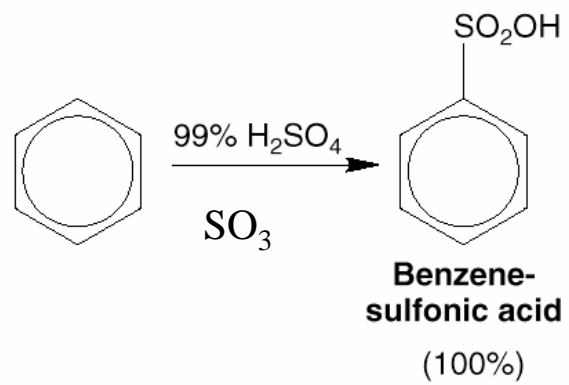
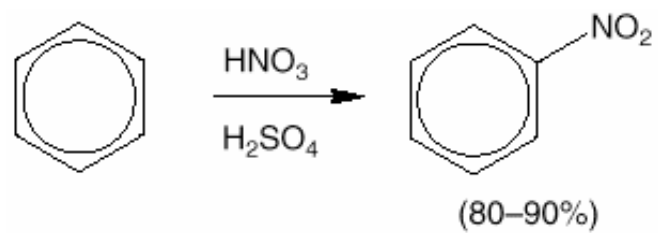
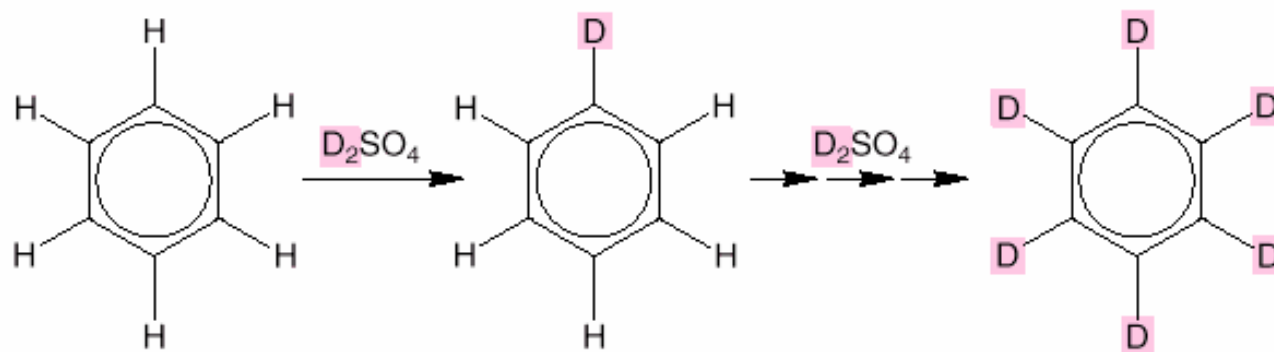
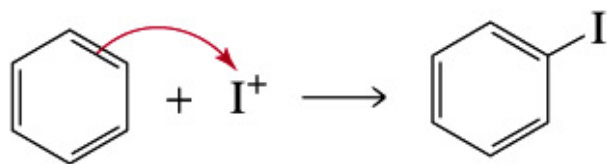
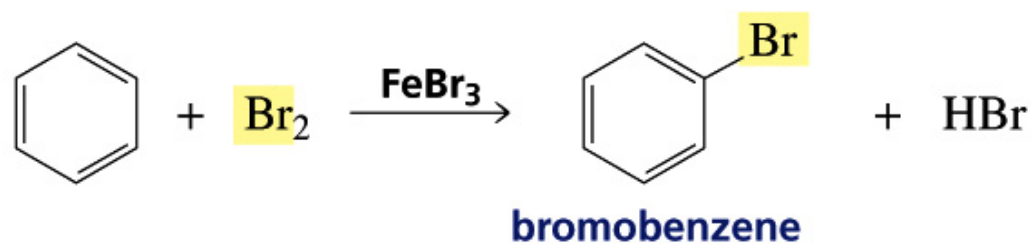
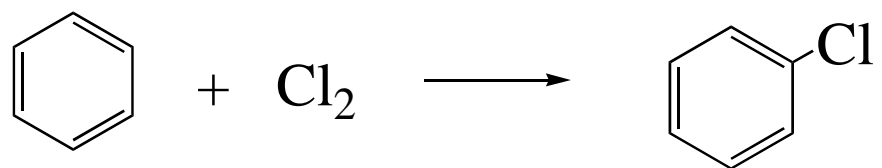
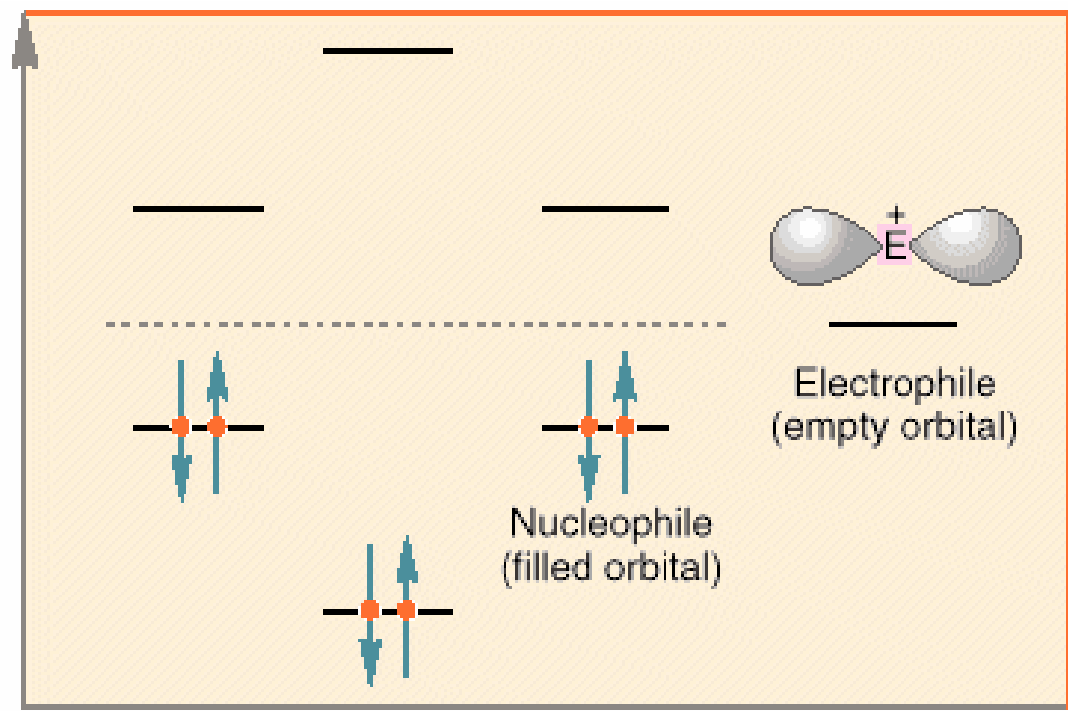
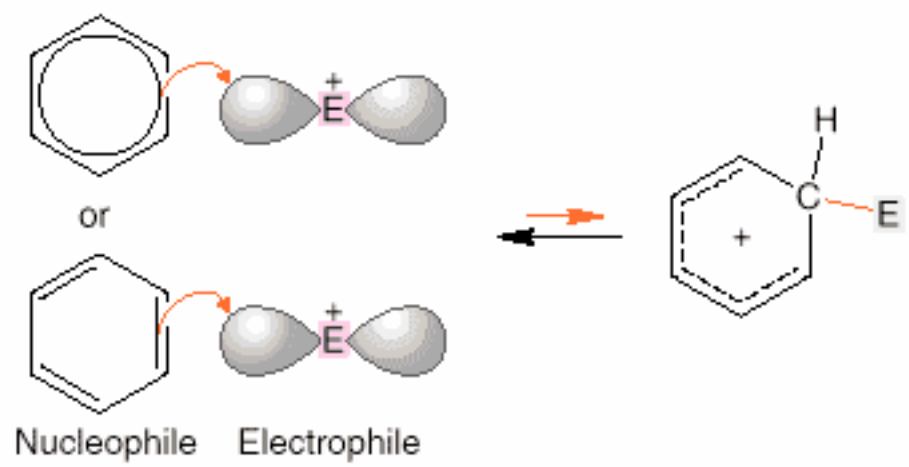


