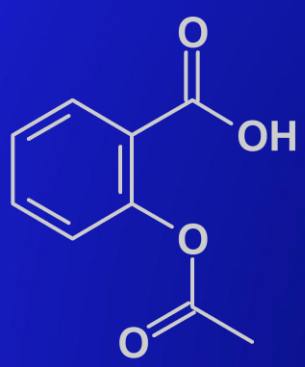
Chapter 18

Reactions of Aromatic Compounds



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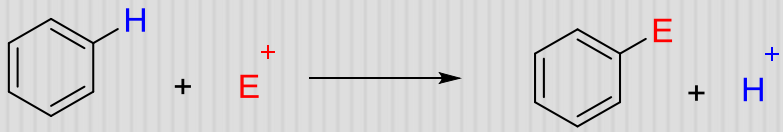
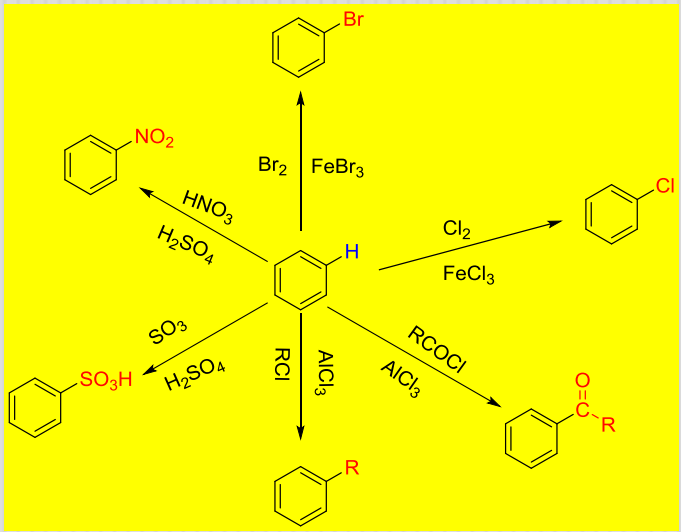
Electrophilic Aromatic Substitution





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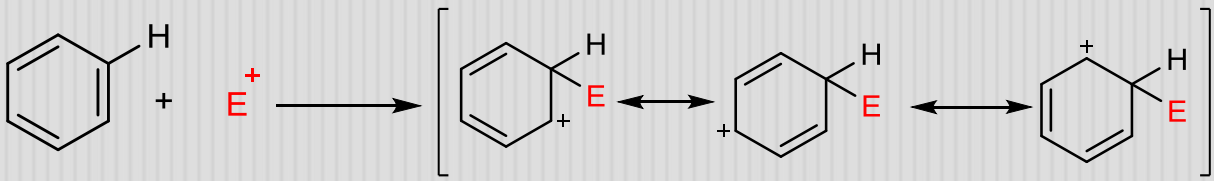
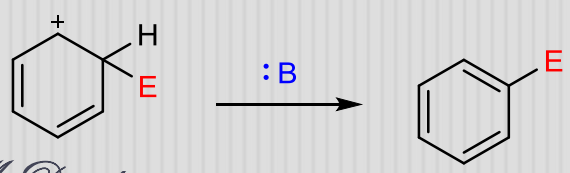
General Mechanism of Electrophilic Aromatic Substitution

3

Step 1: Attack on the electrophile forms the resonance stabilized carbocation.



Step 2: Loss of a proton gives the substitution product.



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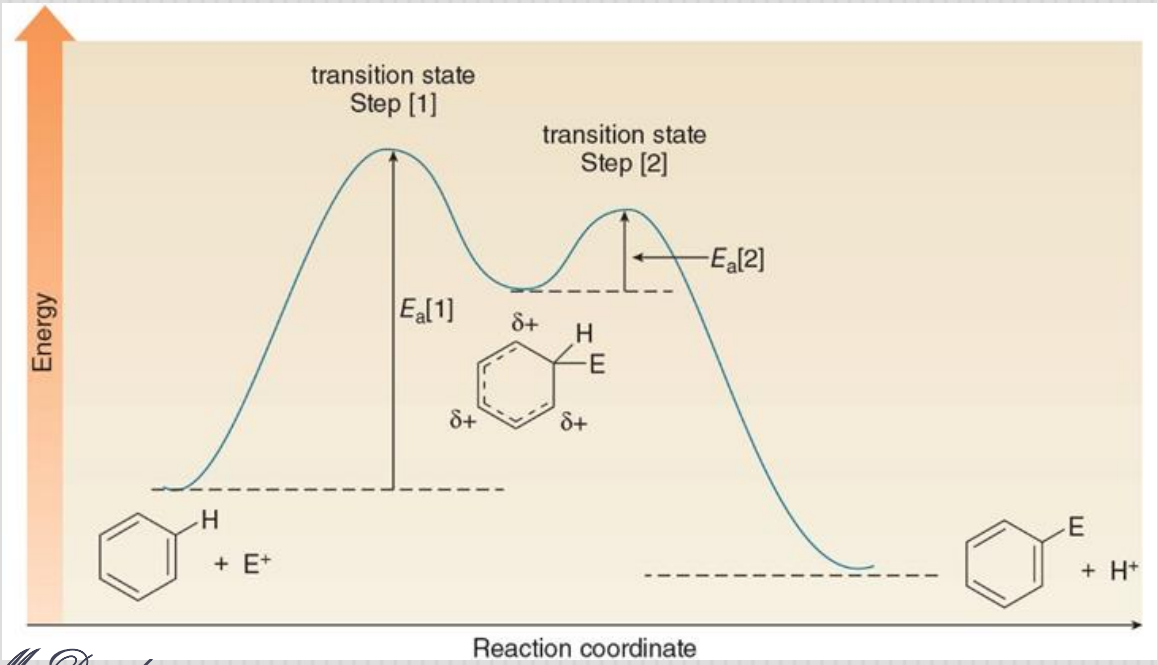
Energy Diagram for Electrophilic Aromatic Substitution



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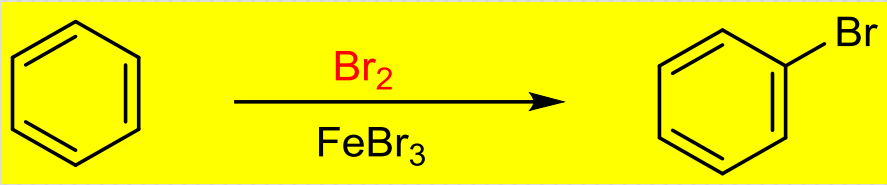
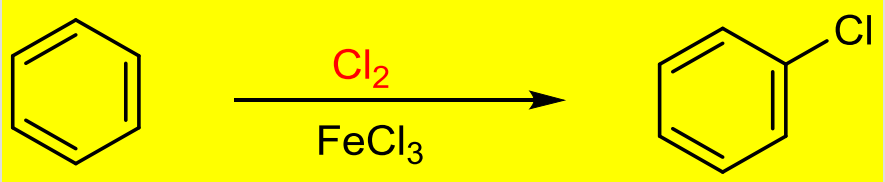
Halogenation





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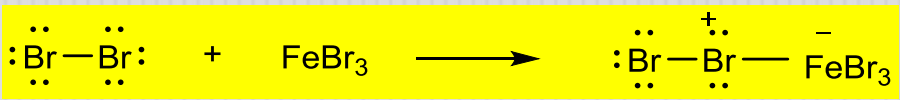
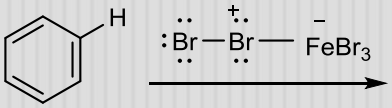
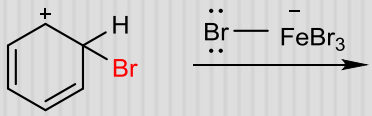
Bromination Mechanism







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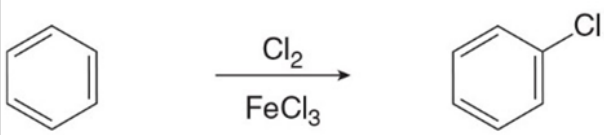
Chlorination Mechanism



- Chlorination requires $AlCl_3/FeCl_3$

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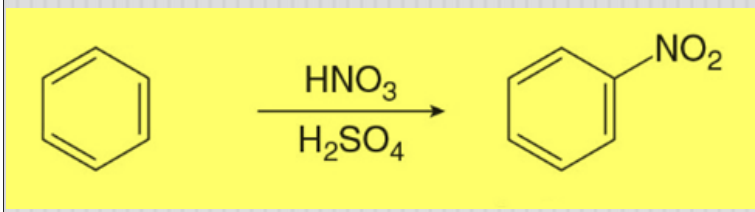
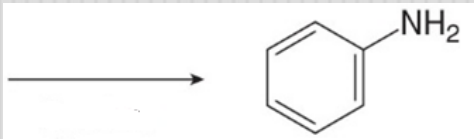
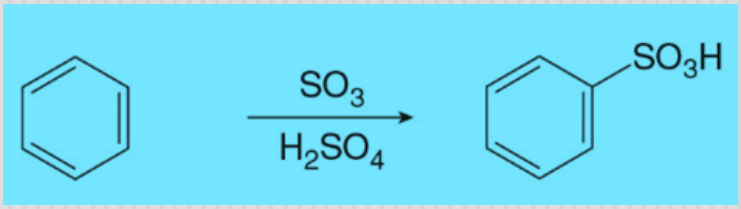
Nitration and sulfonation







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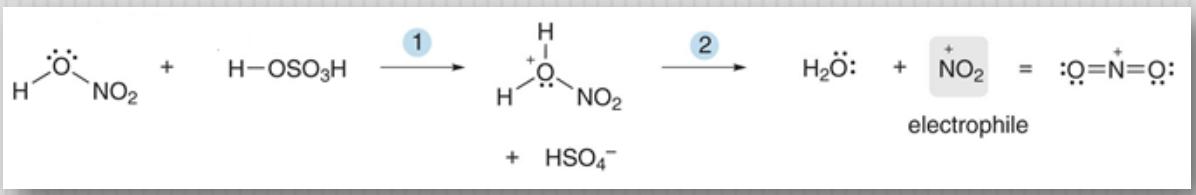
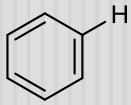
Nitration Mechanism





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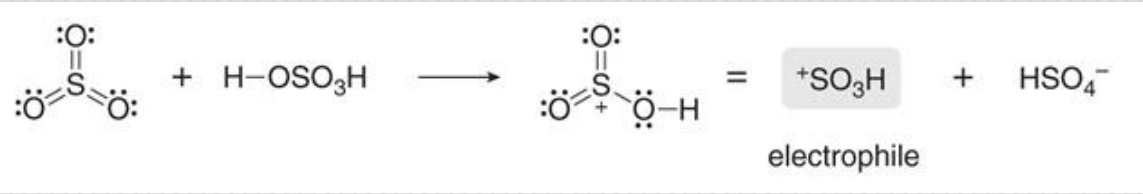
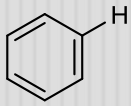
Sulfonation Mechanism





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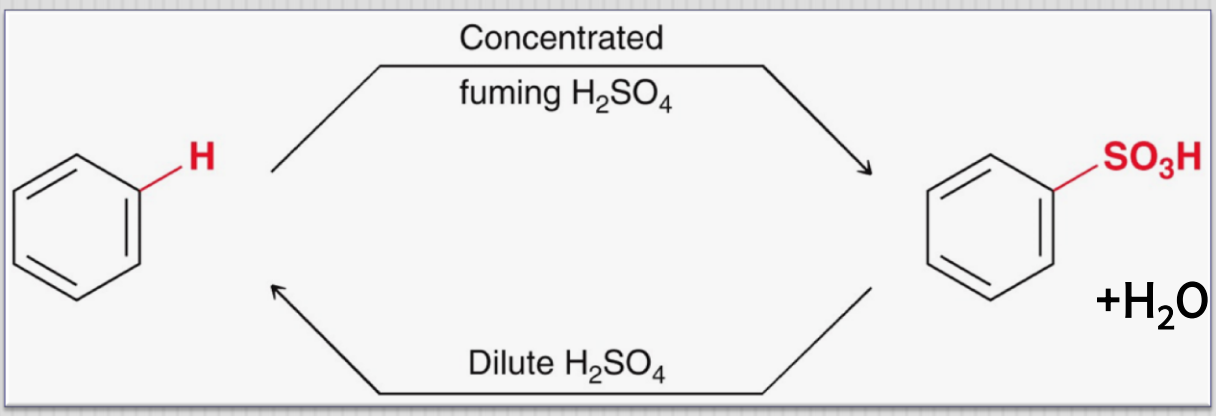
Sulfonation

- The sulfonation of an aromatic ring is reversible.



