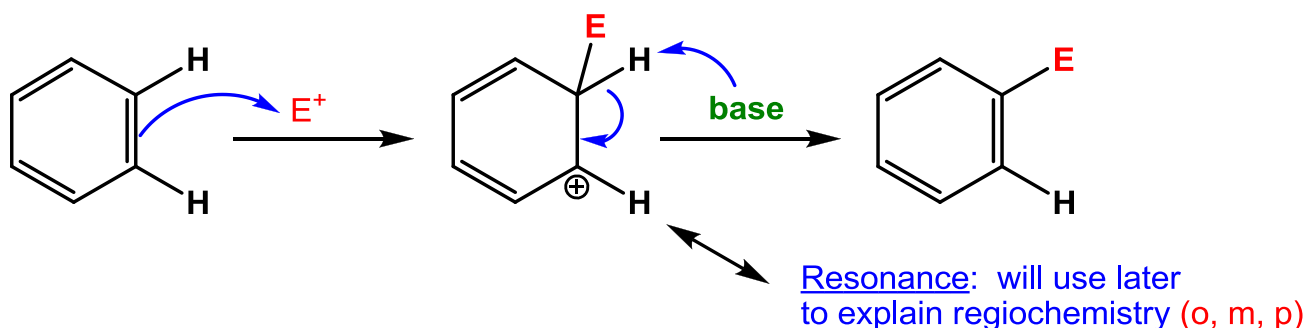


## Overheads: - Outline

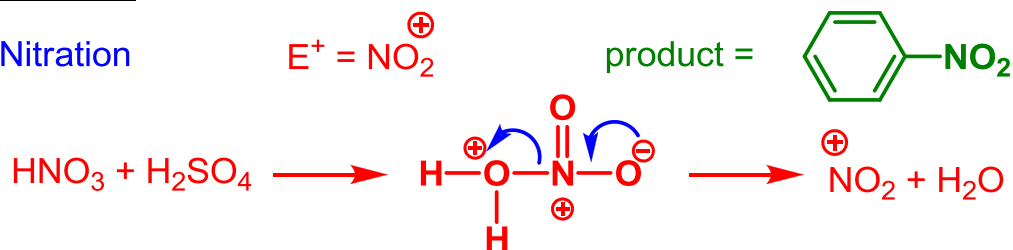
## Recap Wednesday: Reactions of Benzene

- less reactive than “normal” C=C
- need very strong  $E^+$

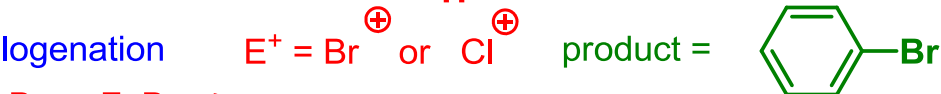
General Reaction: Called Electrophilic Aromatic Substitution  
 - replace  $H^+$  with  $E^+$

5 types of  $E^+$ :

