



Chem 342 • Organic Chemistry II

Lecture Summary II - 09 Feb 2009

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.


Activating Electron Donating Groups

ortho, para directors

- OR strongest (resonance)
- NR₂
- SR
- alkyl weakest (inductive)

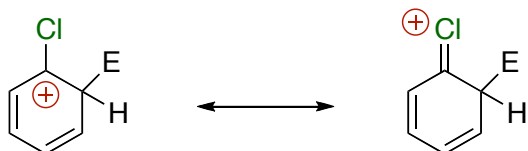
Deactivating Electron Withdrawing Groups

meta directors

- NO₂ strongest (resonance)
- SO₃H
- 
- CN

—X weak
ortho, para directors
but deactivating

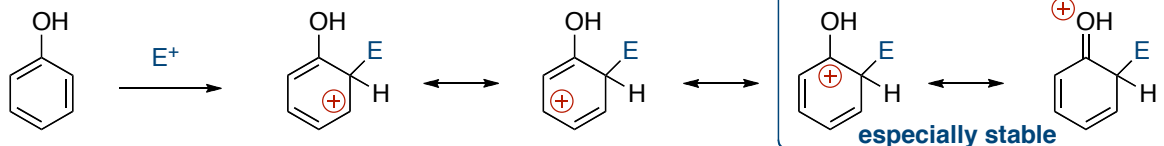
Halogens are the exception to the rule - it is deactivating (electron withdrawing), but due to resonance effects, is an ortho-para director.



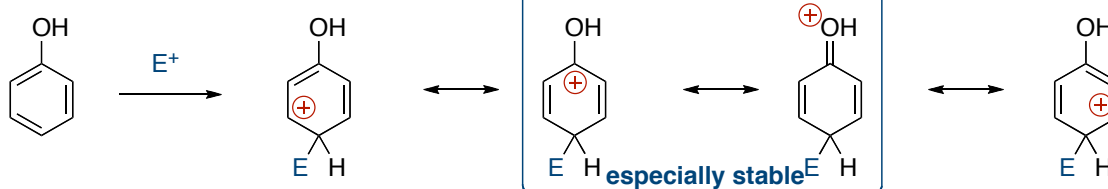
halogens, while inductively electron withdrawing groups, they can stabilize plus charge through resonance. Thus, they are an exception and are ortho-para directors