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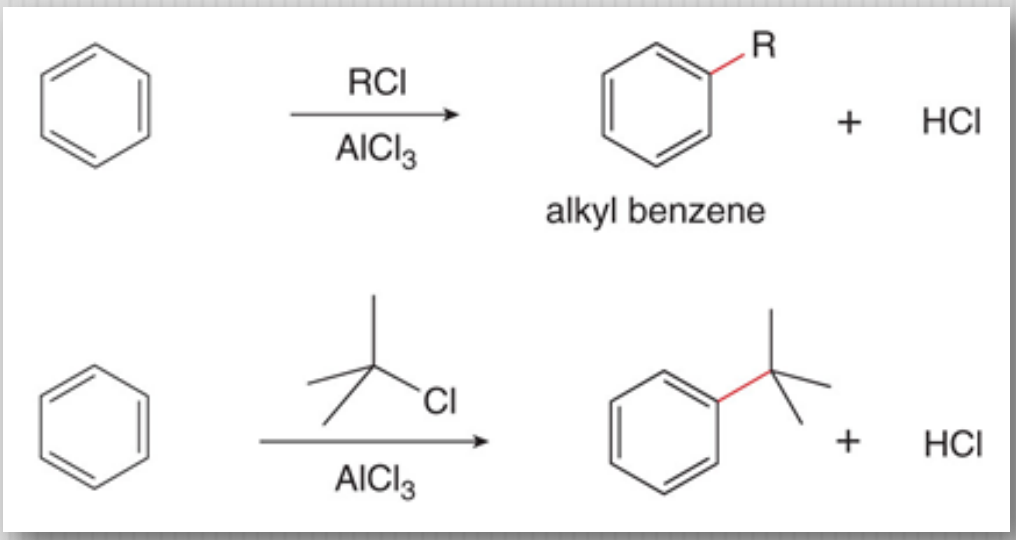
Friedel-Crafts Alkylation



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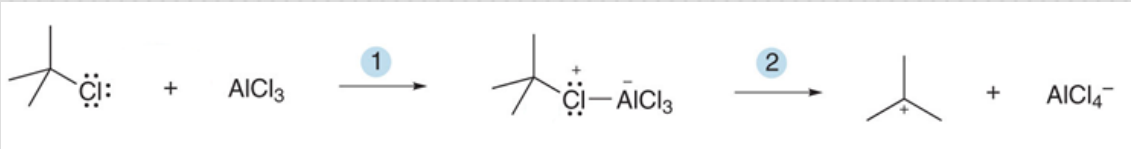
Alkylation Mechanism

Formation of the Electrophile

1. Methyl and 1° Alkyls

2. 2° and 3° Alkyls



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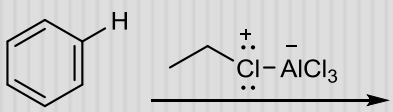
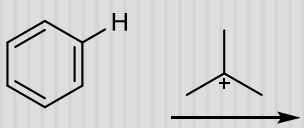
Alkylation Mechanism





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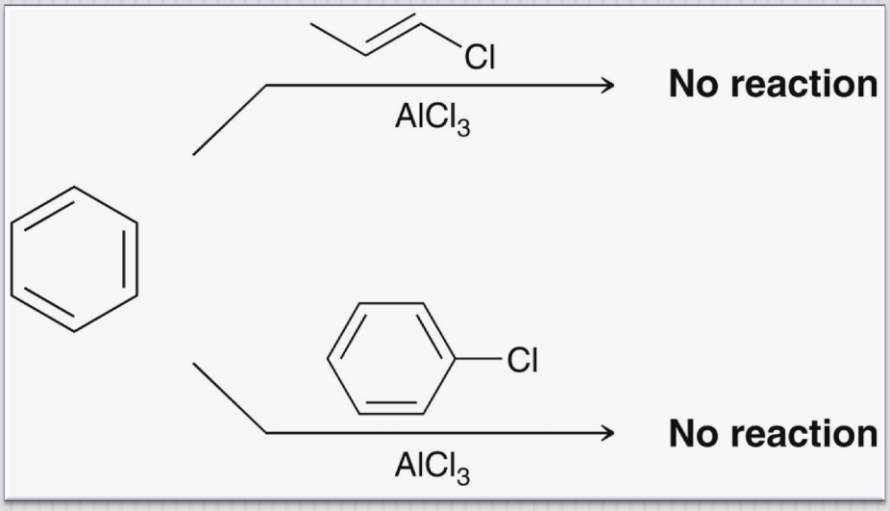
Limitations of the Friedel-Crafts Alkylation

1. The halide leaving group must be attached to an *sp*^{3} hybridized carbon



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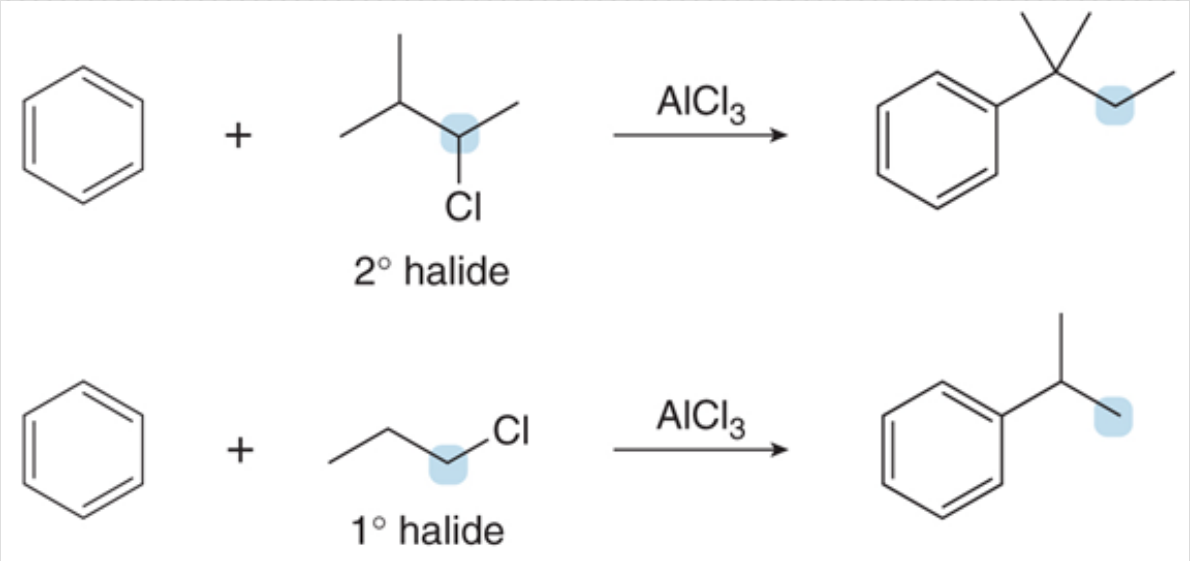
Limitations of the Friedel-Crafts Alkylation

2. Rearrangement can occur



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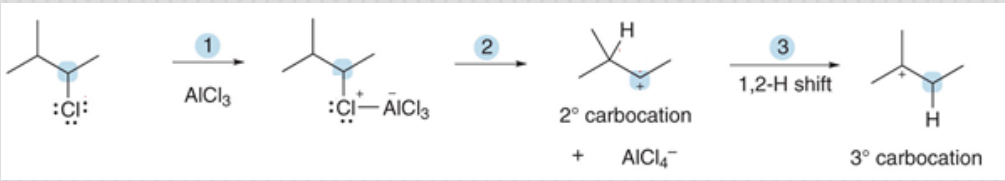
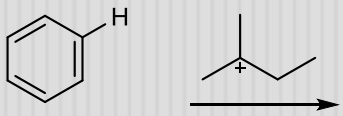
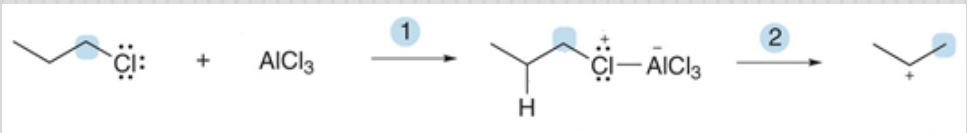
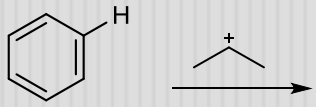
Mechanism with Rearrangement









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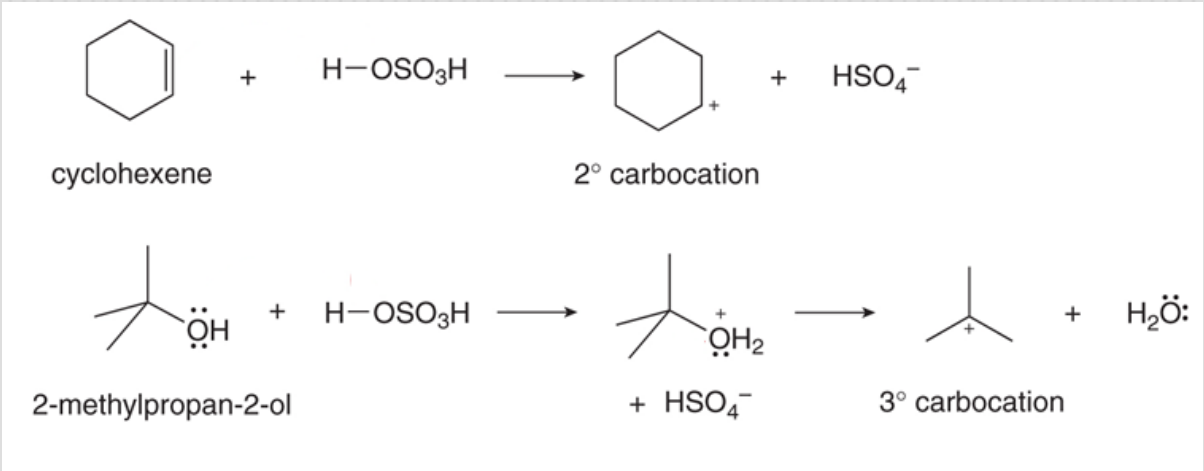
Other Carbocations in Friedel–Crafts Alkylation



