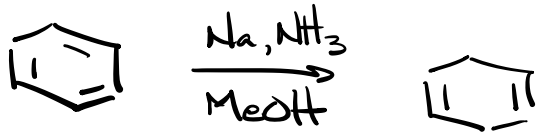
Last week - What is aromaticity

This week - Reactions of aromatic molecules

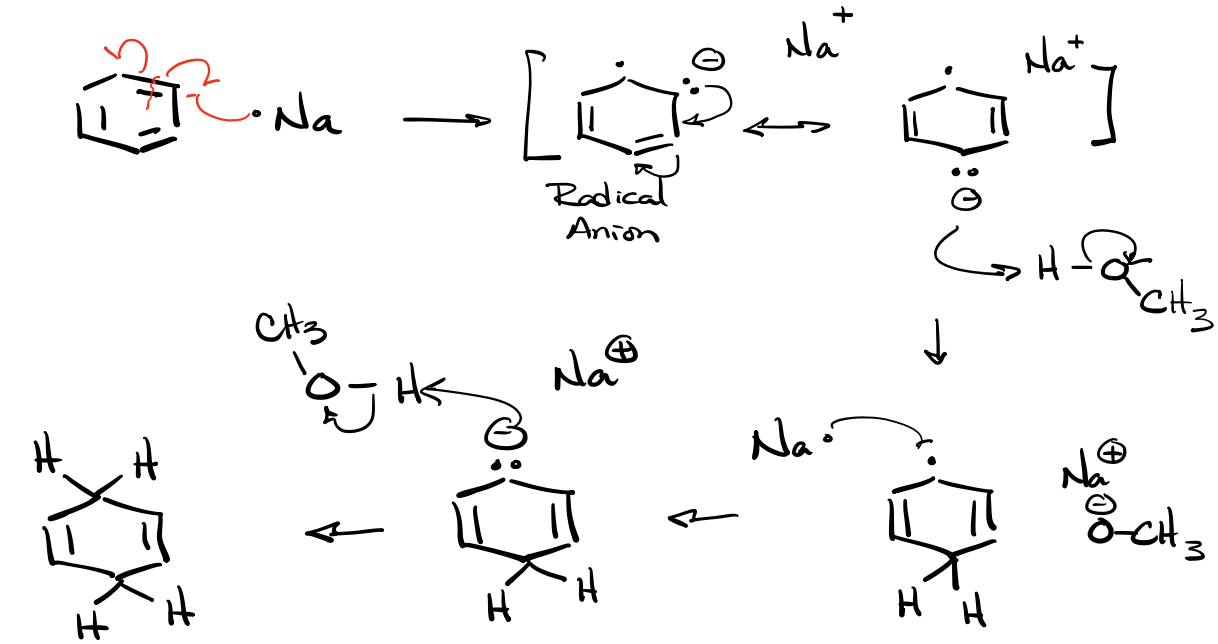
- Birch reduction
- * Electrophilic Aromatic Substitution

