

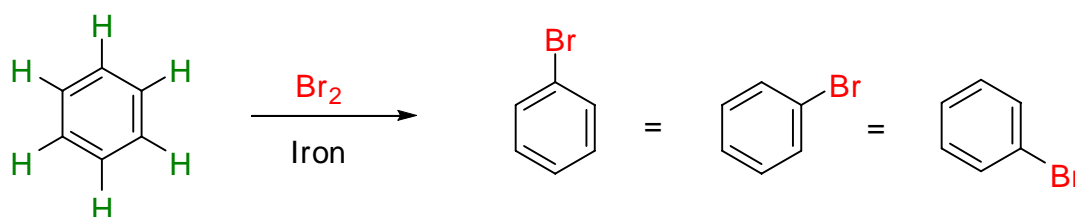
Chapter 5. Aromatic Compounds

5.1 Structure of Benzene: The Kekule Proposal

Mid-1800s, benzene was known to have the **molecular formula C_6H_6** .

Benzene reacts with Br_2 in the presence of iron to give **substitution product C_6H_5Br** (only one isomeric form) rather than the addition product $C_6H_6Br_2$.

1865, **August Kekule** proposed that benzene contains a ring of carbon atoms and can be formulated as **cyclohexa-1,3,5-triene**, in which all six carbon atoms and all six hydrogens are equivalent



Two critical questions

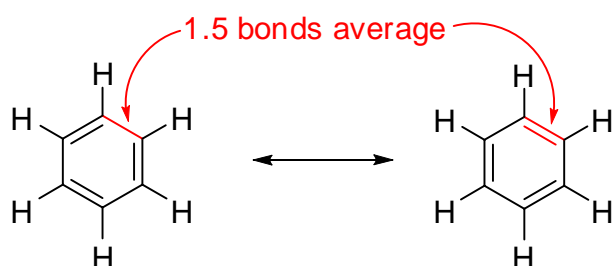
Why is benzene **unreactive** compared with alkenes? Benzene does not undergo electrophilic addition reactions with $KMnO_4$, H_3O^+ , HCl .

Why does benzene give a **substitution product** on reaction with Br_2 ?

All carbon-carbon bonds in benzene have the same length (139 pm), intermediate between typical single bond (154 pm) and a typical double bond (134 pm).

5.2 Structure of Benzene: The Resonance Proposal

Benzene is a **resonance hybrid** of the following two forms.

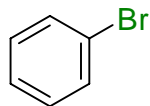


Benzene is a flat, symmetrical molecule with the shape of a regular hexagon. All C-C-C bond angles are 120° , each carbon atom is sp^2 -hybridized, and each carbon has a p orbital perpendicular to the plane of the six-membered ring.

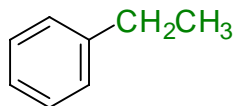
Each p orbital overlaps equally well with both neighboring p orbitals, leading to the structure in which the π electrons are shared around the ring in two doughnut-shaped clouds. [chapter 05 01 benzene.ppt](#)

5.3 Naming Aromatic Compounds

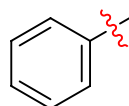
1. Monosubstituted benzenes: **-benzene** used as the parent name.



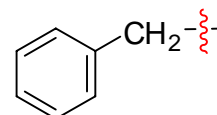
Bromobenzene



Ethylbenzene

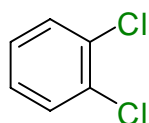


A phenyl group

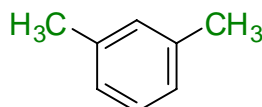


A benzyl group

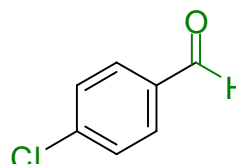
2. Disubstituted benzenes: use the prefixes **ortho- (o)**, **meta- (m)**, or **para- (p)**.



ortho-Dichlorobenzene

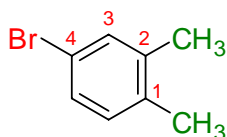


meta-Xylene

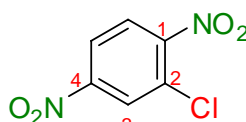


para-Chlorobenzaldehyde

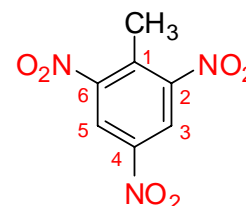
3. Benzenes with more than two substituents: named by **numbering** the position of each substituent on the ring so that the lowest possible numbers are used.



