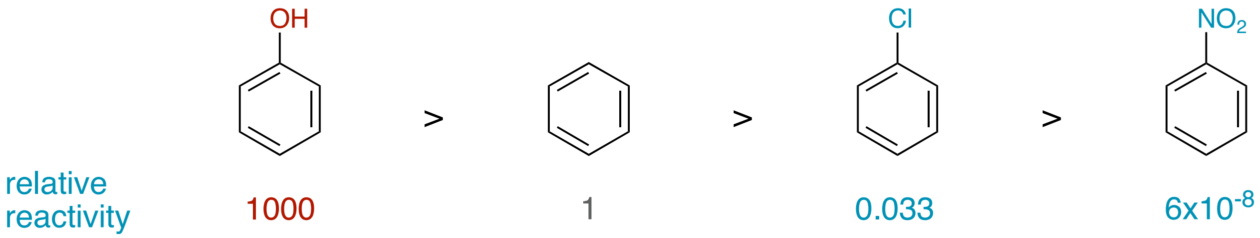
Chem 342

Lecture Summary 12
February 11, 2004

Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

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).



Electron Donating Groups will direct additions to occur in the Ortho and Para positions, while Electron Withdrawing Groups direct additions to the Meta position. The exception is the halogens, which are deactivating, but are ortho-para directors. Resonance effects are largely responsible for this, however there are some cases where it is an inductive effect. In the resonance structures of the carbocation intermediate, those that place the plus charge next to an EDG are especially stable and if it is next to an EWG, it is especially destabilized.

Electron Donating Groups

alkyl —OR —NR_2

—SR

ortho-para directors

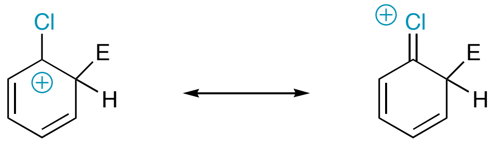
Electron Withdrawing Groups

acyl —CN —NO_2 —SO_3H

meta directors

—X ortho-para director

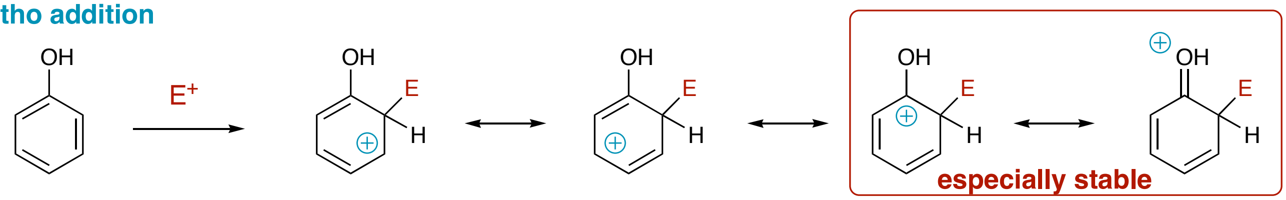
Chlorine is the oddball - it is deactivating (electron withdrawing), but due to resonance effects, is an ortho-para director.



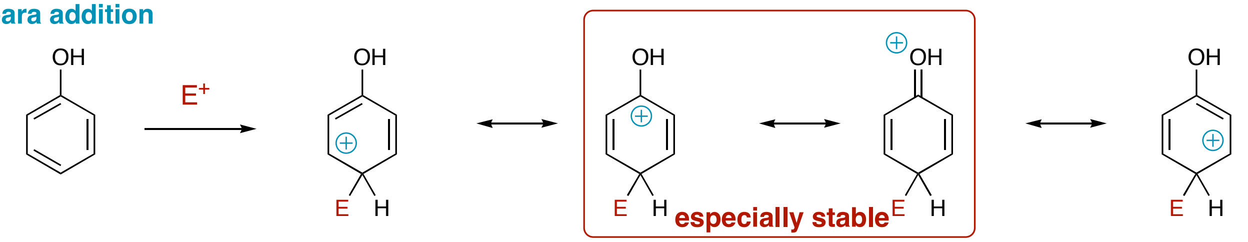
halogens, while inductively electron withdrawing groups, they can stabilze plus charge through resonance. Thus, they are an exception and are ortho-para directors

Activating Groups

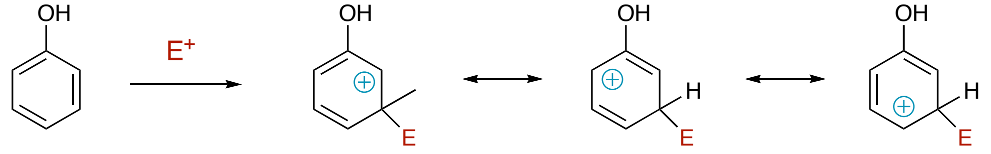
ortho addition



para addition



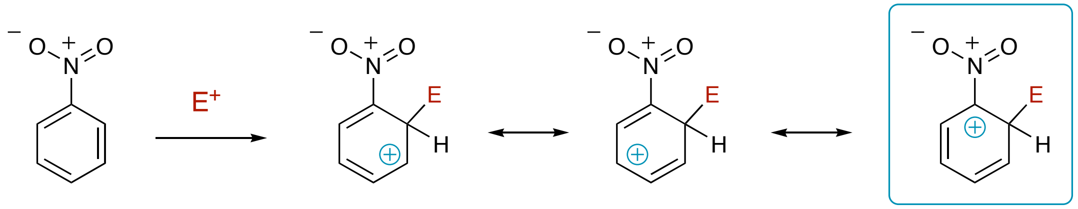
meta addition



none especially stable

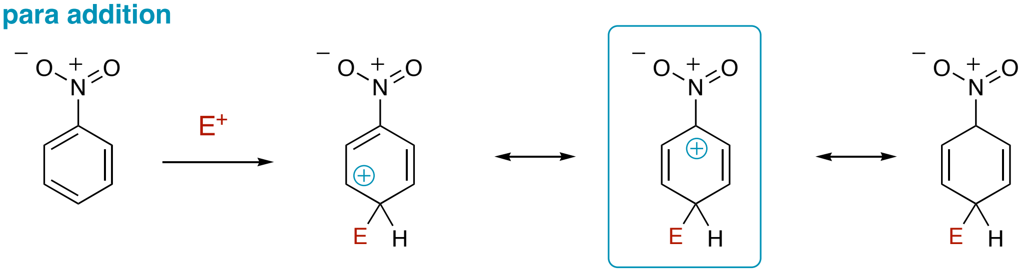
Deactivating Groups

ortho addition



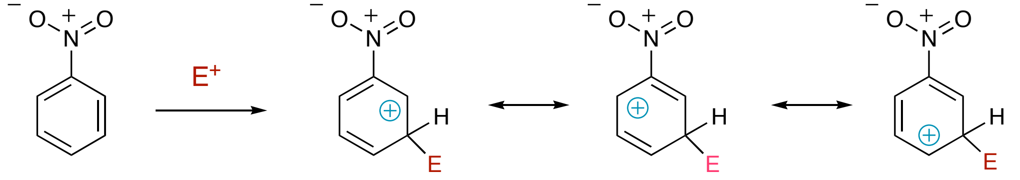
especially UNstable

para addition



especially UNstable

meta addition



none especially UNstable
the lesser of the evils