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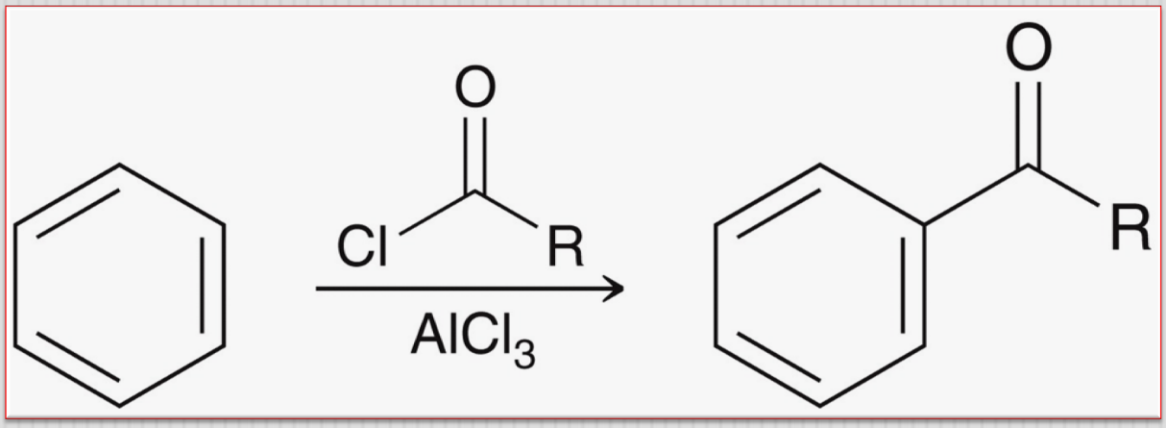
Friedel-Crafts Acylation



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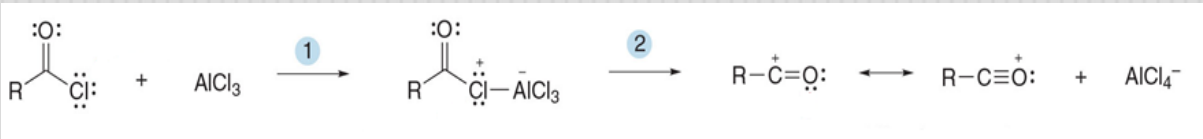
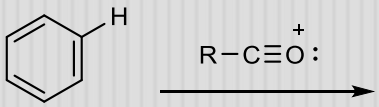
Mechanism of Friedel-Crafts Acylation





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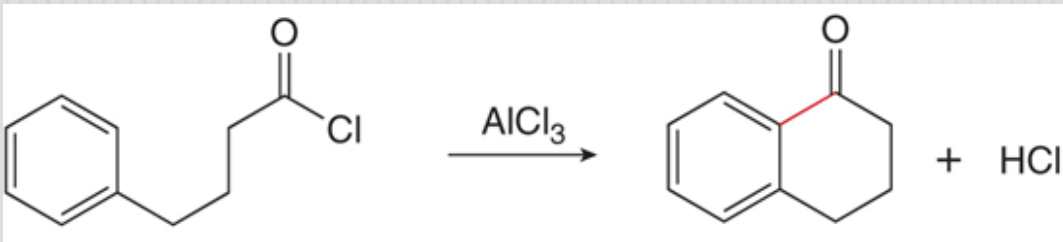
Intramolecular Friedel–Crafts Reactions



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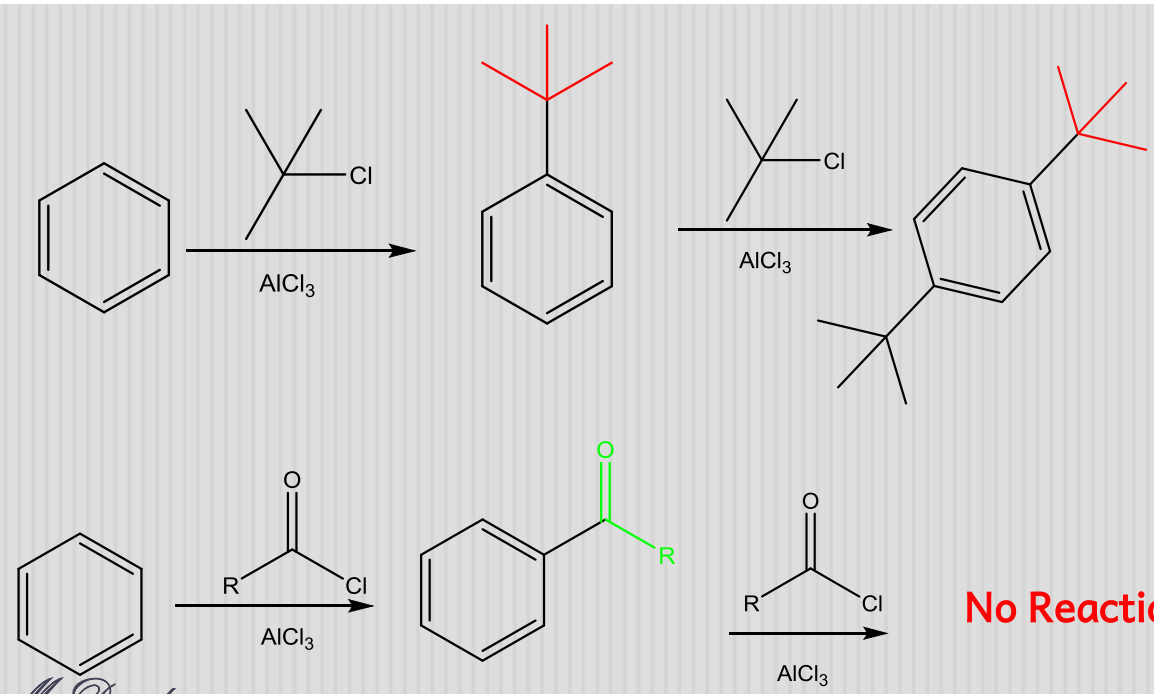
Substituent Effects in Aromatic Rings



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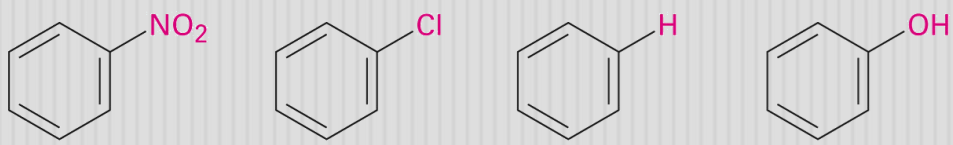
Substituent Effects in Aromatic Rings



Relative rate of nitration	6×10^{-8}	0.033	1	1000

Reactivity

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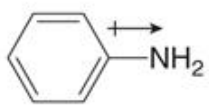
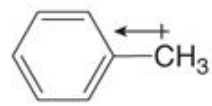
Inductive Effects

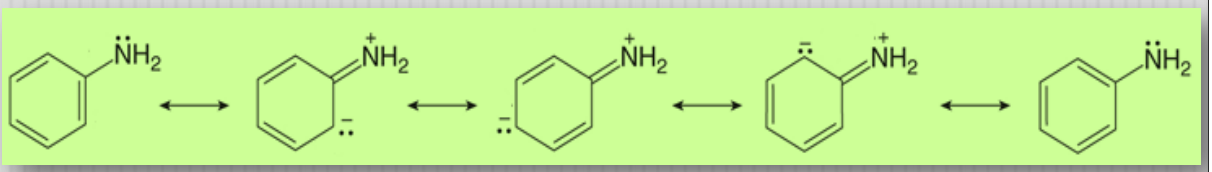
Electron-withdrawing inductive effect

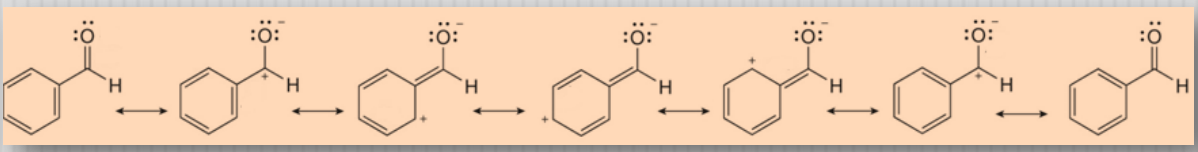


Electron-donating inductive effect



Resonance Effects





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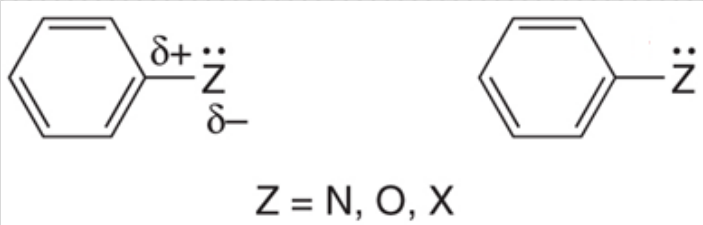
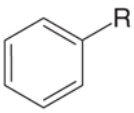
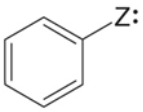
Inductive and Resonance Effects



Electron-donating groups

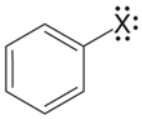


R = alkyl

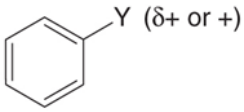


Z = N or O

Electron-withdrawing groups



X = halogen



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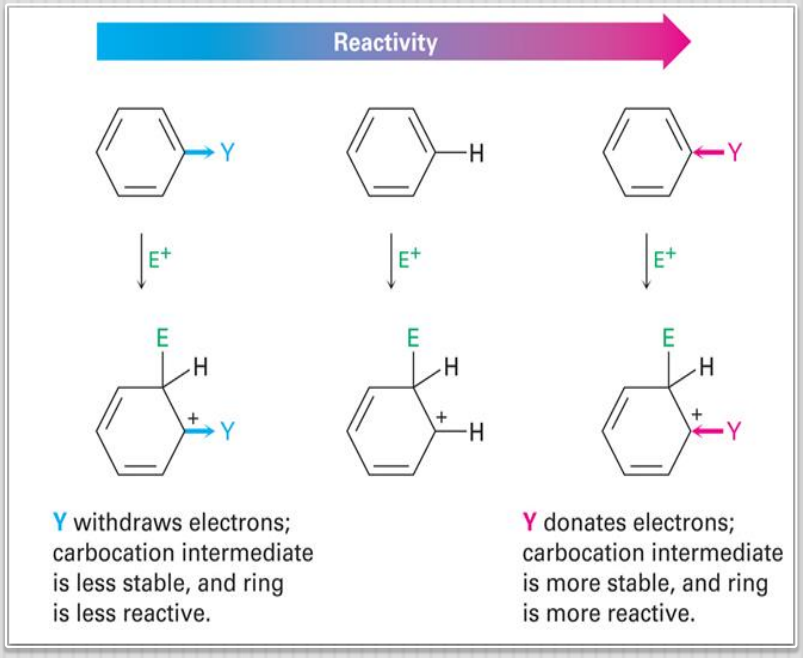
An Explanation of Substituent Effects