4-Bromo-1,2-dimethylbenzene

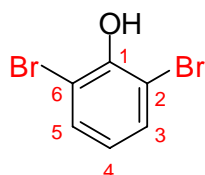


4-Chloro-1,4-dinitrobenzene

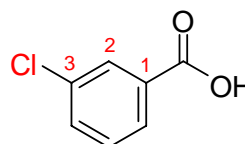


2,4,6-Trinitrotoluene

Monosubstituted aromatic compounds such as Toluene (CH₃), Phenol (OH), Aniline (NH₂), Acetophenone (acetyl), Benzaldehyde (CHO), Benzoic acid (CO₂H), Benzonitrile (CN) can serve as a parent name, with the principle substituent being the carbon #1.



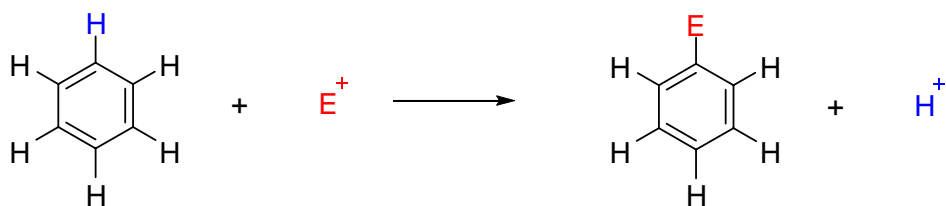
2,6-Dibromophenol



3-Chlorobenzoic acid

5.4 Electrophilic Aromatic Substitution Reactions: **Bromination**

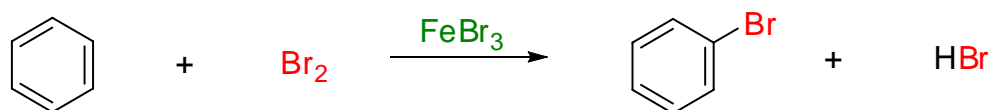
Electrophilic aromatic substitution: an electrophile (E⁺) reacts with the electron-rich aromatic ring (a nucleophile) and substitutes for one of the ring hydrogens.



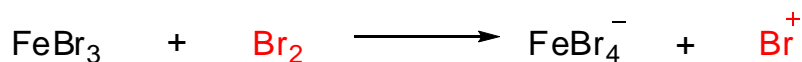
Many different substituents can be introduced: Halogenation (E = F, Cl, Br, I), nitration (E = NO₂), sulfonation (E = SO₃H), Alkylation (E = R), Acylation (E = C(O)R).

Bromination of Benzene

Aromatic rings are less reactive toward electrophiles than alkenes are (Br₂ in CH₂Cl₂ solution does not react with benzene). A catalyst such as FeBr₃ is required for bromination of benzene.



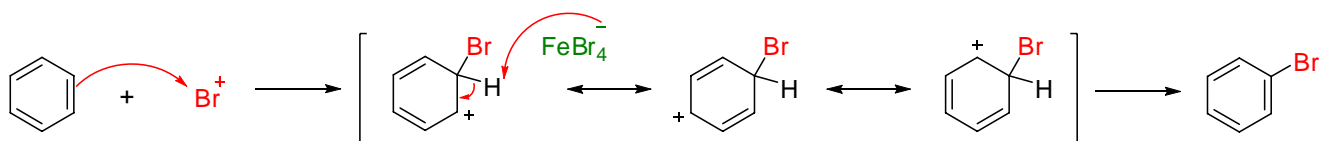
The catalyst makes the Br₂ molecule more electrophilic by reacting with it to give Br⁺.



or by forming Lewis Acid-Base pair.



The electrophile Br⁺ (or Br-Br⁺-FeBr₃) then reacts with benzene ring to yield an allylic carbocation intermediate. Since the intermediate carbocation is much less stable than the starting aromatic benzene, **the reaction has a relatively high activation energy and is rather slow.**

