

# CHEM 222 section 01

## LECTURE #20

Thurs., Nov.08, 2007

### Lecture topics & readings

#### Today's class

- rxns of substituted benzenes: Ch. 15...

#### Before next class

- **master electrophilic substitution mechanism for benzenes with pre-existing substituents**  
(including resonance structures for sigma complex)
- master substituent effects: ortho-para vs. meta directing activators vs. deactivators

#### Next class

- finish Ch.15 & start carbonyl compounds (Ch.16)

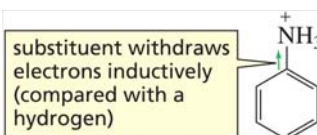
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### Ch.15 Adding additional substituents onto substituted benzenes

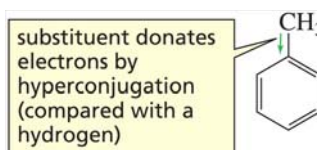
*Some substituents activate the ring, others deactivate it*

#### Important effects to consider:

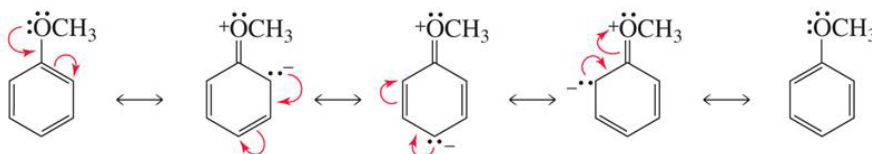
1. Inductive electron withdrawal



2. Inductive electron donation (= hyperconjugation)

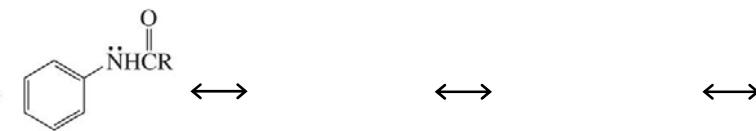


3. Resonance electron donation & withdrawal = **MOST IMPORTANT**



## 15.4 - 15.5: Effects on reactivity & regiochemistry

EDGs: ↑ ring's reactivity towards E<sup>+</sup>philic aromatic substitution

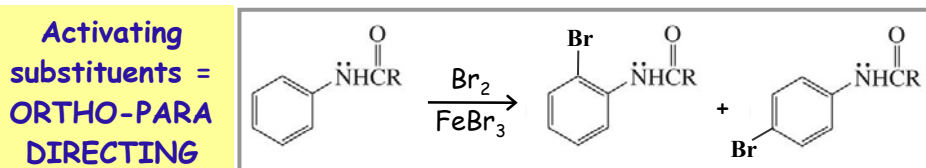


If brominating ring: to which site(s) would  $\text{Br}^+\text{Br}^-\text{FeBr}_3$  be attracted?

EDGs described as: activating & "ortho-para directing"

Which site is preferentially substituted?

- Ortho (2:1...), unless attack is sterically hindered (ring or E<sup>+</sup>)



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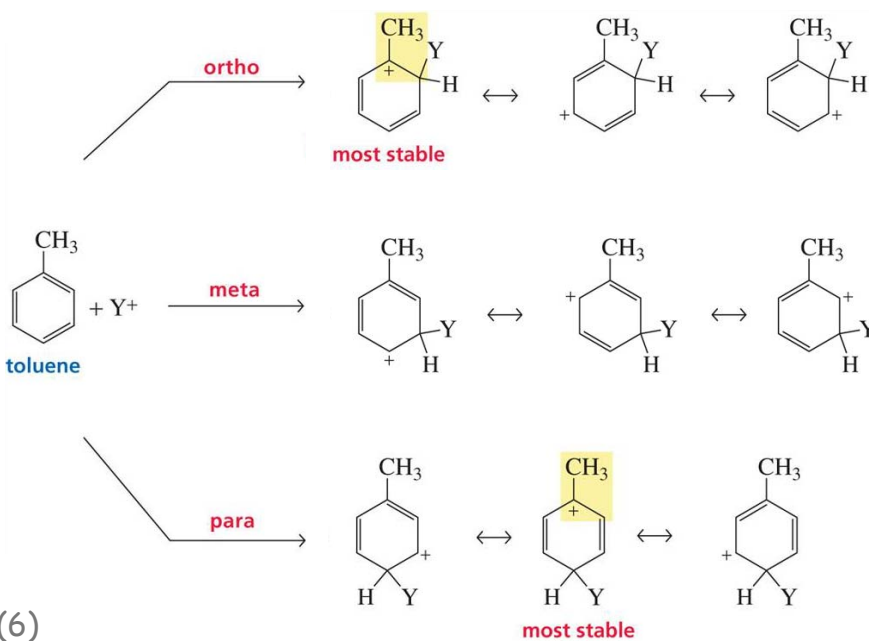
## Summary of ACTIVATING substituents