Birch Reduction

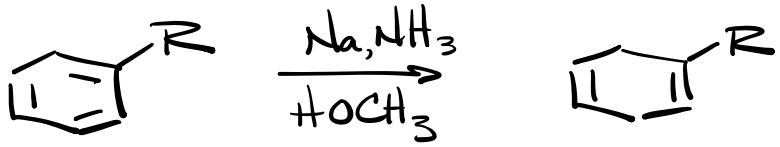


1,4 - Cyclohexadiene

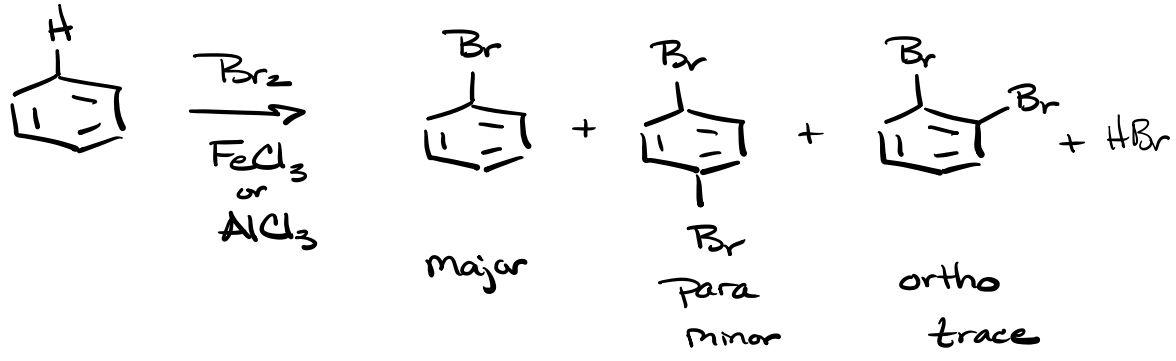
Mechanism

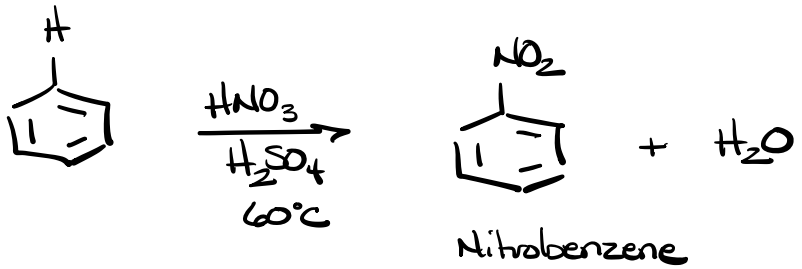


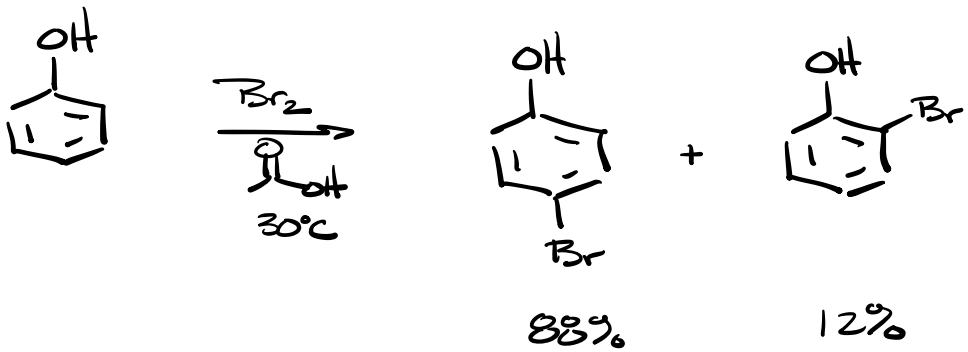
+ 2 $Na^{\oplus}\ {}^{\ominus}OMe$

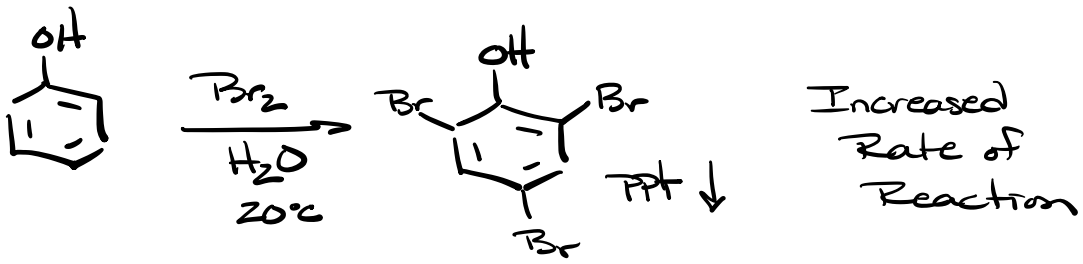