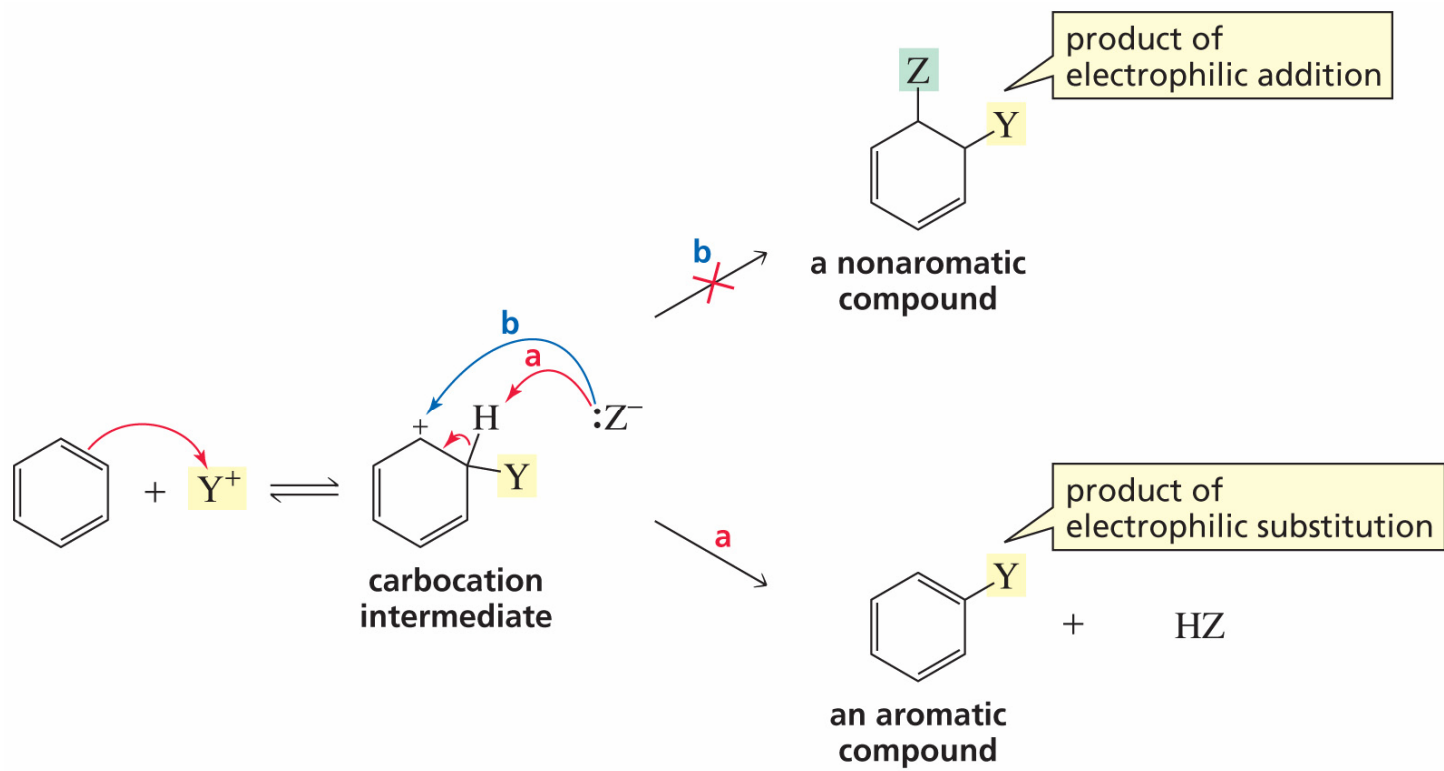


Instead of Br⁻ adding to the carbocation intermediate to yield an addition product, a base removes H⁺ from the bromine-bearing carbon to yield the neutral aromatic substitution product.