# Chapter 17

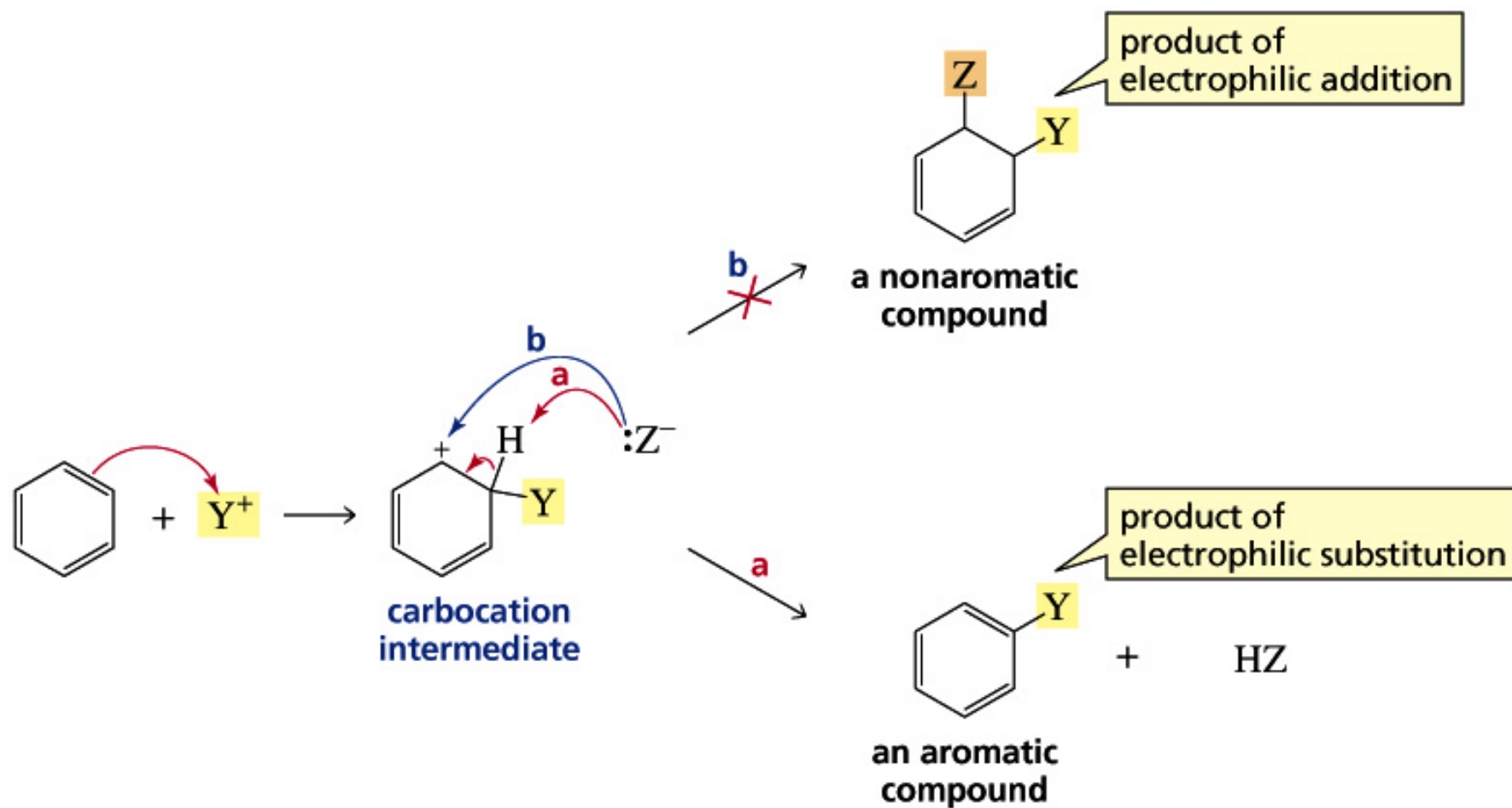
## Reactions of Aromatic Compounds



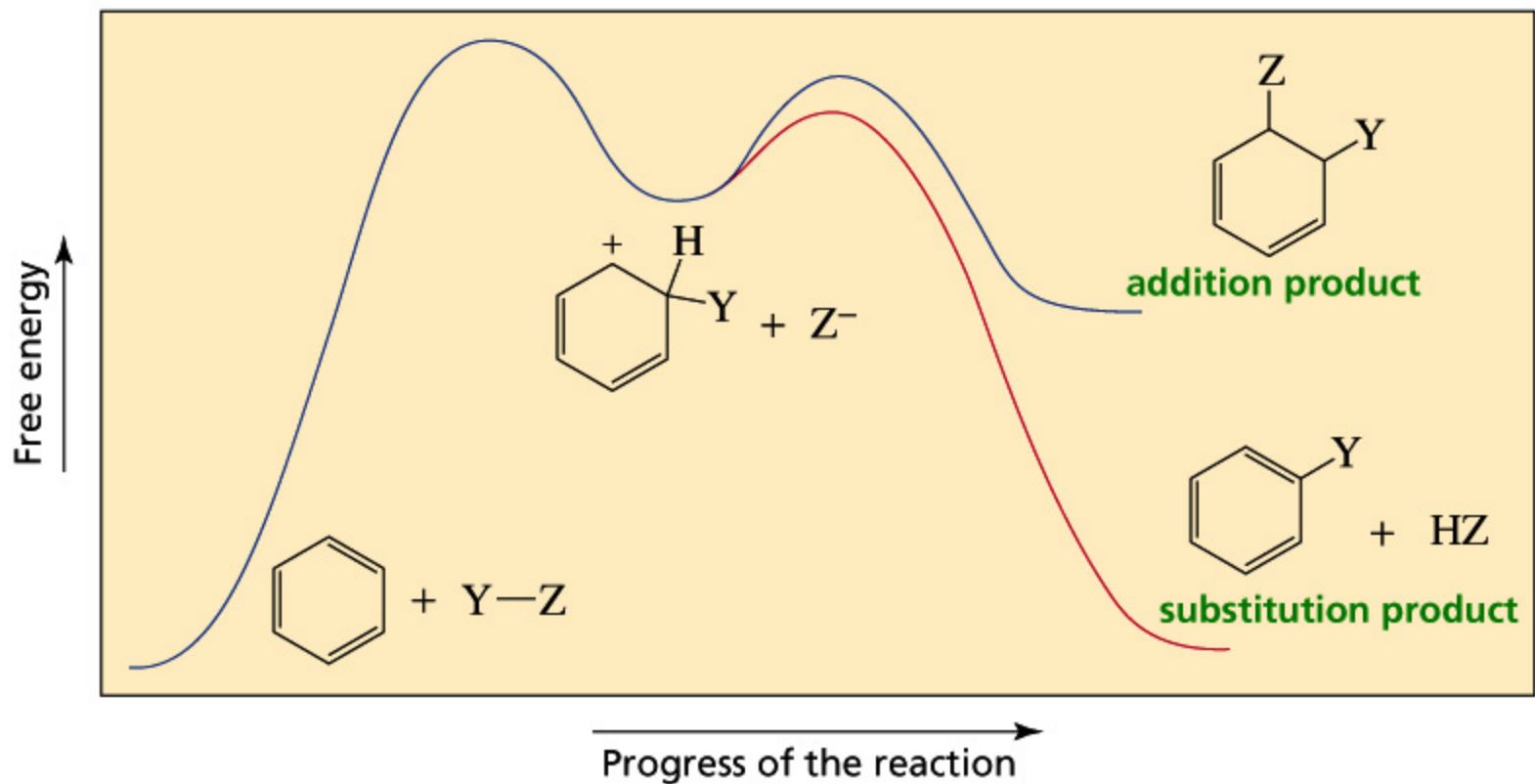




# Benzene is a nucleophile that reacts with an electrophile

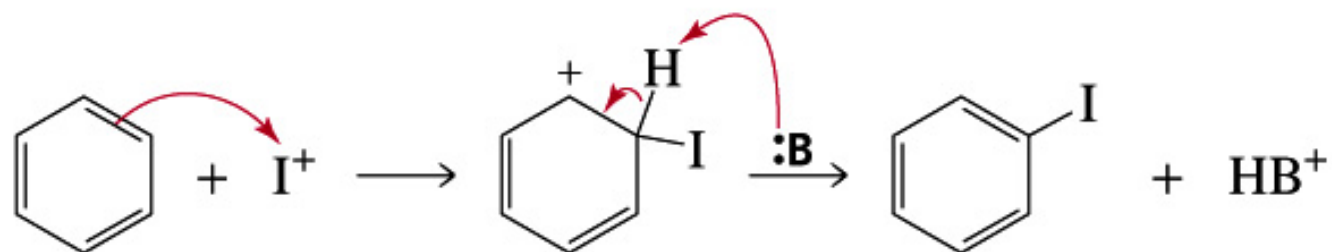


# Reaction Coordinate Diagrams for the Two Benzene Reactions



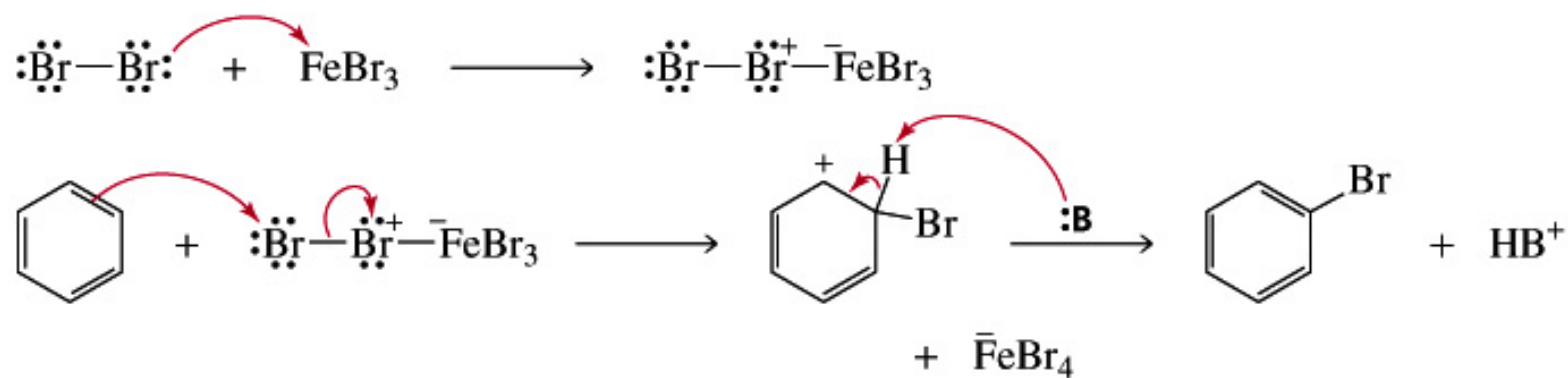
# Iodination of Benzene

mechanism for iodination



# Bromination of Benzene

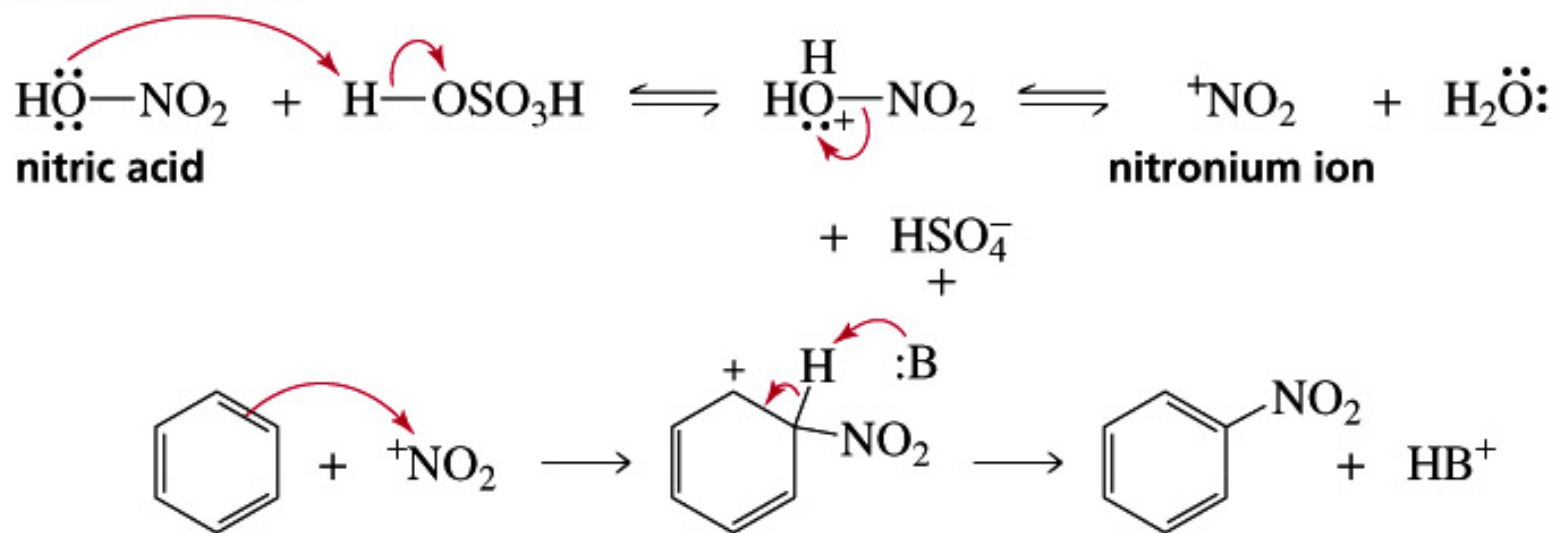
mechanism for bromination





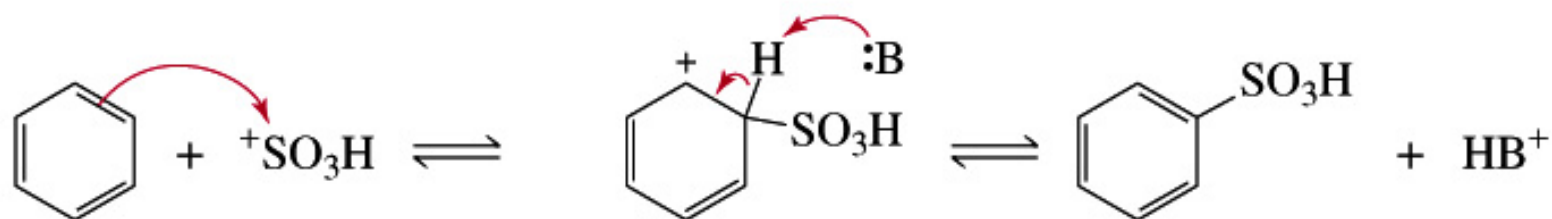