Electrophilic Aromatic Substitution

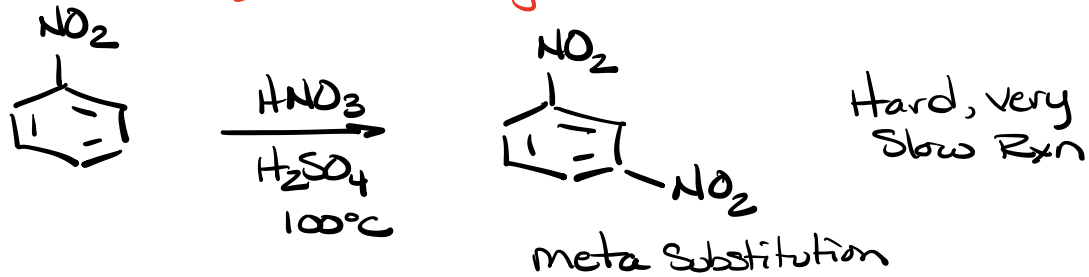


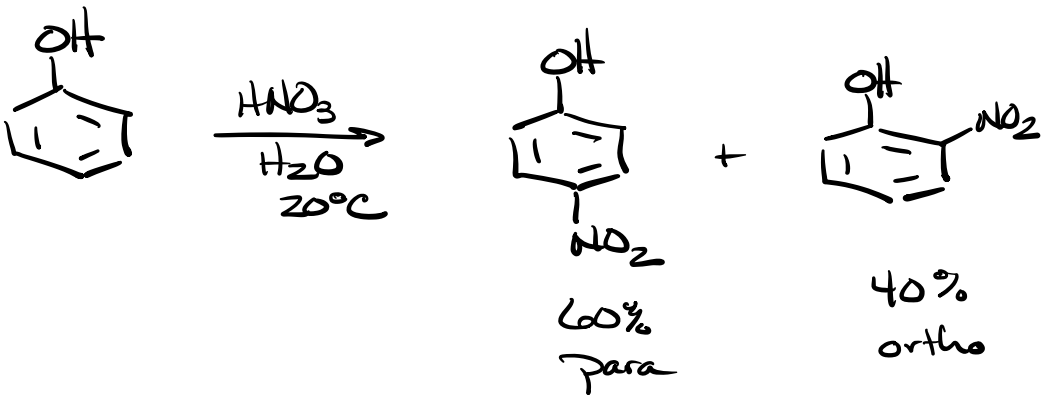






* only one showing meta substitution

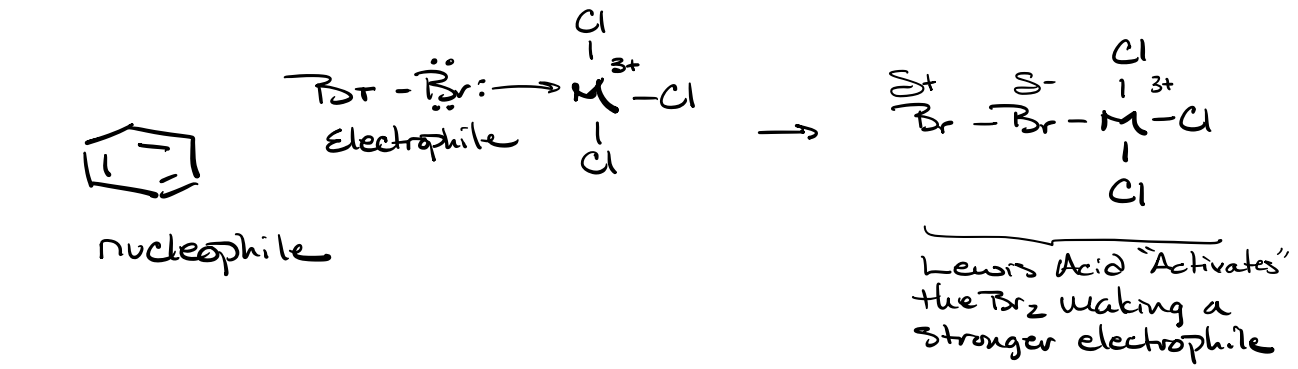


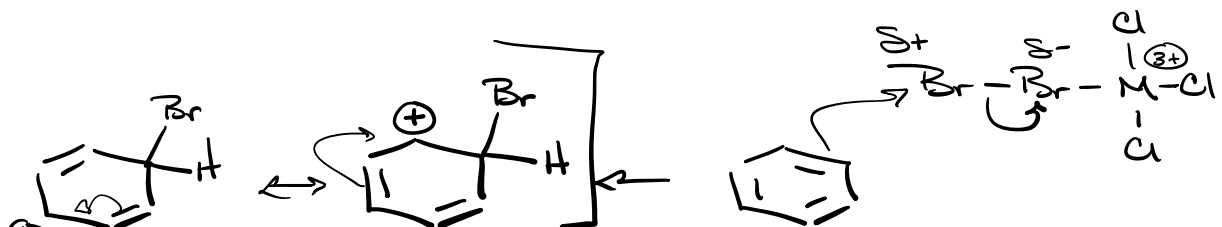