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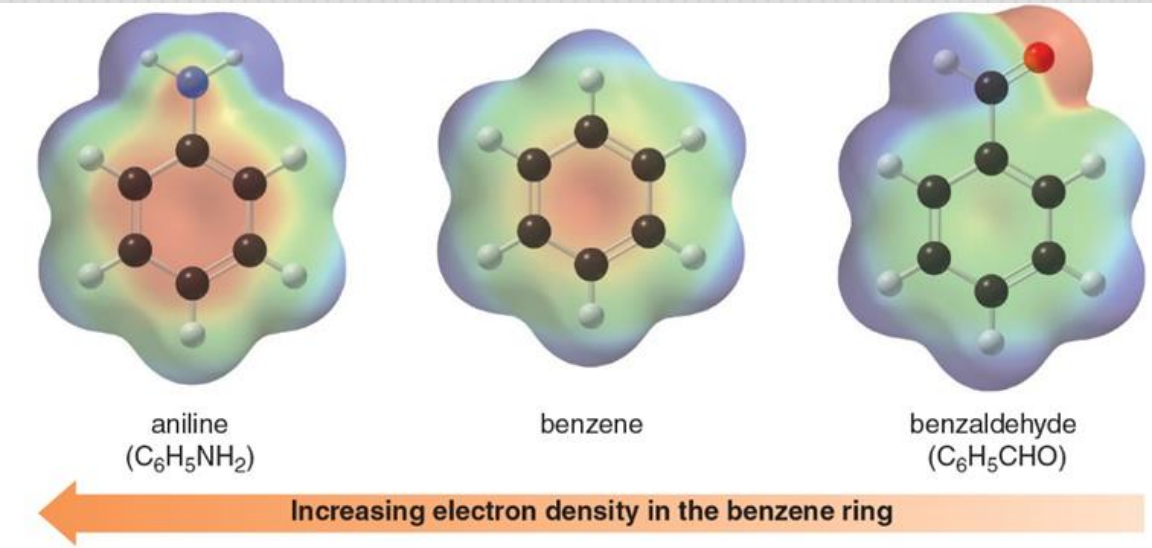
Electron-Donating and Electron-Withdrawing Groups



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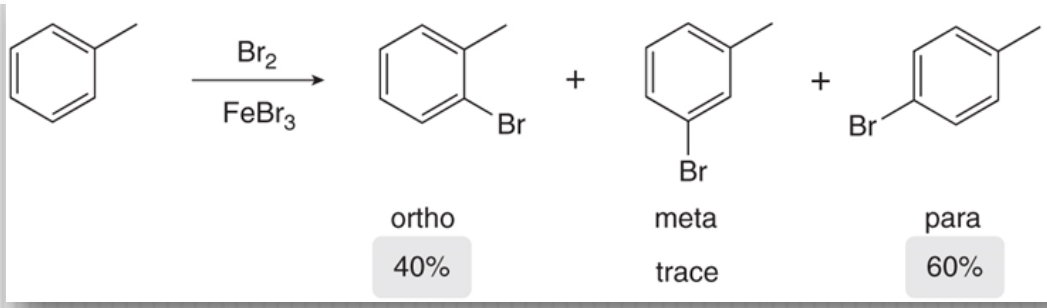
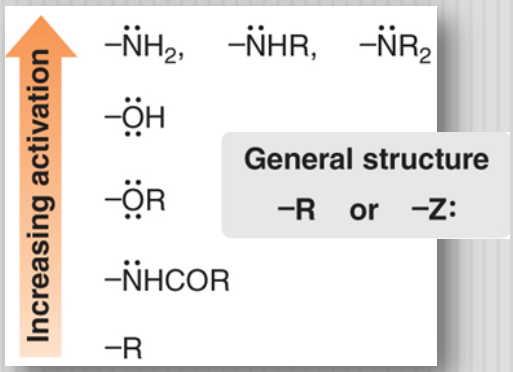
Ortho,Para Directors—Activators

29



The CH_3 group is called an ortho, para director.



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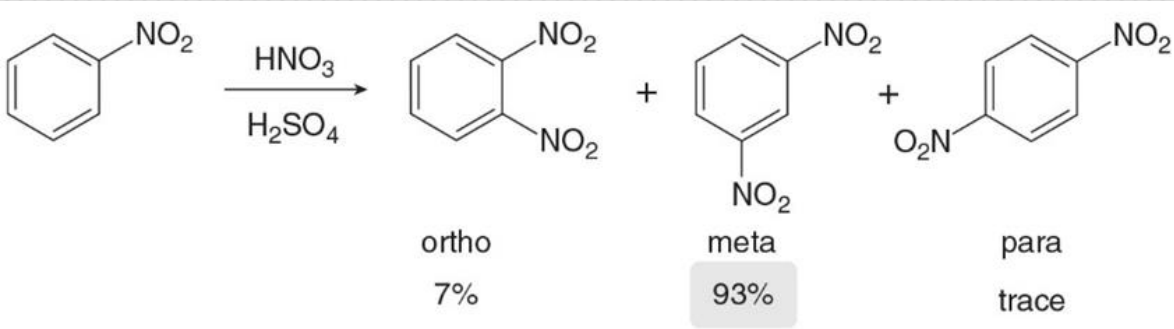
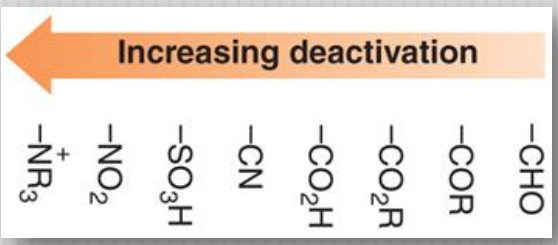
Meta Directors—Deactivators



The NO_2 group is called a meta director.



General structure

–**Y** (δ+ or +)

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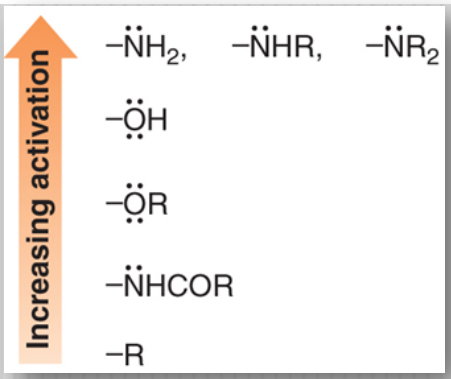
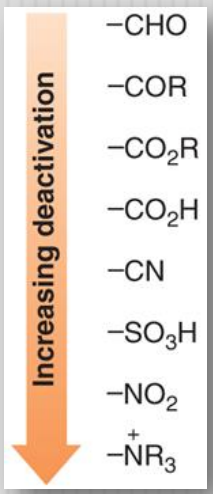
Directors—Activator, Deactivators

31

Ortho, para **activators and directors**



Meta **deactivators**



Ortho, para **deactivators**

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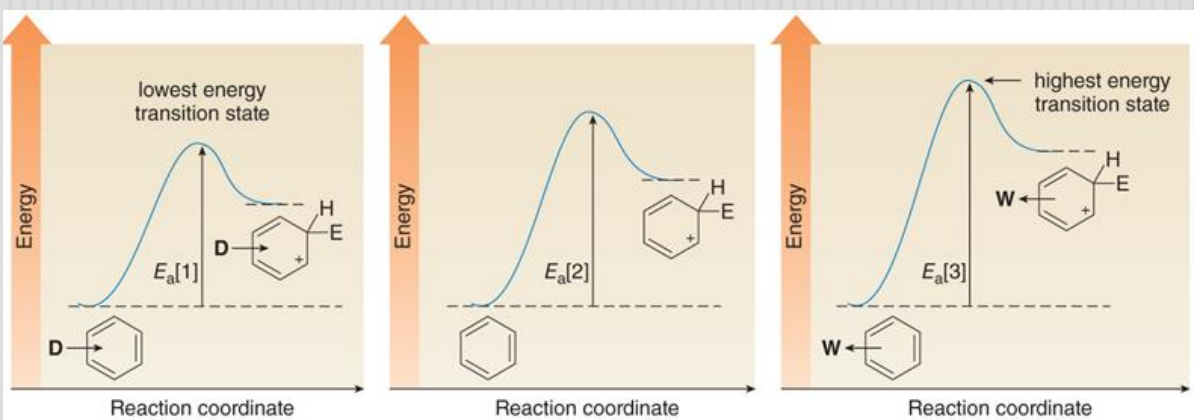
Energy Diagrams of Substitution



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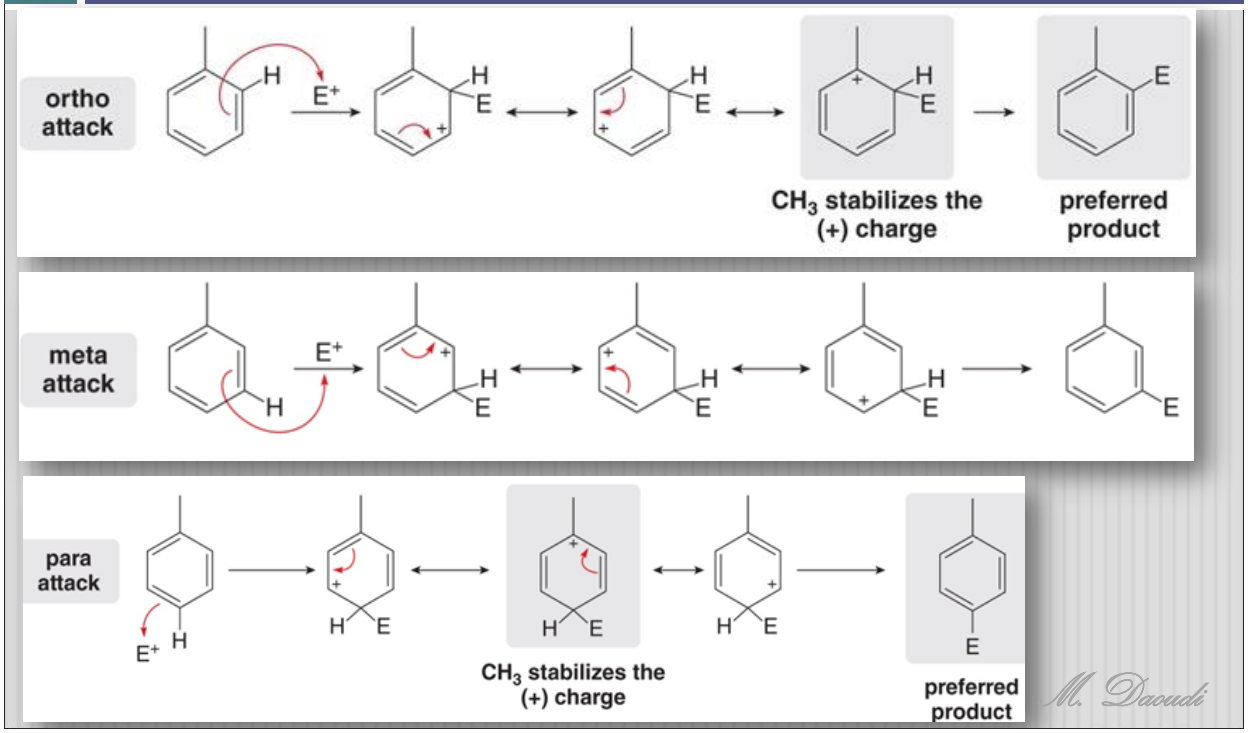
Methyl Carbocation Stabilization