Activating Groups

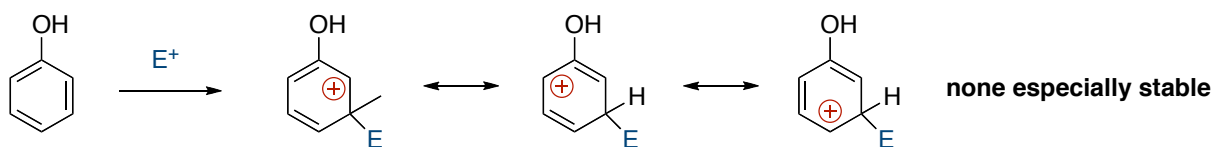
ortho addition



para addition

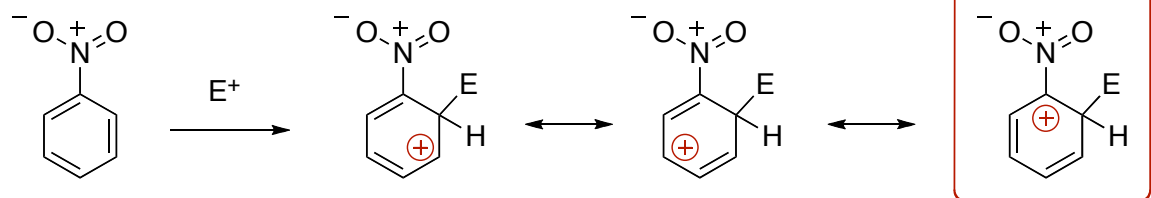


meta addition

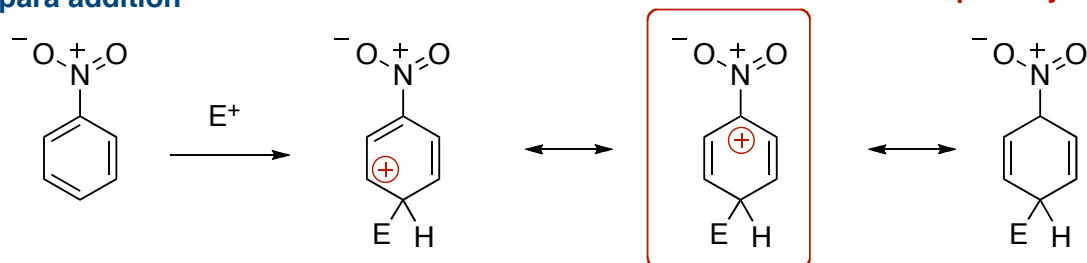


Deactivating Groups

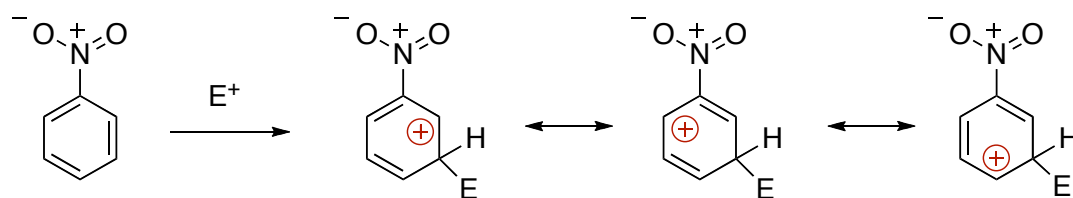
ortho addition



para addition



meta addition



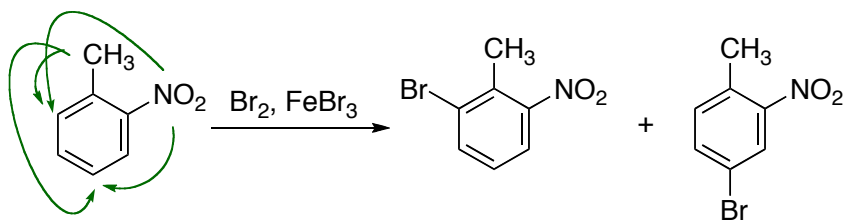
none especially UNstable
the lesser of the evils

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 (strong) usually win against Electron Withdrawing Groups. Resonance Effects are Stronger than Inductive Effects.

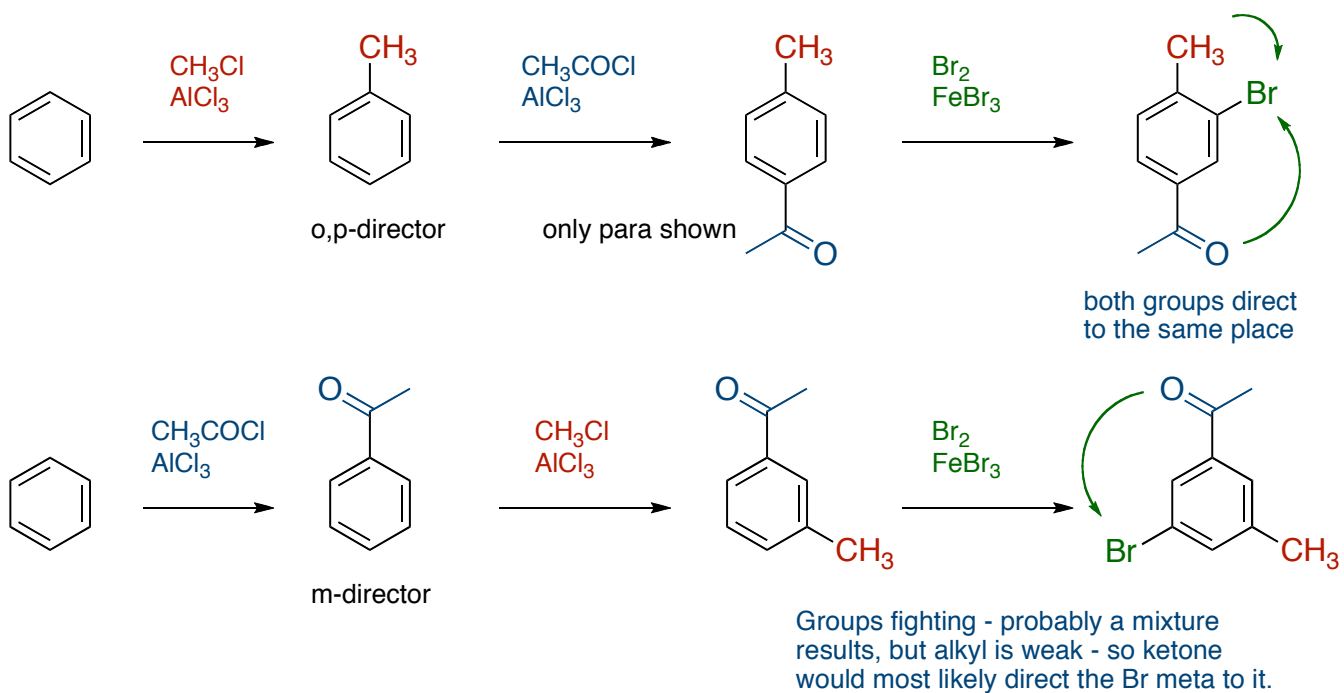


OH is the stronger director (resonance) so it will be the important director for the substitution with bromine.



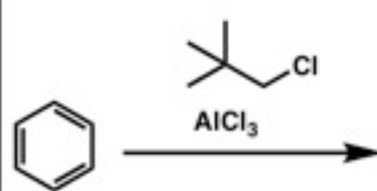
CH_3 and NO_2 are both directing to the same positions and are thus working together

Because substituents direct in different ways, the order of addition can have a large influence on the product outcome.



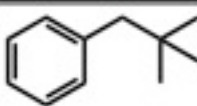
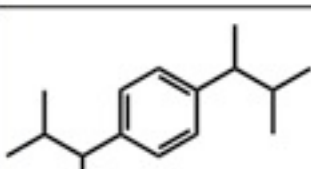
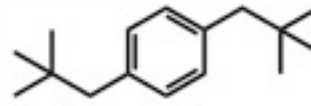
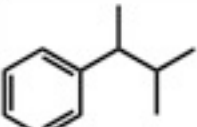
Daily Quiz

Q: What is the major product expected from the following reaction?



Reaction: Benzene + tert-butyl chloride $\xrightarrow{\text{AlCl}_3}$?

Options:

- 1: 
- 2: 
- 3: 
- 4: 

NOTE: I made a mistake on the structure of the answer. The actual major product is shown below. Full credit will be given if you answered number 2 or number 3.