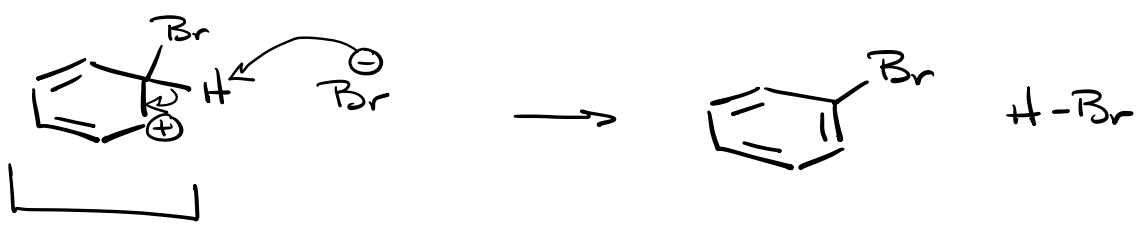
- Some groups (OH) speed Rxn up
- Some groups ($-NO_2$) Slow Rxn down
- Most disubstitutions go ortho, para
- very few disubstitutions go meta

} ?

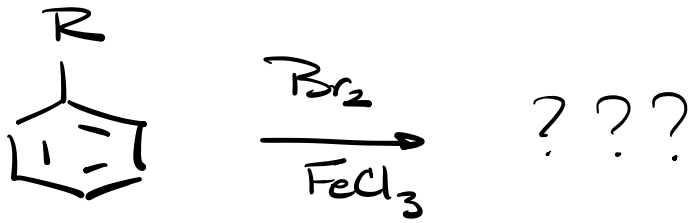
Mechanism (Electrophilic Aromatic Substitution)