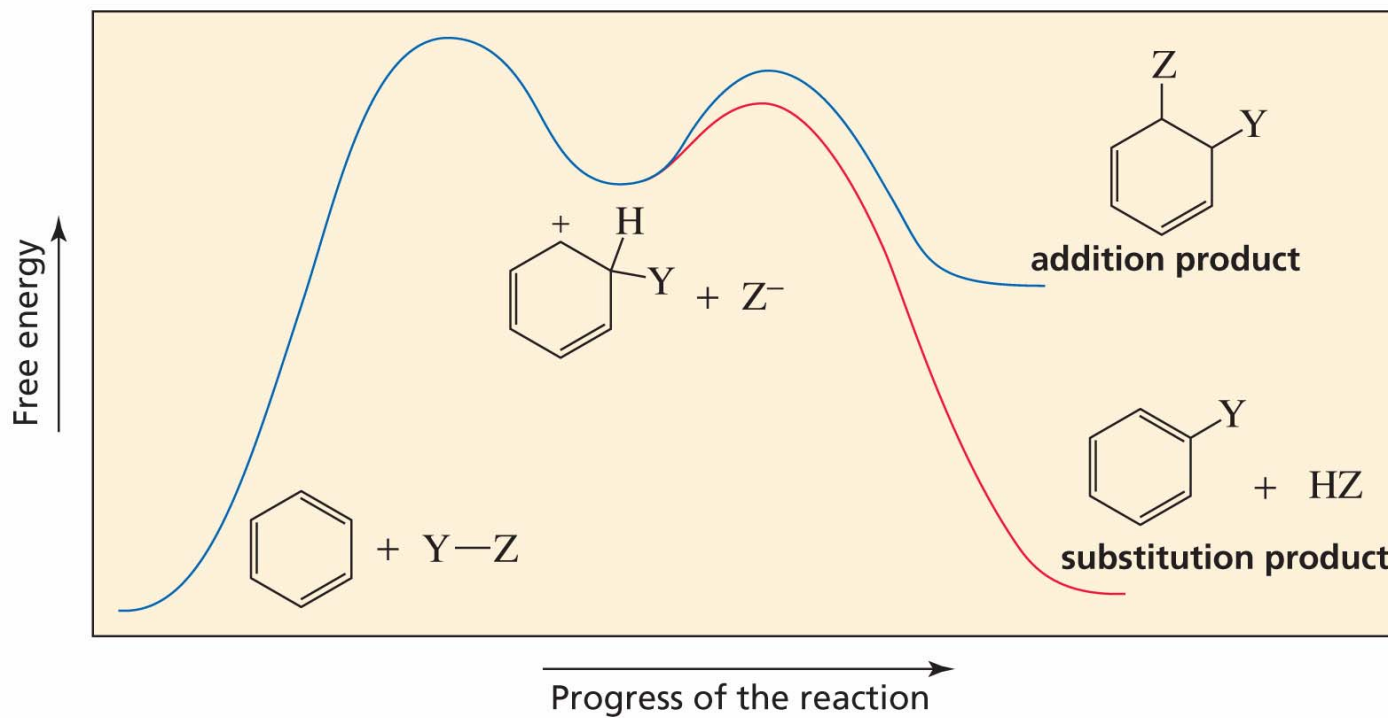
Why substitution than addition in the reaction of Br₂ with benzene?

If addition occurred, the stability of the aromatic ring would be lost, energy would be absorbed, and the overall reaction would be unfavorable.

When substitution occurs, the stability of the aromatic ring is retained, energy is released, and the reaction is favorable.



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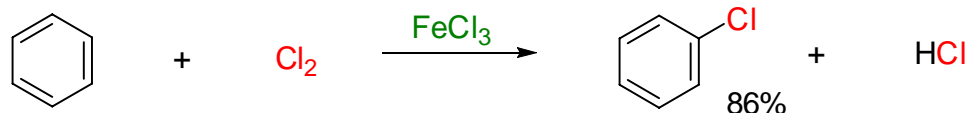


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5.5 Other Electrophilic Aromatic Substitution Reactions

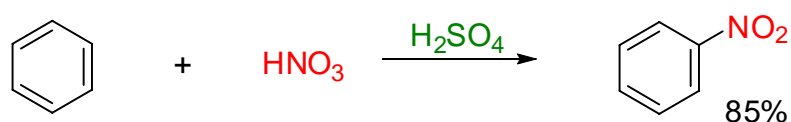
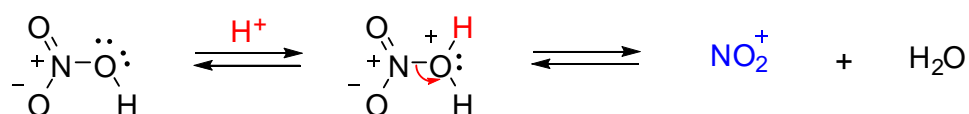
Electrophilic aromatic substitutions occur by the same general mechanism as bromination. The only real variation is how the electrophile is generated.

Chlorination



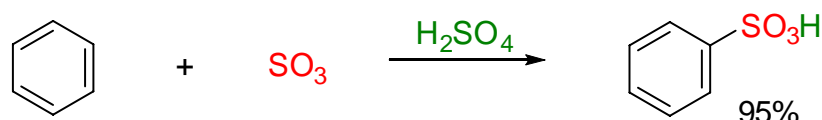
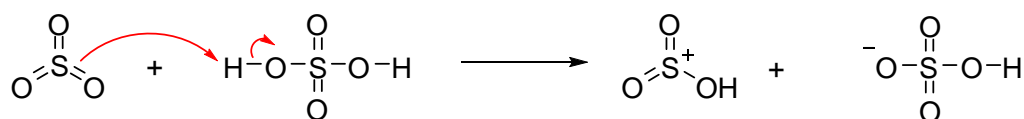
Nitration

Electrophilic species: **nitronium ion, NO_2^+** by the reaction of HNO_3 with H_2SO_4 .