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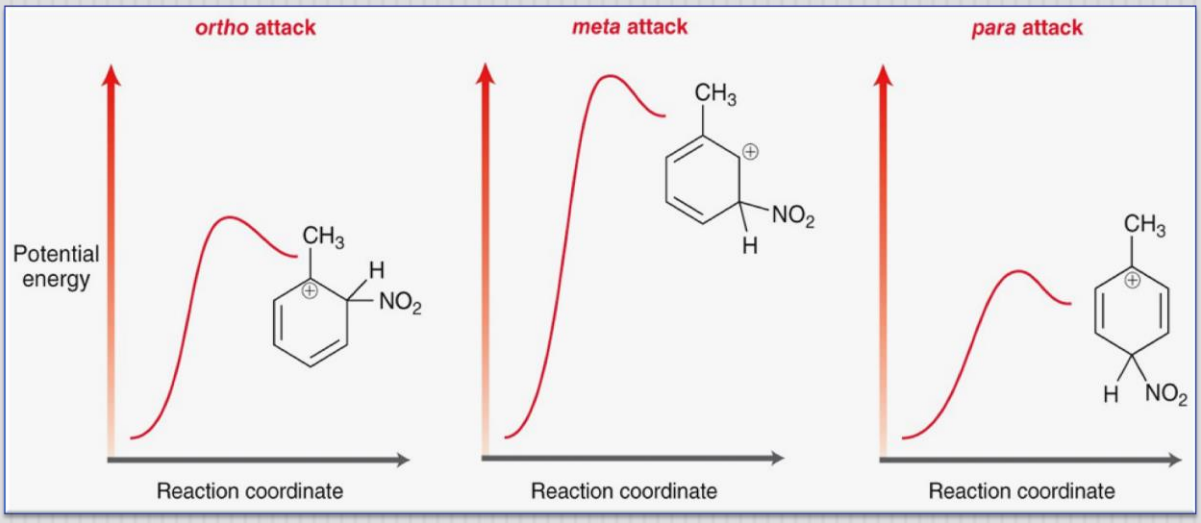
Nitration of Toluene



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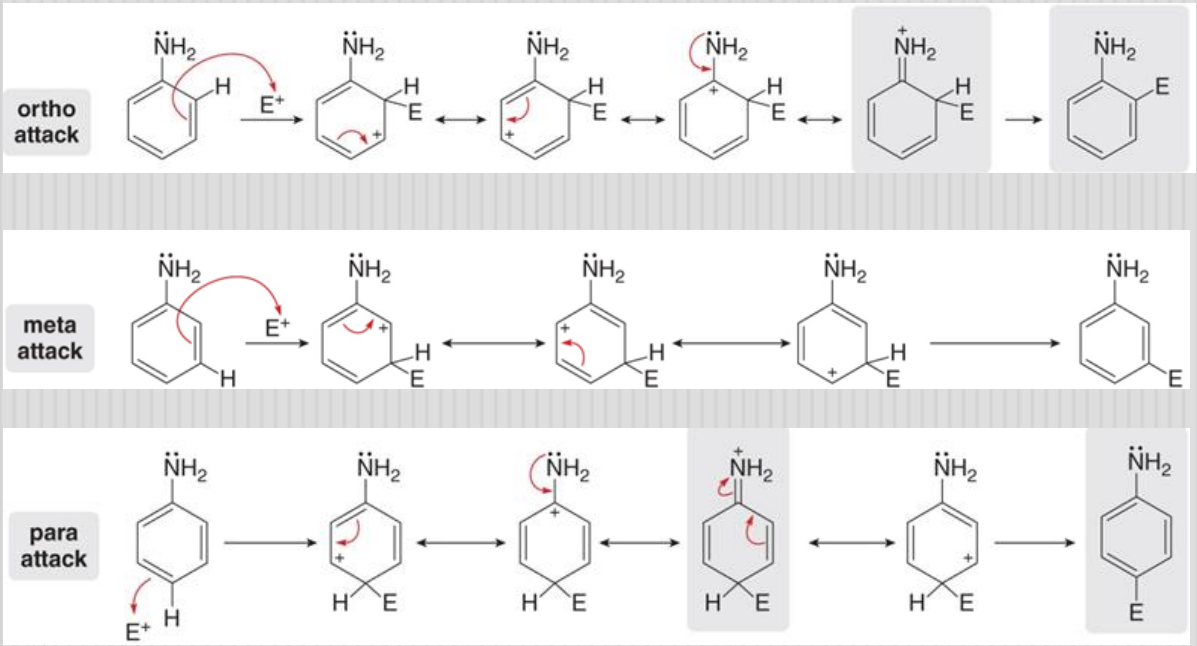
Amine Carbocation Stabilization



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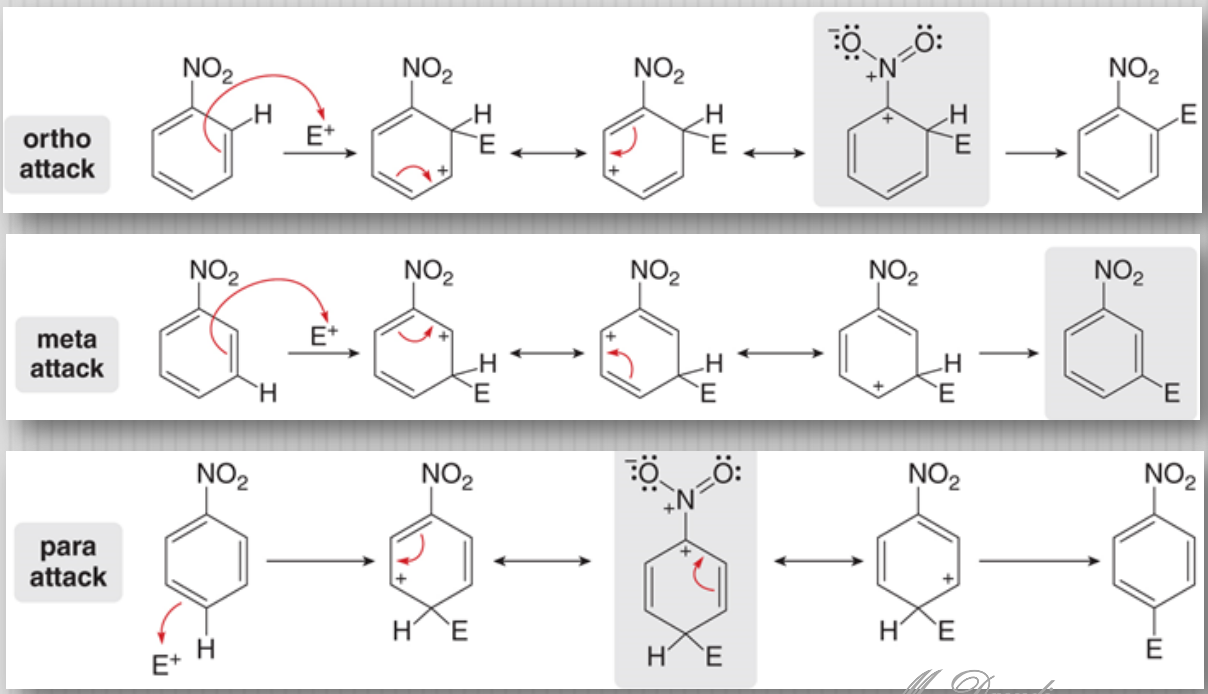
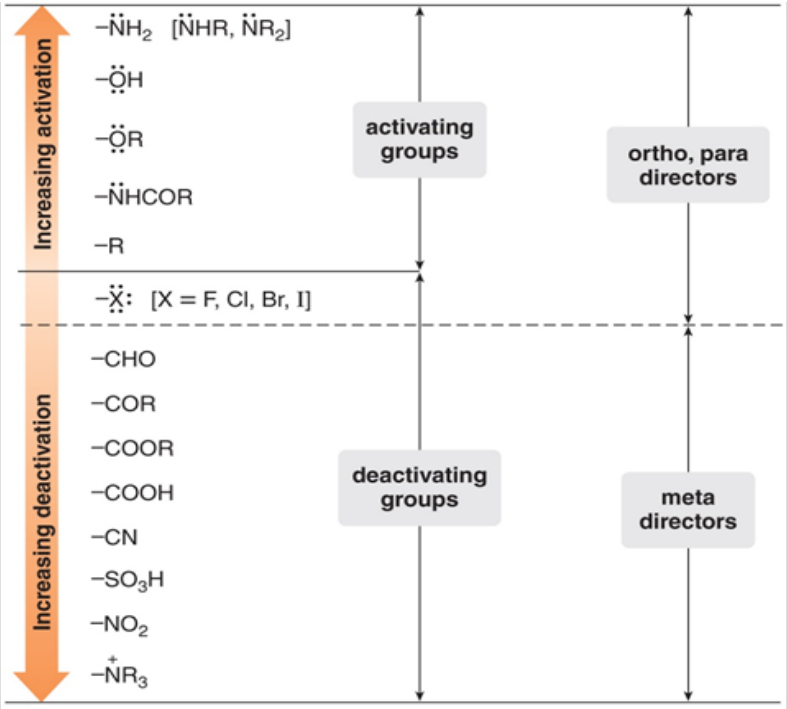
Nitro Carbocation Stabilization



