very strong acid: pKa = -0.6!

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⁺:

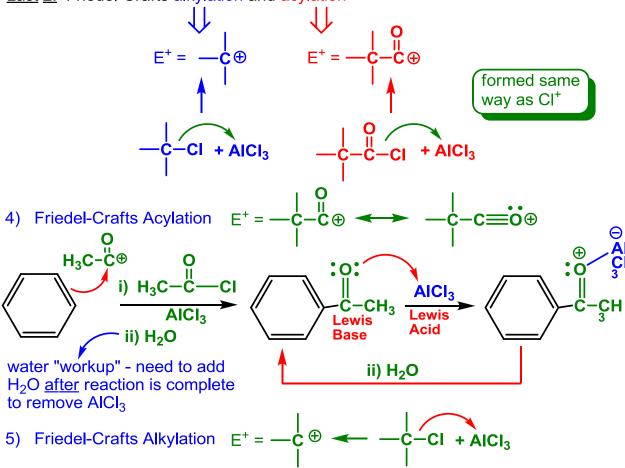
1) Nitration
$$E^{+} = NO_{2}$$
 product = NO_{2}
 $HNO_{3} + H_{2}SO_{4}$ HOO_{2}

2) Halogenation $E^{+} = Br$ or CI product = Br
 $Br_{2} + FeBr_{3}$ Don't mix Br/CI or get mixture

 $CI_{2} + AICI_{3}$ NOTE: F^{\oplus} too reactive enough F^{\oplus} will see how to make later

3) Sulfonation $E^{+} = SO_{3}H$ product = $FOO_{3}H$
 $SO_{3} + H_{2}SO_{4} = \text{"fuming sulfuric acid" (actually fumes!)}$
 $SO_{3} + H^{+}$ FOO_{4} FOO_{5} FOO_{5} FOO_{6} FO

Last 2: Friedel-Crafts alkylation and acylation



More about F-C Alkylation

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

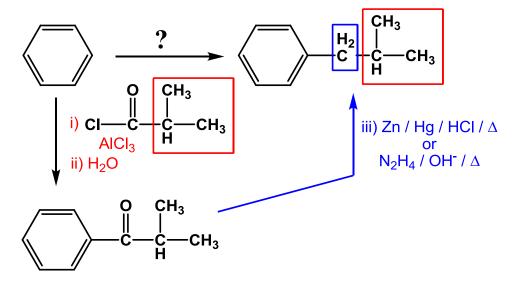
NOTE: no C=O so don't need H₂O after

$$H_{3}C-CI + AICI_{3} \longrightarrow [H_{3}C-----CI-----AICI_{3}] \longrightarrow H_{\oplus}$$

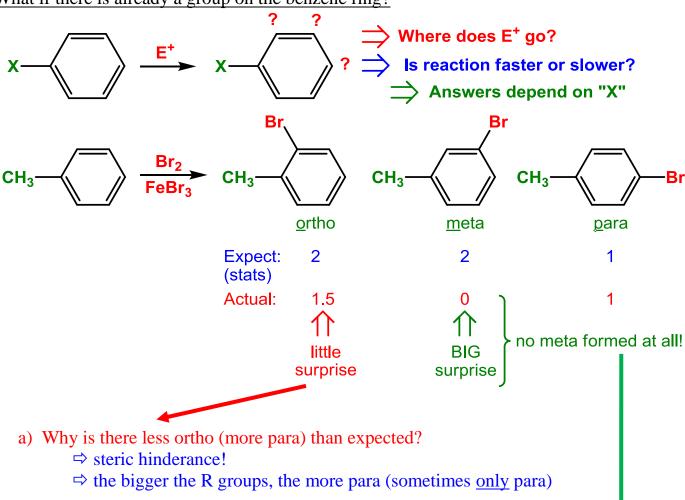
$$\longrightarrow Can use \underline{any} C^{+} (eg ROH + H^{+})$$

Complication with F-C Alkylation: What can C⁺ do? CH₃ AICI₄ CH₃ How do we make CH₂CH₂CH₃ this one? only 30% 70% (major) ** can't introduce 1° R (> ethyl) by FC alkylation ➤ Do FC <u>Acylation</u> with correct number of C's, then remove O from C=O → including C of C=O reduction CH₂CH₃ ii) H₂O need to add 3 C's! reduce C=O to CH₂ group CH₃CH₂−C≡O[⊕] does not rearrange → 2 ways (resonance stabilized!) **≡** Called Acylation-Reduction 1) Clemmensen Reduction "zinc amalgam" = Zn "dissolved" in $Hg(1) \square$ better reducing agent 2) Wolff-Kishner Reduction N_2H_4 = hydrazine: reduces all ketones mechanism Ch 17.8 (18.6 old book)

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



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



- b) Why is there no meta?
 - ⇒ Resonance! (next class!)