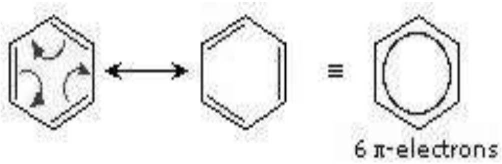
1,4-dibromobenzene
para-dibromobenzene
p-dibromobenzene

The relative positions of two substituents on a benzene ring can be indicated either by numbers or by the prefixes ortho, meta, and para. Adjacent substituents are called ortho, substituents separated by one carbon are called meta, and substituents located opposite one another are designated para. Often, only their abbreviations (o, m, p) are used in naming compounds.

However, that two 1,2-dibromo isomers differing in the positions of bromine relative to the double bonds, should be possible:



On the other hand, it is believed by some that Kekule had unthinkingly anticipated our present concept of *delocalized electrons*, and drew two pictures (as shown above). The currently accepted structure did not arise from the discovery of new facts about benzene, but is the result of an extension or modification of the structural theory; this extension is the concept of *resonance*.



OR


I


II

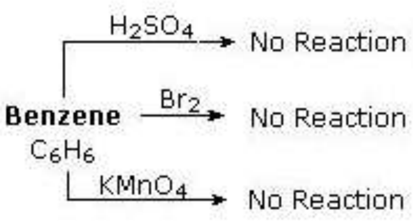
Resonance: structures that differ only in the arrangement of electrons. Benzene is a hybrid of I and II. Since; I and II are exactly equivalent, and hence of exactly the same stability, they make equal contributions to the hybrid.

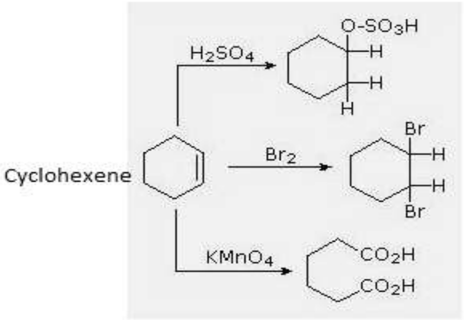
Stability:

The most striking evidence to unusual stability of benzene ring is found in the chemical reactions of benzene & the heat released in a hydrogenation reaction of one mole of an unsaturated compound.

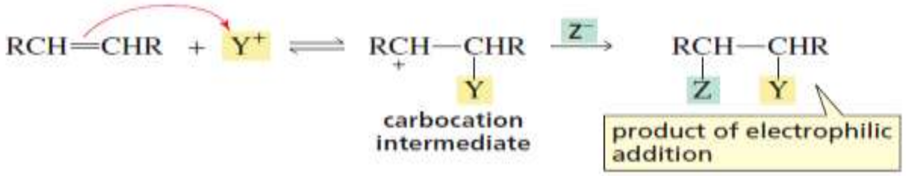
(a) Benzene undergoes substitution rather than addition.

- Kekule's structure of benzene is one that we would call "cyclohexatriene." We would expect this cyclohexatriene, like the very similar compounds, cyclohexadiene and cyclohexene, to undergo readily the addition reactions characteristic of the alkene structure.
- Example: cyclohexene an alkene undergoes rapid addition reaction, under same conditions were benzene reacts either not at all or very slowly and this exhibited a high degree of unusual chemical stability of benzene compared with known alkenes and cycloalkenes (aliphatic compounds).

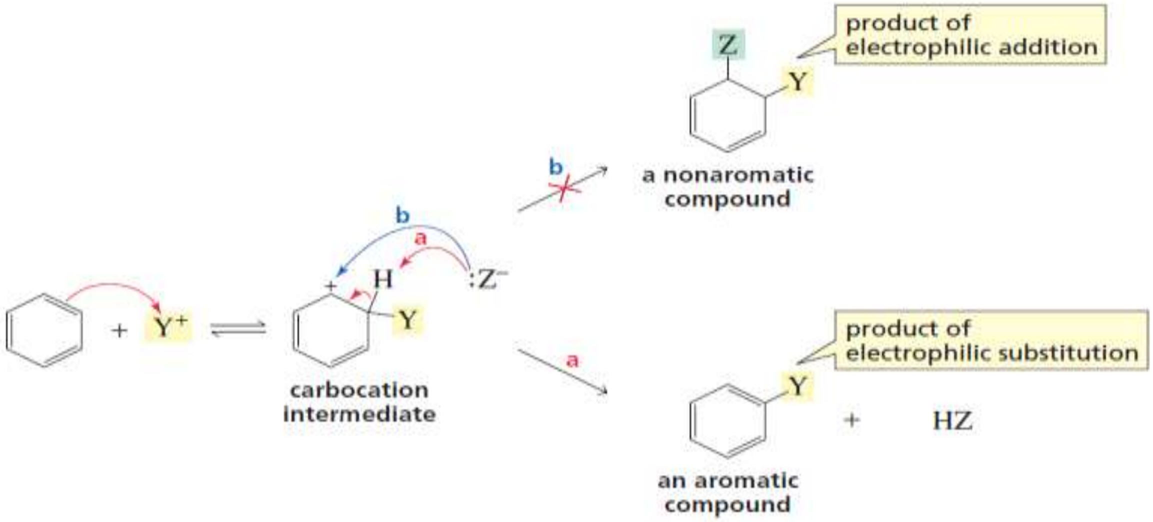




- Example: In addition reaction an alkene reacts with an electrophile, thereby forming a carbocation intermediate. In the second step of an electrophilic addition reaction, the carbocation reacts with a nucleophile to form an addition product.



If the carbocation intermediate formed from the reaction of benzene with an electrophile were to react similarly with a nucleophile (depicted as event b in Figure below), the addition product would not be aromatic. If, however, the carbocation loses a proton from the site of electrophilic attack (depicted as event a in Figure below), the aromaticity of the benzene ring is restored. Because the aromatic product is much more stable than the nonaromatic addition product, the overall reaction is an electrophilic substitution reaction rather than an electrophilic addition reaction. In the substitution reaction, an electrophile substitutes for one of the hydrogens attached to the benzene ring.



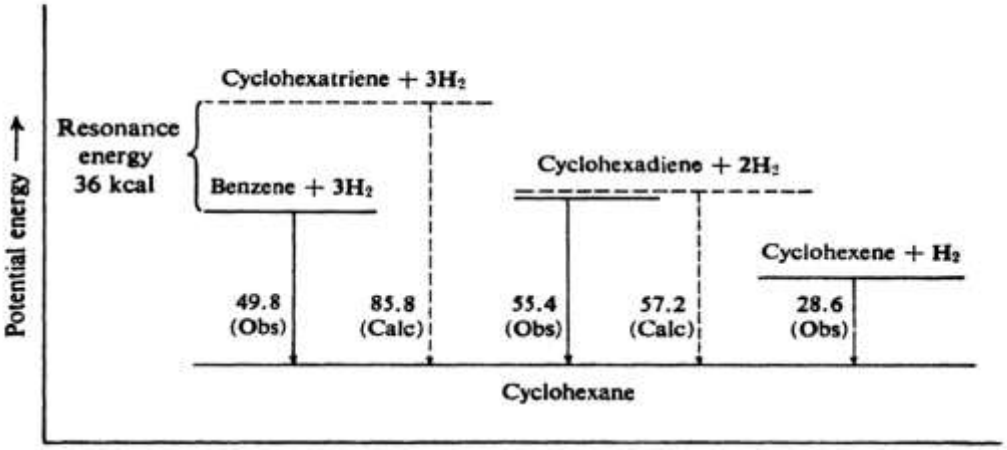
In place of addition reactions, benzene readily undergoes a new set of reactions, all involving substitution. The most important are **Halogenation, Nitration, Sulfonation, Friedel–Crafts acylation & Friedel–Crafts alkylation.**

In an electrophilic aromatic substitution reaction, an electrophile is put on a ring carbon, and the H^+ comes off the same ring carbon.

(b) Heat of hydrogenation (resonance energy) and combustion.

- The heat released in a hydrogenation reaction of one mole of an unsaturated (double bonded) compound is called the **heat of hydrogenation**.
- A quantitative data which show how much more stable is benzene.
- Cyclohexene has a heat of hydrogenation of 28.6 kcal and cyclohexadiene has one about twice that (55.4 kcal.)

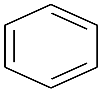
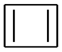
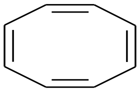
- We expected cyclohexatriene (i.e. in imagine that benzene contains three double bonds in it) to have a heat of hydrogenation about three times as large as cyclohexene, that is, about 85.8 kcal. Actually the value for benzene (49.8 kcal) is 36 kcal less than this expected amount.
- The fact that benzene evolves 36 kcal less energy than predicted can only mean that benzene contains 36 kcal less energy than predicted; in other words, *benzene is more stable* by 36 kcal than we would have expected cyclohexatriene to be.