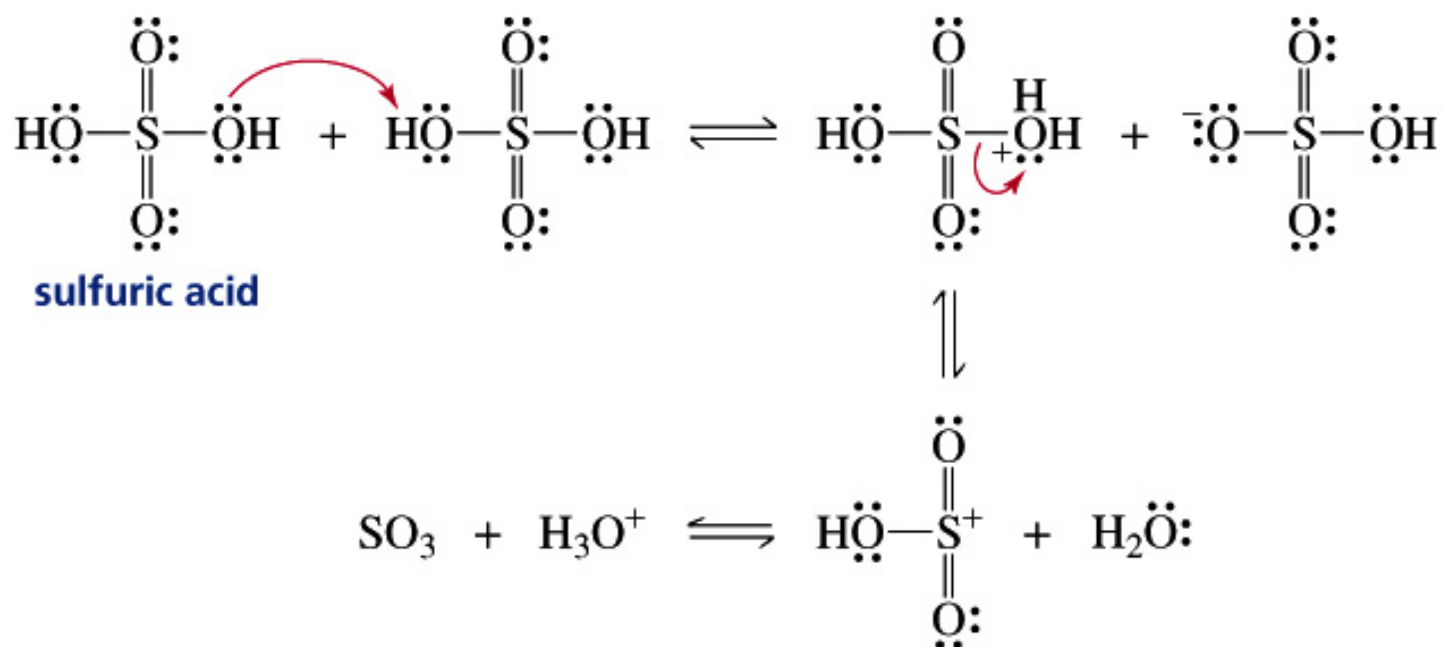
# Nitration of Benzene

mechanism for nitration

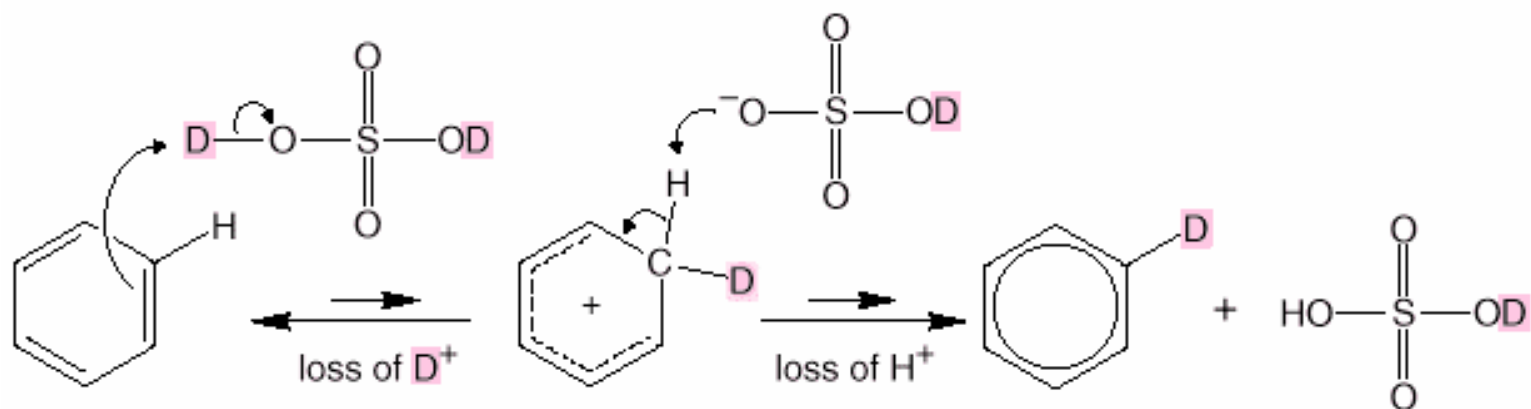
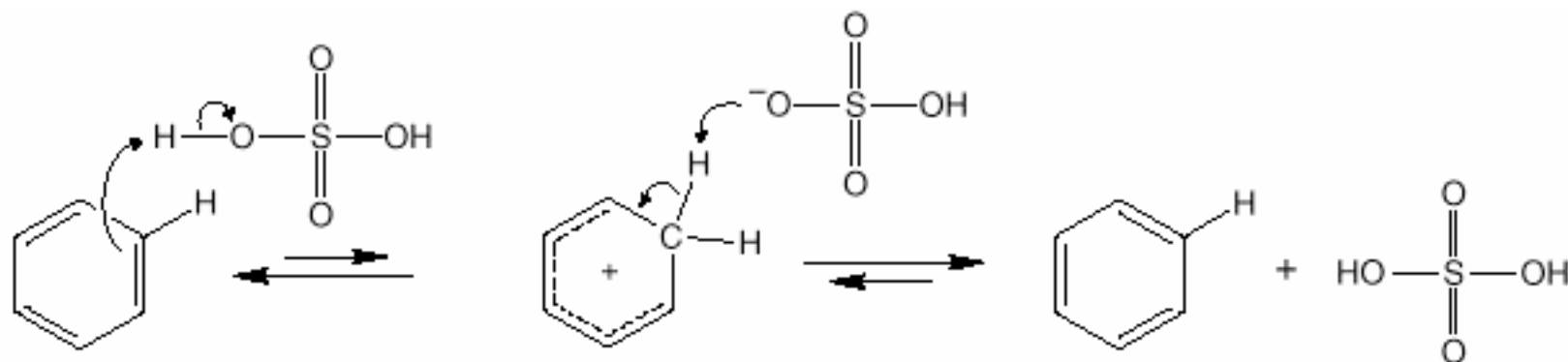


# Sulfonation of Benzene

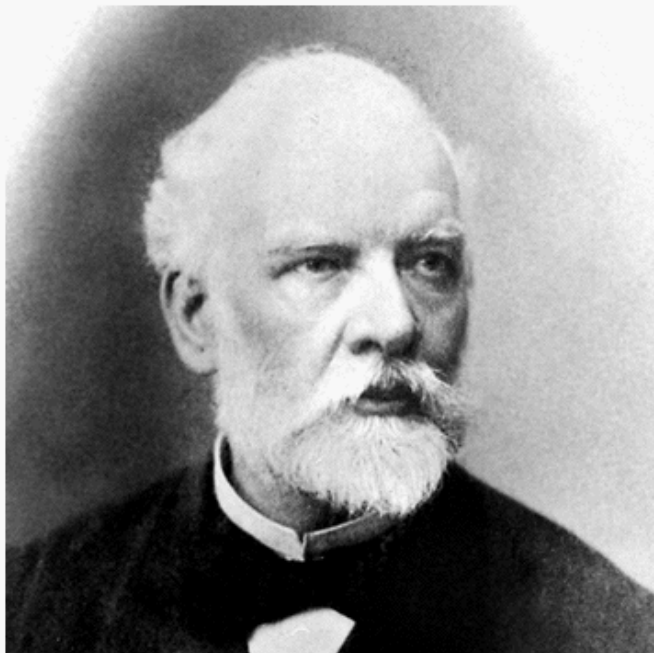
mechanism for sulfonation



# Protonation of Benzene

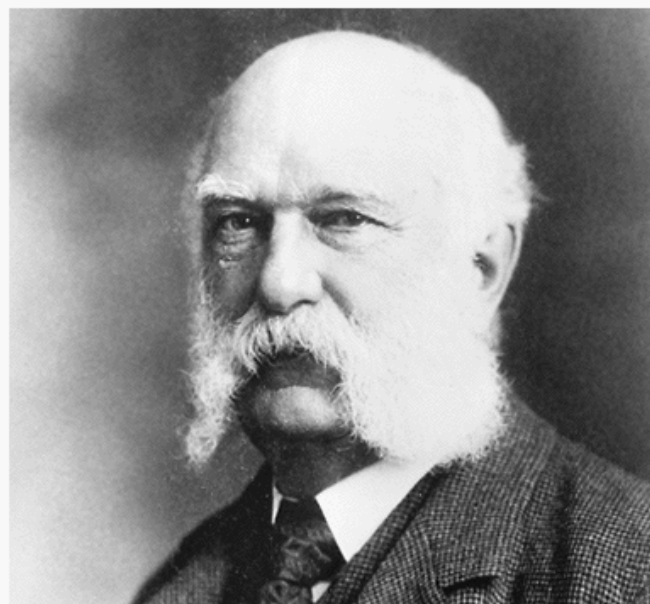


# Friedel-Crafts Reaction



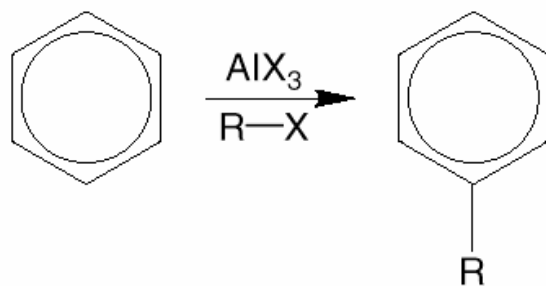
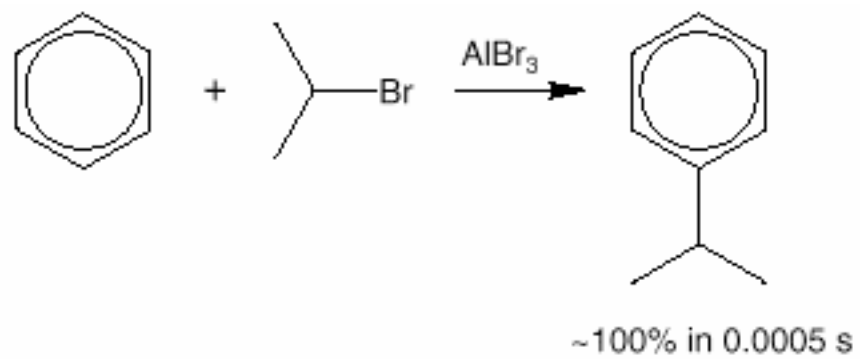
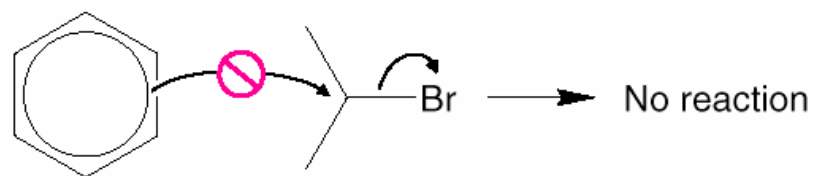
Courtesy Edgar Fahs Smith Collection,  
Van Pelt Library, University of Pennsylvania

