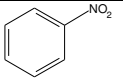
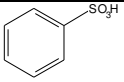
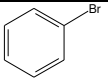
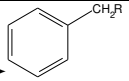
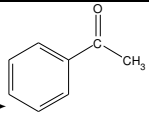
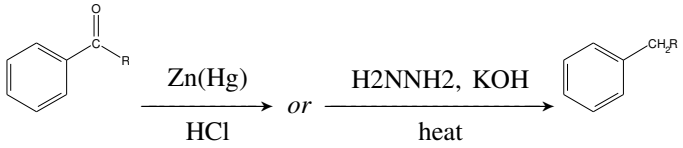
CHEM 20481 - Basic Organic Chemistry - Chapter 12 Review
Electrophilic Aromatic Substitution

Electrophilic Aromatic Substitution: Be able to show mechanisms.

Reagent	E^+	Ex.
HNO_3/H_2SO_4	$NO_2{}^+$	benzene $\xrightarrow[H_2SO_4]{HNO_3}$ 
H_2SO_4/heat or H_2SO_4/SO_3	SO_3	benzene $\xrightarrow[SO_3]{H_2SO_4}$ 
X_2/FeX_3	X^+	benzene $\xrightarrow[FeBr_3]{Br_2}$ 
$RX/AlCl_3$	R^+	benzene $\xrightarrow[AlCl_3]{RCH_2Cl}$ 
$RC(=O)X/AlCl_3$	$RC{=}O^+$	benzene $\xrightarrow[AlCl_3]{CH_3C(=O)Cl}$ 

Acyl Reduction: A reaction of a acyl side chain.



Substituent Effects: Two results to consider:

- *ortho/para*- vs. *meta*-directing substituents: Group is *ortho/para* directing if substituent is either a simple alkyl group *or* any group where <u>atom directly bonded to ring</u> contains a lone pair.
- *activating* vs. *deactivating* substituents: All *ortho/para*-directing groups are activating <u>except</u> halides and alkyl halides.

(A more complete list given in text Table 12.2, p. 495)

ACTIVATING *(halogens deactivating)* **DEACTIVATING**

$-NR_2$ -OR -R -H -X -C(=O)R $-C{\equiv}N$ $-SO_3H$ $-NO_2$

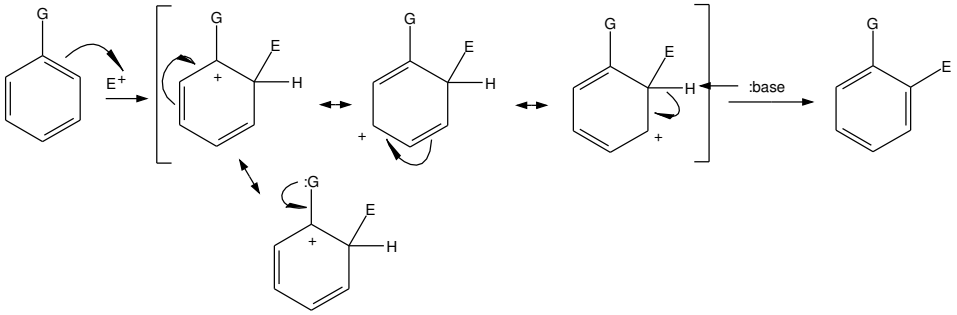
***ortho/para*-directing** *(halogens ortho/para-directors)* ***meta*-directing**

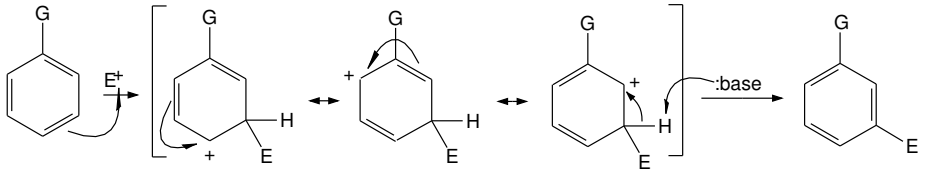
Reaction Order: The order of reaction steps matters in multistep syntheses.

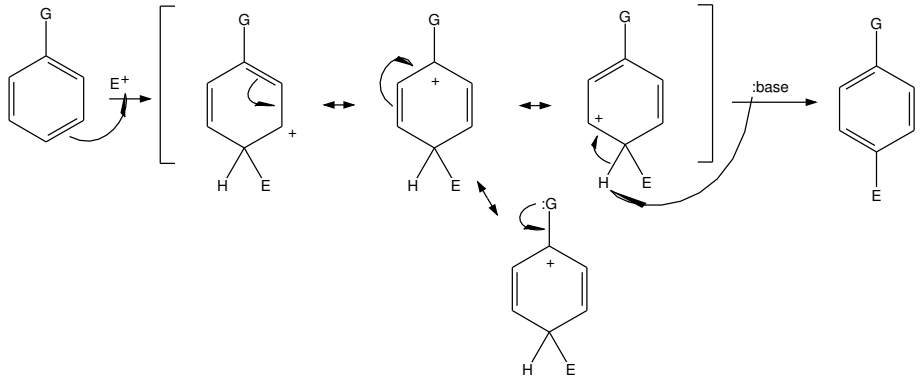
Ex: benzene $\xrightarrow[H_2SO_4]{HNO_3}$ $\xrightarrow[FeBr_3]{Br_2}$ *meta*-substituted product

benzene $\xrightarrow[FeBr_3]{Br_2}$ $\xrightarrow[H_2SO_4]{HNO_3}$ *ortho,para*-substituted products

Mechanisms







Note that both ortho- and para-addition result in the carbocation being delocalized onto the same carbon atoms. Meta-addition places this charge on the other three carbon atoms in the ring.