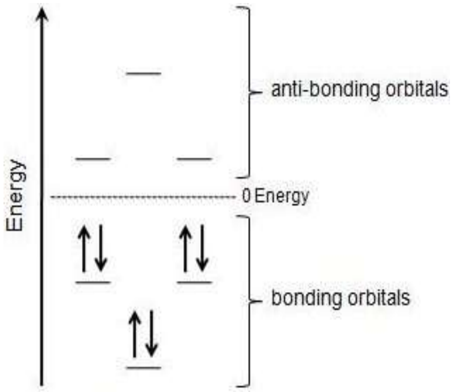
Aromatic character: The Huckel 4n + 2 rule

In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has 4n+2 π (*Pi*) electrons, it is considered aromatic. This rule would come to be known as Hückel's Rule.

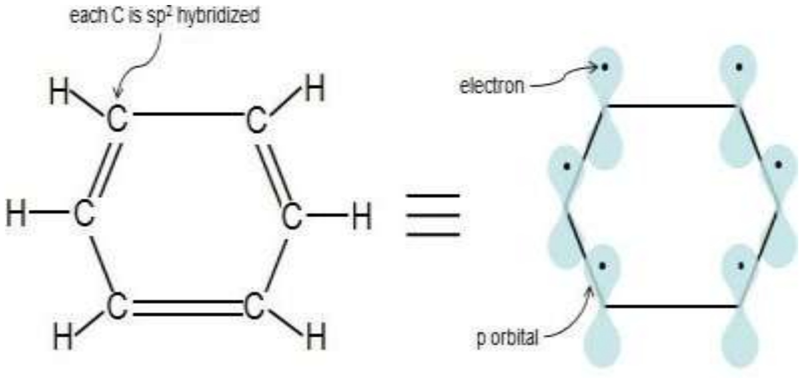
Criteria for Aromaticity & Anti-Aromaticity:

Aromatic	Anti-aromatic	Non-aromatic
The molecule is cyclic (a ring of atoms)	The molecule is cyclic (a ring of atoms)	Fails any one of the criteria on the left OR everything else
The molecule is planar or flat (all atoms in the molecule lie in the same plane)	The molecule is planar or flat (all atoms in the molecule lie in the same plane)	
The molecule is fully conjugated (p orbitals at every atom in the ring)	The molecule is fully conjugated (p orbitals at every atom in the ring)	
The molecule has 4n+2 π electrons (n=0 or any positive integer)	The molecule has 4n π electrons	
Unusually stable	Unusually stable	
 Benzene	 Cyclobutadiene	 Cyclooctatetraene
Resonance energy (heat of hydrogenation energy) 36 kcal/mol	Only stable below -100°C	

- According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons.
- With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n) leaving all bonding orbitals filled and no anti-bonding orbitals occupied.
- This gives a total of 4n+2 π electrons.
- In benzene, each double bond (π bond) always contributes 2 π electrons. Benzene has 3 double bonds, so it has 6 π electrons.
- Its first 2 π electrons fill the lowest energy orbital, and 4 π electrons remaining fill in the orbitals of the succeeding energy level.
- Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.



molecular orbital diagram for benzene



benzene has 6 π electrons

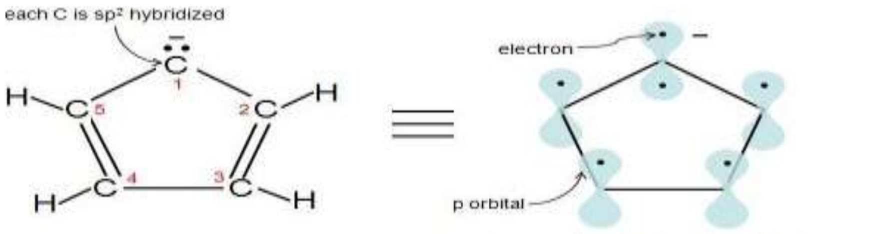
- To apply the 4n+2 rule, first count the number of π electrons in the molecule. Then, set this number equal to 4n+2 and solve for n. If is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six π electrons:

$$4n+2=6$$
$$4n=4$$
$$n=1$$

For benzene, we find that n=1, which is a positive integer, so the rule is met. Benzene is aromatic compound.

Aromatic Ions

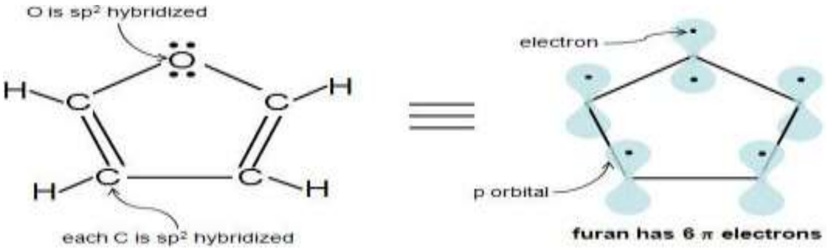
- Hückel's Rule also applies to ions especially aromatic ions. As long as a compound has 4n+2 π electrons, it does not matter if the molecule is neutral or has a charge.
- For example, cyclopentadienyl anion is an aromatic ion.
- Carbons 2-5 are sp2 hybridized because they have 3 attached atoms and have no lone electron pairs.
- If an atom has 1 or more lone pairs and is attached to an sp2 hybridized atom, then that atom is sp2 hybridized also.
- Therefore, carbon 1 also sp2 hybridized, it has a p orbital. Cyclopentadienyl anion has 6 π electrons and fulfills the 4n+2 rule.



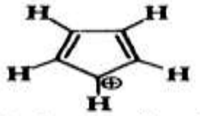
cyclopentadienyl anion has 6 π electrons

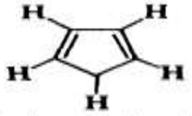
Heterocyclic Aromatic Compounds

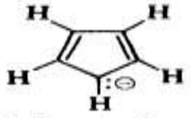
- Heterocyclic compounds contain 1 or more different atoms other than carbon in the ring. A common example is furan, which contains an oxygen atom.
- All carbons in furan are sp2 hybridized.
- The oxygen has at least 1 lone electron pair and is attached to an sp2 hybridized atom, so it is sp2 hybridized as well.
- Notice how oxygen has 2 lone pairs of electrons. How many of those electrons are π electrons?
- A sp2 hybridized atom only has 1 p orbital, which can only hold 2 electrons, so we know that 1 electron pair is in the p orbital, while the other pair is in an sp2 orbital. So, only 1 of oxygen's 2 lone electron pairs are π electrons.
- So, Furan has 6 π electrons and fulfills the 4n+2 rule

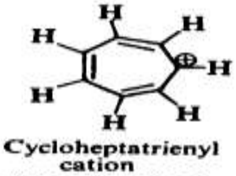


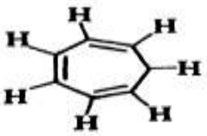
Working example I: Using the criteria for aromaticity, determine if the following molecules are aromatic:

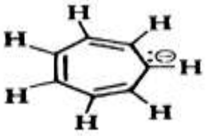

Cyclopentadienyl cation


Cyclopentadienyl radical


Cyclopentadienyl anion


Cycloheptatrienyl cation (Tropylium ion)


Cycloheptatrienyl radical


Cycloheptatrienyl anion

Working example II: Using the criteria for aromaticity, determine if the following molecules are aromatic:

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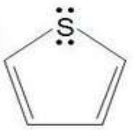

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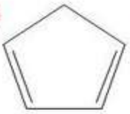

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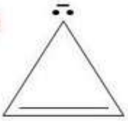

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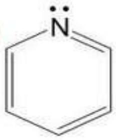

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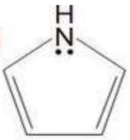

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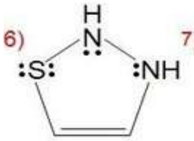

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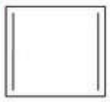

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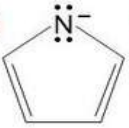

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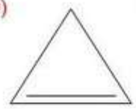


10)

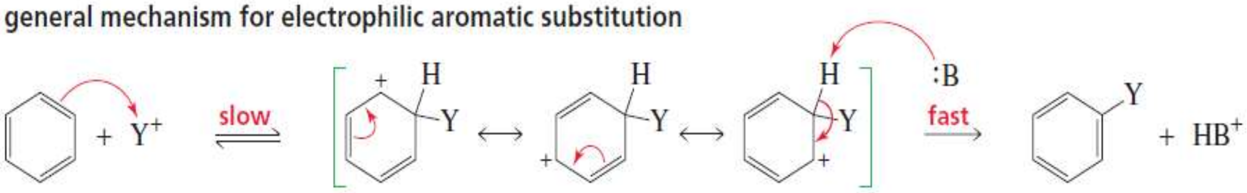

Reactions of Benzene:

Benzene readily undergoes a new set of reactions, all involving substitution i.e. Electrophilic Aromatic Substitution Reactions. It involves the reaction of an electrophile with an aromatic compound, were electrophile substitutes for a hydrogen of an aromatic compound.

General Mechanism for Electrophilic Aromatic Substitution Reactions:

- Similar to alkenes, benzene (aromatics) has a cloud of π electrons available to attack electrophiles (the aromatic ring is nucleophilic)
- The resulting carbocation is stabilized by resonance and is called: Sigma complex
- These reactions are greatly facilitated by addition of Lewis acid catalyst.
- Key bonds formed C-Y and key bonds broken C-H
- Electron donating substituents increase the rate of substitution reaction by activating the benzene ring to electrophilic attack.
- Electron withdrawing substituents decrease the rate of substation reaction by deactivating the benzene ring to electrophilic attack.

general mechanism for electrophilic aromatic substitution



The general mechanism can be applied to the following reactions and the only difference will be the nature of the electrophile, and how it is formed.