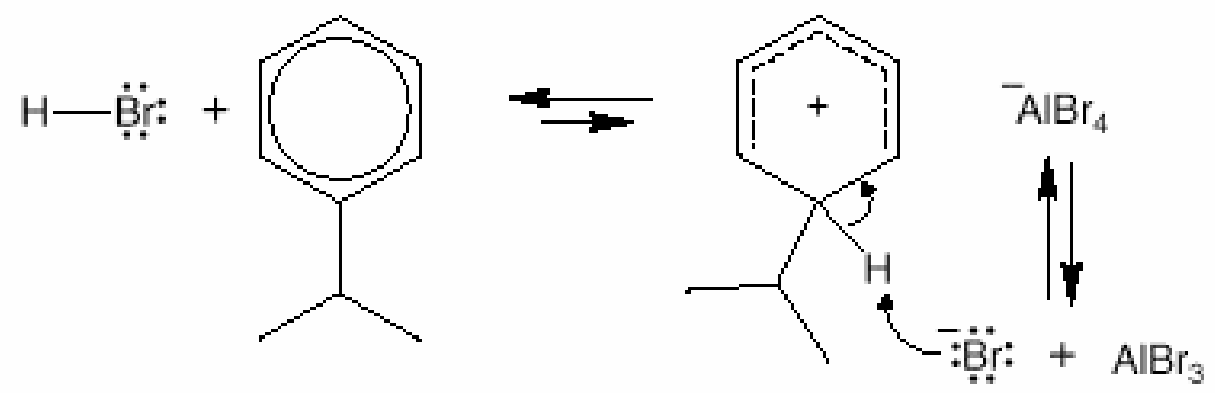
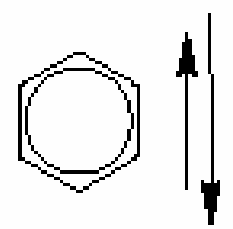
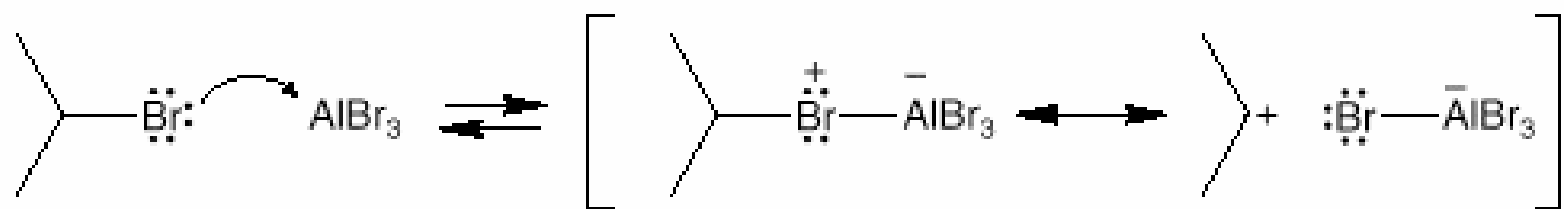
Friedel



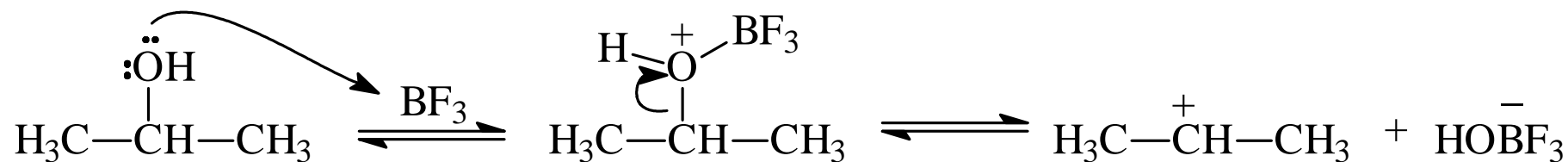
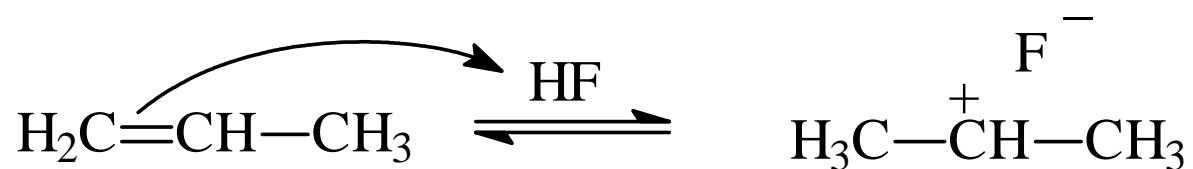
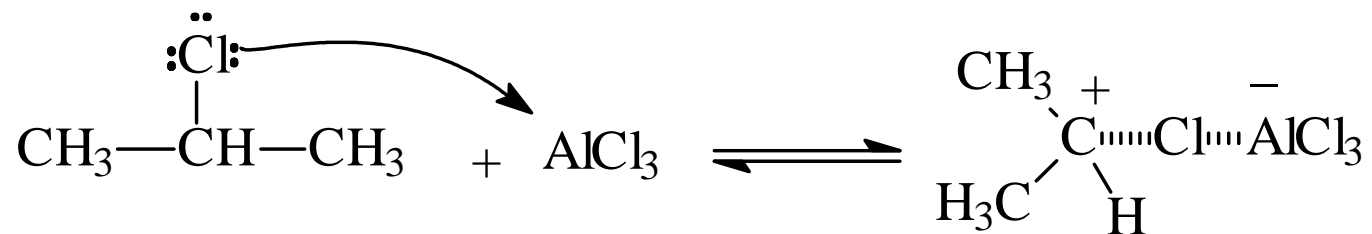
Courtesy Edgar Fahs Smith Collection,  
Van Pelt Library, University of Pennsylvania

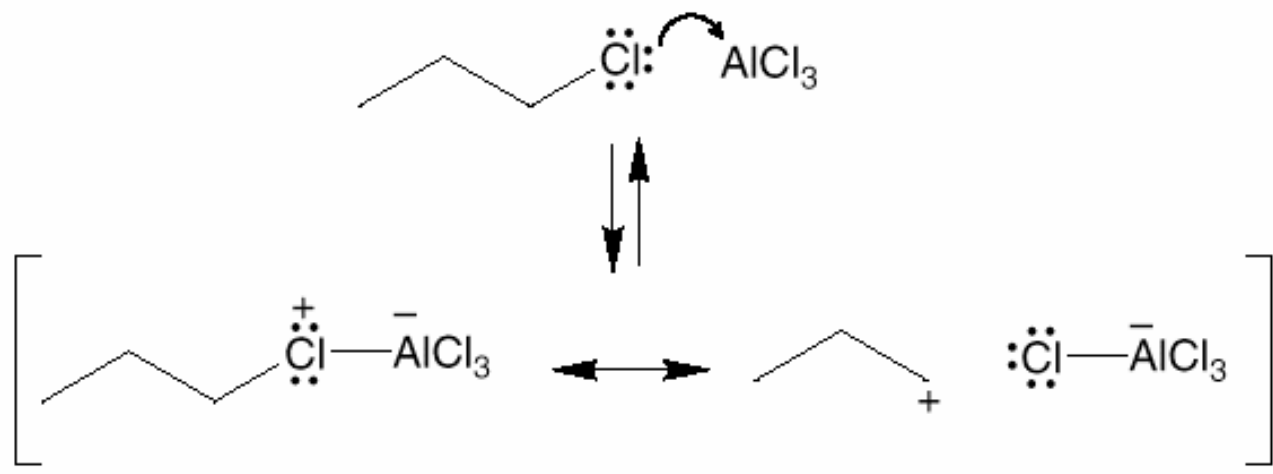
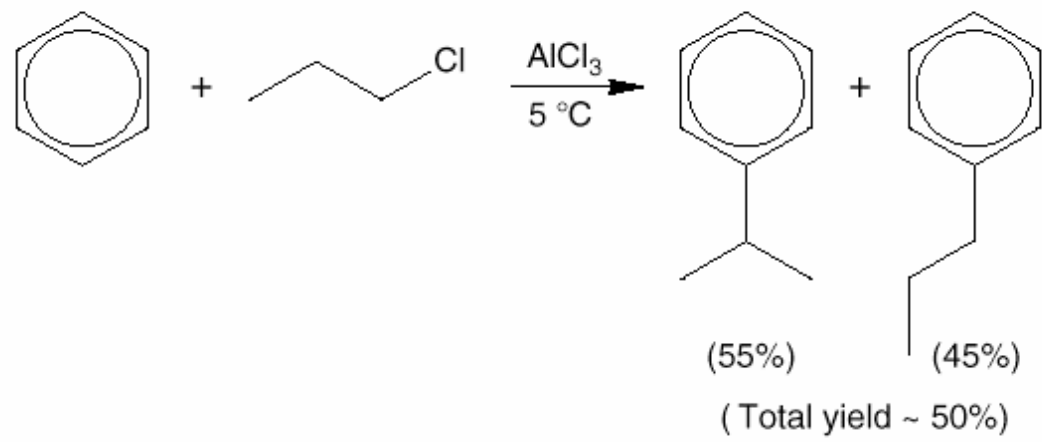
Crafts



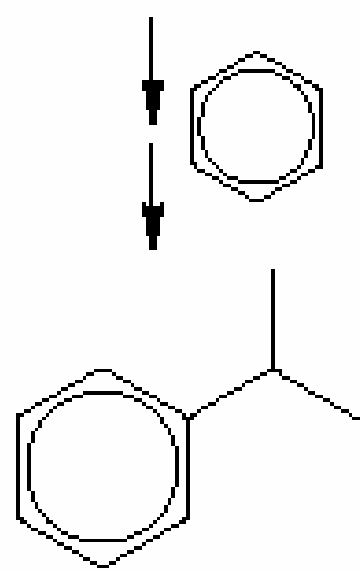
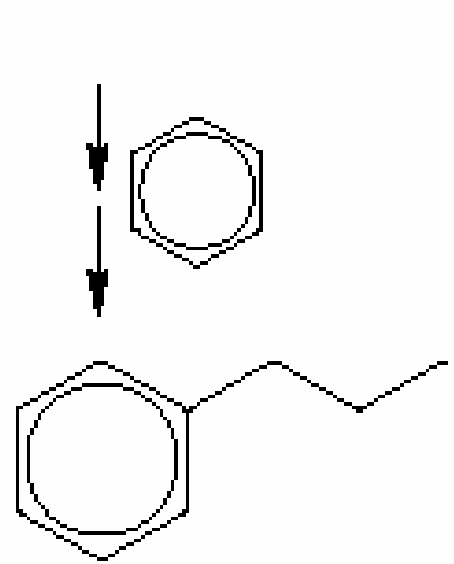
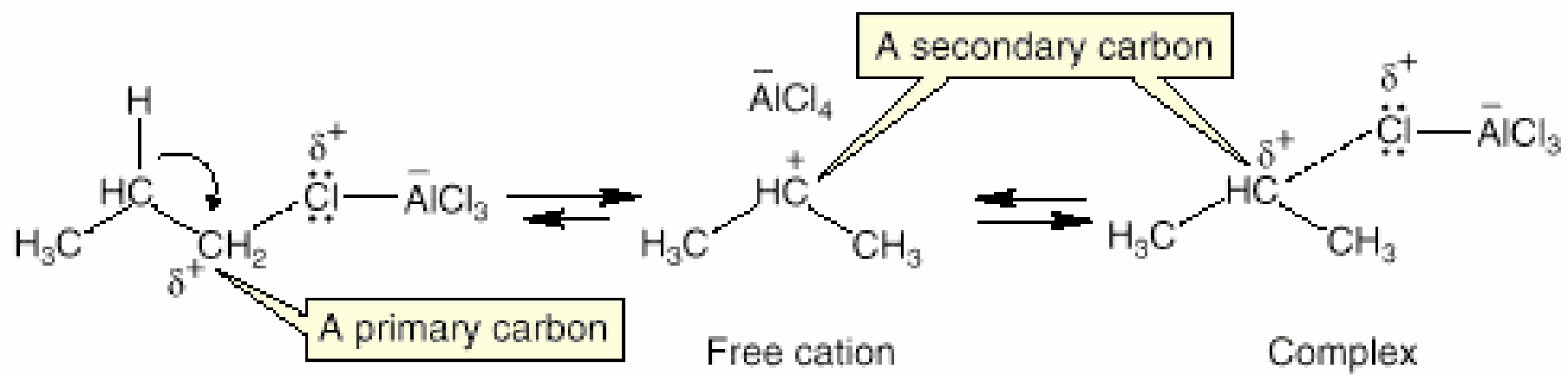