Summary of Reactivity and Directing Effects



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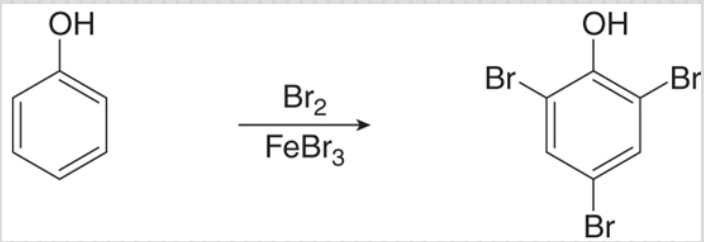
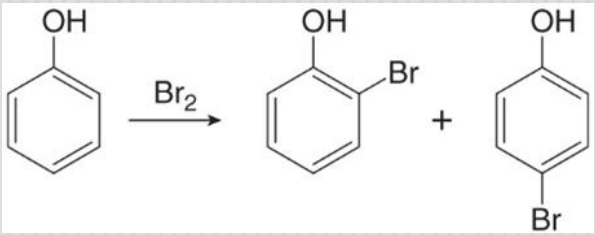
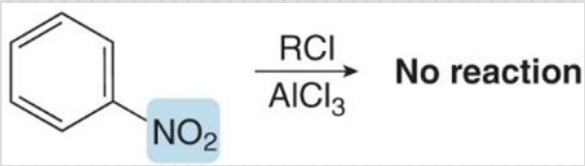
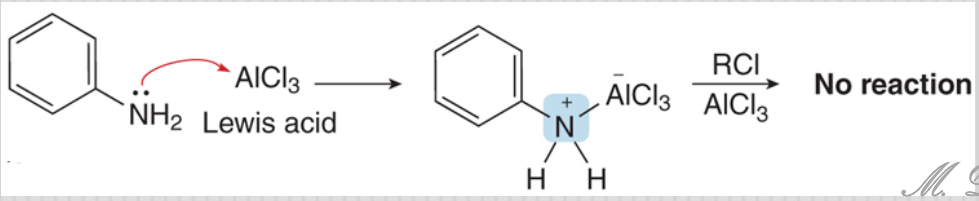
Reactions of Activated/Deactivated Rings









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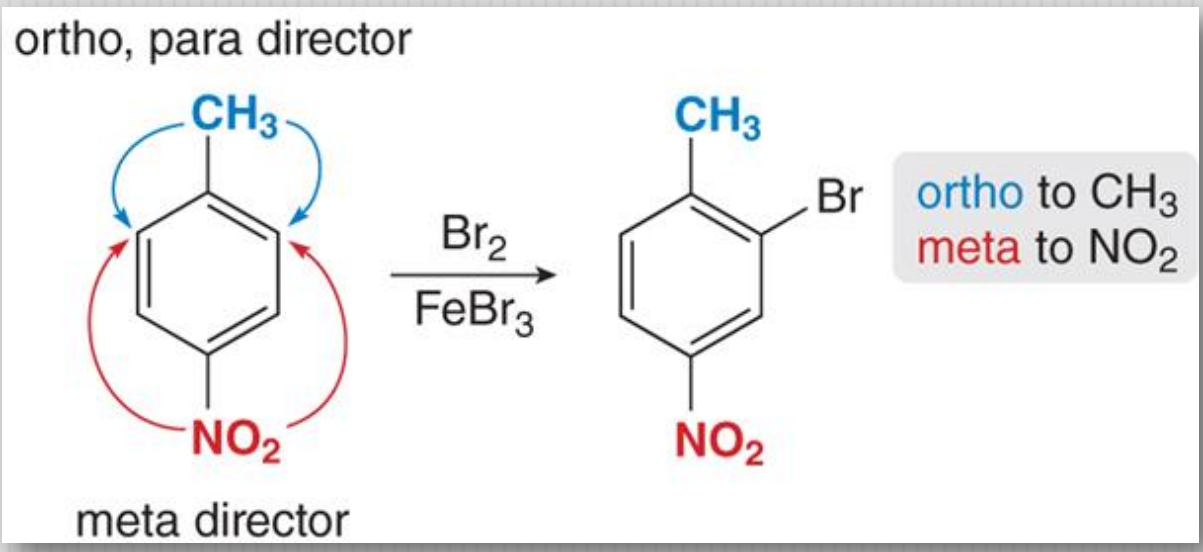
Reinforcing Directing Effects



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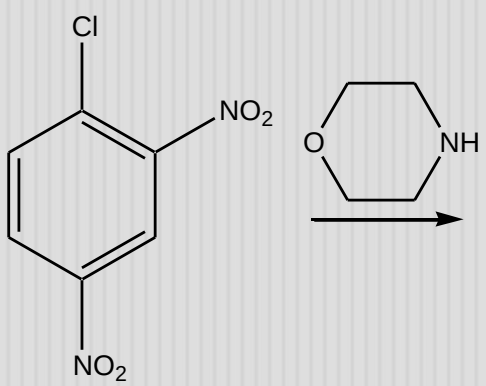
Example



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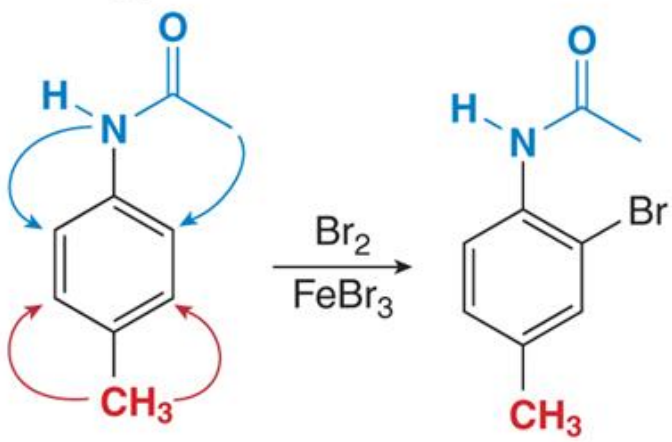
Opposing Directing Effects

stronger ortho, para director



ortho to the stronger activator

weaker ortho, para director

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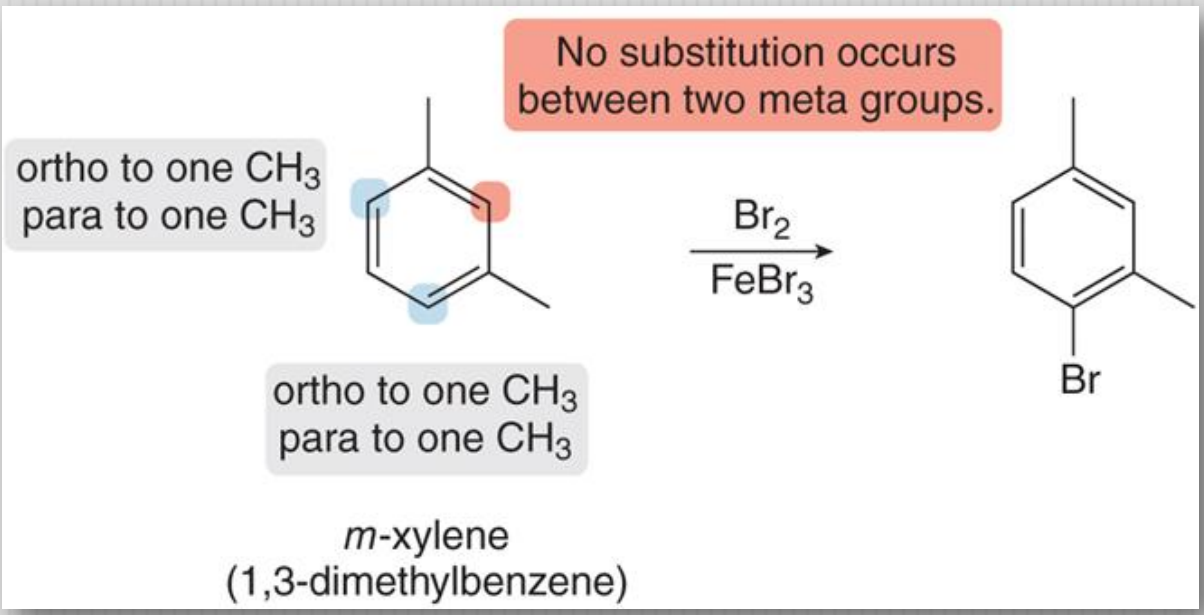
Steric Limitations to Directing Effects



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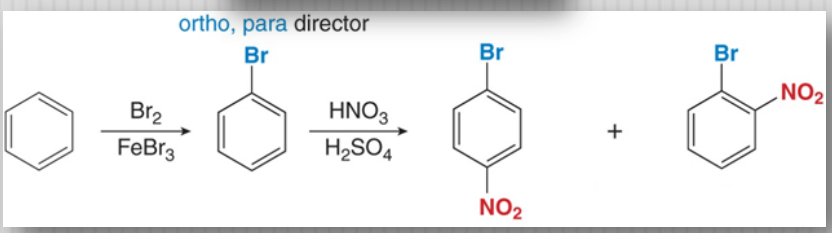
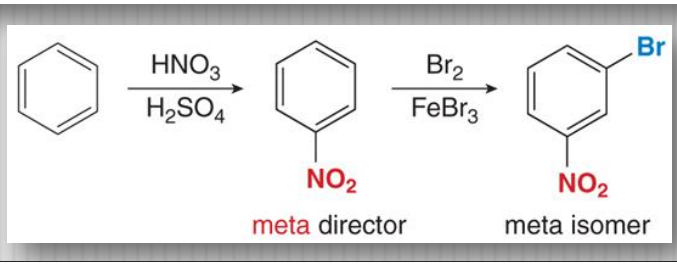
Synthesis of Benzene Derivatives





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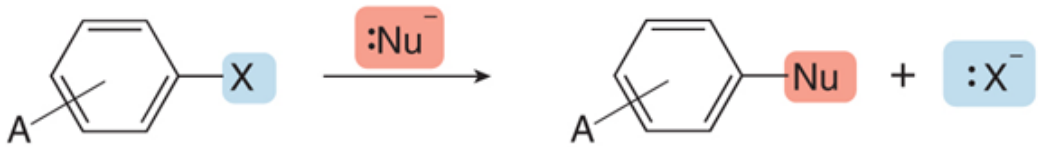
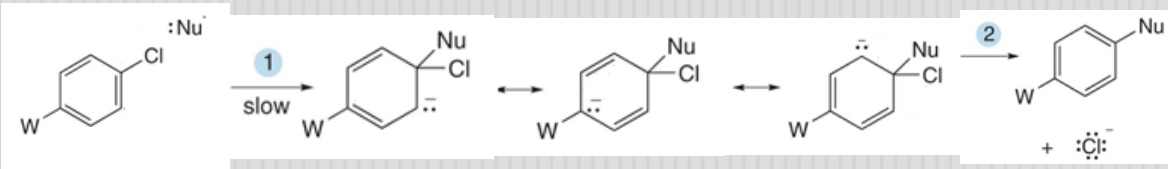
Nucleophilic Aromatic Substitution