1. **Halogenation:** A bromine (Br), a chlorine (Cl), or an iodine (I) substitutes for a hydrogen (Lewis acid: $AlCl_3$/$FeCl_3$/$AlBr_3$/$FeBr_3$, etc.)

2. **Nitration:** A nitro (NO_2) group substitutes for a hydrogen (acid: H_2SO_4).

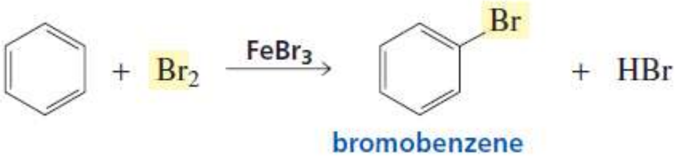
3. **Sulfonation:** A sulfonic acid (SO_3H) group substitutes for a hydrogen (acid: H_2SO_4).

4. **Friedel–Crafts acylation:** An acyl (RC=O) group substitutes for a hydrogen (Lewis acid: $AlCl_3$/$FeCl_3$)

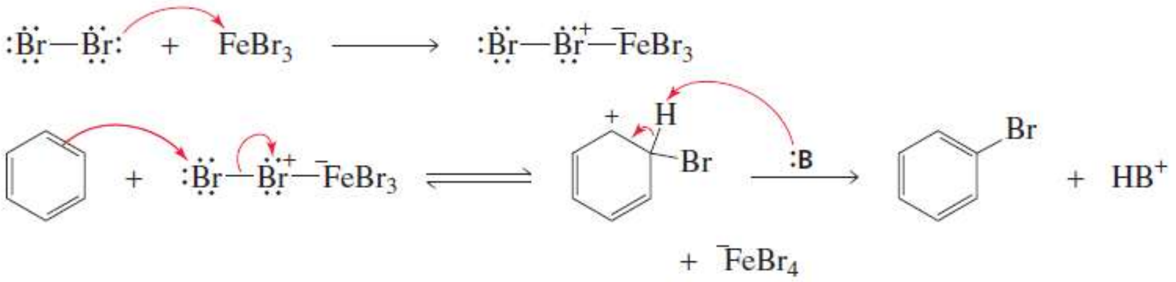
5. **Friedel–Crafts alkylation:** an alkyl (R) group substitutes for a hydrogen (Lewis acid: $AlCl_3$/$FeCl_3$)

Halogenation of Benzene: The bromination or chlorination of benzene requires a Lewis acid such as ferric bromide or ferric chloride. Recall that a Lewis acid is a compound that accepts a share in a pair of electrons.

Bromination: Electrophile Br^+

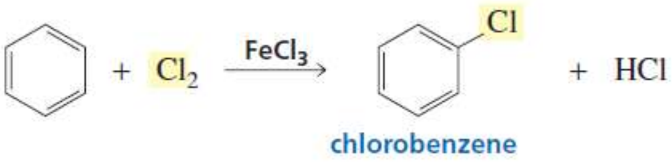


mechanism for bromination

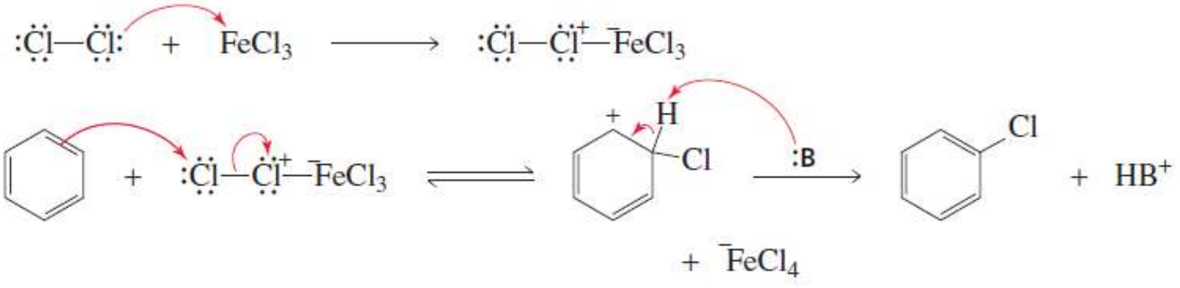


$$\bar{F}eBr_4 \quad + \quad HB^+ \quad \longrightarrow \quad HBr \quad + \quad FeBr_3 \quad + \quad :B$$

Chlorination: Electrophile Cl^+



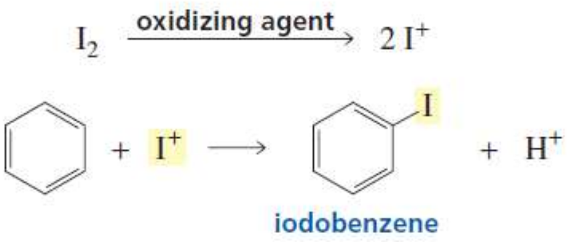
mechanism for chlorination



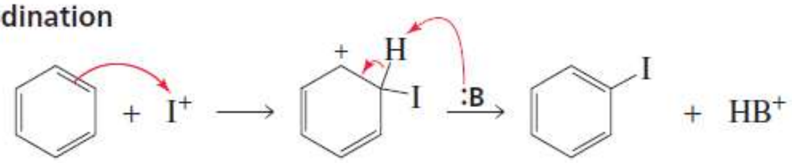
Iodination: For iodination, iodine is simply oxidized with nitric acid (HNO_3) to liberate the I^+, which is then used as the electrophile.

$$H^+ + HNO3 + ½ I_2 \rightarrow I^+ + NO_2 + H_2O$$

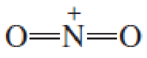
OR



mechanism for iodination

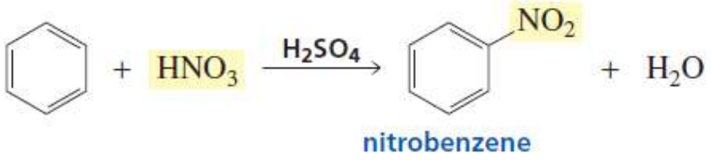


Nitration of Benzene: Nitration of benzene with nitric acid requires sulfuric acid as a catalyst.

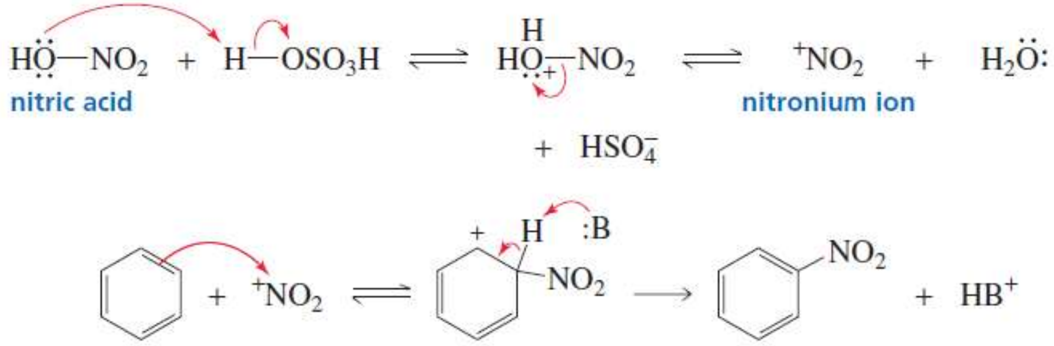
Electrophile: 