Table 15.1

Activating substituents	Most activating	
↑	-NH <sub>2</sub>	Strongly activating
	-NHR	
	-NR <sub>2</sub>	
	-OH	
	-OR	
	-NHCO-R	Moderately activating
	-O-CO-R	
	-R	Weakly activating
	-Ar	
	-CH=CHR	
	Standard of comparison →	-H

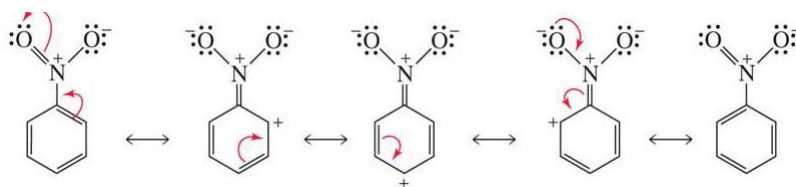
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Alkyl substituents = weak inductive e<sup>-</sup> donors (hyperconjugation)



**EWGs: ↓ ring's reactivity towards E<sup>+</sup>philic aromatic substitution**

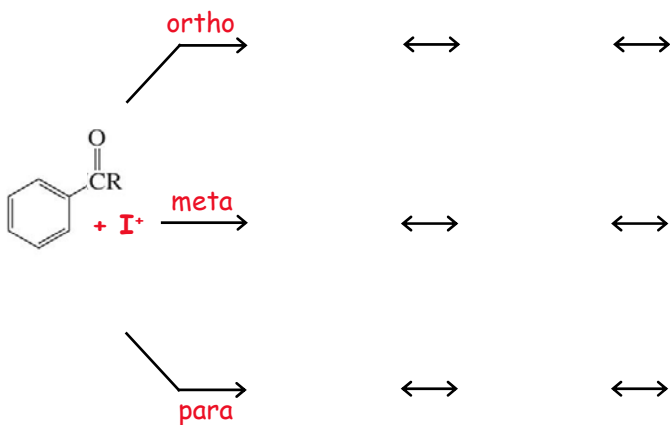
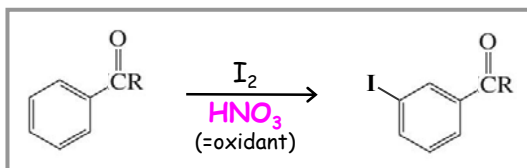
withdrawal of electrons from a benzene ring by resonance



If alkylating this ring: to which site(s) would "R<sup>+</sup>" be attracted?

**EWGs described as: deactivating & "meta directing" (usually)**

**Deactivating substituents**  
(groups that do not donate e<sup>-</sup>s via resonance)  
= **META DIRECTING**

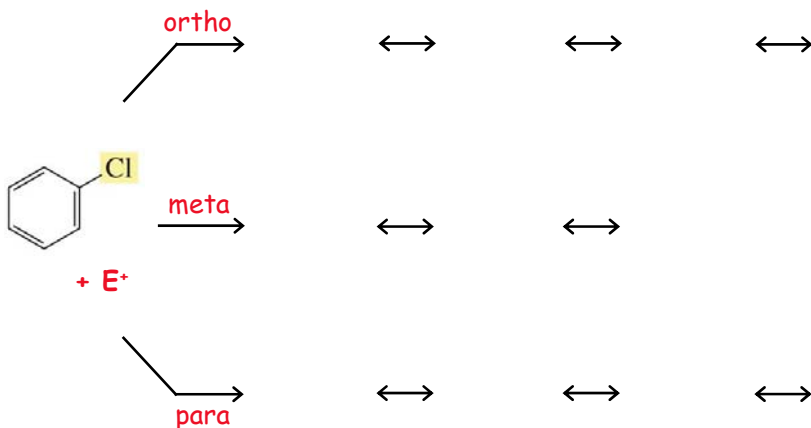


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## Summary of DEACTIVATING substituents

