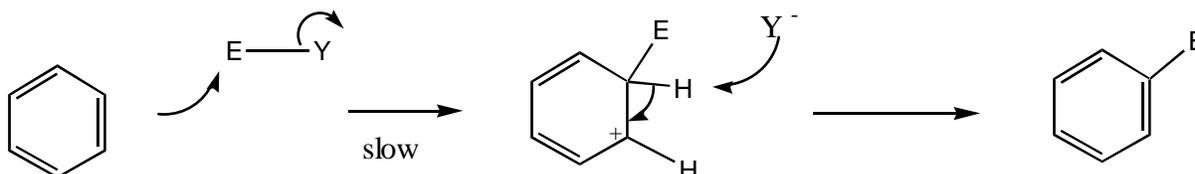


Electrophillic Aromatic Substitution Chapter 18

- As we look at the aromatic ring we see that it is full of double bonds; it is electron rich and will probably be nucleophilic. It should react with electrophiles. Review reactions of alkenes
- Aromatic rings are especially stable. It will be difficult to remove the aromaticity.
- They will react with only especially strong electrophiles. Will not react the same way as alkenes.

Electrophillic Aromatic Substitution follows the same general mechanism although there are many different reactions.

General Electrophillic Aromatic Substitution Mechanism

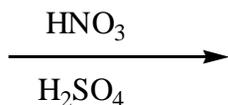


Note the following things:

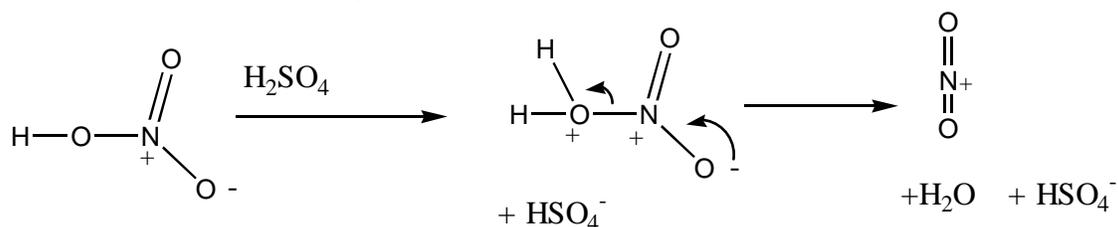
1. The E is a general electrophile and will be substituted for a H in the aromatic ring. We will learn a number of specific electrophiles next.
2. The first step is a slow step or the rate determining step.
3. The carbocation is a reactive intermediate
4. The re-aromatization is the fast step.

Nitrating the ring:

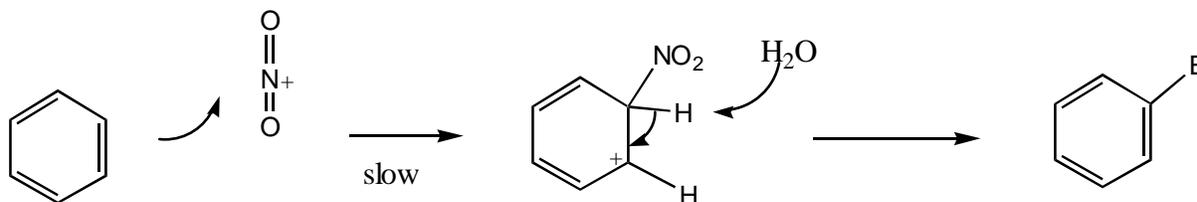
1. The reagents



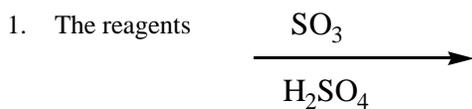
2. Formation of the "hot electrophile"