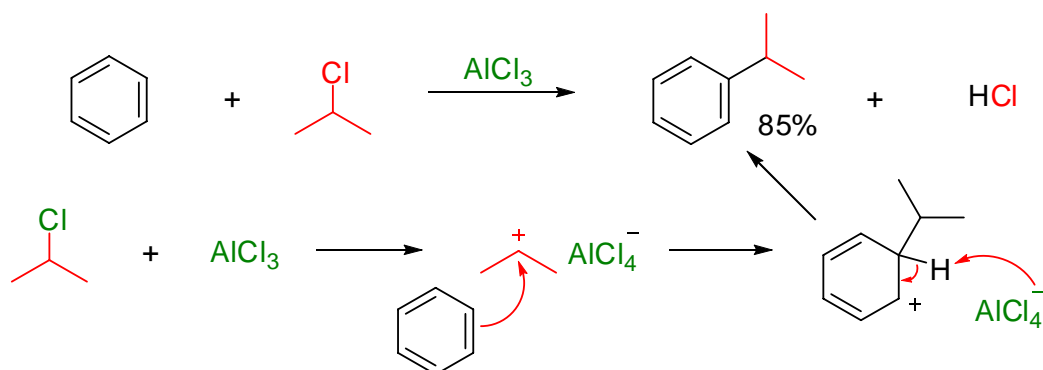
Sulfonation

Electrophilic species: **HSO_3^+** from a mixture of SO_3 and H_2SO_4 (fuming sulfuric acid).



5.6 The Friedel-Crafts Alkylation and Acylation Reactions

Friedel-Crafts Alkylation: An alkyl group is attached to an aromatic ring on reaction with an alkyl chloride, RCl , in the presence of AlCl_3 catalyst.



Aluminum chloride catalyzes the reaction by helping the alkyl chloride ionize.

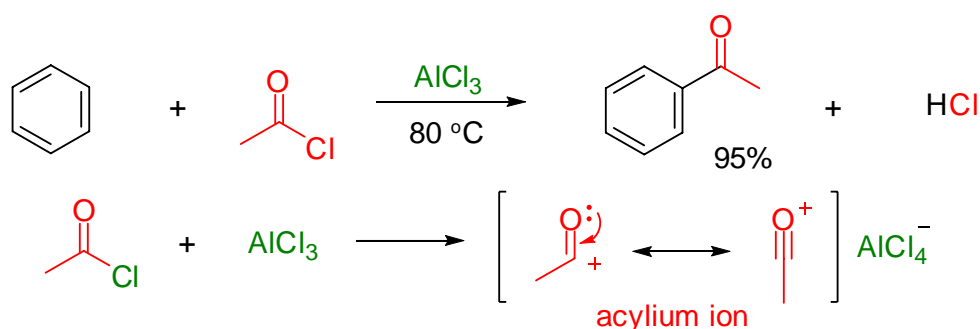
Limitations:

Aryl halides don't react, only alkyl halides can be used.

Don't work for aromatic rings that are substituted by the electron withdrawing groups – NO₂, C≡N, SO₃H, or COR.

Polyalkylation problem.

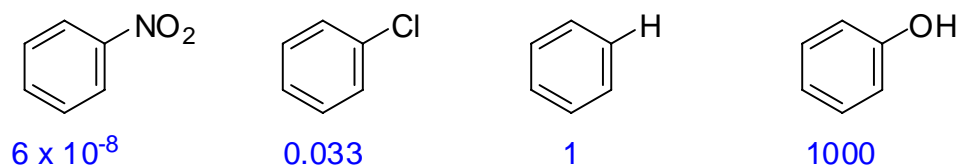
Friedel-Craft acylation reaction: When an aromatic compound is treated with carboxylic acid chloride, RCOCl, in the presence of AlCl₃, an acyl group is introduced onto the ring.



5.7 Substituent Effects in Electrophilic Aromatic Substitution

★ Substituents affect the reactivity of the aromatic ring.

Relative rate of nitration



★ Substituents affect the orientation of the reaction.

An OH group directs further substitution toward the **ortho** and **para** positions, while a CN group directs further substitution primarily toward the **meta** position.