## 1) Nitration



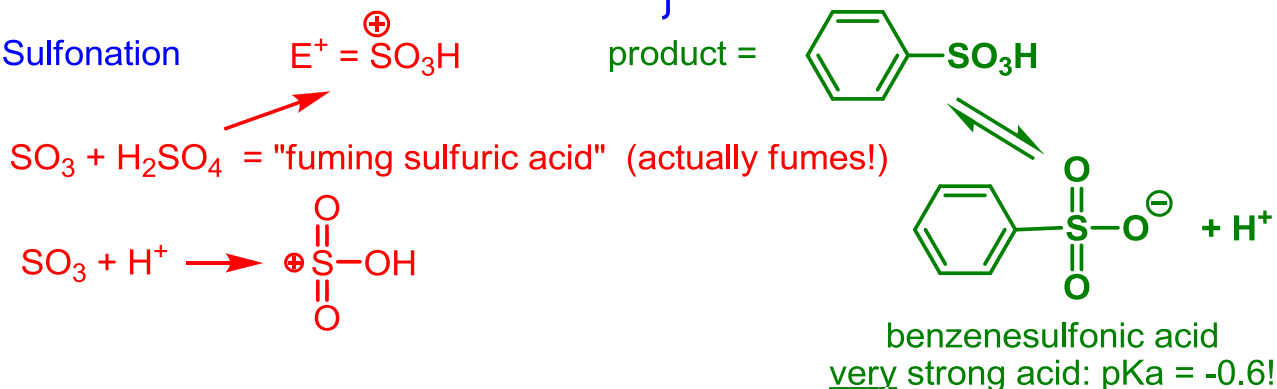
## 2) Halogenation



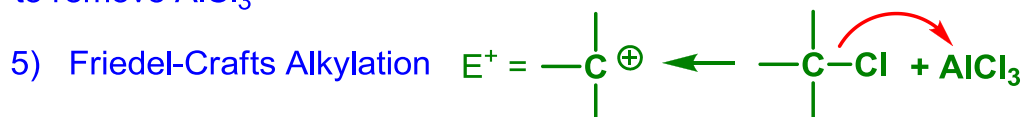
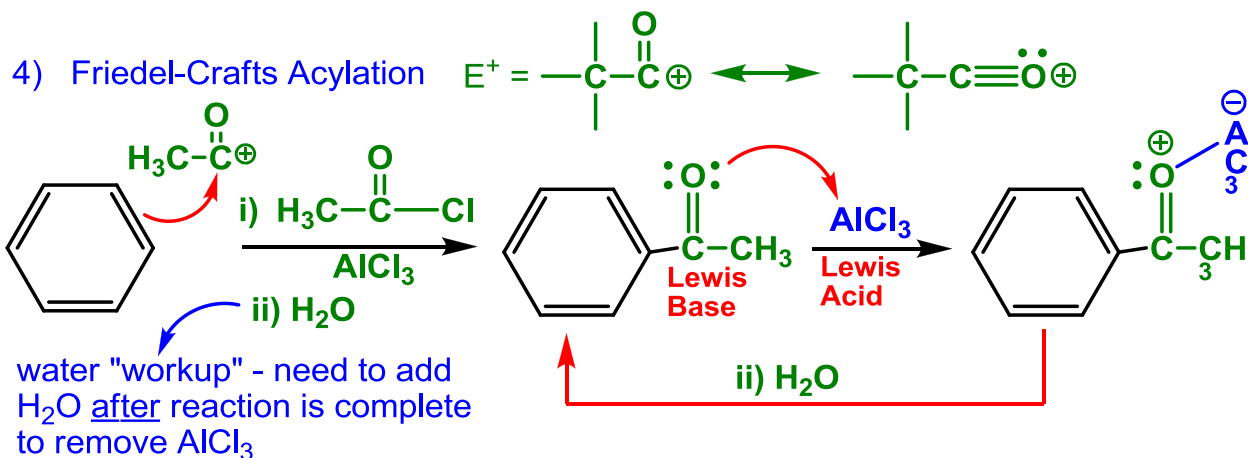
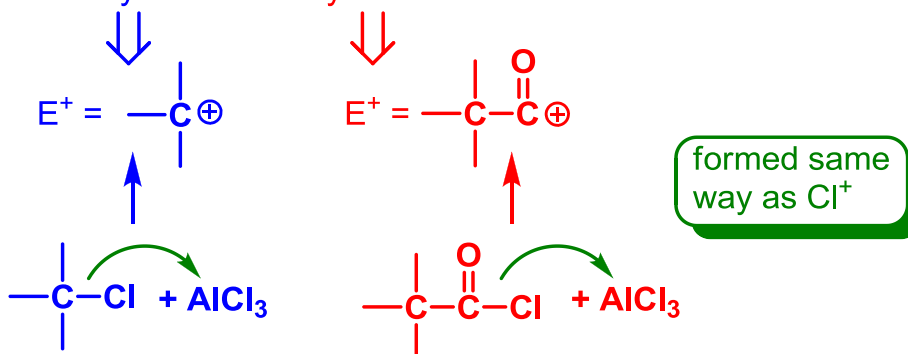
$Br_2 + FeBr_3$   
 $Cl_2 + AlCl_3$  } Don't mix Br/Cl or get mixture

NOTE:  $F^+$  too reactive  
 $I^+$  not reactive enough } Will see how to make later