## Examples of Carbocation Formation



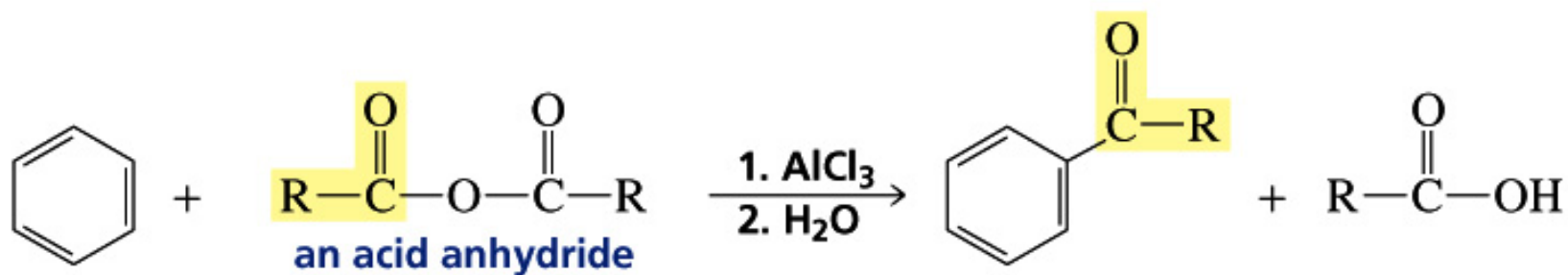
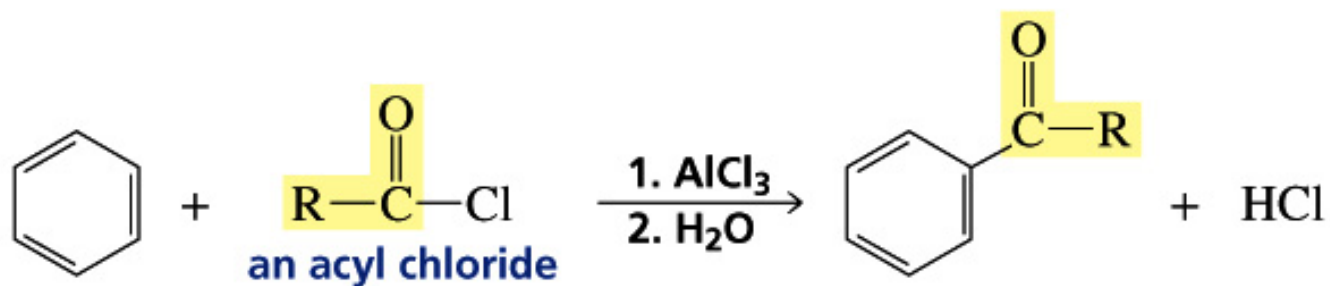


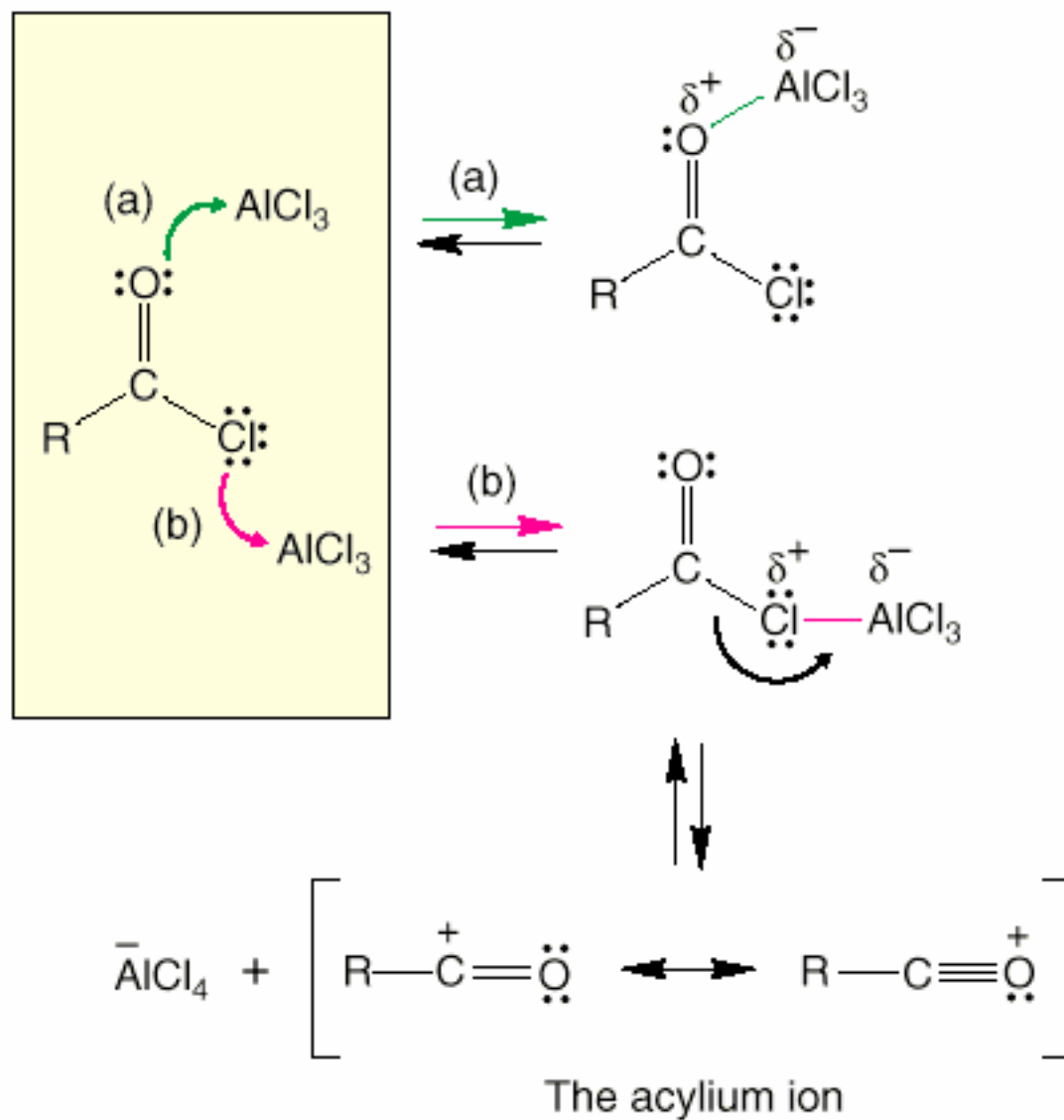


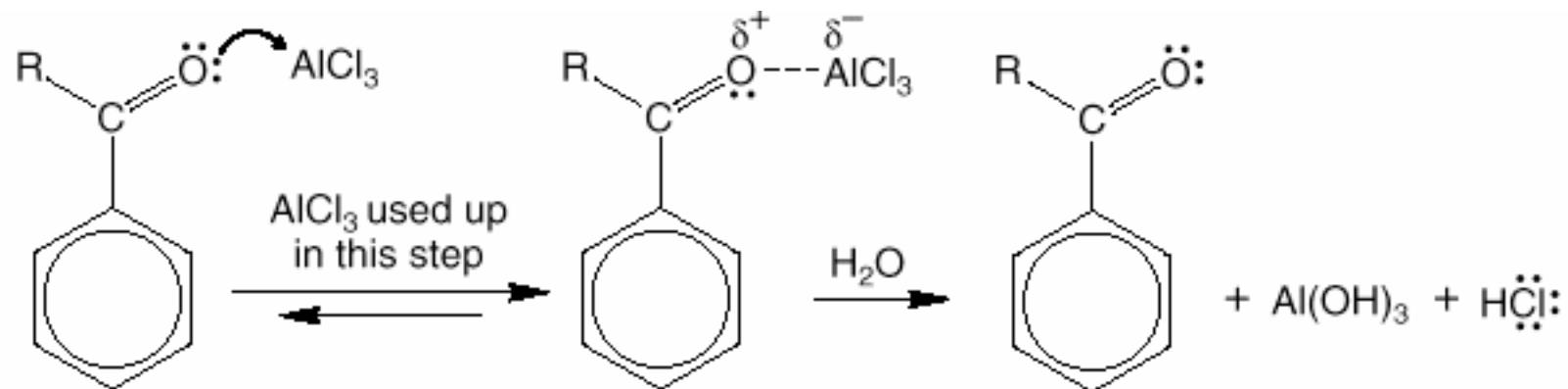
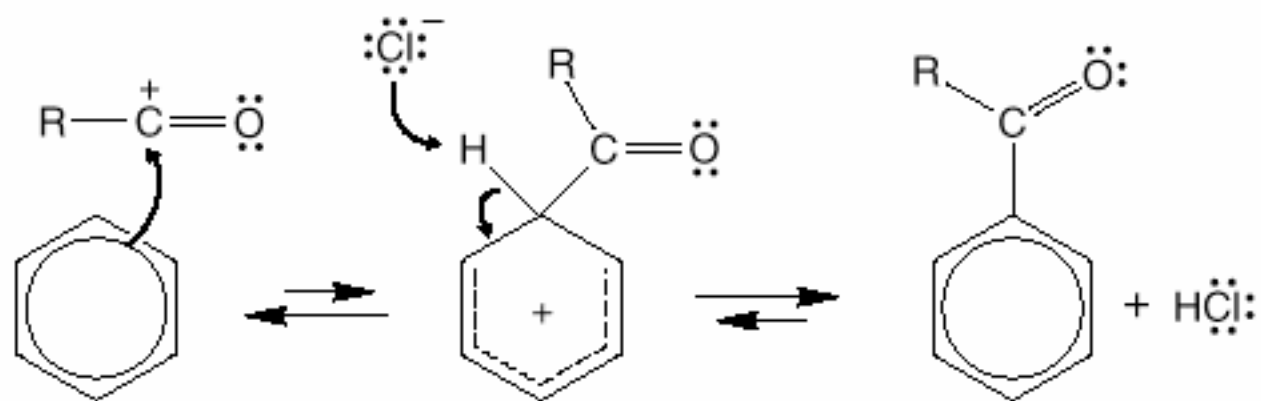