$$O=\overset{+}{N}=O$$

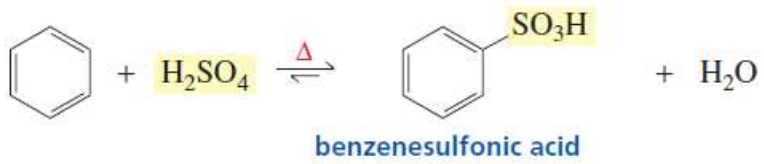
nitronium ion



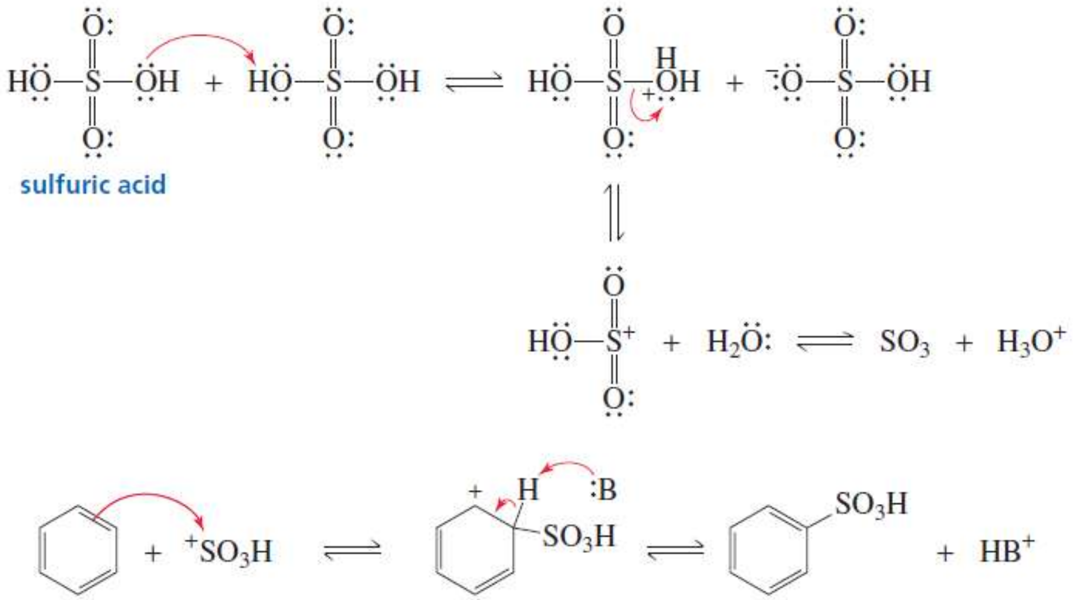
mechanism for nitration



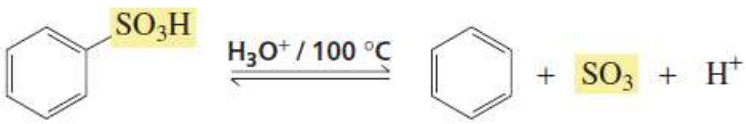
Sulfonation of Benzene: Fuming sulfuric acid (a solution of in sulfuric acid) or concentrated sulfuric acid is used to sulfonate aromatic rings. Electrophile: HSO_3^+



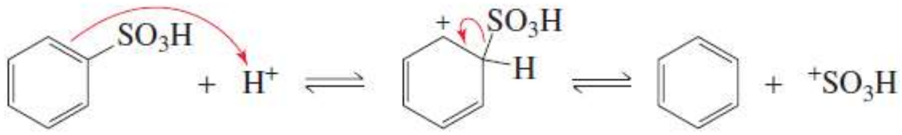
mechanism for sulfonation



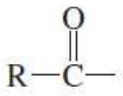
Sulfonation of benzene is a reversible reaction. If benzenesulfonic acid is heated in dilute acid, the reaction proceeds in the reverse direction.



mechanism for desulfonation

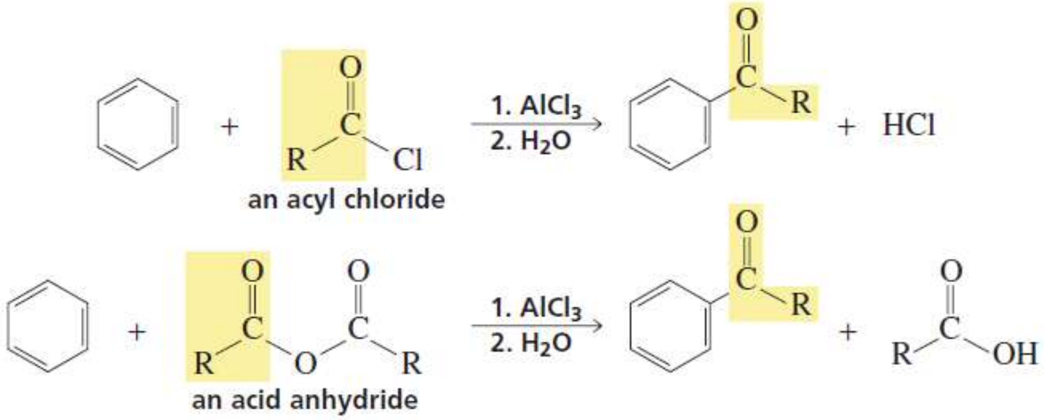


Friedel–Crafts Acylation: Friedel–Crafts acylation places an acyl group on a benzene ring.



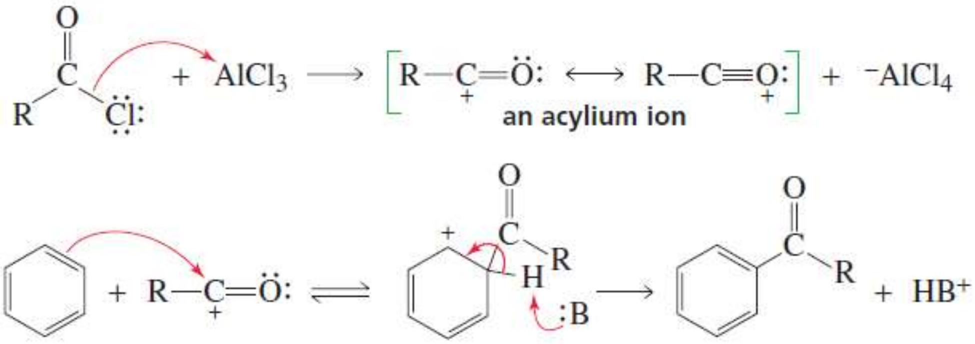
an acyl group

Either an acyl halide or an acid anhydride can be used for Friedel–Crafts acylation.



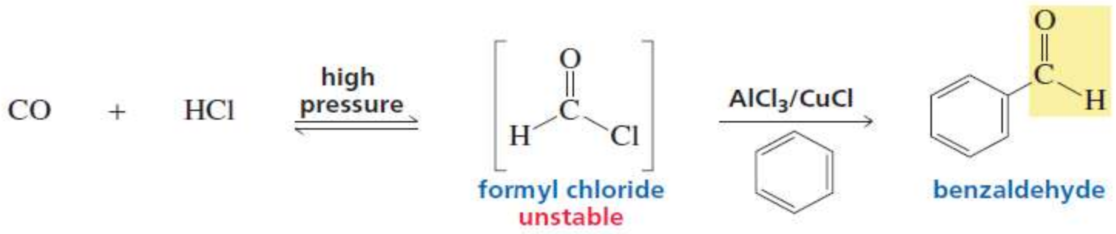
An acylium ion is the electrophile required for a Friedel–Crafts acylation reaction. This ion is formed by the reaction of an acyl chloride or an acid anhydride with $AlCl_3$ a Lewis acid.

mechanism for Friedel–Crafts acylation

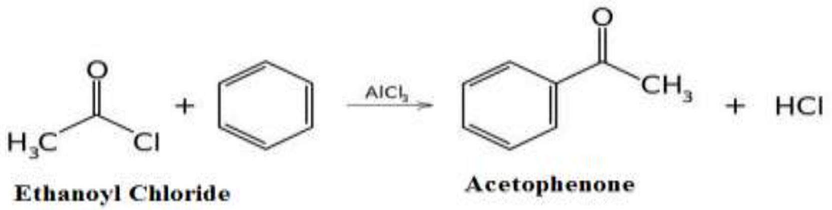


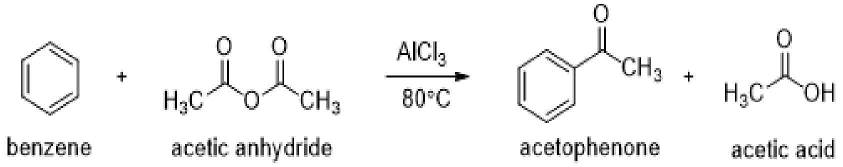
Example:

The synthesis of benzaldehyde from benzene and formyl chloride (the acyl halide required for the reaction), which is unstable and obtained by means of the Gatterman–Koch formylation reaction. This reaction uses a high-pressure mixture of carbon monoxide and HCl to generate formyl chloride, along with an aluminum chloride–cuprous chloride catalyst to carry out the acylation reaction.



Example: Preparation of Acetophenone from alkyl halide and acid anhydride.



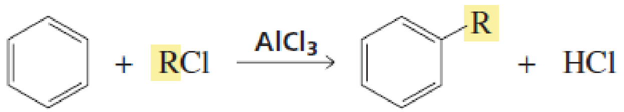


LIMITATIONS of Friedel-Crafts acylation:

1. Acylation can only be used to give ketones. This is because HCOCl decomposes to CO and HCl under the reaction conditions.
2. Deactivated benzenes are not reactive to Friedel-Crafts conditions, the benzene needs to be as or more reactive than a mono-halobenzene.
3. The Lewis acid catalyst AlCl3 often complexes to aryl amines making them very unreactive.
4. Amines and alcohols can give competing N or O acylations rather than the require ring acylation

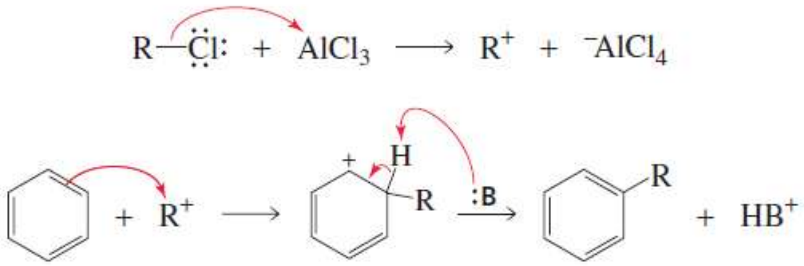
Friedel–Crafts alkylation: Friedel–Crafts alkylation places an alkyl group on a benzene ring.

