

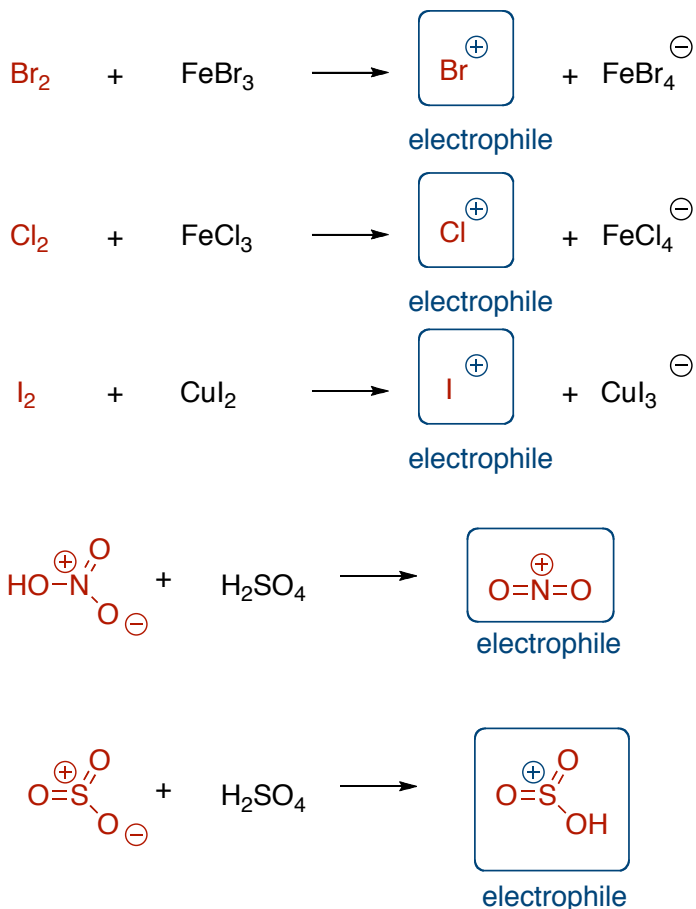
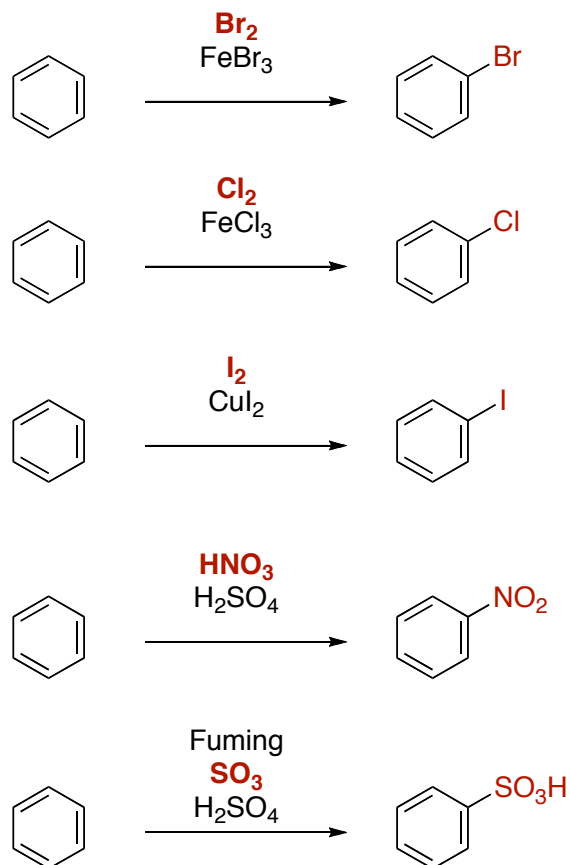


Chem 342 • Organic Chemistry II

Lecture Summary 10 - 06 Feb 2009

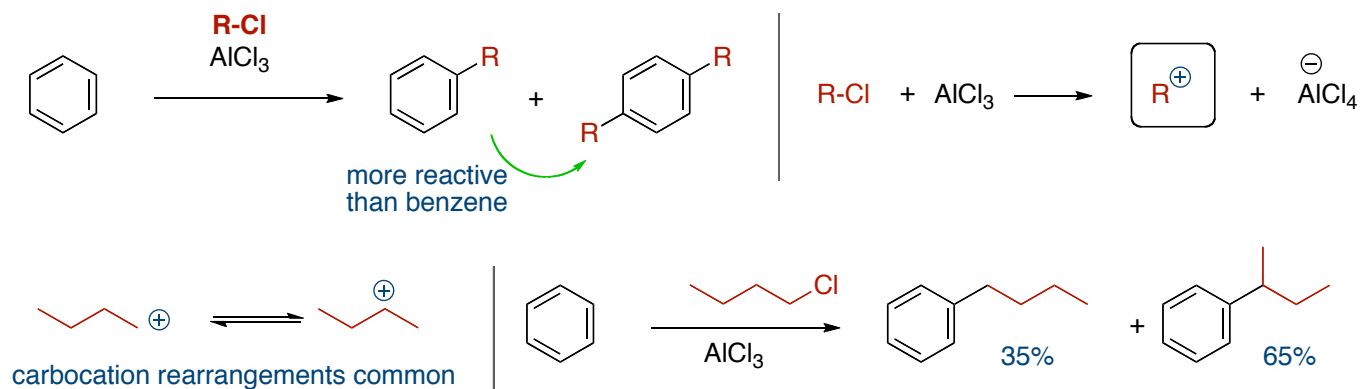
Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

Electrophilic substitution will occur with many reactive electrophiles. Here is a list of some of the more common reagents for electrophilic aromatic substitution.