3. The mechanism:

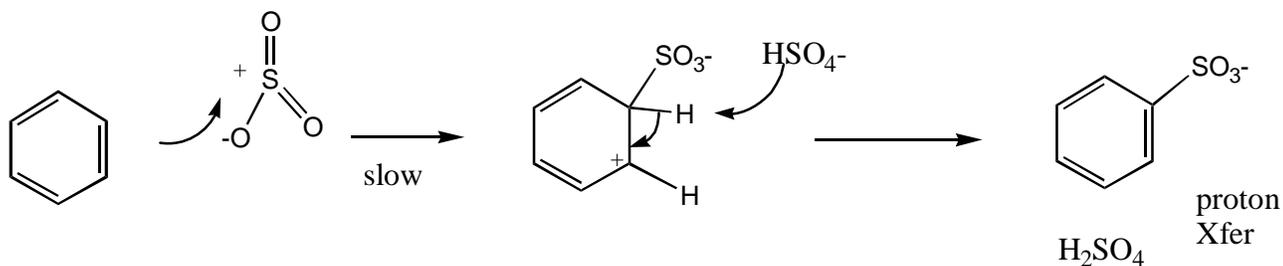


Sulfonation



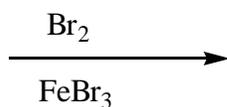
2. Formation of the "hot electrophile" : (SO_3 is already hot)

3.

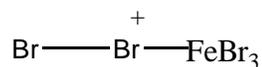


Bromination (and chlorination)

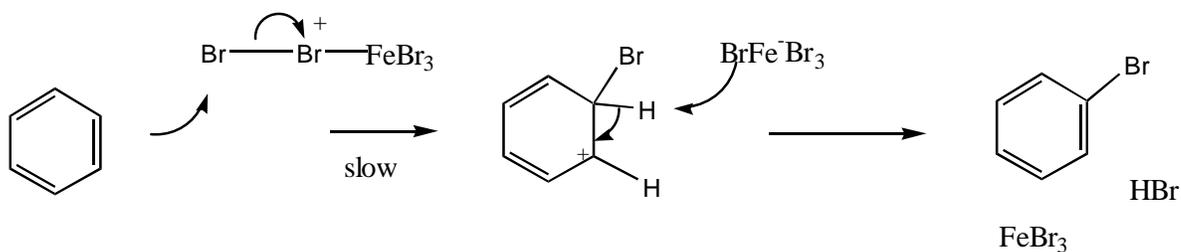
1. F too fast, I too slow ($\text{I}_2/\text{Cu}^{2+}$ works for I)
2. The reagents



3. Formation of the "hot electrophile"

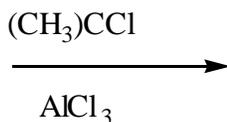


4. mechanism

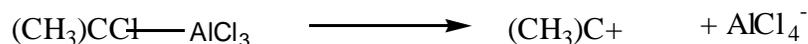


Friedel Crafts Alkylation

1. Similar to bromination
2. No electron withdrawing groups allowed on ring
3. Difficult to stop at mono alkylation
4. rearrangements of alkyl group can occur so be careful with primary alkyl halides
5. Reagents: alkyl only