R—
an alkyl group



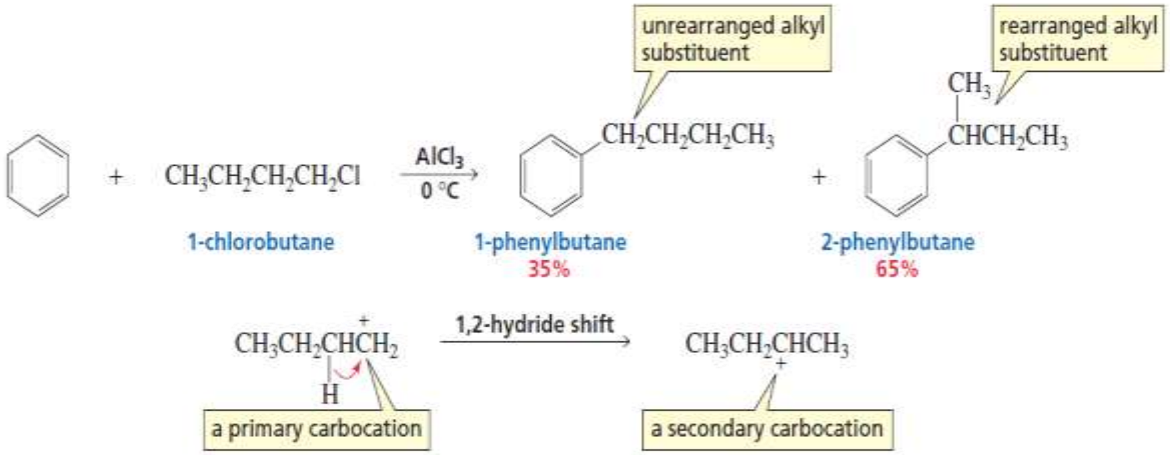
- A carbocation is formed from the reaction of an alkyl halide with $AlCl_3$, Alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides can all be used. Vinyl halides and aryl halides cannot be used because their carbocations are too unstable to be formed.

mechanism for Friedel–Crafts alkylation

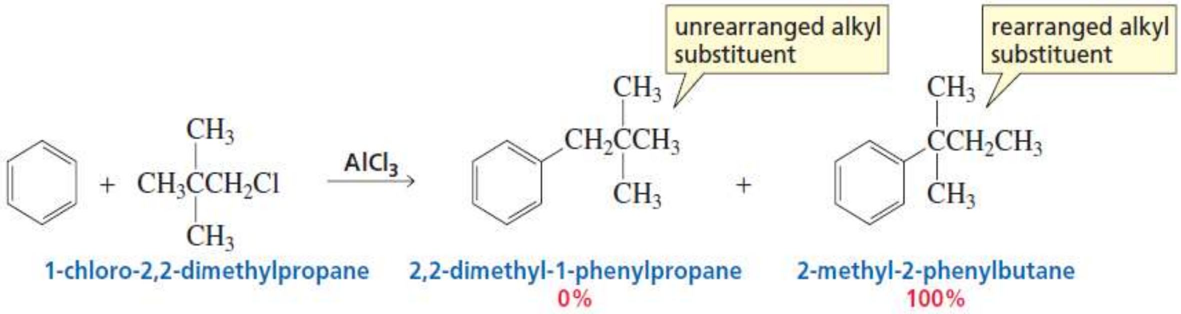


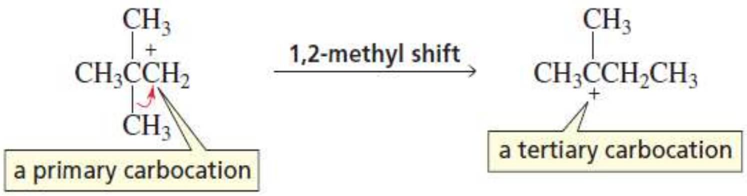
- An alkyl-substituted benzene is more reactive than benzene. Therefore, to prevent further alkylation of the alkyl-substituted benzene, a large excess of benzene is used in Friedel–Crafts alkylation reactions.
- A carbocation will rearrange if rearrangement leads to a more stable carbocation.
- When the carbocation can rearrange in a Friedel–Crafts alkylation reaction, the major product will be the product with the rearranged alkyl group on the benzene ring.

Example: less stable primary carbocation to stable secondary carbocation



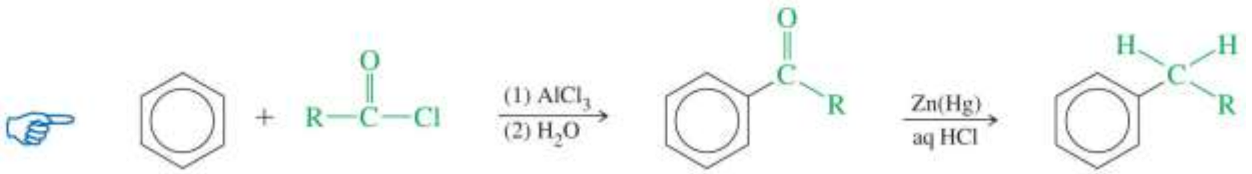
Example: less stable primary carbocation to stable tertiary carbocation





- We have just seen that Friedel-Crafts alkylation rarely provides a straight chain alkyl function on the aromatic (due to rearrangement)
- To avoid this problem, one can use either of the Clemmensen reduction of acyl benzene to form the desired alkylated aromatic.
- The Clemmensen reduction is a series of 2 reaction, (1) Friedel-Crafts Acylation, (2) decarbonylation of the resulting ketone.

Example 1:



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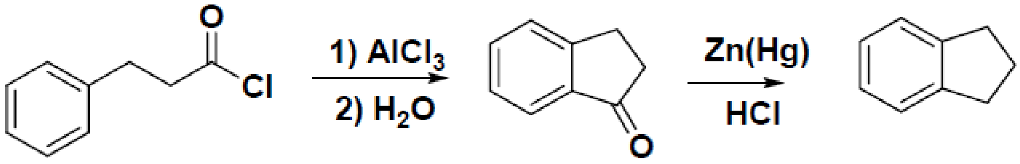
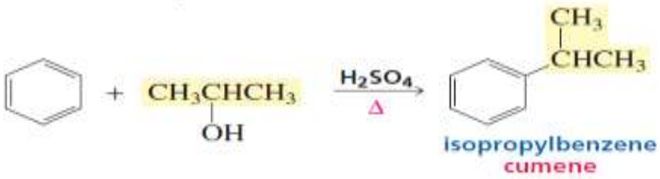
Example 2:

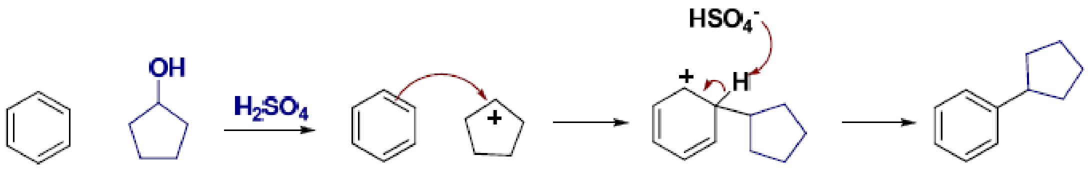


Any other carbocation source can be used in the presence of an aromatic ring to give Friedel Crafts substitution products.