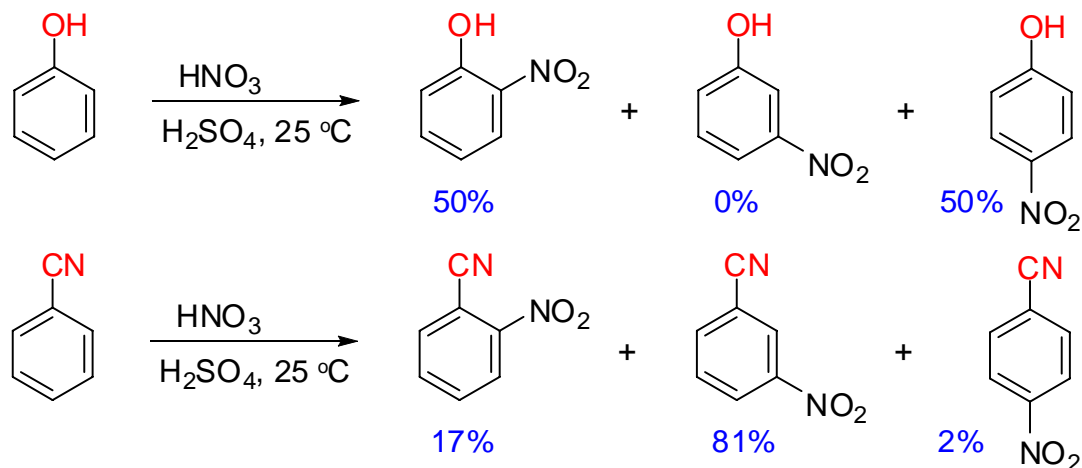


Table 7.1 The Effects of Substituents on the Reactivity of a Benzene Ring Toward Electrophilic Substitution

<p>Activating substituents</p> <p>↑</p>	<p>Most activating</p> <p>—$\ddot{\text{N}}\text{H}_2$ —$\ddot{\text{N}}\text{HR}$ —$\ddot{\text{N}}\text{R}_2$ —$\ddot{\text{O}}\text{H}$ —$\ddot{\text{O}}\text{R}$</p> <p>—$\ddot{\text{N}}\text{H}\overset{\text{O}}{\parallel}\text{CR}$</p> <p>—$\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{CR}$ —R</p>	<p>Strongly activating</p> <p>Moderately activating</p> <p>Weakly activating</p>	<p>Ortho/para directing</p>
<p>Standard of comparison →</p> <p>—H</p>	<p>—H</p>		
<p>Deactivating substituents</p> <p>↓</p>	<p>—$\ddot{\text{F}}:$ —$\ddot{\text{Cl}}:$ —$\ddot{\text{Br}}:$ —$\ddot{\text{I}}:$ —$\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{CH}$ —$\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{CR}$ —$\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{COR}$ —$\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{COH}$ —$\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{CCl}$ —$\text{C}\equiv\text{N}:$ —SO_3H —NH_2R —NR_3 —NO_2</p>	<p>Weakly deactivating</p> <p>Moderately deactivating</p> <p>Strongly deactivating</p>	<p>Meta directing</p>
<p>—NH_3^+ —NHR_2^+</p> <p>Most deactivating</p>			

Classification of substituents

1. **Ortho- and para-directing activators:** electron donating groups such as OH, NH₂.
2. **Ortho- and para-directing deactivators:** halogens
3. **Meta-directing deactivators:** electron withdrawing groups such as a CN or a carbonyl group.

5.8 An Explanation of Substituent Effects

Reactivity: Activating and Deactivating Effects in Aromatic Rings

What makes a group either activating or deactivating?

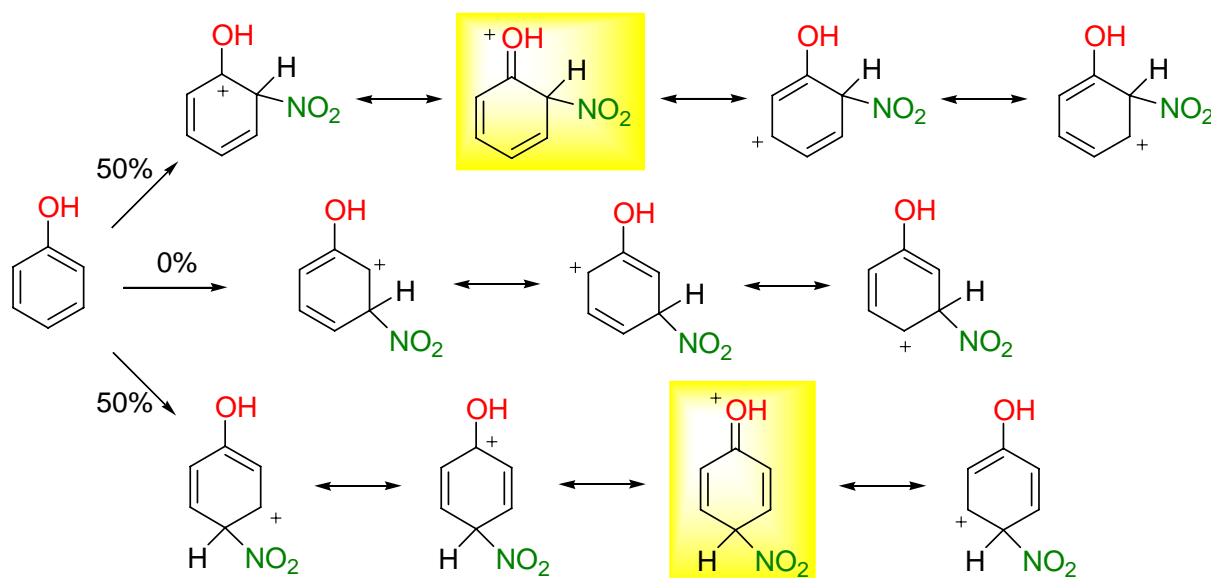
All activating groups donate electrons to the ring (**resonance effect**).