# Friedel-Crafts Acylation

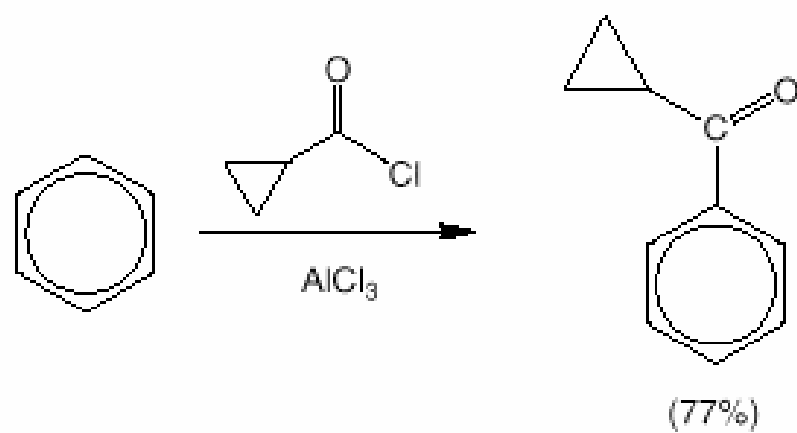
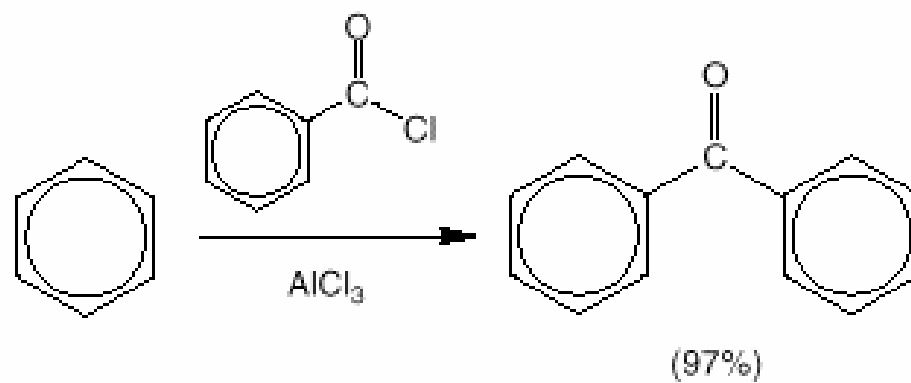
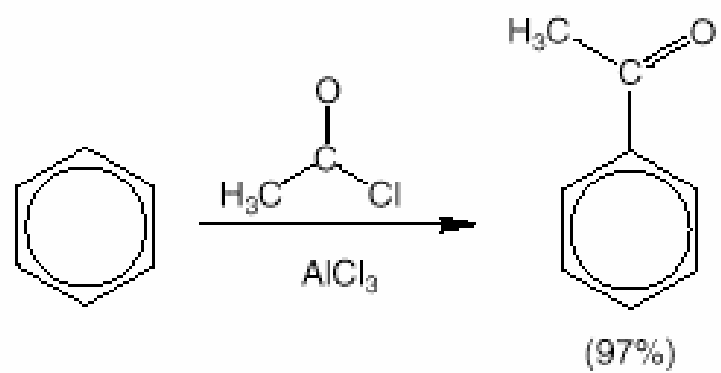
## Friedel-Crafts acylation





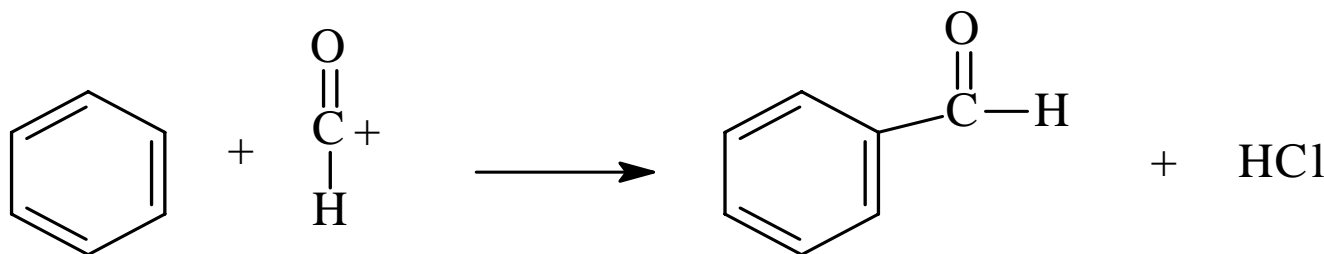
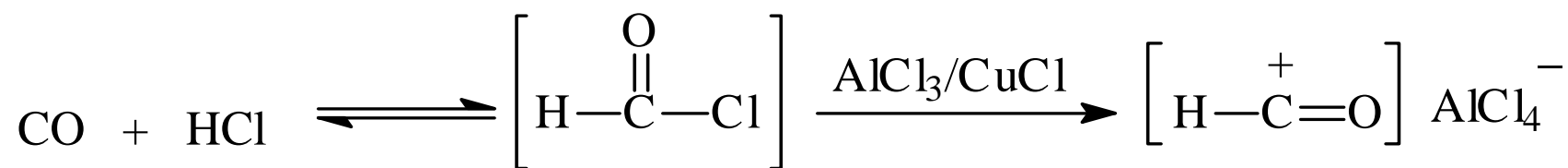


A final hydrolysis step liberates the ketone, an acyl benzene

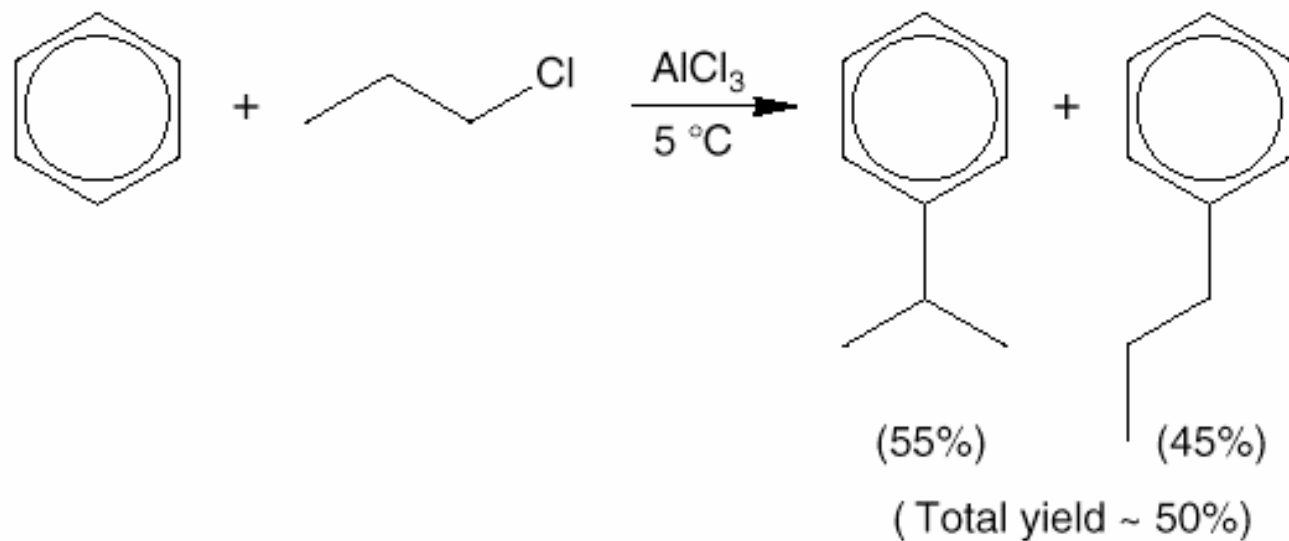


## Gatterman-Koch Formylation

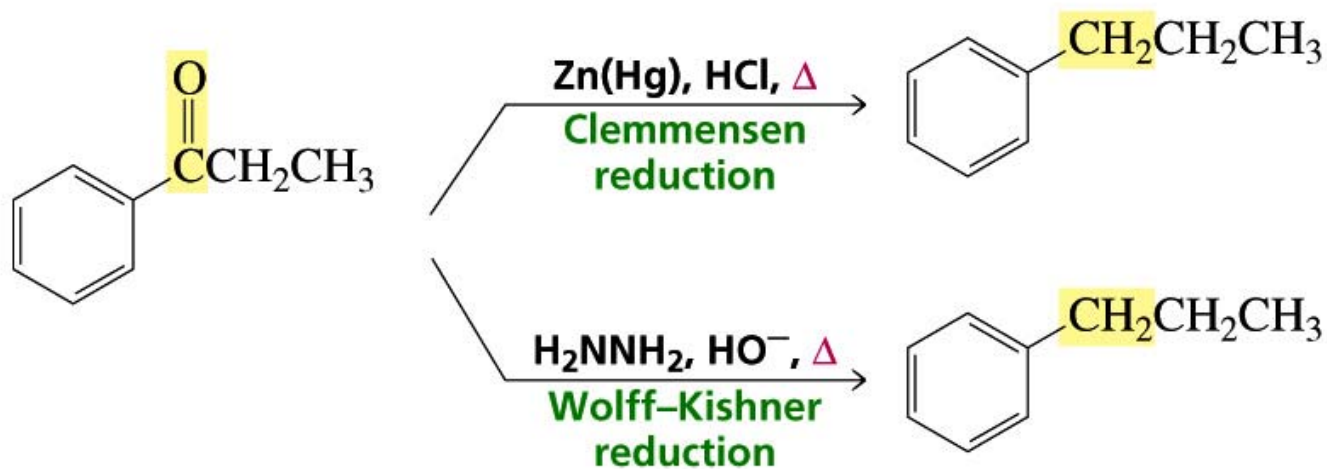
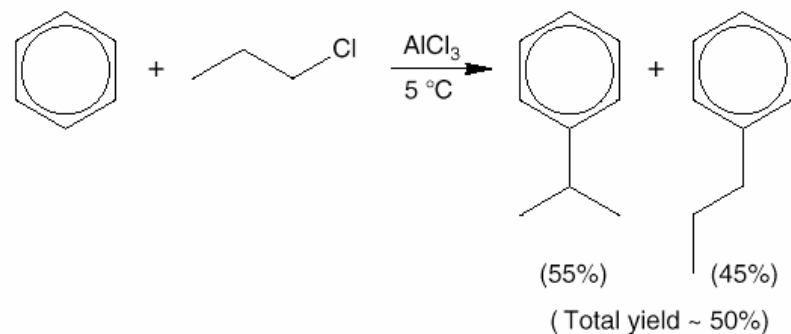
- Formyl chloride is unstable. Use a high pressure mixture of CO, HCl, and catalyst.
- Product is benzaldehyde.