alkylation of benzene by an alkene

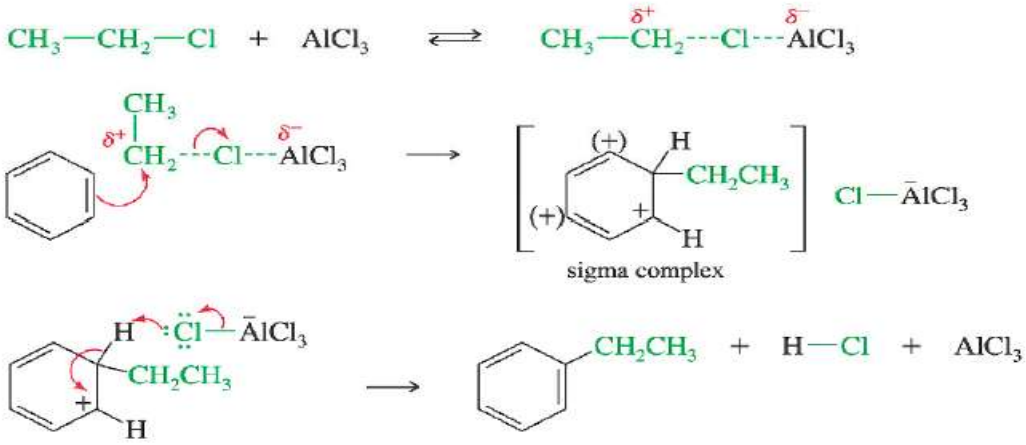
alkylation of benzene by an alcohol



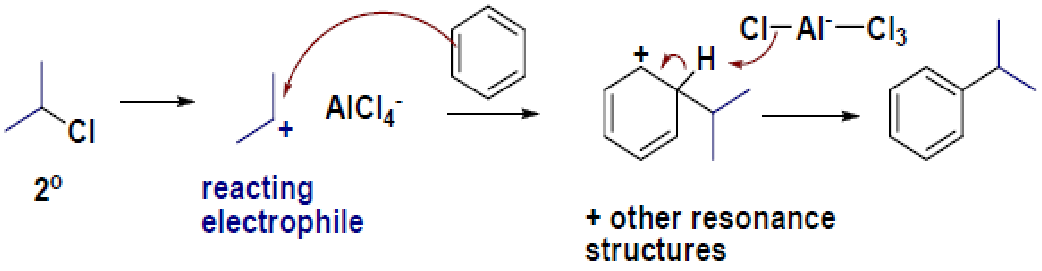


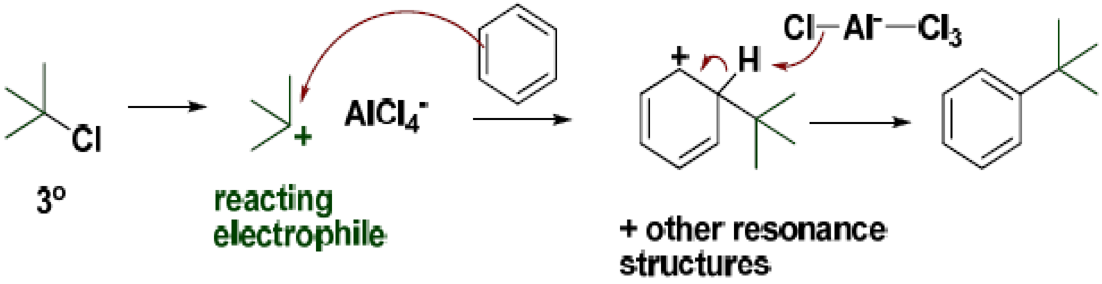
Example: Friedel–Crafts alkylation

Mechanism of Friedel-Crafts Alkylation (1° halides)



Example: When secondary and tertiary alkyl halides are used, the electrophile is the corresponding carbocations.





There are 3 important LIMITATIONS to the Friedel-Crafts Alkylation:

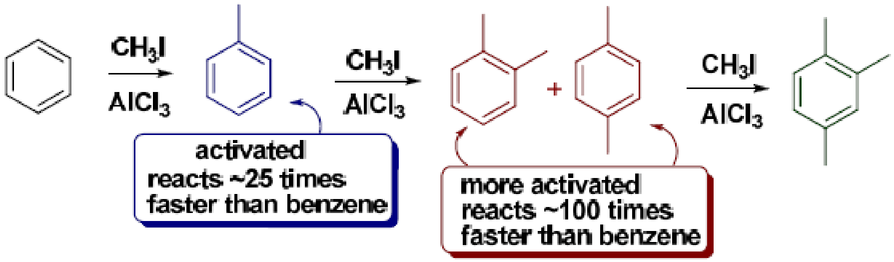
1. Works only with benzene and activated derivatives (no reaction when deactivators are present).

2. Rearrangements of carbocations or carbocation like species is common.

3. Vinyl or aryl halides do not react (their intermediate carbocations are too unstable).

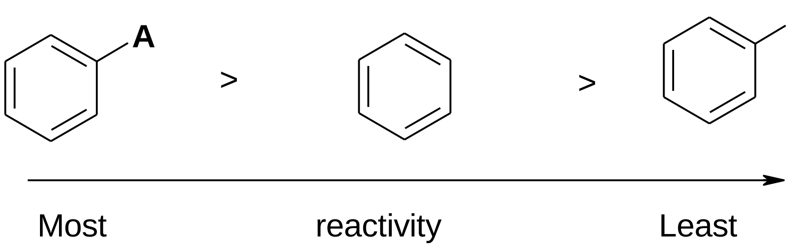
4. The Lewis acid catalyst AlCl3 often complexes to aryl amines making them very unreactive.

5. Poly-alkylation is often the result since the alkylation product is more reactive than the original compound (Note: This can usually be controlled with an excess of the benzene). For example:



Effect of Substituents on Reactivity and Orientation of Mono Substituted Benzene Compounds towards Electrophilic Substitution Reaction

- The reactions of substituted benzenes are similar to those of benzene, but can take place faster or slower than benzene depending on the substitution pattern.
- The substituent can either increase or decrease the rate of the reaction depending on its nature.



- Activating (**A**) if the benzene ring it is attached to is more reactive than benzene i.e. one that provides more electrons (electron donating groups) to the aromatic system
- Deactivating (**D**) if the ring it is attached to is less reactive than benzene i.e. one that pulls electrons away from the aromatic system.
- Substituent(s) direct the incoming electrophile to a specific location.
- As shown in **Table 1**, nearly all groups fall into one of two glasses: activating and ortho, para directing, or deactivating and meta-directing. The halogens are in a class by themselves, being deactivating but ortho, para-directing.

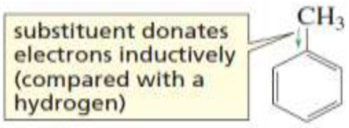
The Effect of Substituents on Reactivity

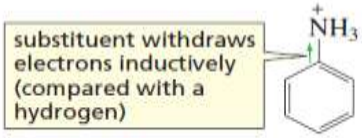
There are two ways substituents can donate electrons into a benzene ring: inductive electron donation and electron donation by resonance. There are also two ways substituents can withdraw electrons from a benzene ring: inductive electron withdrawal and electron withdrawal by resonance.

Inductive Electron Donation and Withdrawal

- It is a permanent effect
- It operates on sigma bonded electrons
- Electron shift take place towards more electro negative atom

If a substituent that is bonded to a benzene ring is less electron withdrawing than a hydrogen, the electrons in the sigma bond that attaches the substituent to the benzene ring will move toward the ring more readily. Such a substituent donates electrons inductively compared with a hydrogen.





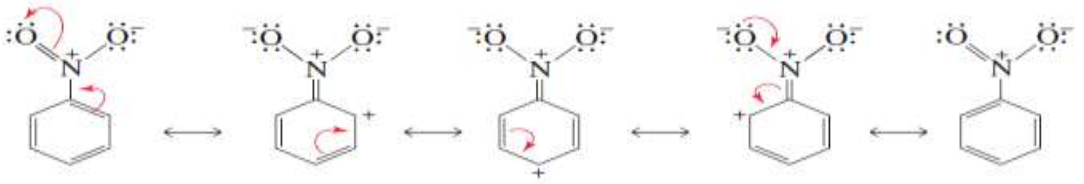
If a substituent is more electron withdrawing than a hydrogen, it will withdraw the sigma electrons away from the benzene ring more strongly than will a hydrogen. Withdrawal of electrons through a sigma bond is called **inductive electron withdrawal**. The NH_3^+ group is a substituent that withdraws electrons inductively because it is more electronegative than a hydrogen.

Resonance Electron Donation and Withdrawal

If a substituent has a lone pair on the atom that is directly attached to the benzene ring, the lone pair can be delocalized into the ring; these substituents are said to donate electrons by resonance. Substituents such as OH, OR, and Cl donate electrons by resonance.


donation of electrons into a benzene ring by resonance

If a substituent is attached to the benzene ring by an atom that is doubly or triply bonded to a more electronegative atom, the pi electrons of the ring can be delocalized onto the substituent; these substituents are said to withdraw electrons by resonance. Substituents such as C=O, C≡N, O=N-O (NO_2) and withdraw electrons by resonance.



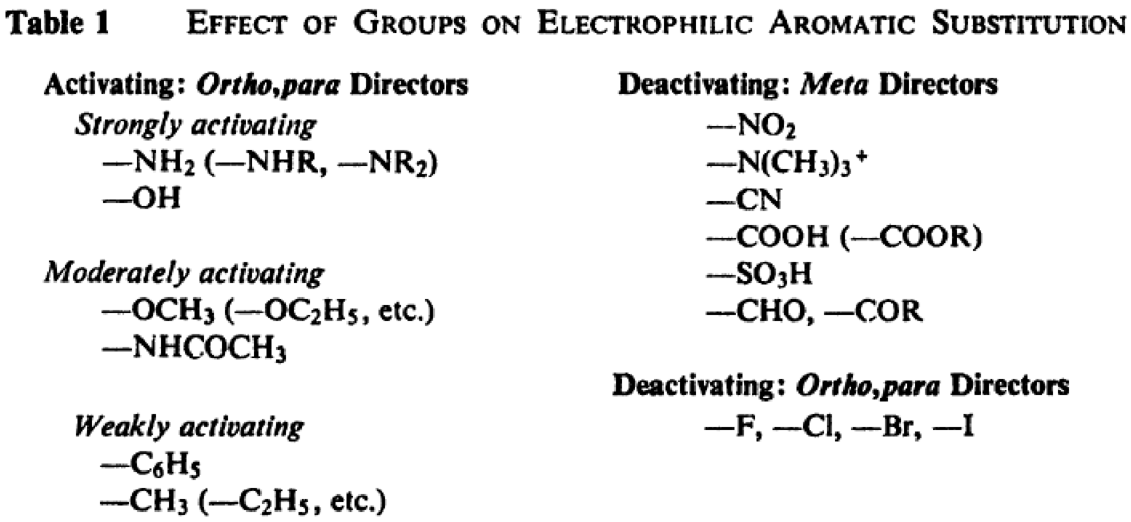


Table 1 EFFECT OF GROUPS ON ELECTROPHILIC AROMATIC SUBSTITUTION

Activating: *Ortho,para* Directors

Strongly activating
- $—NH_2$ ($—NHR$, $—NR_2$)
- $—OH$

Moderately activating
- $—OCH_3$ ($—OC_2H_5$, etc.)
- $—NHCOCH_3$

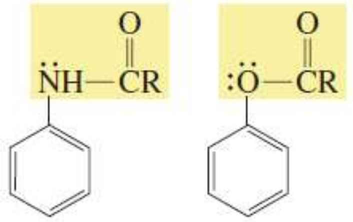
Weakly activating
- $—C_6H_5$
- $—CH_3$ ($—C_2H_5$, etc.)