If the aromatic ring is electron-rich, **the carbocation intermediate will be more stable** and the activation energy barrier for its formation will be lower.

All deactivating groups withdraw electrons from the ring, thereby making the ring more electron-poor, **destabilizing the carbocation intermediate**, and raising the activation energy for its formation (**inductive effect**).

Site of Reaction: Ortho and Para Directors

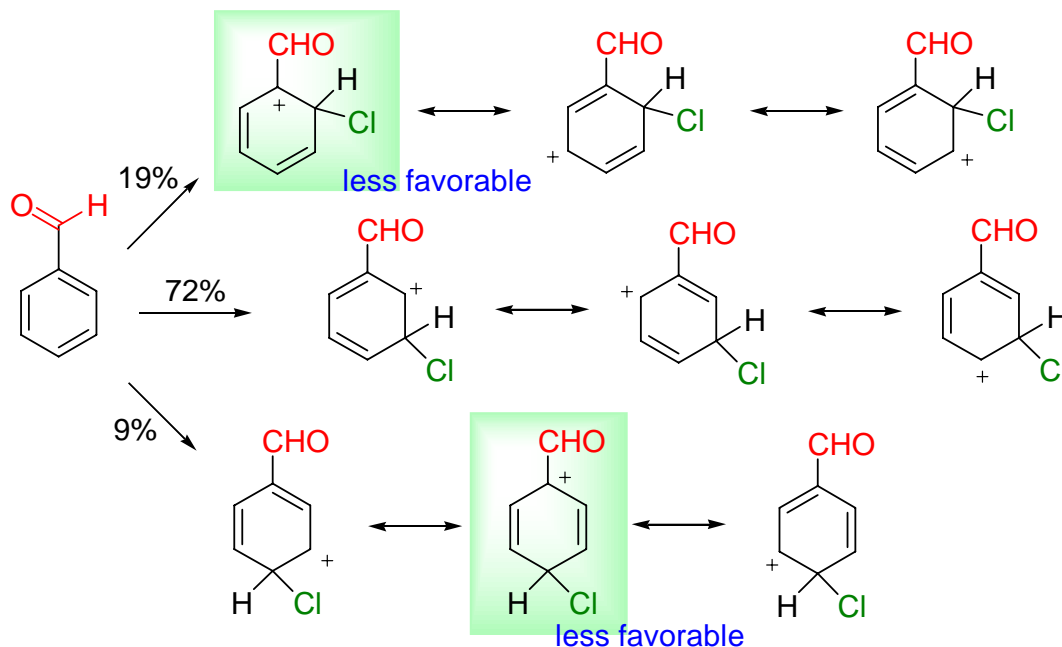
Any substituent that has **a lone pair of electrons on the atom directly bonded to the aromatic ring** (–OH, –NH₂, –Cl, –Br etc) allows an electron-donating resonance interaction to occur and thus acts as an **ortho and para director**.



The ortho and para intermediates are more stable than the meta intermediate because they have more resonance forms.

Site of Reaction: Meta Directors

Any substituent that has a **positively polarized atom directly attached to the ring** ($-\text{COR}$, $-\text{COOR}$, $-\text{CN}$, $-\text{NO}_2$ etc) makes one of the resonance forms of the ortho and para intermediate unfavorable and thus acts as a **meta director**.