It is not possible to obtain a good yield of an alkylbenzene containing a straight-chain group via Friedel-Crafts alkylation

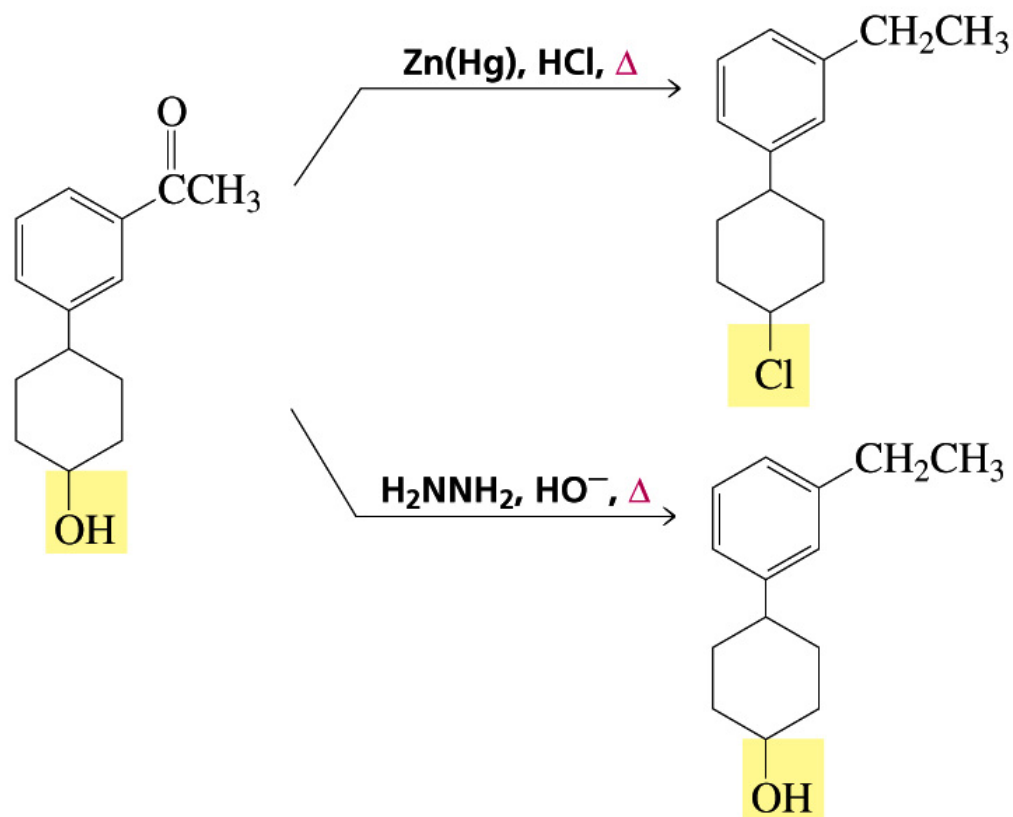


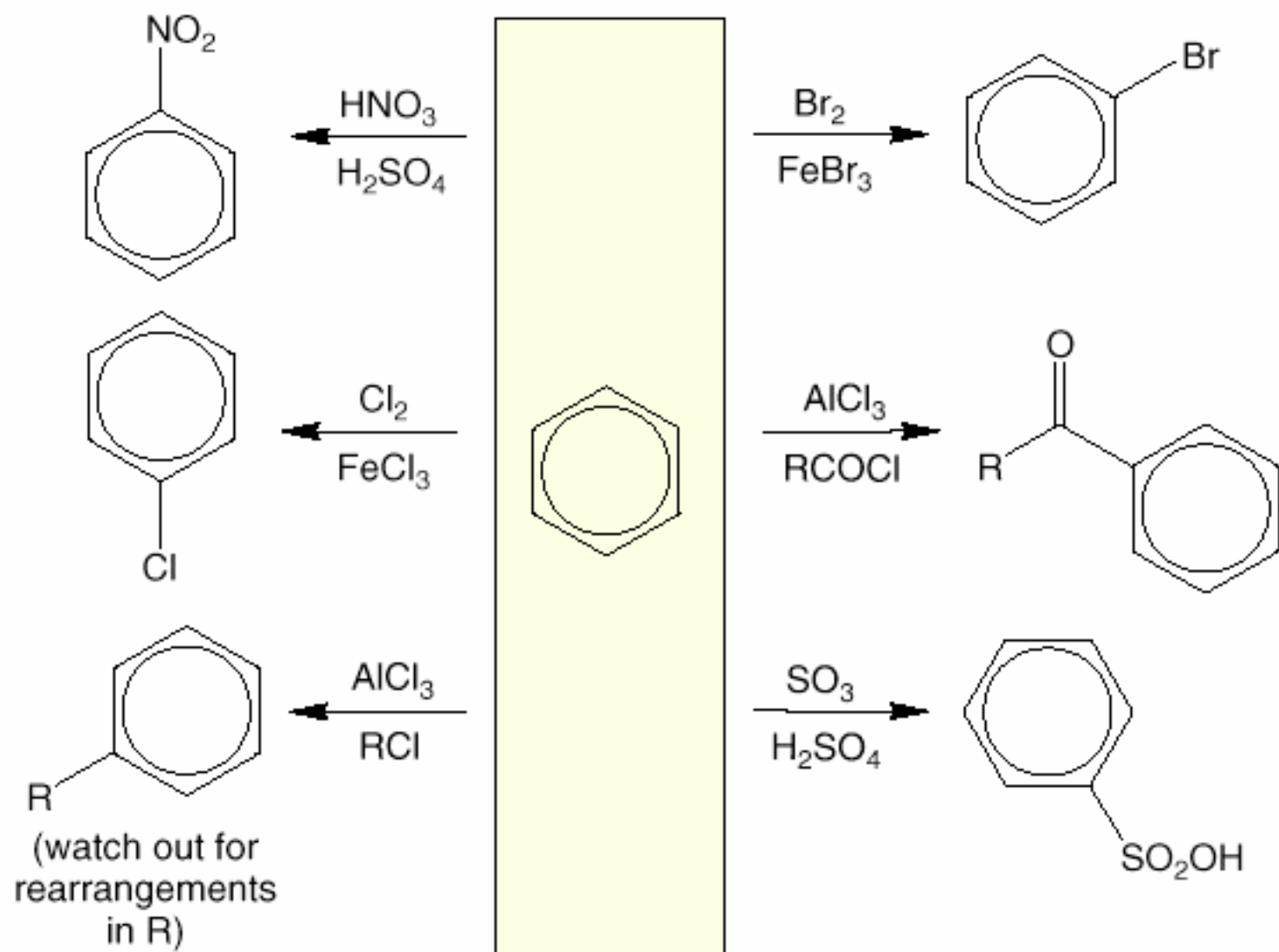
However the same goal is achieved through a Friedel-Crafts Acylation-reduction works well



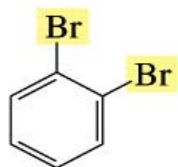
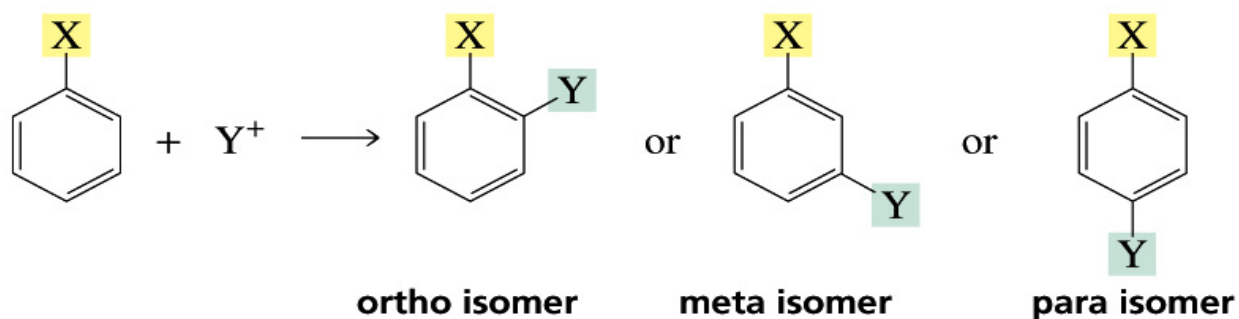


One needs to consider an alternative if there is another functional group present in the compound

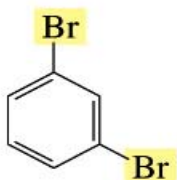




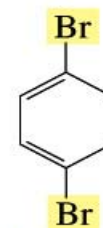
## Three isomers with two substituents



**1,2-dibromobenzene**  
*ortho*-dibromobenzene  
*o*-dibromobenzene



**1,3-dibromobenzene**  
*meta*-dibromobenzene  
*m*-dibromobenzene

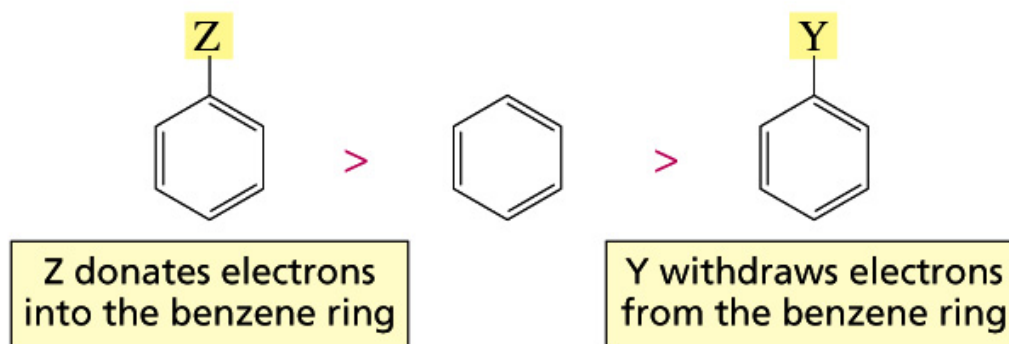


**1,4-dibromobenzene**  
*para*-dibromobenzene  
*p*-dibromobenzene

## Substituent controls the

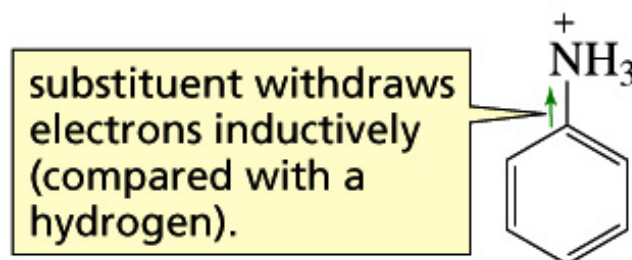
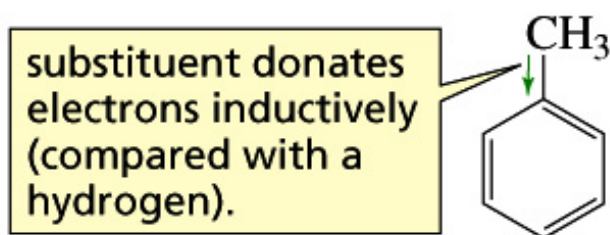
- Relative rates of electrophilic substitution
- Location of the attack

relative rates of electrophilic substitution



Donation of electrons through a  $\sigma$  bond is called **inductive electron donation**

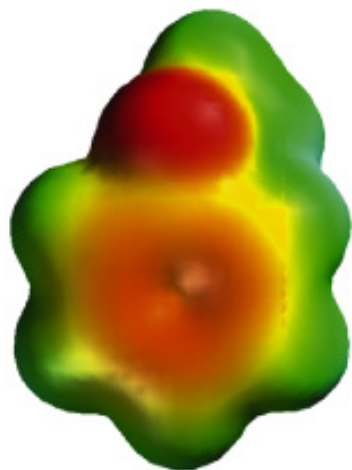
An alkyl group is more electron donating than hydrogen because of hyperconjugation



Withdrawal of electrons through a  $\sigma$  bond is called **inductive electron withdrawal**

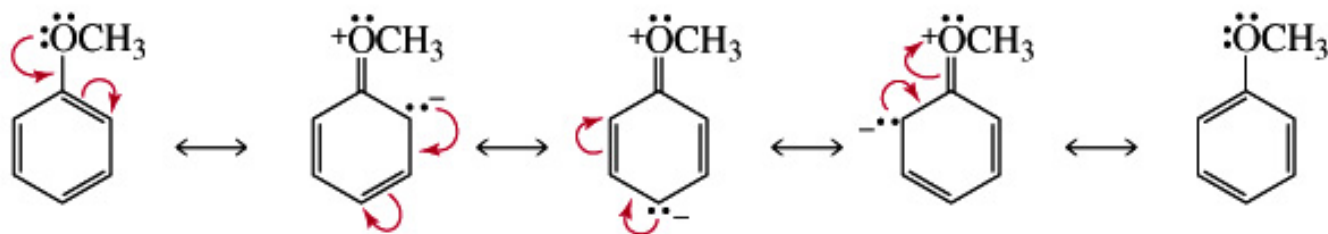
The  $\text{NH}_3$  group is more electronegative than a hydrogen

