CHEM 222 section 01

LECTURE #19 Tues., Nov.06, 2007

Lecture topics & readings

Today's class

- rxns of benzene & its substituents: finish Ch. 14…

Before next class

- **master** the electrophilic substitution **mechanisms** (including resonance structures for sigma complex)
- **master** the **reagents** used to functionalize benzene
- practice using reagents to modify substituents

Next class

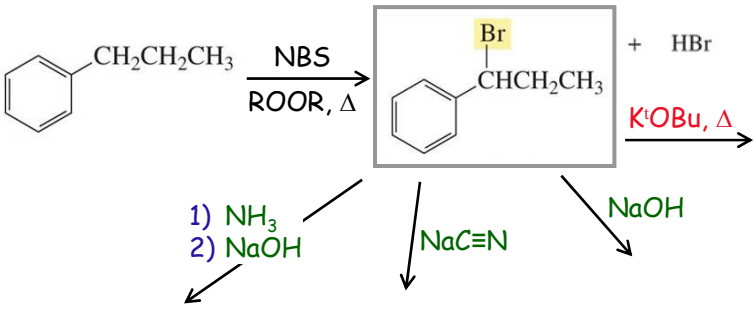
- further substitutions on substituted Ph rings (Ch.15)

14.19 Chemical modification of substituents on benzene

Standard organic rxns do not affect aromatic ring itself…

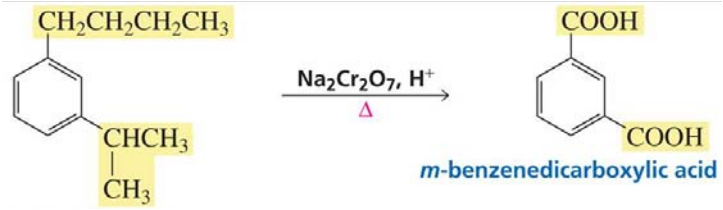
Reactions of alkyl substituents:

- **Bromination:**
  1. **Benzylic position (= allylic…):** using NBS } **Followed by:** substitution by Nu OR elimination…

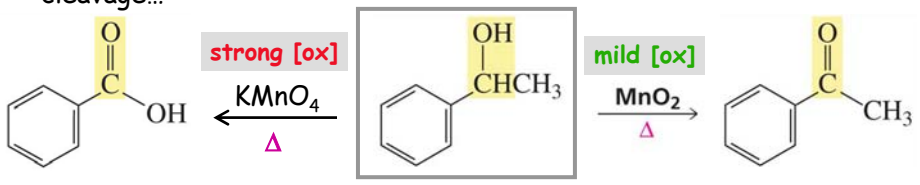


- **Oxidation of substituents:**

1. **If benzylic H present** ⇨ oxidative cleavage yields PhCOOH…
strong oxidant: $KMnO_4/\Delta$ *OR* $Na_2Cr_2O_7/H^+/\Delta$

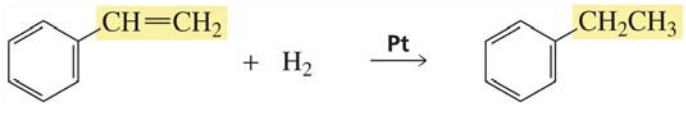


2. **If benzylic OH present** ⇨ **mild oxidant** yields ketone / aldehyde without cleavage…

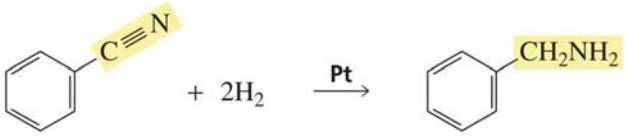


- **Reduction of multiple bonds in substituents:** catalytic hydrogenation

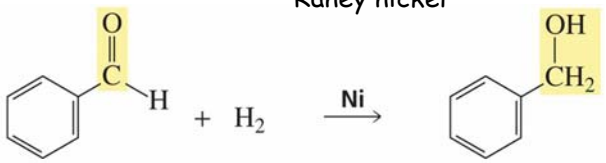
1. **Substituent = alkene, nitrile:** use H_2 & Pt(s)