X = F, Cl, Br, I
A = H or electron-withdrawing group

- Addition-elimination
- Elimination-addition



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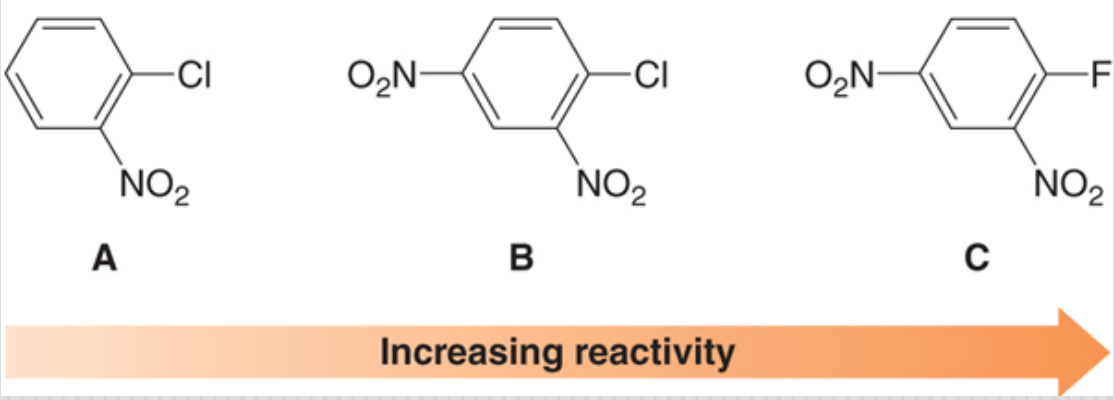
Reactivity Trends in Nucleophilic Aromatic Substitution



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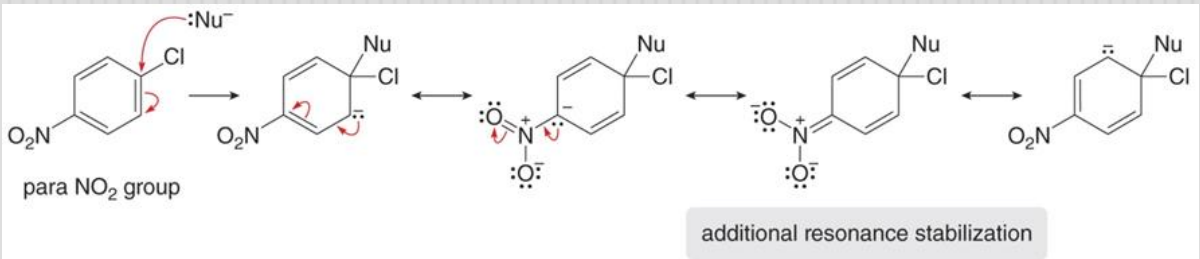
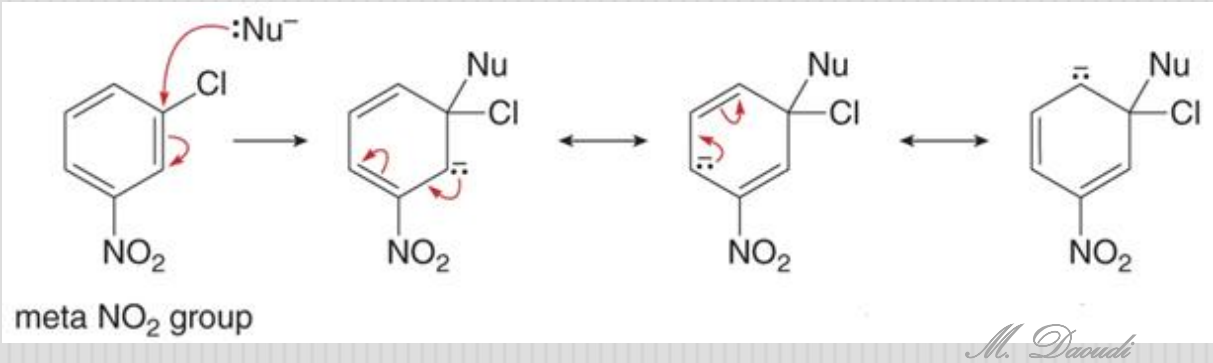
Orientation for Addition-Elimination





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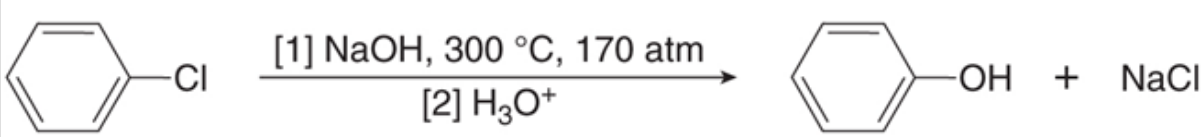
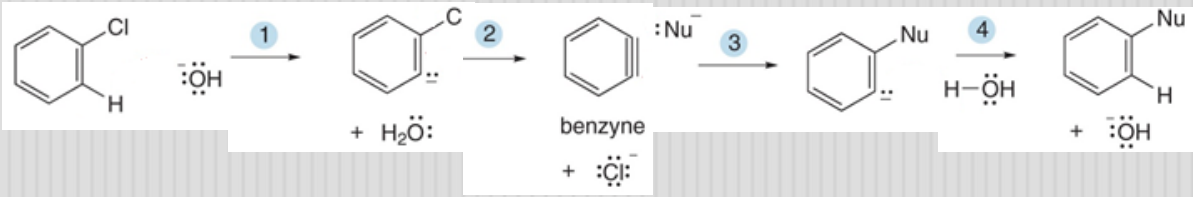
Nucleophilic Aromatic Substitution by Elimination-Addition





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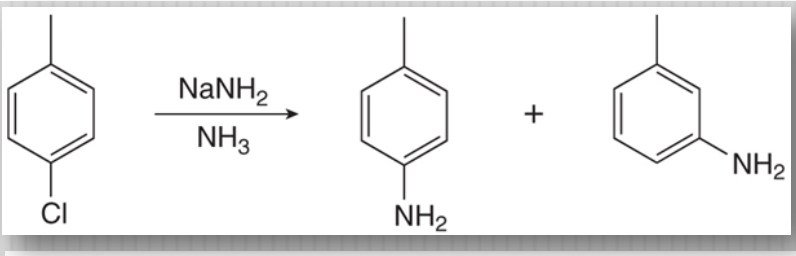
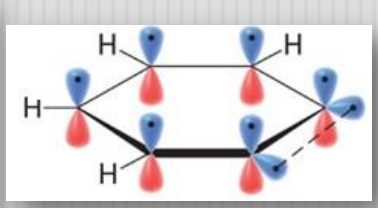
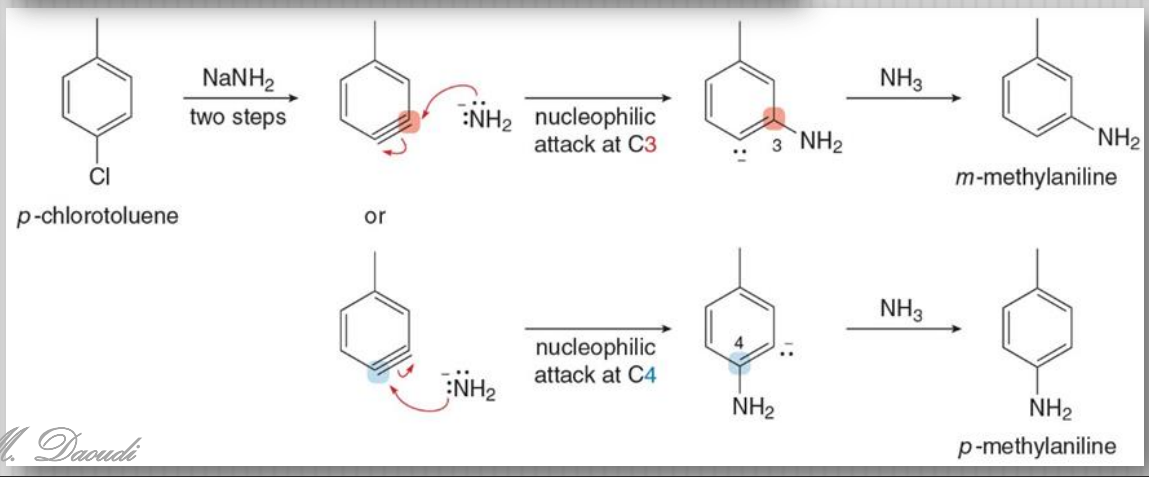
Products of Elimination-Addition







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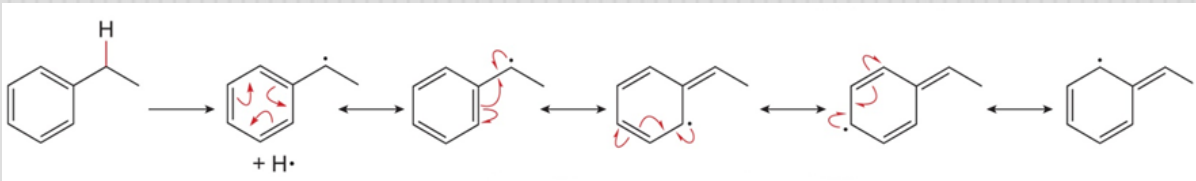
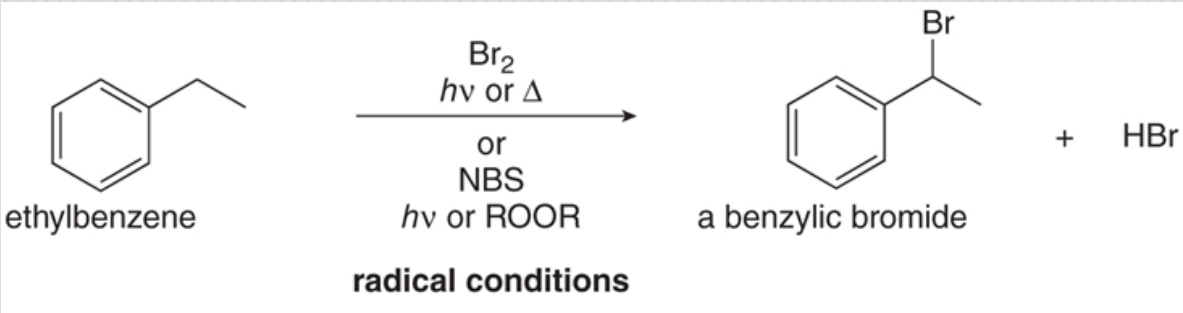
Halogenation of Alkyl Benzenes





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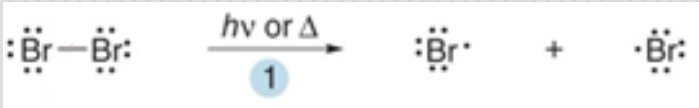
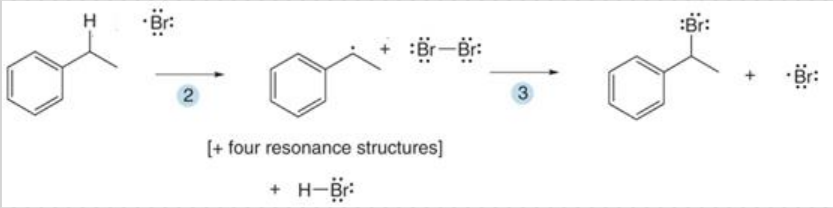
Benzylic Bromination