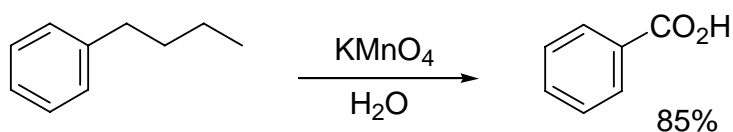


The meta intermediate has three favorable resonance forms, while the ortho and para intermediates have only two favorable forms. The meta intermediate is more favored and is formed faster. [chapter_05_02_Electrophilic Substitution.ppt](#)

5.9 Oxidation and Reduction of Aromatic Compounds

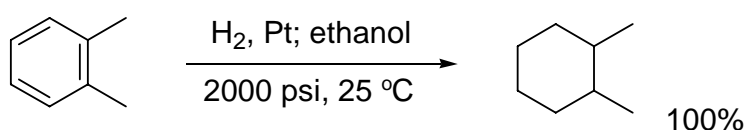
Oxidation

A benzene ring does not usually react with strong oxidizing agent such as KMnO_4 . Alkyl groups attached to the aromatic ring are readily attacked by KMnO_4 to give carboxyl groups.

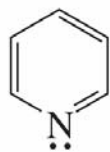


Reduction

A benzene ring is inert to reduction under typical alkene hydrogenation conditions. Reduction of an aromatic ring occurs only if high temperatures and pressure are used.



5.10 Aromaticity in Nonbenzene Rings heterocyclic compounds



pyridine



pyrrole

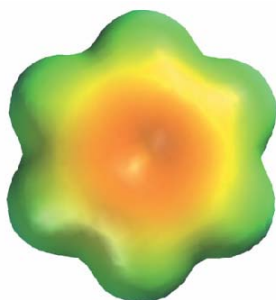


furan

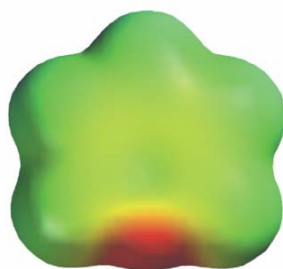


thiophene

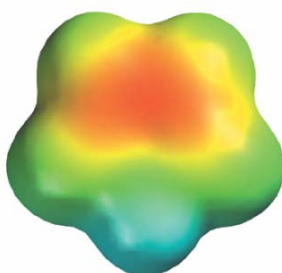
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benzene

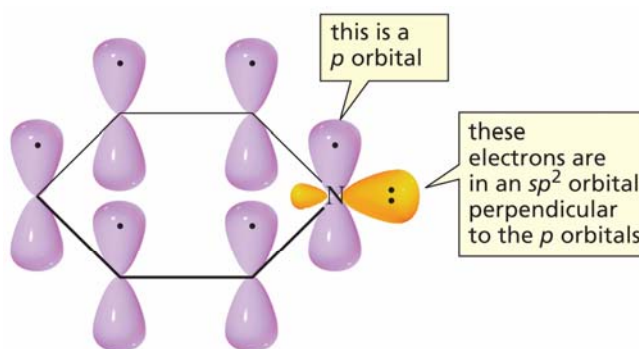


pyridine



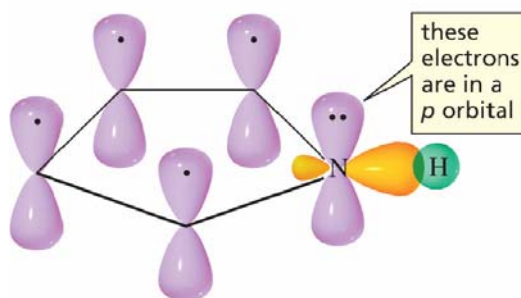
pyrrole

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orbital structure of pyridine

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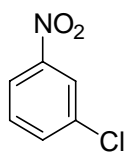
orbital structure of pyrrole

[4n + 2] π Electron Rule: If the number of π electrons in a flat, cyclic, conjugated molecule is an equal to $4n + 2$, the molecule is aromatic.

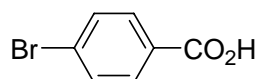
5. 11 Organic Synthesis (Home Works – due date: October 21, 2007)

Synthesize the following compound starting from benzene

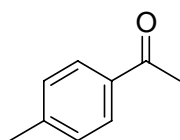
(1) *m*-chloronitrobenzene



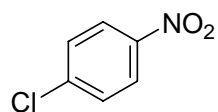
(2) *p*-bromobenzoic acid



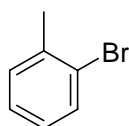
(3) *p*-methylacetophenone



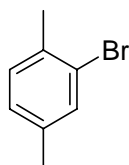
(4) *p*-chloronitrobenzene



(5) *o*-bromotoluene



(6) 2-bromo-1,4-dimethylbenzene



(7) *m*-bromobenzoic acid