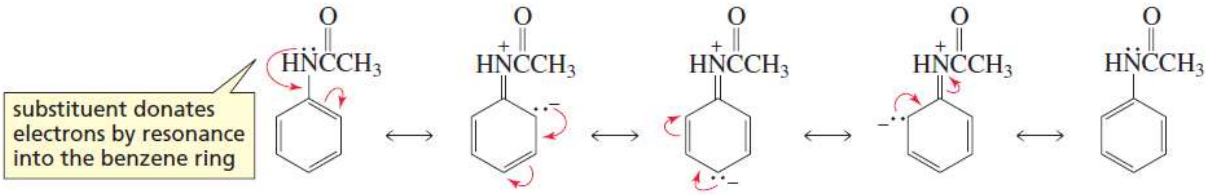
Deactivating: *Meta* Directors
- $—NO_2$
- $—N(CH_3)_3^+$
- $—CN$
- $—COOH$ ($—COOR$)
- $—SO_3H$
- $—CHO$, $—COR$

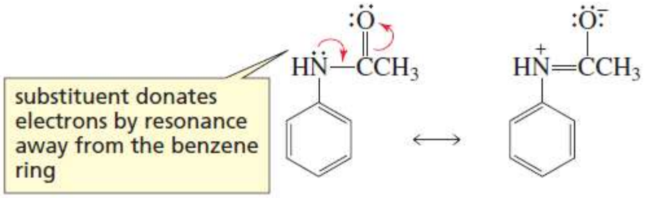
Deactivating: *Ortho,para* Directors
- $—F$, $—Cl$, $—Br$, $—I$

Note: The **moderately activating substituents** also donate electrons into the ring by resonance and withdraw electrons from the ring inductively. These substituents are less effective at donating electrons into the ring by resonance because, unlike the strongly activating substituents that donate electrons by resonance only into the ring, the moderately activating substituents can donate electrons by resonance in two competing directions: into the ring and away from the ring.

moderately activating substituents

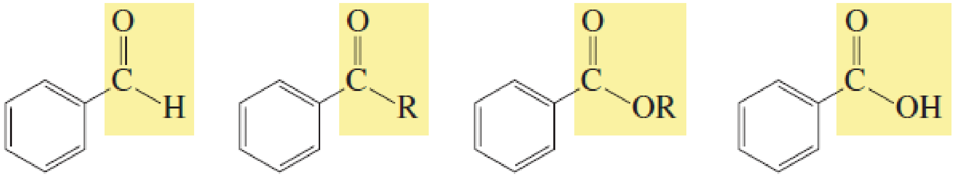



substituent donates electrons by resonance into the benzene ring

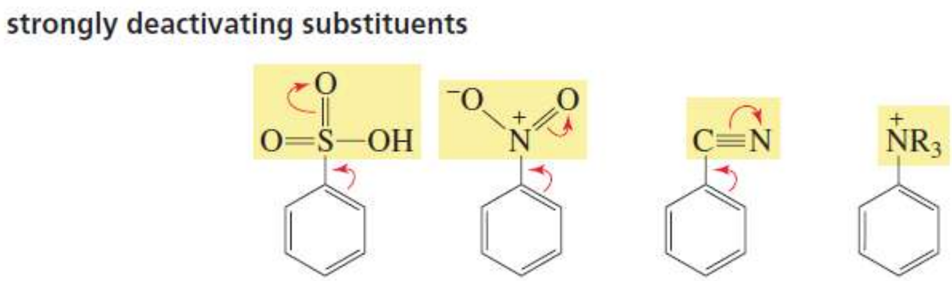

substituent donates electrons by resonance away from the benzene ring

The moderately deactivating substituents all have carbonyl groups directly attached to the benzene ring. Carbonyl groups withdraw electrons both inductively and by resonance.

moderately deactivating substituents



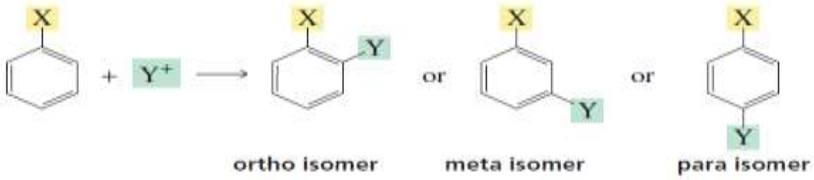
The strongly deactivating substituents are powerful electron withdrawers. Except for the ammonium ions ($^{+}NH_3$, $^{+}NH_2R$, $^{+}NHR_2$ and $^{+}NR_3$), these substituents withdraw electrons both inductively and by resonance. The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electrons inductively.



The Effect of Substituents on Orientation

When a substituted benzene undergoes an electrophilic substitution reaction, The substituent already attached to the benzene ring determines the location of the new substituent.

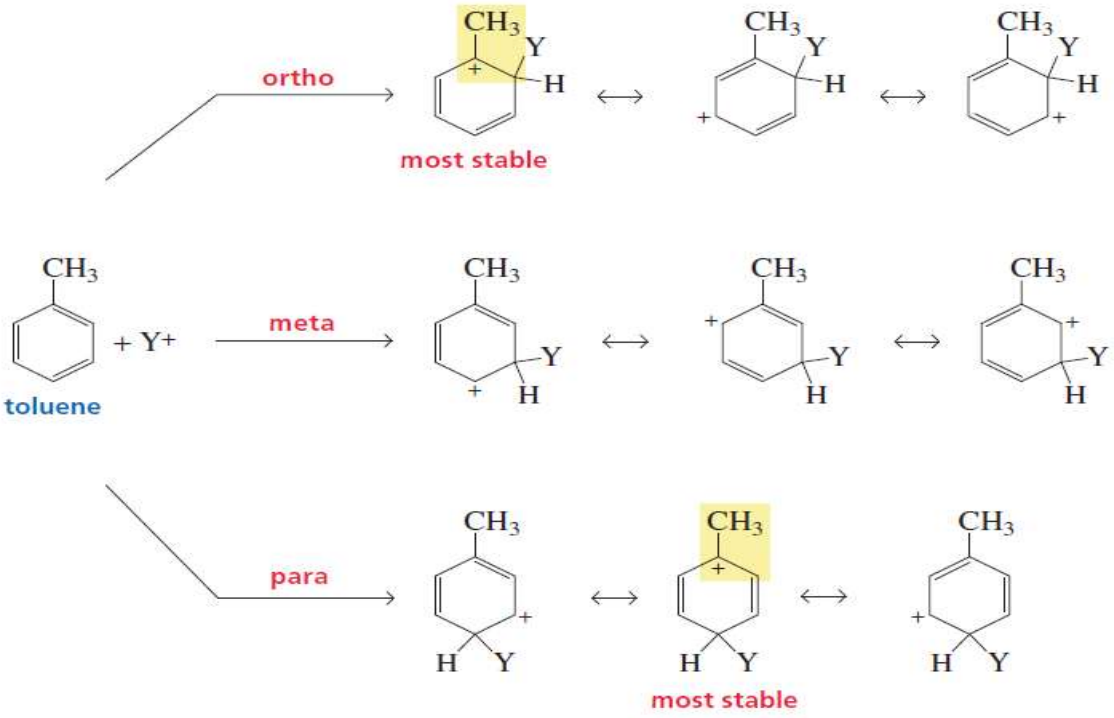
All activating substituents and the weakly deactivating halogens are ortho–para directors, and all substituents that are more deactivating than the halogens are meta directors. Thus, the substituents can be divided into three groups:



The above classification is based on the stability of the carbocation intermediate that is formed in the rate-determining step.