A substituent can also donate electrons into the ring by delocalizing its lone-pair electrons  
**Resonance effect**



anisole

donation of electrons into a benzene ring by resonance

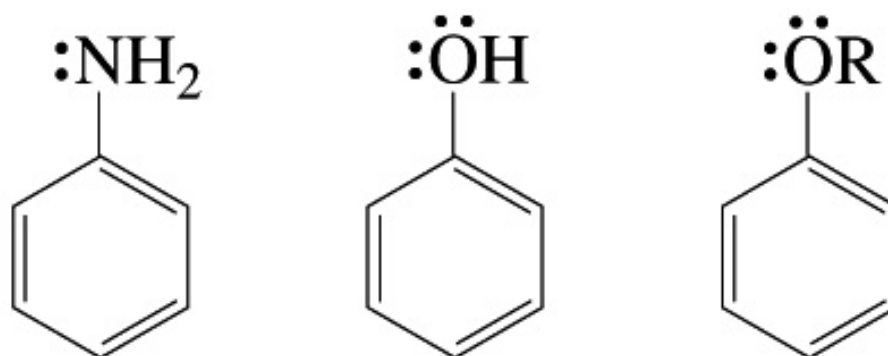


**Table 16.1 The Effects of Substituents on the Reactivity of a Benzene Ring Toward Electrophilic Substitution**

<b>Activating substituents</b> ↓	<b>Most activating</b>			
		-NH <sub>2</sub>	} <b>Strongly activating</b>	} <b>Ortho/para directing</b>
		-NHR		
		-NR <sub>2</sub>		
		-OH		
		-OR		
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-NHCR} \end{array}$	} <b>Moderately activating</b>	
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-OCR} \end{array}$		
		-R	} <b>Weakly activating</b>	
		-Ar		
	-CH=CHR			
<b>Standard of comparison</b> →	-H			
<b>Deactivating substituents</b> ↓		-F	} <b>Weakly deactivating</b>	} <b>Meta directing</b>
		-Cl		
		-Br		
		-I		
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-CH} \end{array}$		
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-CR} \end{array}$	} <b>Moderately deactivating</b>	
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-COR} \end{array}$		
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-COH} \end{array}$		
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{-CCl} \end{array}$		
		-C≡N		
		-SO <sub>3</sub> H	} <b>Strongly deactivating</b>	
		$\begin{array}{c} + \\ \text{-NH}_3 \end{array}$		
		$\begin{array}{c} + \\ \text{-NHR}_2 \end{array}$		
		$\begin{array}{c} + \\ \text{-NR}_3 \end{array}$		
		-NO <sub>2</sub>		
	<b>Most deactivating</b>			

The strongly activating substituents make the benzene ring more reactive toward electrophilic substitution

**strongly activating substituents**

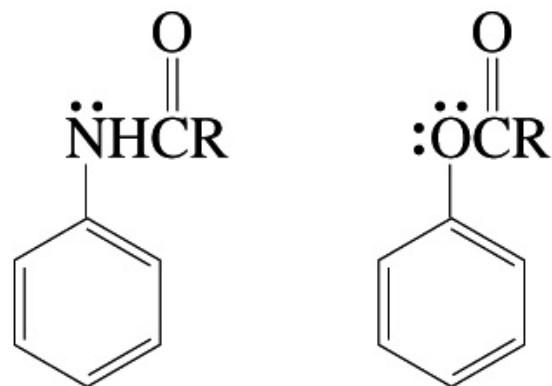


All the strongly activating substituents donate electrons by resonance and withdraw electrons inductively

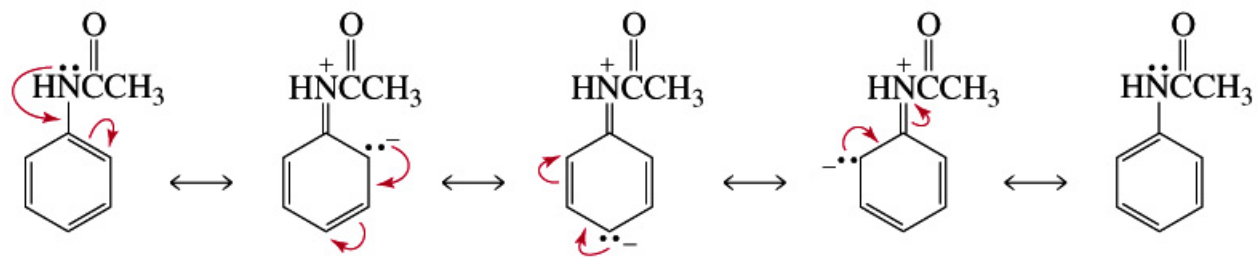


The moderately activating substituents can donate electrons into the ring and away from the ring

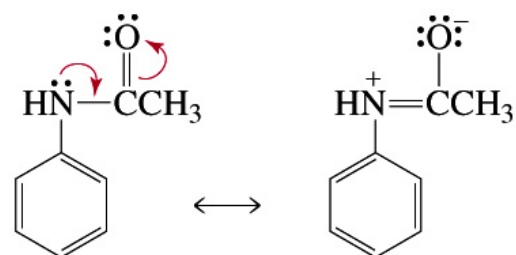
moderately activating substituents



Overall, they donate electrons by resonance more strongly than they withdraw electrons inductively



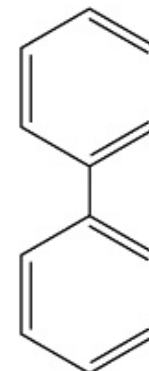
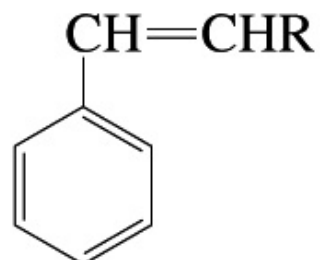
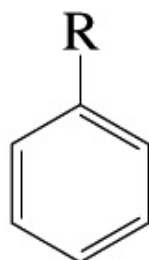
substituent donates electrons by resonance into the benzene ring



substituent donates electrons by resonance away from the benzene ring

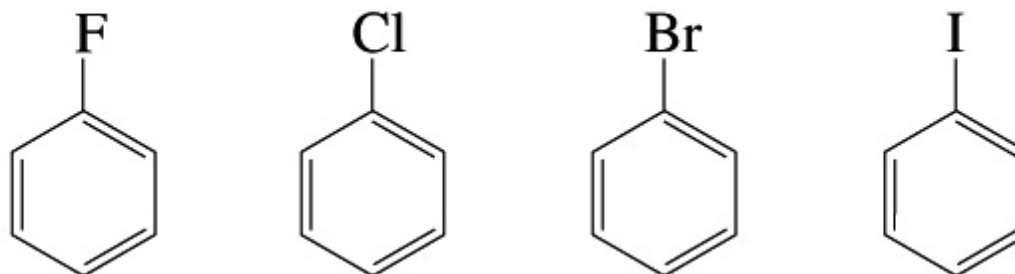
These substituents are slightly more electron donating than they are electron withdrawing

weakly activating substituents



These substituents donate into the ring by resonance and withdraw electrons from the ring inductively

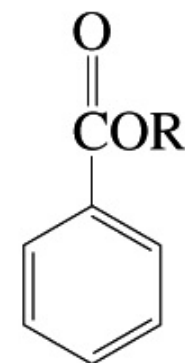
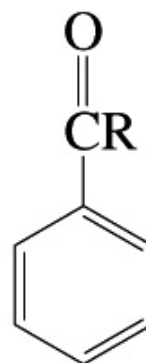
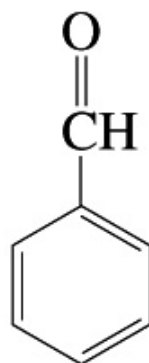
**weakly deactivating substituents**



They withdraw electrons inductively more strongly than they donate electrons by resonance

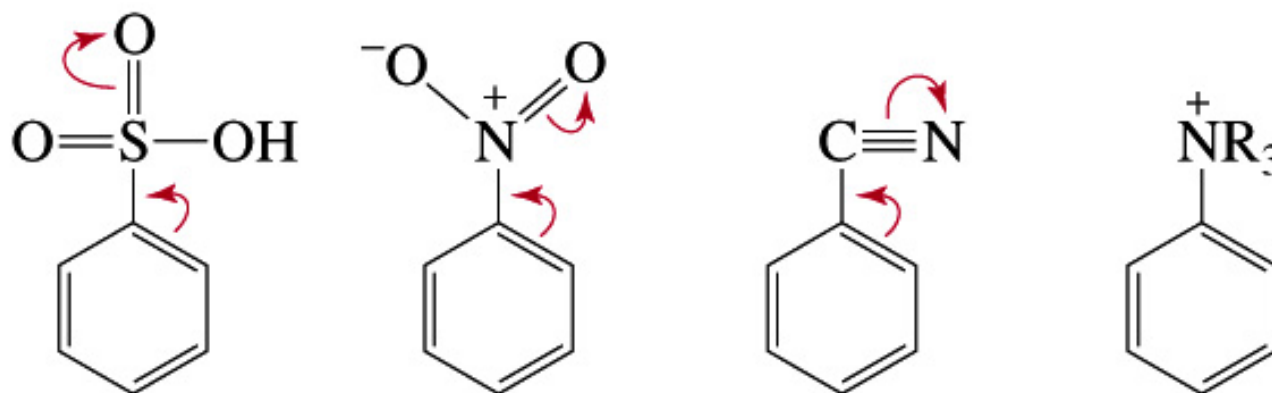
These substituents withdraw electrons both inductively and by resonance

moderately deactivating substituents



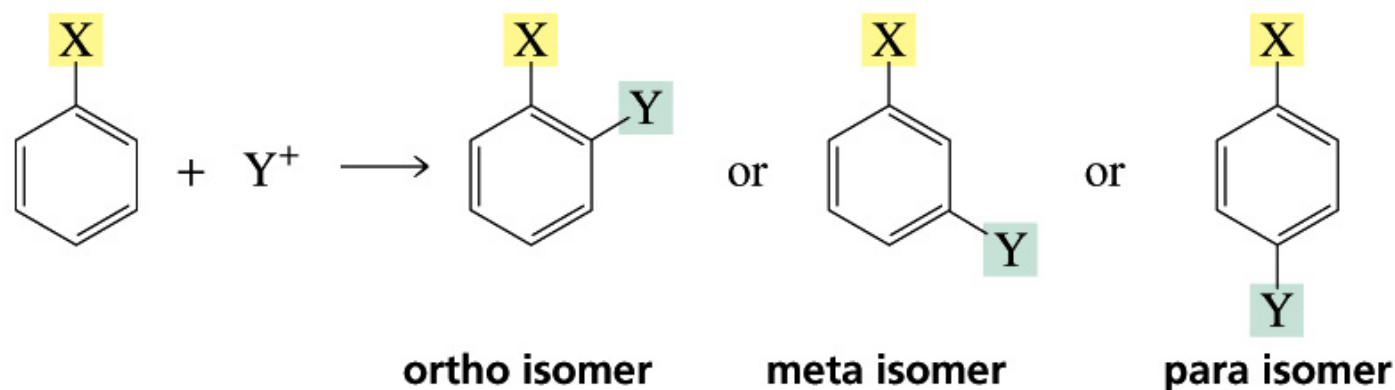
These substituents are powerful electron-withdrawing groups

strongly deactivating substituents



These substituents withdraw electrons both inductively and by resonance

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

All substituents that are more deactivating than halogens are meta directors