## 3) Sulfonation



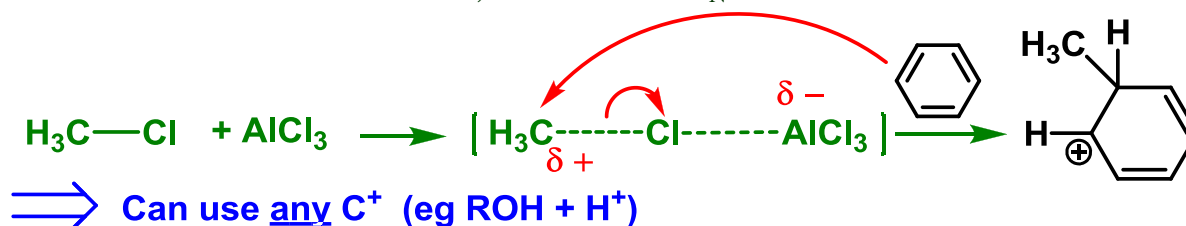
Last 2: Friedel-Crafts alkylation and acylation



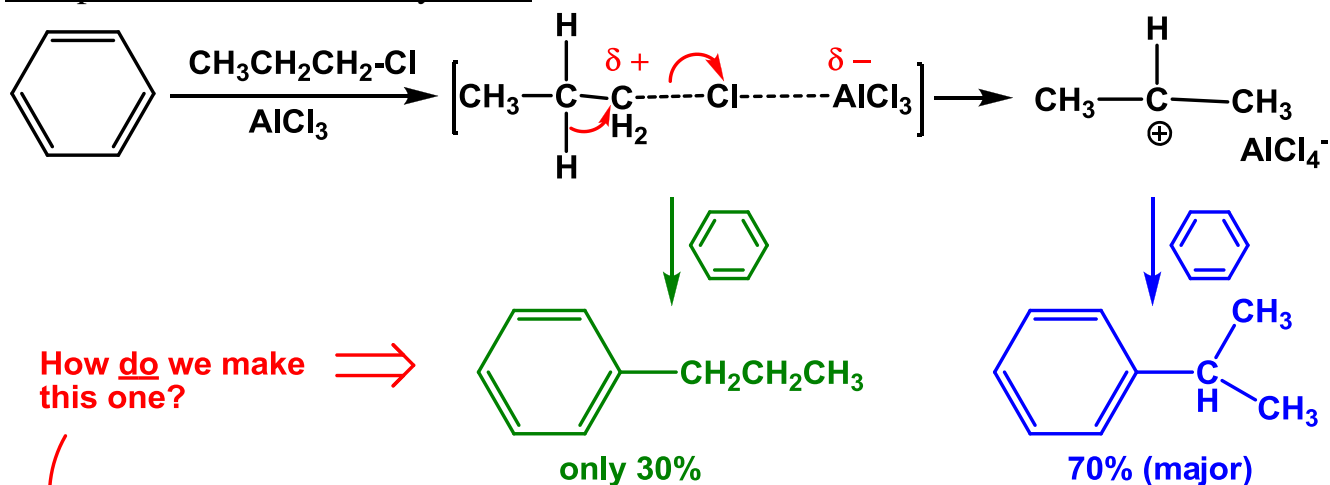
NOTE: no  $C=O$  so don't need  $H_2O$  after

More about F-C Alkylation

$\Rightarrow$  For  $1^\circ$   $R-Cl$ : Can't make  $C^+$ , so more like  $S_N2$



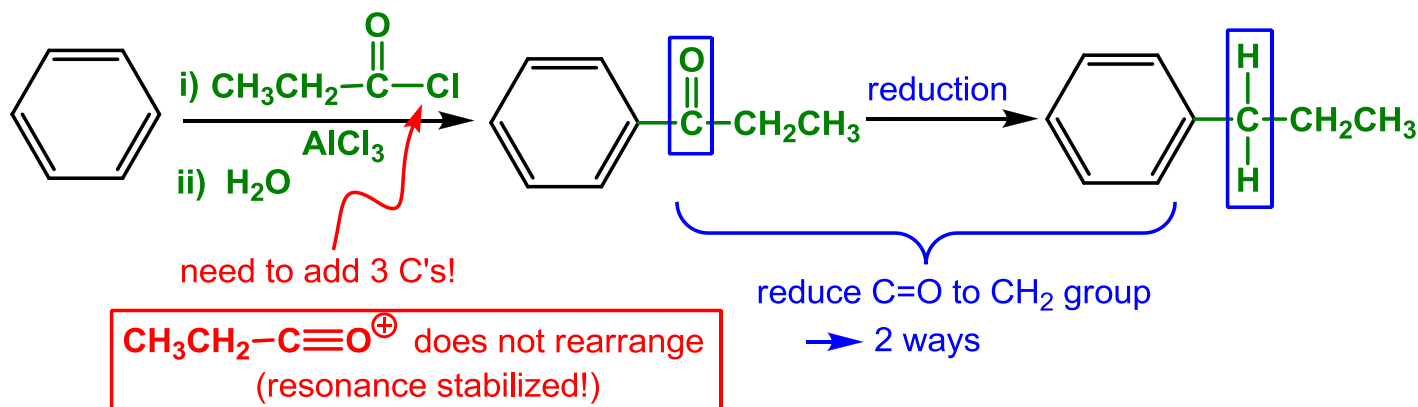
Complication with F-C Alkylation: What can  $C^+$  do?