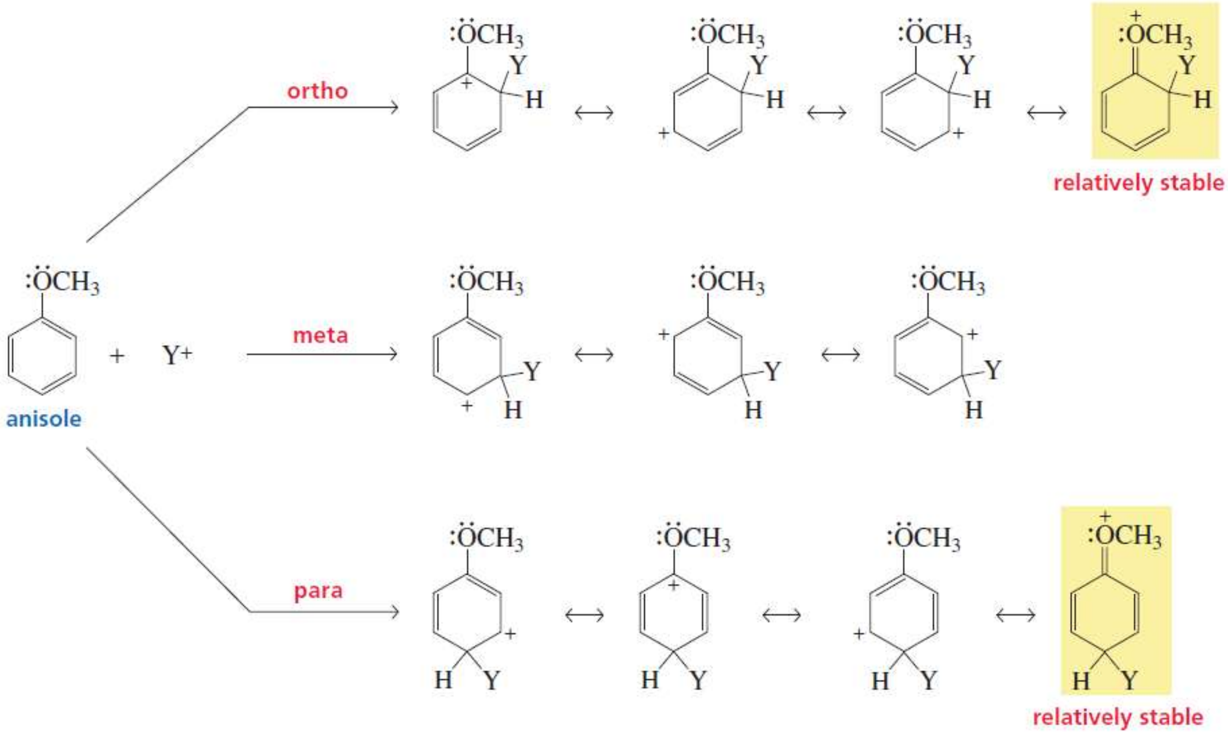
Example:

If a substituent donates electrons inductively like a methyl group, for example in Toulene, the substituent is attached directly to the positively charged carbon, which the substituent can stabilize by inductive electron donation. These relatively stable resonance contributors are obtained only when the incoming group is directed to an ortho or para position.



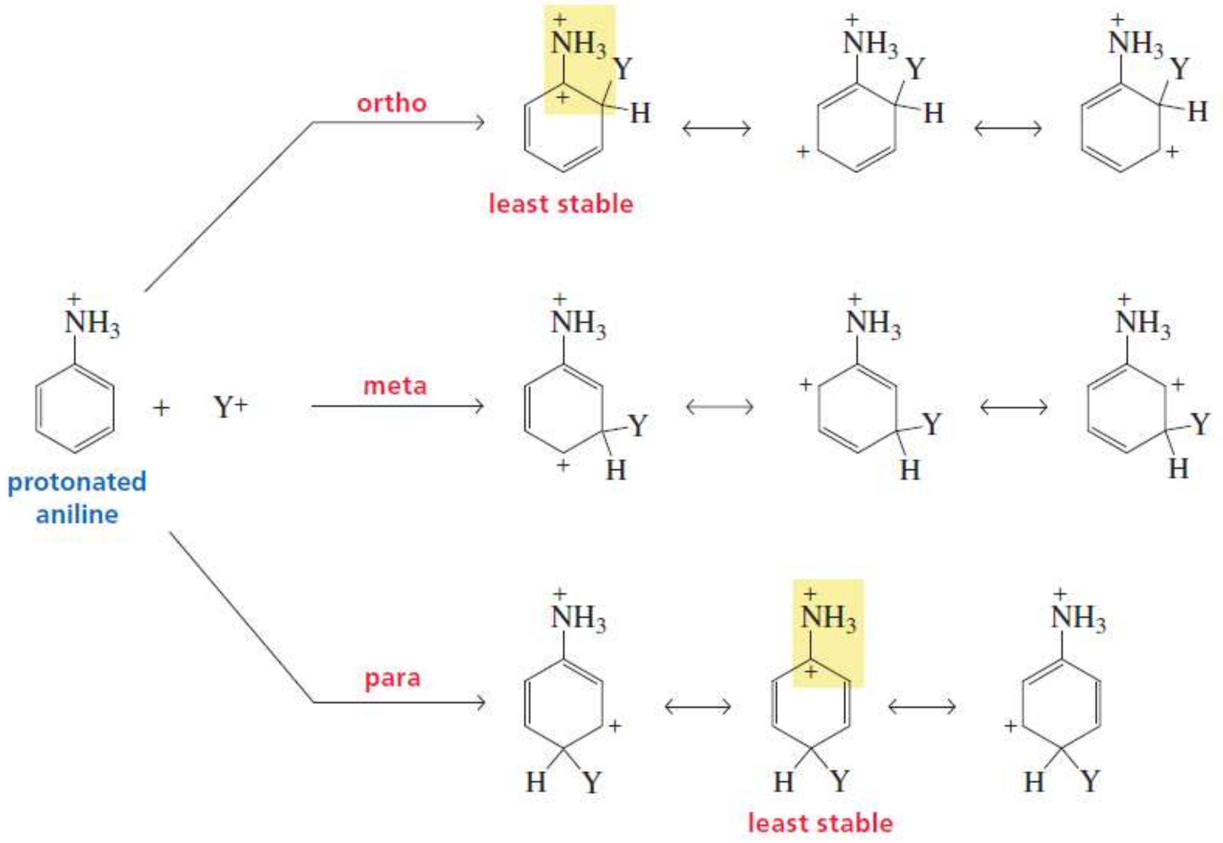
Example:

If a substituent donates electrons by resonance, like a methoxy group, for example in Anisole, the carbocations formed by putting the incoming electrophile on the ortho and para positions have a fourth resonance contributor. This is an especially stable resonance contributor because it is the only one whose atoms (except for hydrogen) all have complete octets. Therefore, all substituents that donate electrons by resonance are ortho–para directors.



Example:

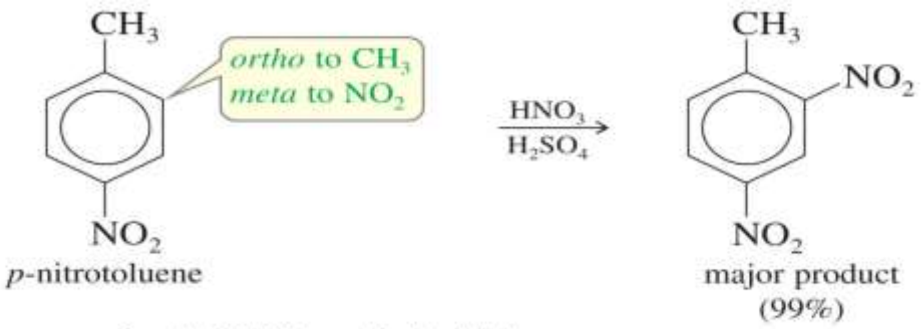
Substituents with a positive charge or a partial positive charge on the atom attached to the benzene ring, withdraw electrons inductively from the benzene ring, and most withdraw electrons by resonance as well. For all such substituents, the indicated resonance contributors in Figure below are the least stable because they have a positive charge on each of two adjacent atoms, so the most stable carbocation is formed when the incoming electrophile is directed to the meta position. Thus, all substituents that withdraw electrons (except for the halogens, which are ortho–para directors because they donate electrons by resonance) are meta directors.



Effect of Multiple Substituents on Electrophilic Aromatic Substitution

When 2 substituents are already on the ring

- the stronger activator usually predominates.
- Steric factors will also play a role in determining the structure of the new product.



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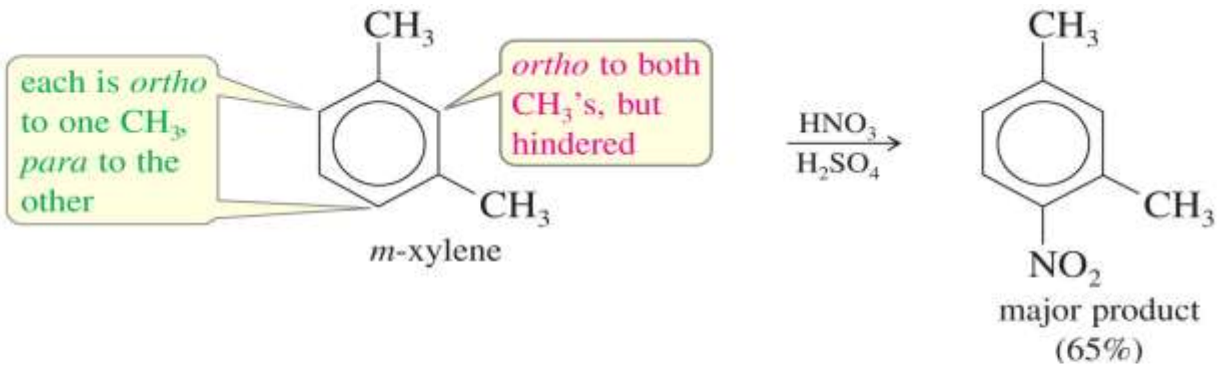

Note: for Unit I subtopic: D, i.e. Structure and uses of DDT, Saccharin, BHC and Chloramine, please refer to/your Unit-I, Activity-I copy for further detail and reference.