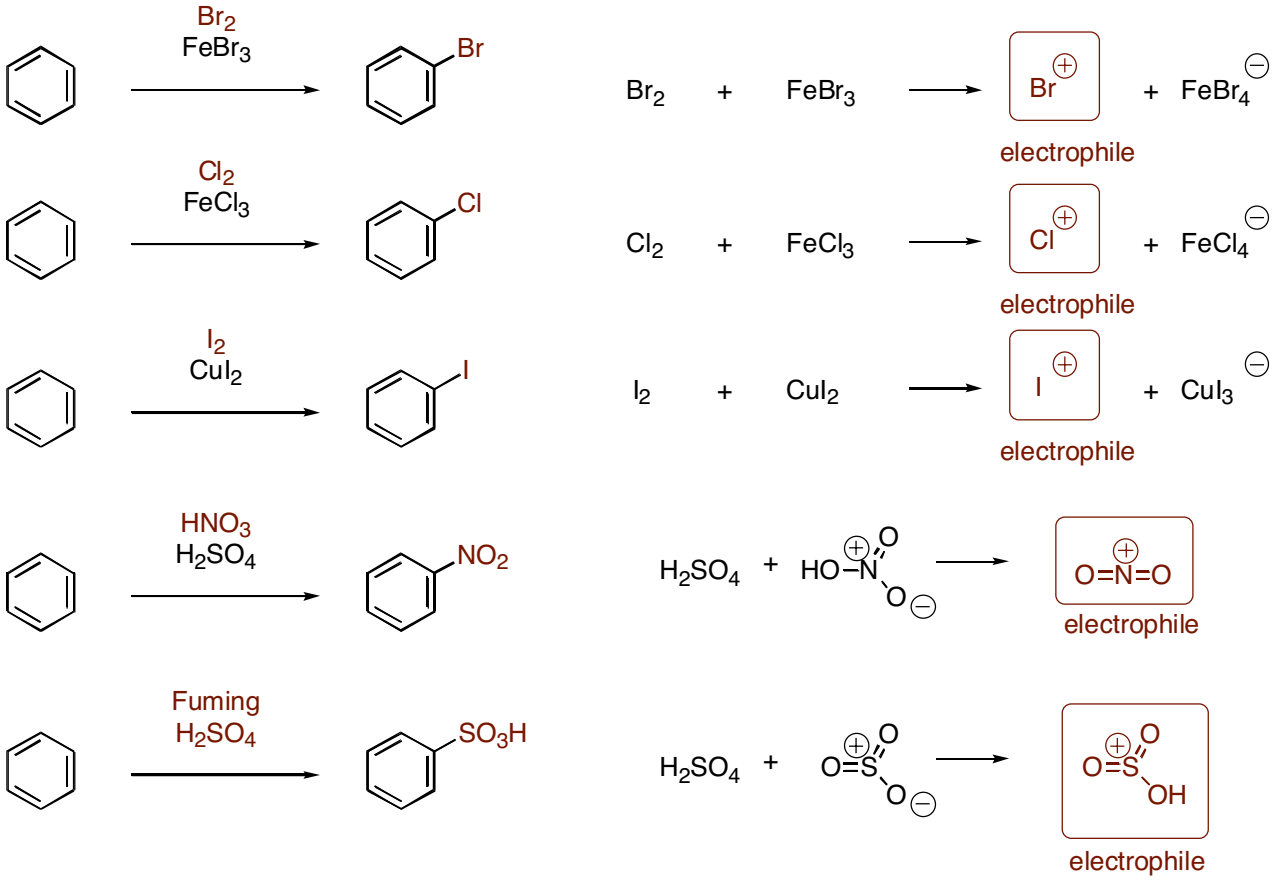
These notes can be obtained at: http://www.ndsu.nodak.edu/instruct/grcook/chem342/notes.shtml