More about nitriles later…



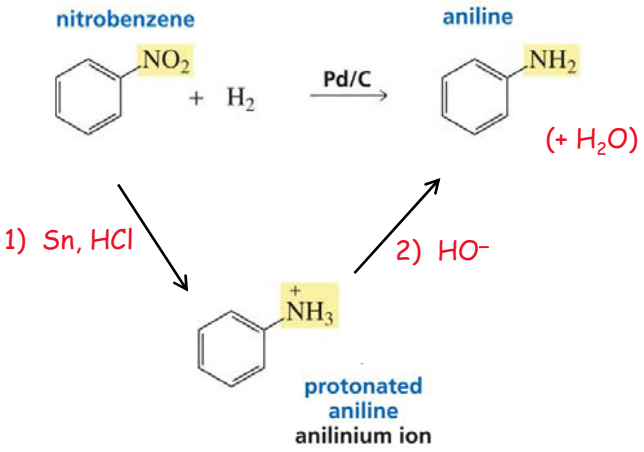
2. **Substituent = carbonyl:** use Ni powder impregnated with H_2 "Raney nickel"



To hydrogenate benzene ring: High T& P (175°C, 180atm H_2, Ni)

- **Reduction: nitrobenzenes to anilines…**

  3. Substituent = nitro: catalytic hydrogenation (H_2 + Pd on carbon)
  OR metal (Sn, Fe or Zn) with acid (HCl)

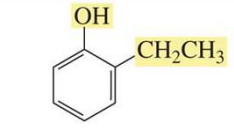


Ch.15 Adding additional substituents onto substituted benzenes

First: naming disubstituted benzenes (15.1)

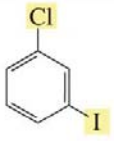
Relative substituent positions:

ORTHO



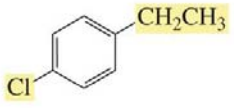
2-ethylphenol
ortho-ethylphenol
not
ortho-ethylhydroxybenzene

META



1-chloro-3-iodobenzene
meta-chloroiodobenzene
not
1-iodo-3-chlorobenzene or
meta-iodochlorobenzene

PARA



1-chloro-4-ethylbenzene
para-chloroethylbenzene

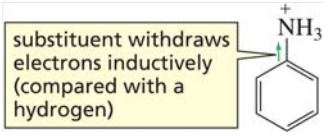
Substituents named alphabetically: but often added to common names

Ch.15 Adding additional substituents onto substituted benzenes

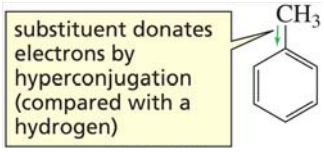
Some substituents activate the ring, others deactivate it

Important effects to consider:

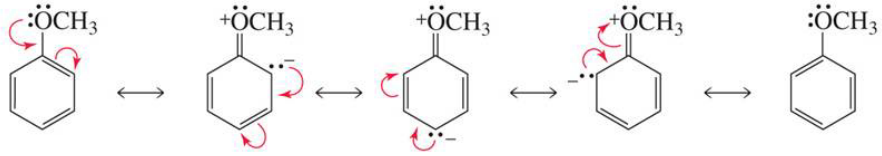
1. Inductive electron withdrawal



2. Inductive electron donation
   (= hyperconjugation)

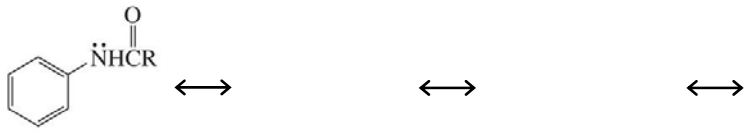


3. **Resonance electron donation & withdrawal** = **MOST IMPORTANT**



15.4 – 15.5: Effects on reactivity & regiochemistry

EDGs: ↑ ring's reactivity towards E⁺philic aromatic substitution

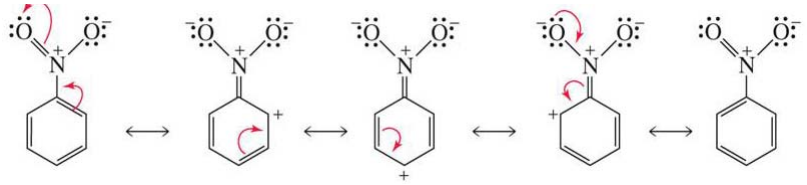


If brominating ring: to which site(s) would $Br\text{-}\overset{+}{B}r\text{-}\overset{-}{F}eBr_3$ be attracted?

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

EWGs: ↓ ring's reactivity towards E^+philic aromatic substitution

withdrawal of electrons from a benzene ring by resonance



If alkylating this ring: to which site(s) would " R^+ " be attracted?

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

Summary of ACTIVATING substituents

Table 15.1

Activating substituents	Most activating		
↑	—NH_2	Strongly activating	Ortho/para directing
	—NHR		
	—NR_2		
	—OH		
	—OR		
	—NHCR (O)	Moderately activating	
	—OCR (O)		
	—R	Weakly activating	
	—Ar		
	—CH=CHR		
Standard of comparison →	—H		

Summary of DEACTIVATING substituents