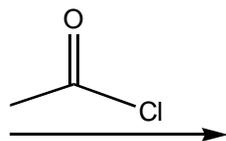


6. Formation of the "hot electrophile"

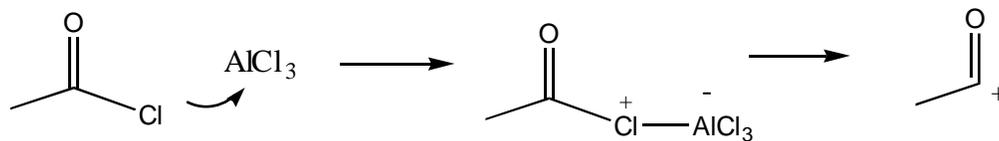


Freidal Crafts Acylation

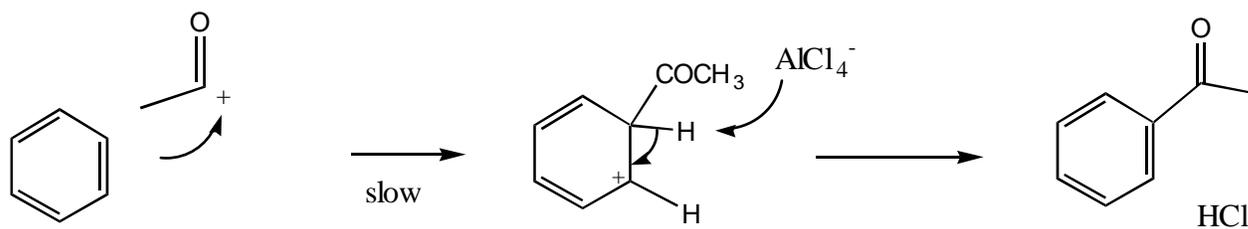
1. No rearrangements
2. Stops at 1 reaction.
3. Reagents:



4. Formation of "Hot electrophile"



5. Reaction



Substituent effects.

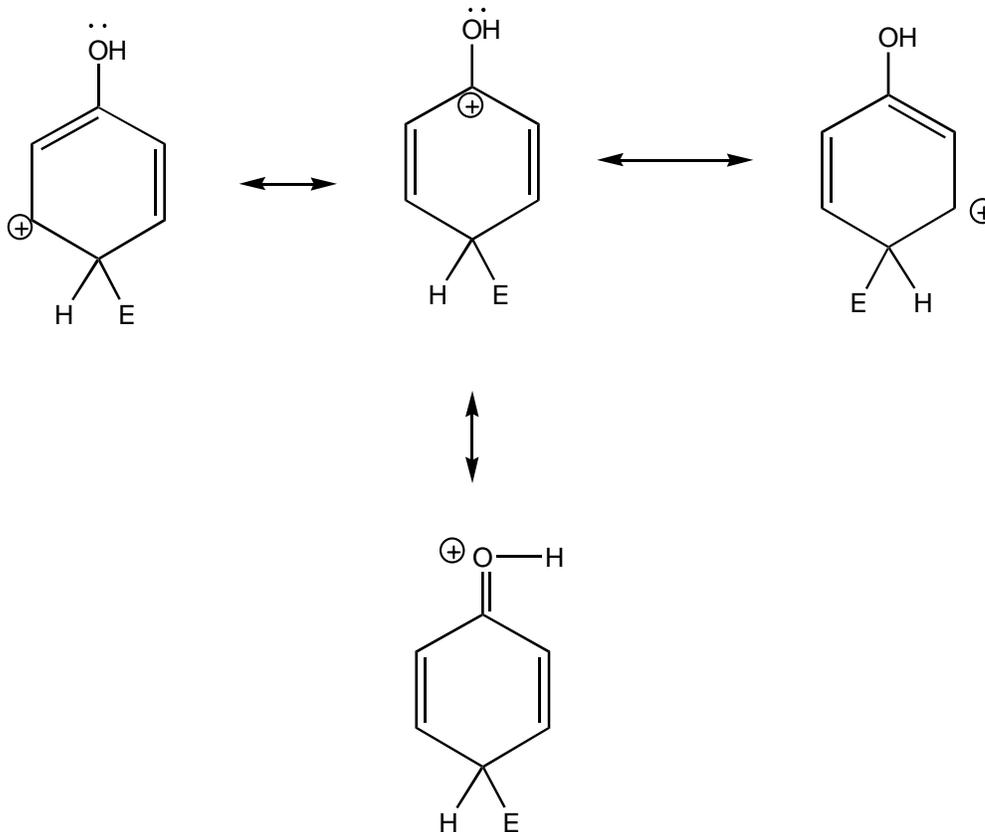
Substituents can be electron donating/Electron Withdrawing

There are two kinds of effects, pi(resonance effect) and sigma (inductive effect) networks.

Activating groups/ o,p directors!!

