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

Chapter 16: Chemistry of Benzene: Electrophilic Aromatic Substitution

Substituent Effects

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

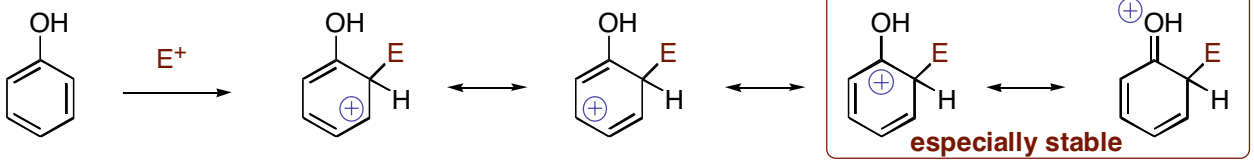
Electron Withdrawing Groups

acyl —CN —NO_2 —SO_3H

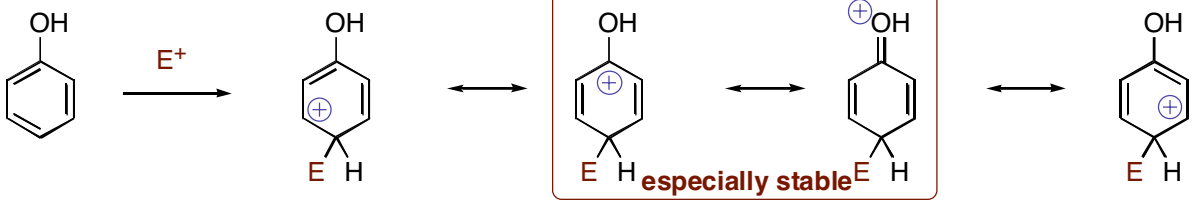
meta directors

—X ortho-para director

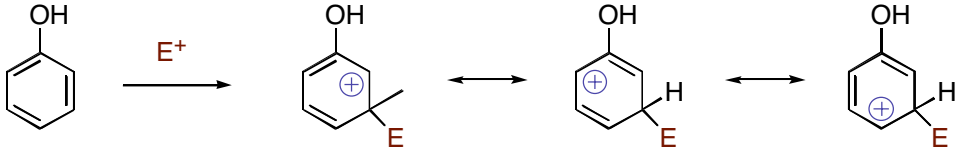
ortho addition



para addition

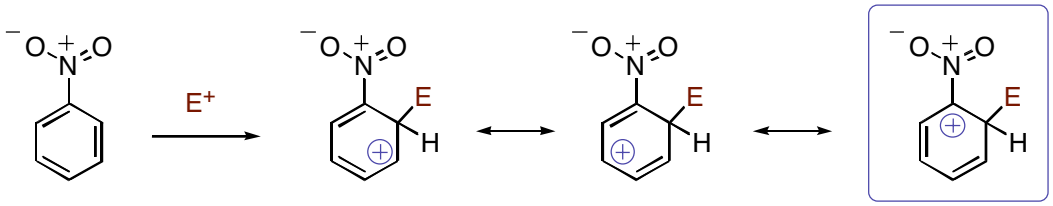


meta addition



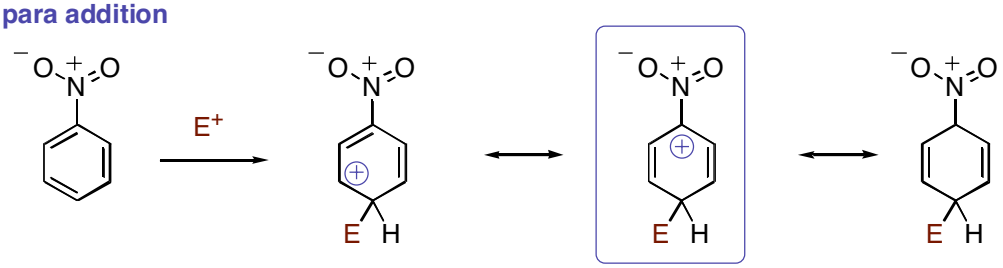
none especially stable

ortho addition



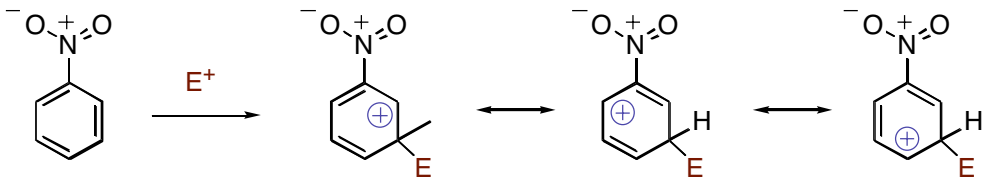
especially UNstable

para addition

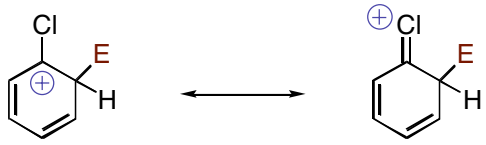


especially UNstable

meta addition



none especially UNstable



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

More than one Substituent

If more than one substituent is present on a benzene ring, they may work together or may be opposing each other for directing electrophilic addition.

Electron Donating Groups win against Electron Withdrawing Groups

Resonance Effects are Stronger than Inductive Effects.