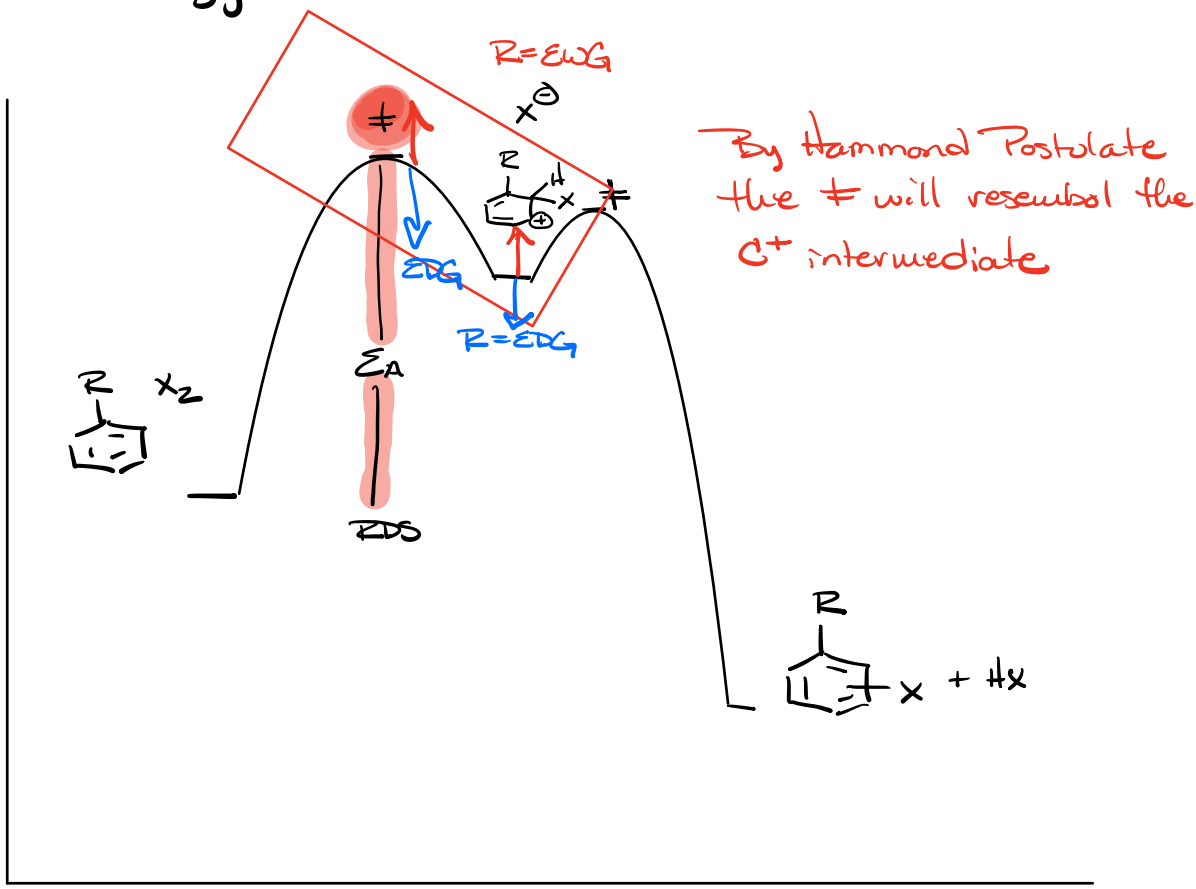


How do different substituents affect the reaction?

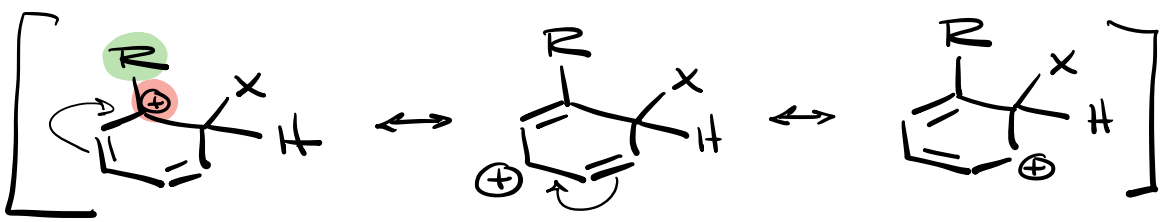


→ mechanism?

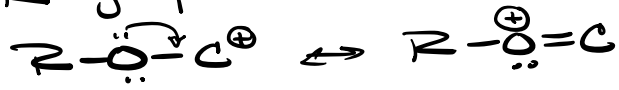
Energy Diagram for EAS Reaction



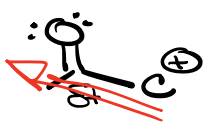
Intermediate



What sort of R-group will stabilize the $C^{\oplus}$?

R = EDG 

What sort of R-group will destabilize the $C^{\oplus}$?

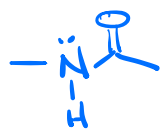
R = EWG 

Activating Groups

EDG ⇒ Speed Rxn up

(ortho, para-directors)

strongest ↑

- $-\ddot{N}R_2$
- $-\ddot{N}H_2$
- $-\ddot{O}H$
- $-\ddot{O}R$
- 
- 
- $-R$ Alkyl

- $-\ddot{C}l:$
- $-\ddot{B}r$
- $-\ddot{I}$

} mildly deactivating but o,p-directors

Deactivating Groups

EWG ⇒ Slow Rxn down

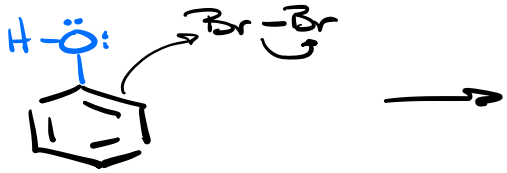
(meta-directors)