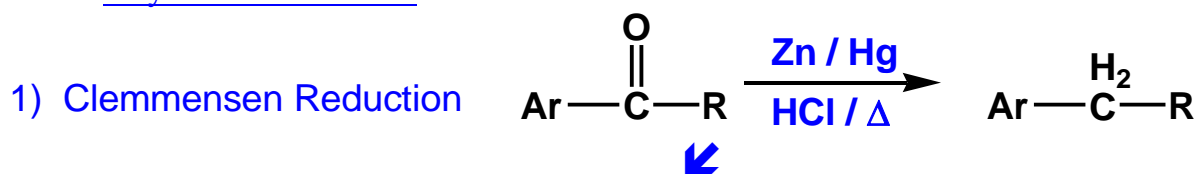
**\*\* can't introduce 1° R (> ethyl) by FC alkylation**

Do FC Acylation with correct number of C's, then remove O from C=O

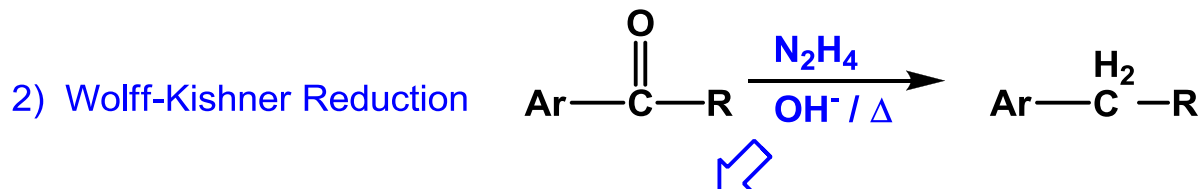
$\hookrightarrow$  including C of C=O



$\equiv$  Called Acylation-Reduction

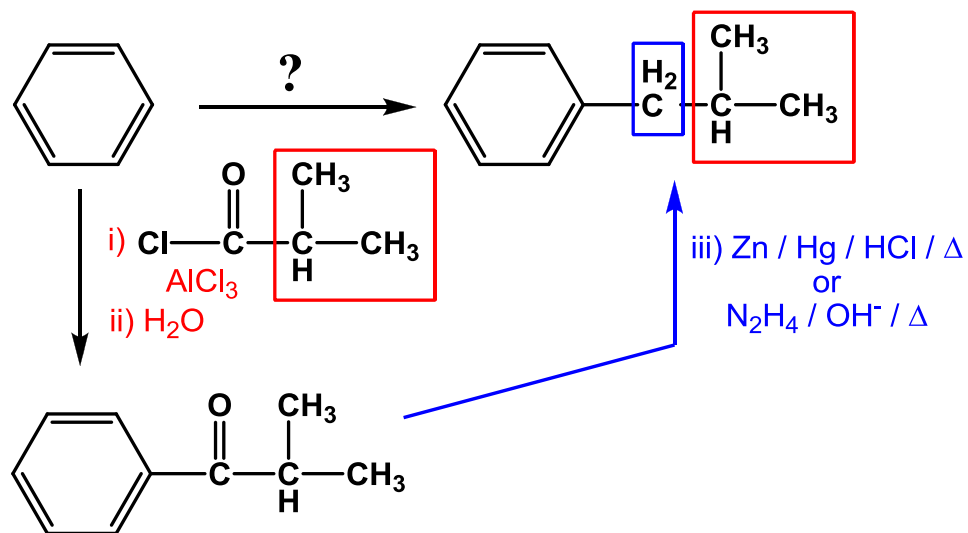


“zinc amalgam” = Zn “dissolved” in Hg(l)  $\square$  better reducing agent

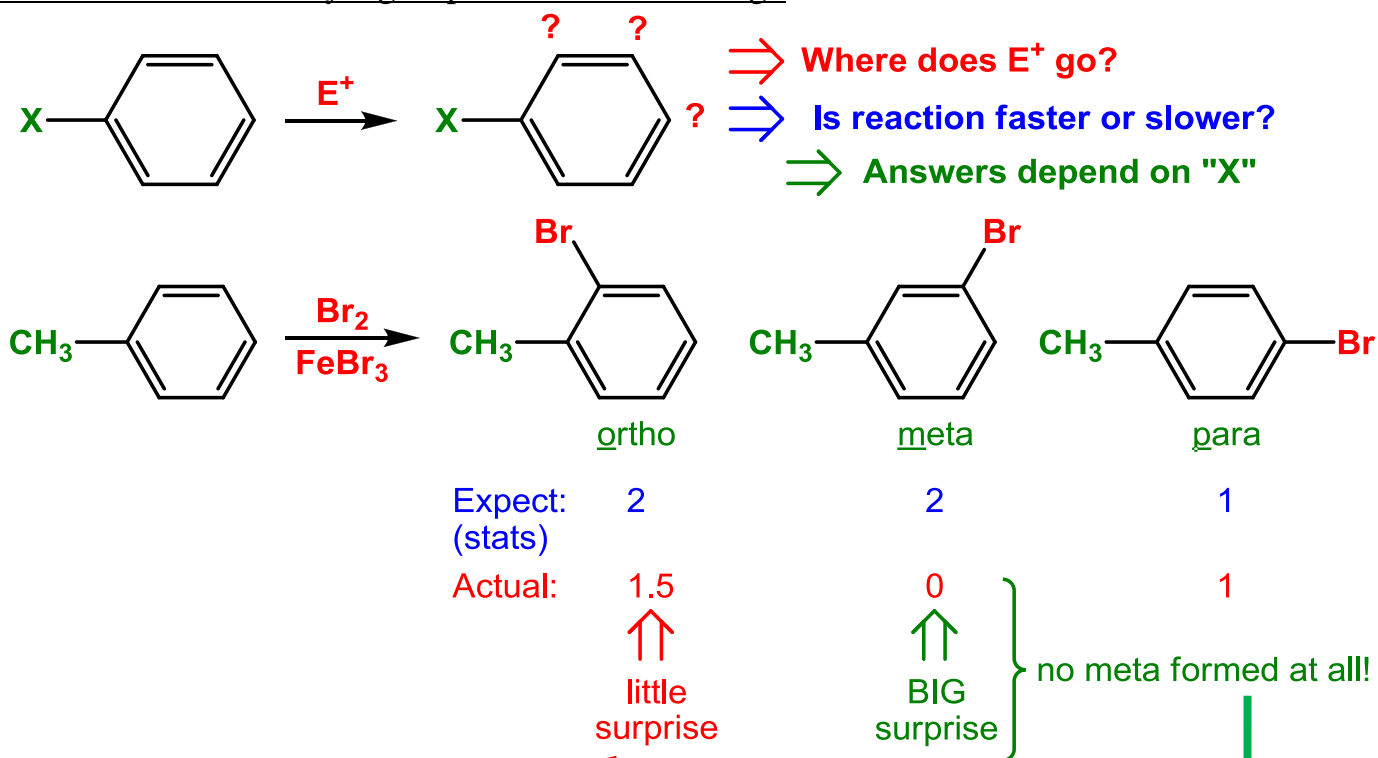


$\text{N}_2\text{H}_4$  = hydrazine: reduces all ketones  
mechanism Ch 17.8 (18.6 old book)

$\Rightarrow$  can use either method: depends on whether acid or base is preferred



What if there is already a group on the benzene ring?



a) Why is there less ortho (more para) than expected?  
 $\Rightarrow$  steric hinderance!  
 $\Rightarrow$  the bigger the R groups, the more para (sometimes only para)

b) Why is there no meta?  
 $\Rightarrow$  Resonance! (next class!)