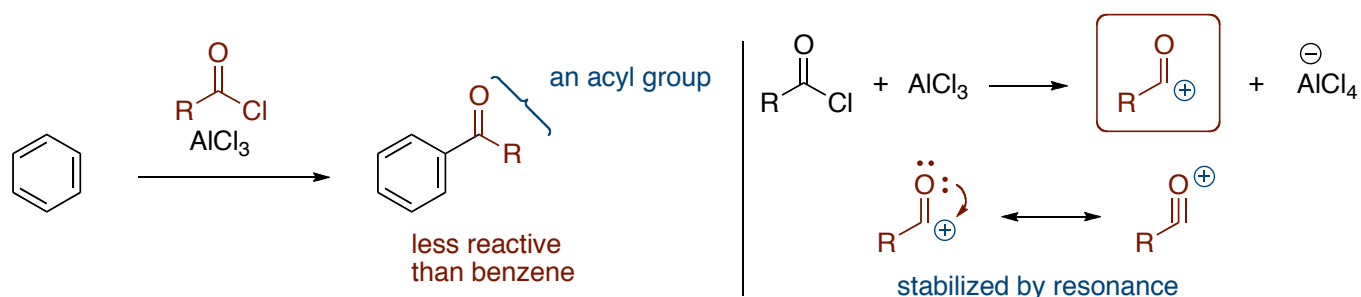
Friedel-Crafts Alkylation

Alkyl halides can be used to generate carbocations which will do substitution. There are two problems with this alkylation reaction. The products are more reactive than the starting material because alkyl groups are electron donating to the ring, so over reaction is common. Also, if possible, carbocations can undergo rearrangements affording a mixture of isomers in the products.



Friedel-Crafts Acylation

The reaction with acid chlorides solves both of the problems associated with alkylation reactions. The reactive acyl electrophile does not undergo rearrangements since it is the most stable cation, and the product is less reactive than benzene due to the electron withdrawing nature of the ketone. Thus, adding a second electrophile can be avoided.



Some notes about electrophilic aromatic substitution

Two step mechanism - E^+ addition followed by H^+ elimination

Reaction requires generation of very reactive electrophiles with strong Brønsted or Lewis acids.

X, NO_2 , SO_3H , R, RCO can all be added to a benzene ring

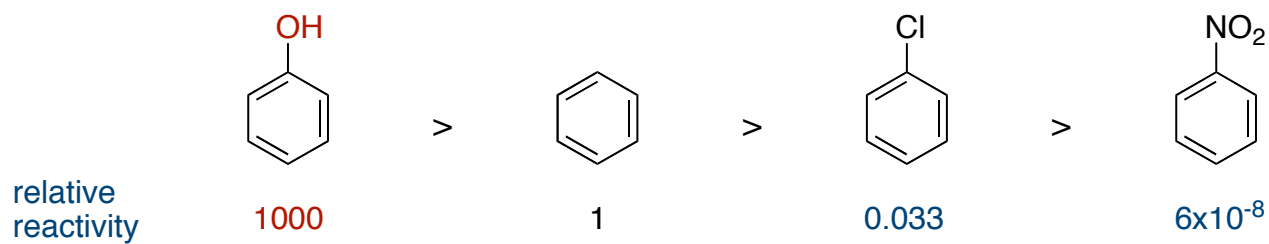
OH and NH_2 cannot be directly added to a benzene ring

F-C Alkylation suffers from carbocation rearrangements and more than one addition

F-C Acylation solves the problems of the alkylation reaction

Substituent Effects


Since the first step in the electrophilic aromatic substitution is the rate determining step, substituents on the ring can influence the rate by stabilizing or destabilizing the cation intermediate. Electron donating groups stabilize the plus charge, thus aromatic rings with electron donating groups react faster than benzene. Electron withdrawing groups destabilize the charged intermediate, thus reactions with these groups on the ring are slower than benzene (these are deactivated).



**Activating
Electron Donating Groups**

alkyl —OR —NR₂ —SR

**Deactivating
Electron Withdrawing Groups**

—X —CN —NO₂ —SO₃H 

Daily Quiz

Q: Which of the following statements is TRUE about electrophilic aromatic substitution?	<input type="checkbox"/> 1:	Bromine easily reacts with benzene.
	<input checked="" type="checkbox"/> 2:	The first step has a large activation energy.
	<input type="checkbox"/> 3:	This is a one step reaction.
	<input type="checkbox"/> 4:	The mechanism involves first elimination, then addition.