Strongest ↑

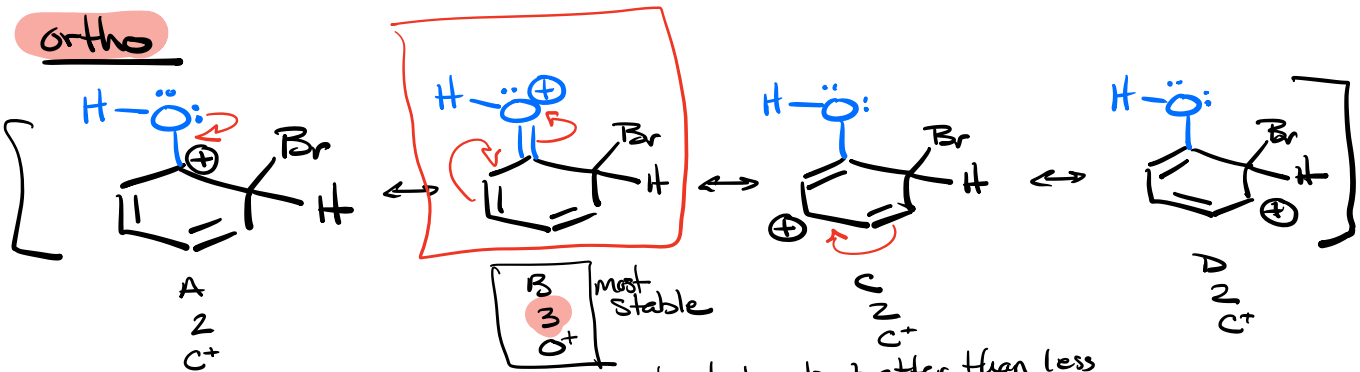
- 
- 
- $-C\equiv N:$
- 
- 
- 
- 
- 
- 

How does EDG vs EWG translate into ortho,para vs. meta director?

EDG Example – ortho, para director

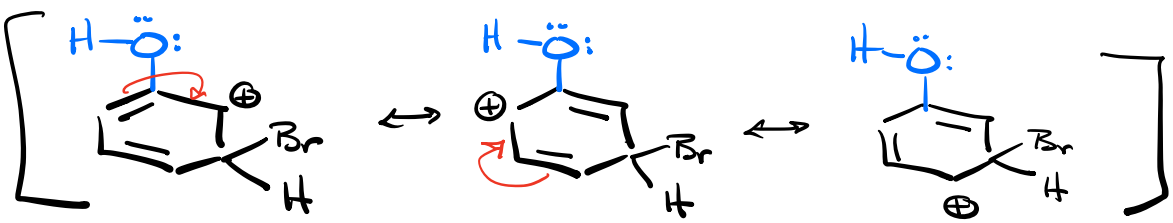


ortho



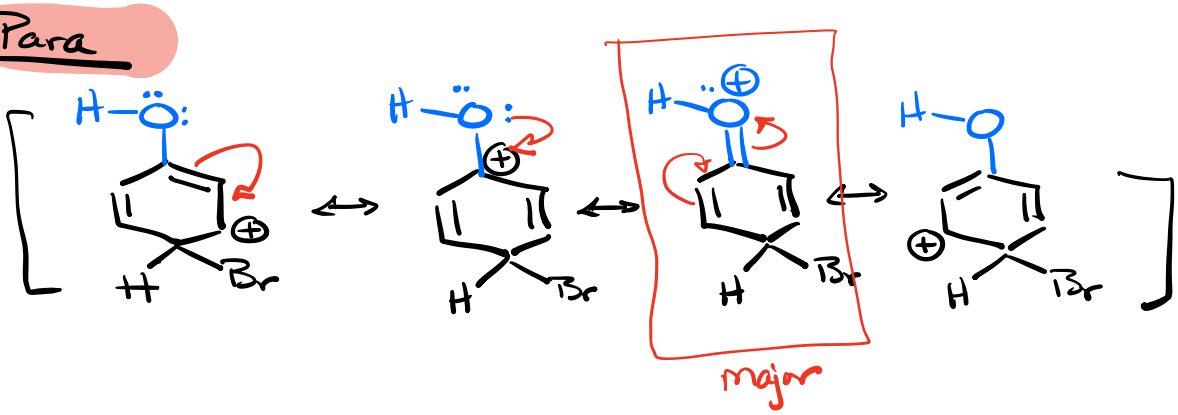
⇒ – more covalent bonds better than less
– neg charge on more EN element (or reverse)
– less seperation of charges