Chapter 16: Chemistry of Benzene: Electrophilic Aromatic Substitution

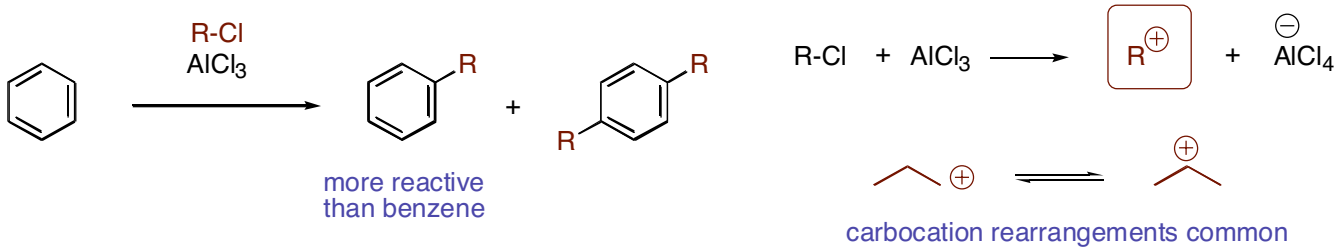
Electrophilic Aromatic Substitution

Electrophilic substitution will occur with many reactive electrophiles.



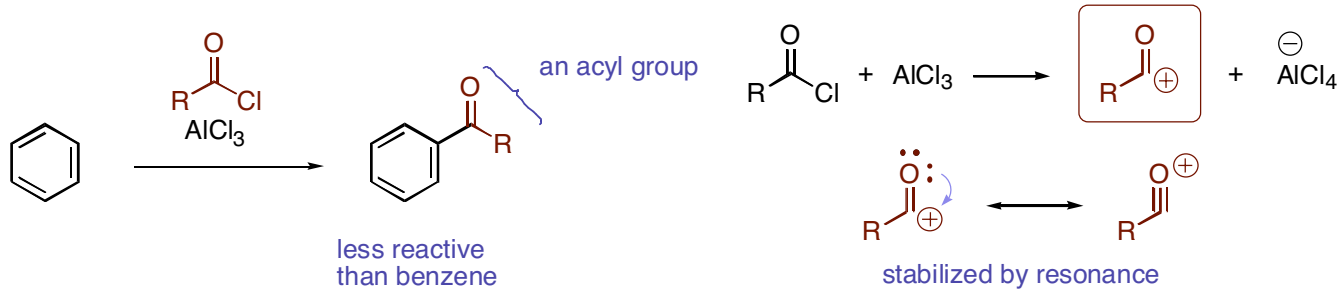
Friedel-Crafts Alkylation

Alkyl halides can be used to generate carbocations which will do substitution. There are two problems with this alkyation reaction. The products are more reactive than the starting material, so over reaction is common. Carbocations can undergo rearrangements affording a mixture of isomers in the products.



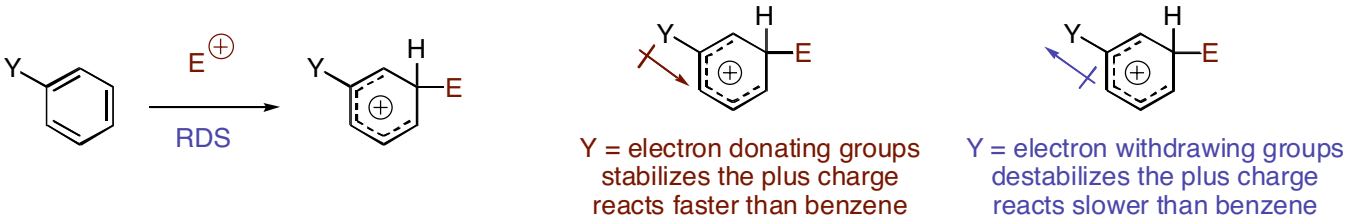
Friedel-Crafts Acylation

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. Thus, adding a second electrophile can be avoided.



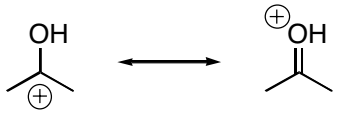
Substituent Effects

Since the first step in the electrophilic aromatic substitution is the rate determing 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 (these are activated). Electron withdrawing groups destabilize the charged intermediate, thus reactions with these groups on the ring are slower than benzene (these are deactiviated). Electron donating or withdrawing effects can be either inductive (through single bonds) or resonance (through pi-bonds). Resonance effects are usually stronger than inductive effects.



Electron Donating Groups

alkyl —OR —NR_2 —SR



resonance makes atoms with lone pairs good electron donating groups

Electron Withdrawing Groups

acyl —X —NO_2 —SO_3H —CN