-NH₂, -OH, -OR, -NR₂

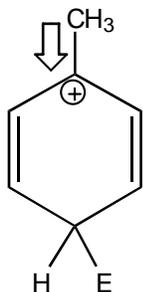
These are all groups with lone pairs next to the ring. They can stabilize the reactive intermediate with an extra resonance structure. They can only do this when E is being added in the o or p position. If it is in the m position the + charge will not line up.



-CH₃ and other alkyl groups.

Donate electron density thru sigma bonds or through the sigma network.

Less effective than the resonance activators. No extra resonance structures

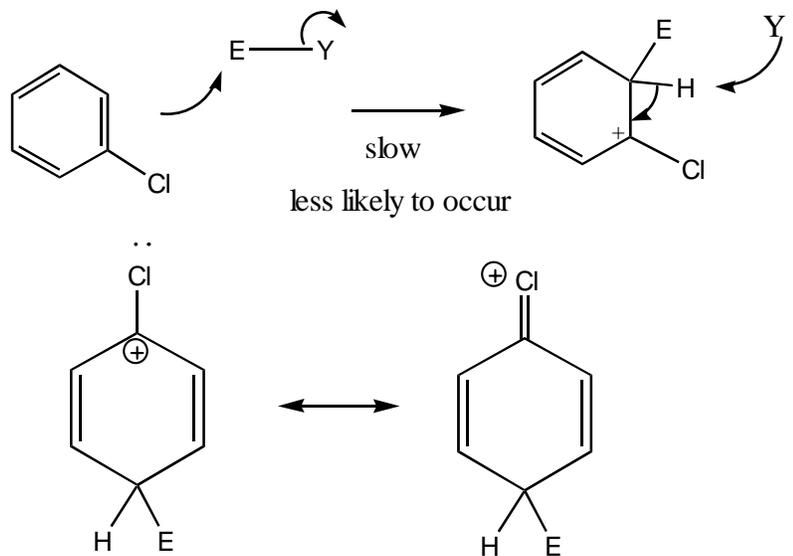


Benzene.

The halogens.

Deactivate because they withdraw electron density through the sigma network.

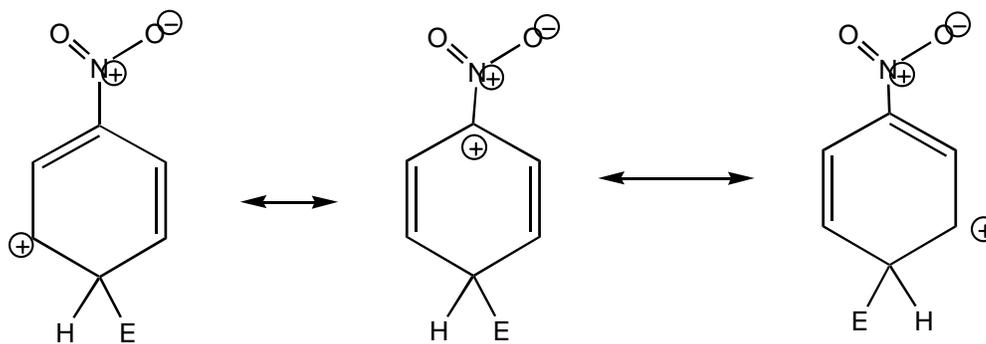
Are o,p directors because they can resonance stabilize.



Deactivators and metadirectors

The whole ring is deactivated by the electron withdrawing nature of the substituent.

The o, and p positions are deactivated even worse by the positive charge next to the ring so if a reaction occurs it will occur in the meta position.



Others in this group are -CN, -CHO and other carbonyls such as acids and esters,

The worst of this group of meta deactivators is -NR₃⁺ which is different mostly in the fact that it has a complete + charge and it is not on a p orbital so there are no resonance effects.

Adding a third substituent:

1. If the first two support each other than it is all good but..
2. If the two are not in support of each other than the more activating group overcomes. (usually)
3. Sterics can play a role

Other reactions