meta

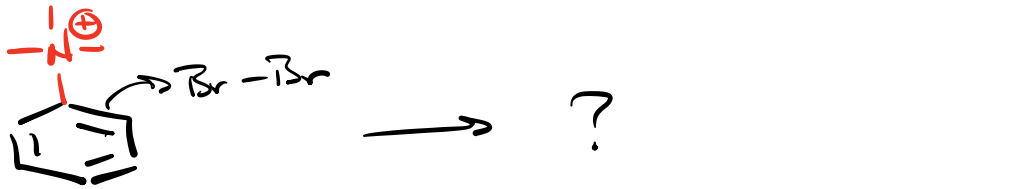


-OH actually an EWG by induction
- only 3 res

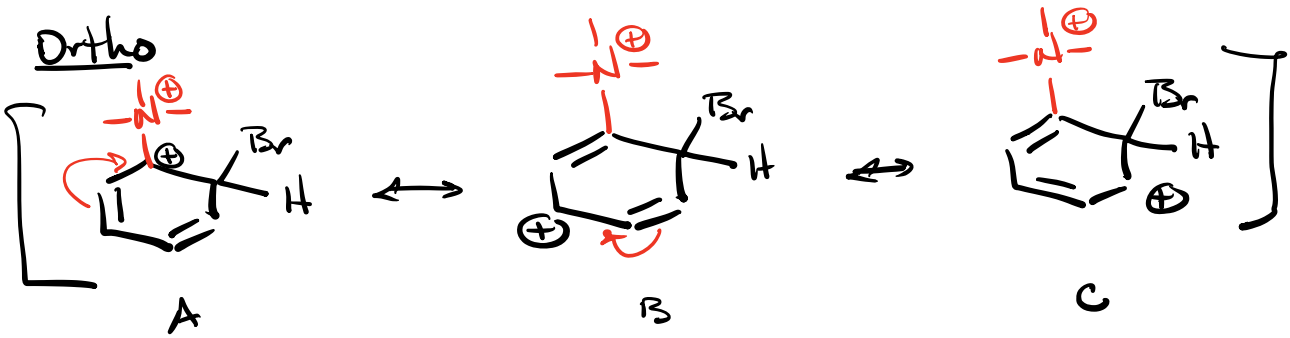
Para



EWG Example - Meta Director



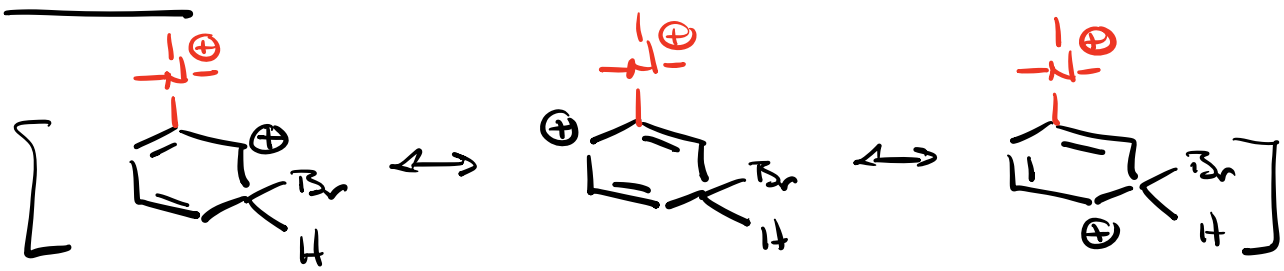
Ortho



A B C

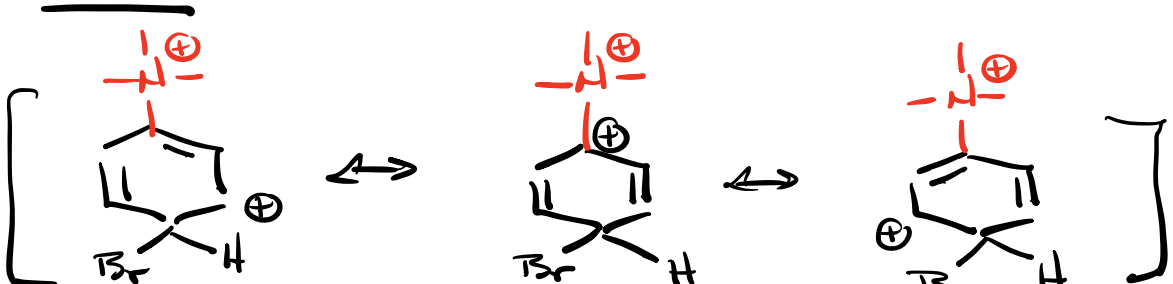
Really Bad

Meta



no Really Bad

Para



Really Bad