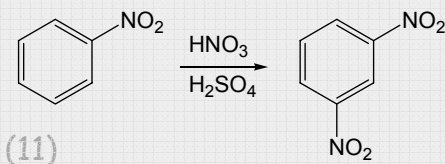
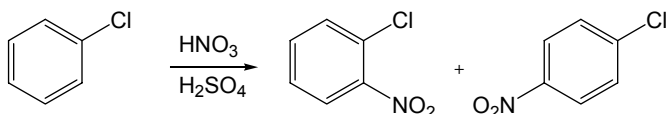
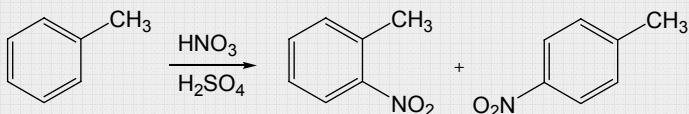
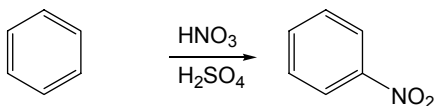
$\downarrow$ Most deactivating	-F	Weakly deactivating	Ortho/para directing
	-Cl		
	-Br		
	-I		
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CH} \end{array}$	Moderately deactivating	Meta directing
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CR} \end{array}$		
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{COR} \end{array}$		
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{COH} \end{array}$		
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CCl} \end{array}$		
	-C≡N		
	-SO <sub>3</sub> H	Strongly deactivating	
	$\begin{array}{c} + \\ -\text{NH}_3 \end{array}$		
	$\begin{array}{c} + \\ -\text{NHR}_2 \end{array}$		
	$\begin{array}{c} + \\ -\text{NR}_3 \end{array}$		
-NO <sub>2</sub>			

Halide substituents: act predominantly as EWGs (deactivators)  
**BUT are ortho-para directing**



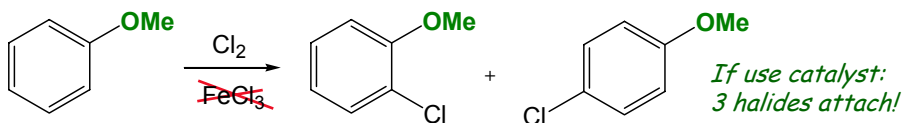
Recall: rarely see halogens engaged in  $\pi$ -bonding...

**Comment on the relative rates & the products of these rxns...**

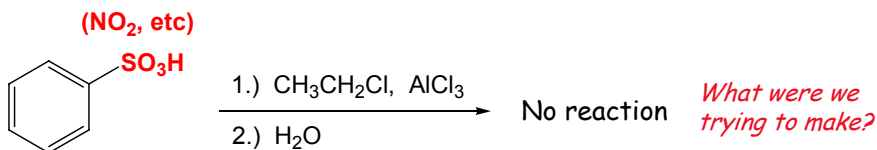


**15.6 Some practical considerations regarding substituent effects**

**Strongly activating substituents:** may not need Lewis acid catalyst...  
(or OH)



**Strongly deactivating substituents:** may make rxn of interest not go...  
▪ Friedel-Crafts acylation & alkylation = slow at the best of times



**Incompatible substituents/reaction conditions:** e.g., with  $\text{PhNH}_2$

- no Friedel-Crafts with anilines:  $\text{N} \rightarrow \text{AlCl}_3 \Rightarrow$  deactivates ring  $\Rightarrow$  no rxn
- do not try to nitrate anilines:  $1^\circ \text{R-NH}_2 + \text{HNO}_3 =$  explosive oxidation

How could the following be synthesized from benzene?

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