Part [1] Initiation



Part [2] Propagation



Part [3] Termination

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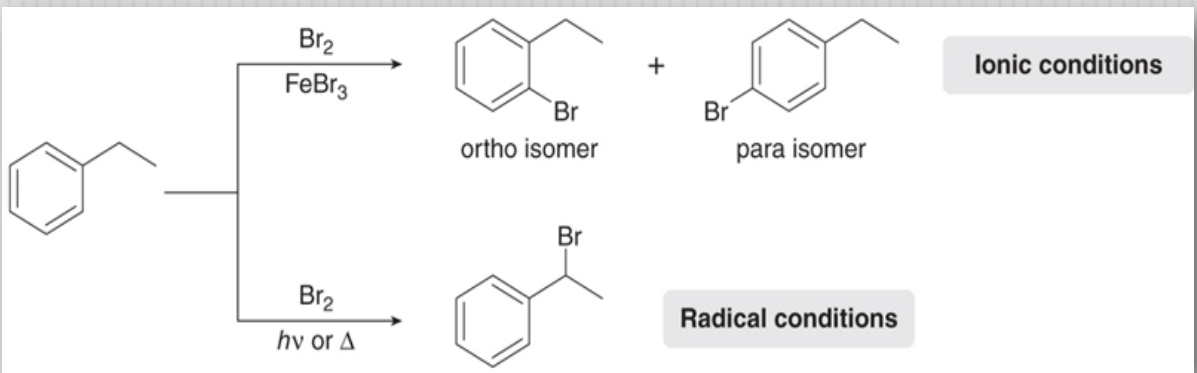
Ionic and Radical Halogenation



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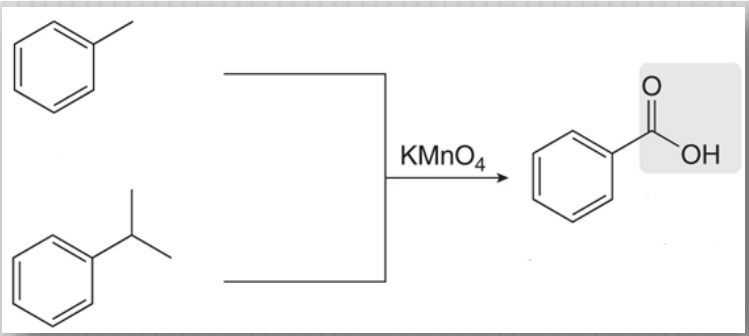
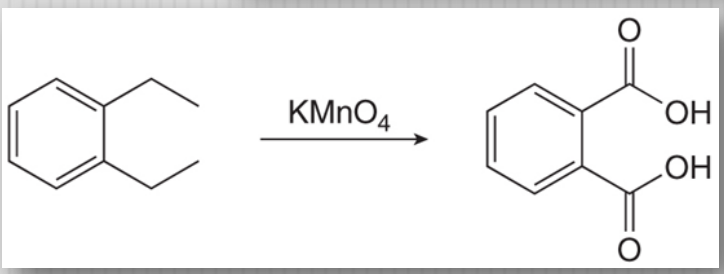
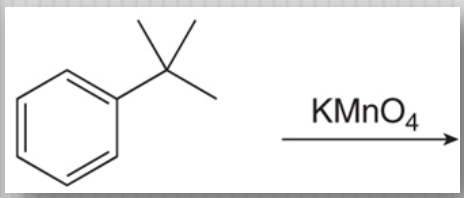
Oxidation of Alkyl Benzenes







No reaction

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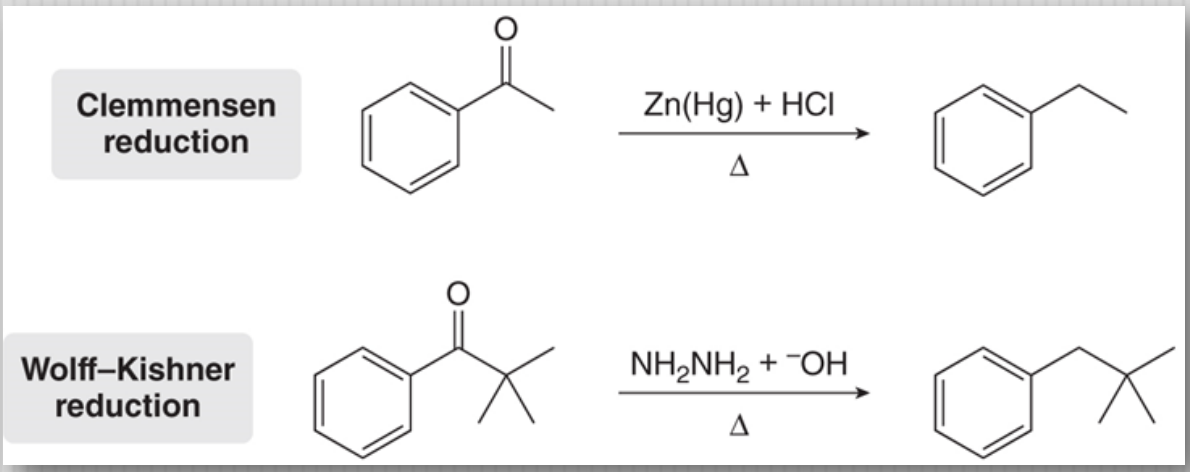
Reduction of Acyl Benzenes



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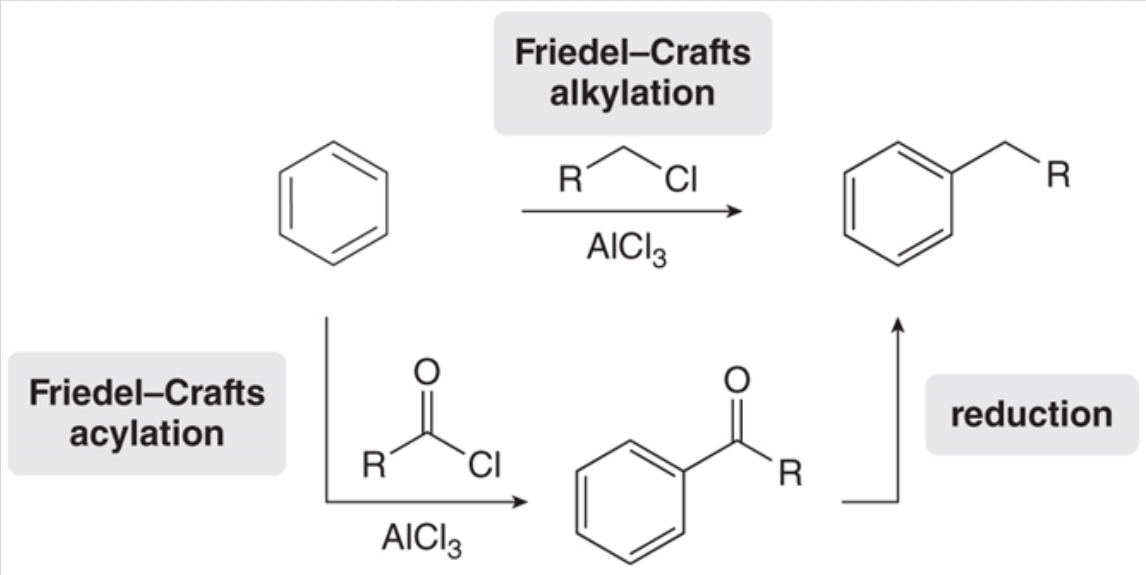
Synthesis of Alkyl Benzenes



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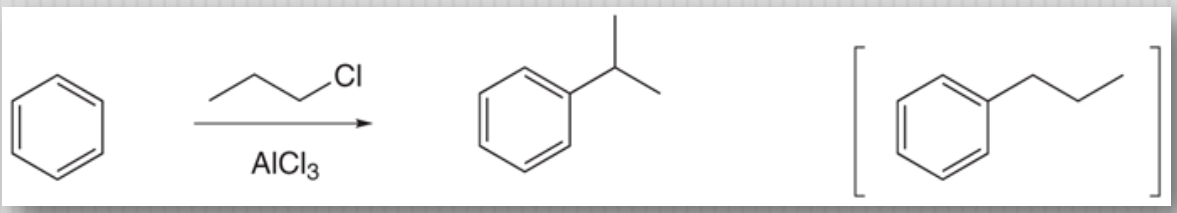
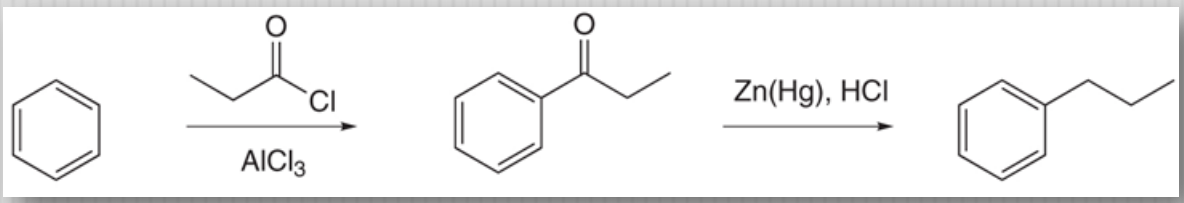
Synthesis of Alkyl Benzenes





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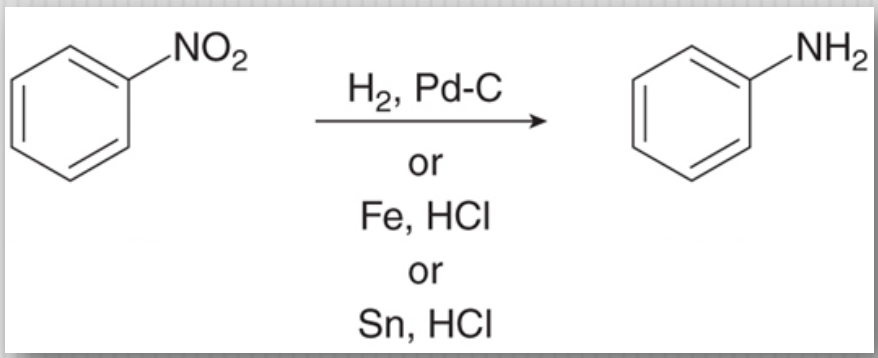
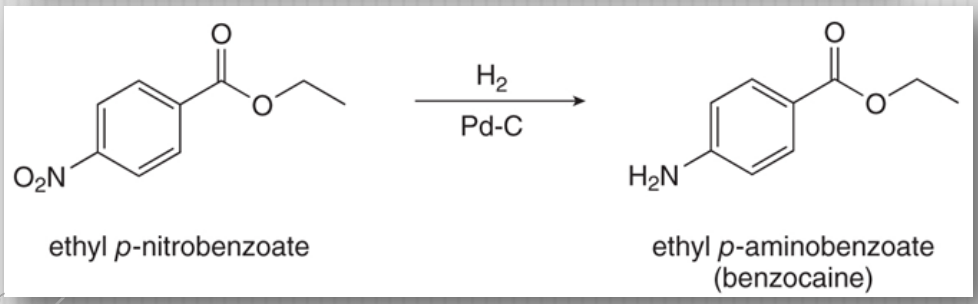
Reduction of Nitro Benzenes





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