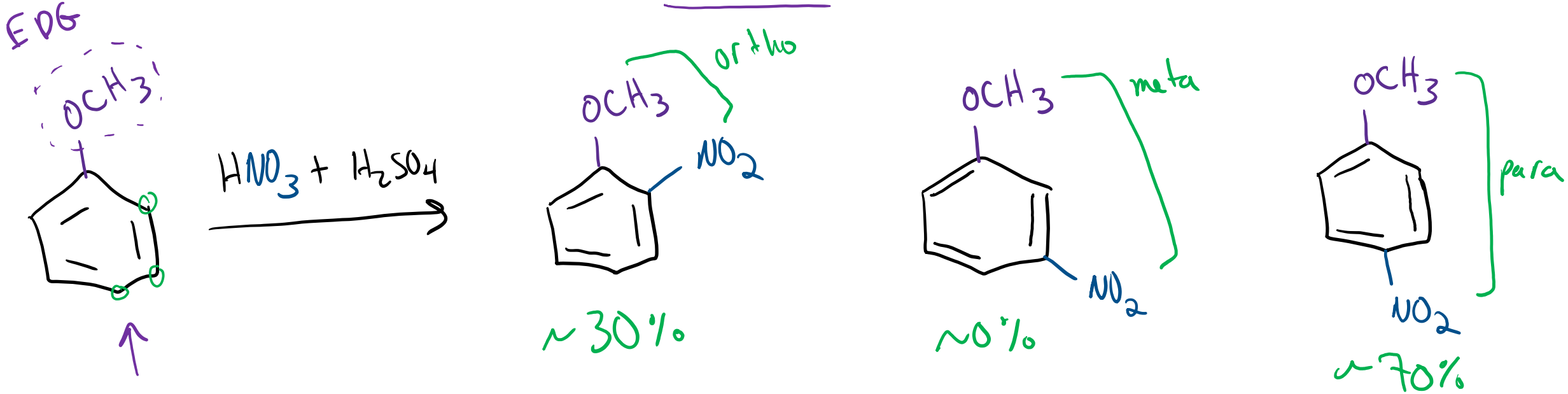
Substituted Benzenes and EAS

Synthesis Strategies

1/25/2023

Electron **Donating** Groups: "Directing" EAS Regioselectivity



- reacts ~400 times faster than regular benzene

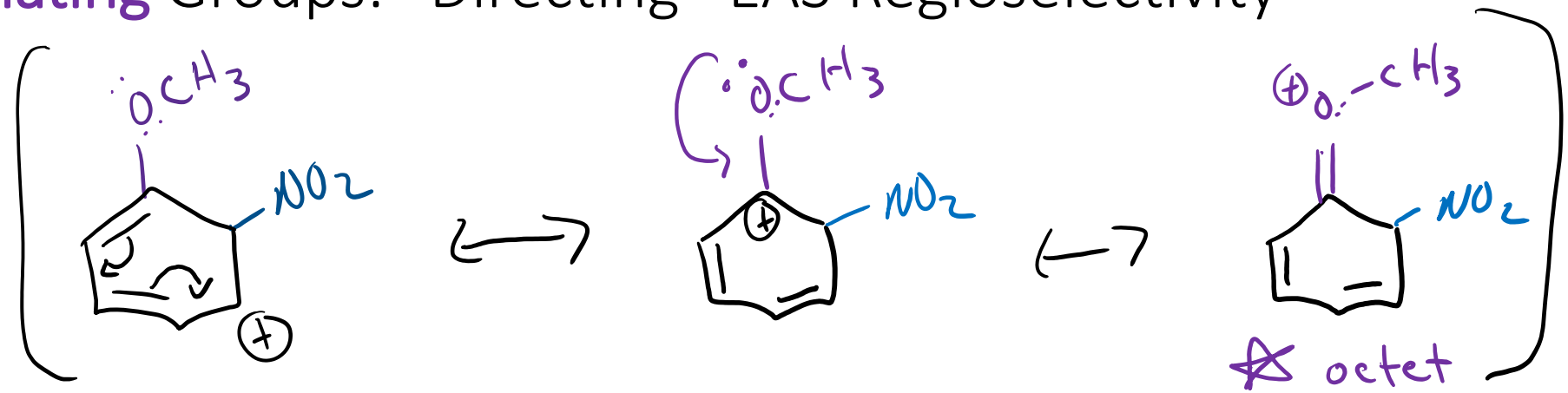
EDG are "activating groups"

- EDG direct new group to ortho + para positions!

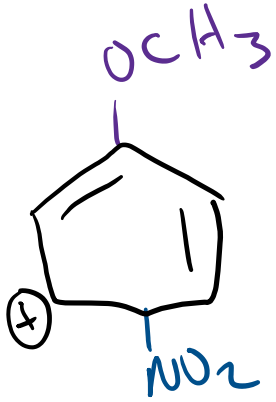
(NO_2 here)

Electron **Donating** Groups: "Directing" EAS Regioselectivity

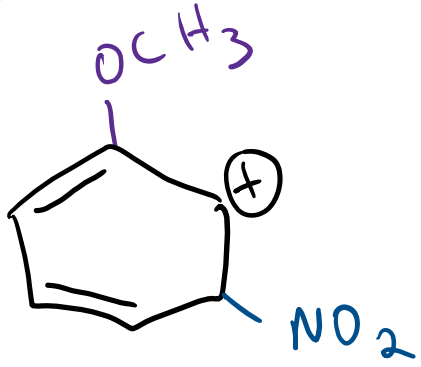
If NO_2 adds ortho:



If NO_2 adds para:



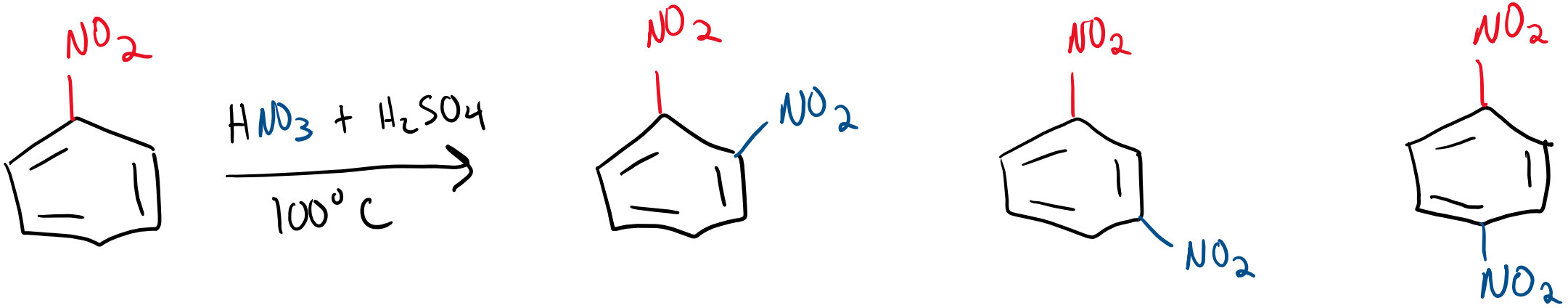
If NO_2 adds ~~meta~~:



can't get ⊕ onto oxygen via resonance!

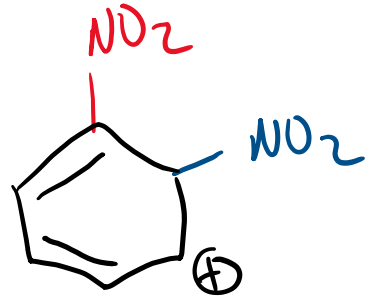
much less stable intermediate vs. ortho- or para-

Electron Withdrawing Groups: "Directing" EAS Regioselectivity

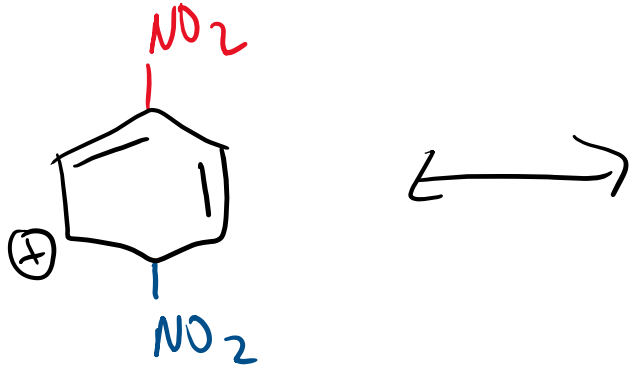


Electron **Withdrawing** Groups: Directing EAS Regioselectivity

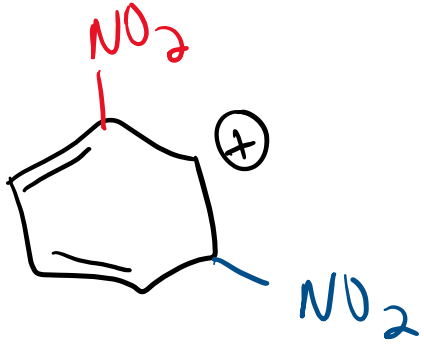
If NO_2 adds ortho:



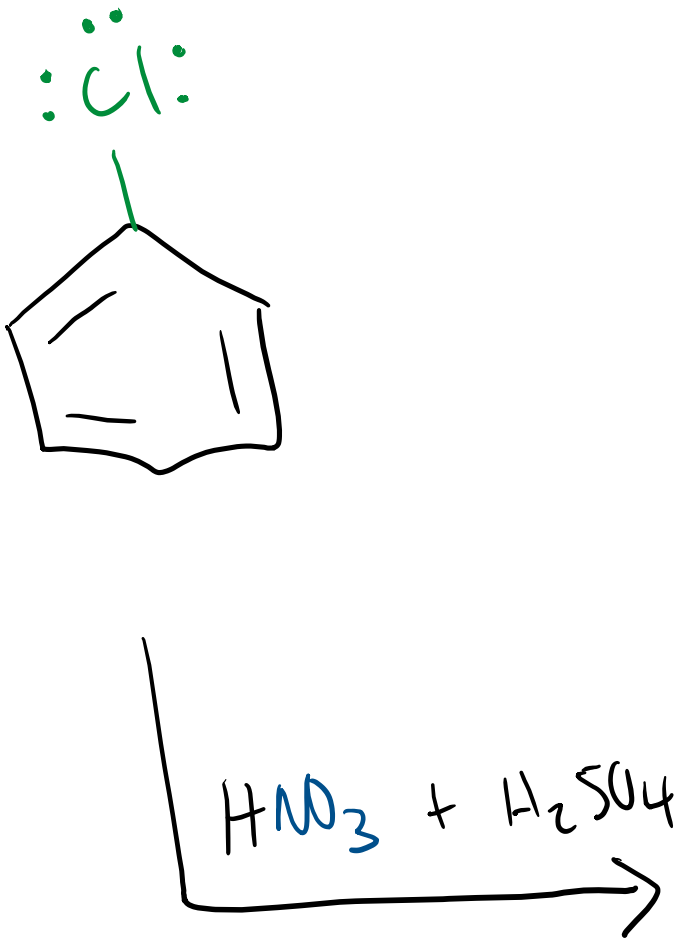
If NO_2 adds para:



If NO_2 adds meta:



Halogens: Directing EAS Regioselectivity (18.9)



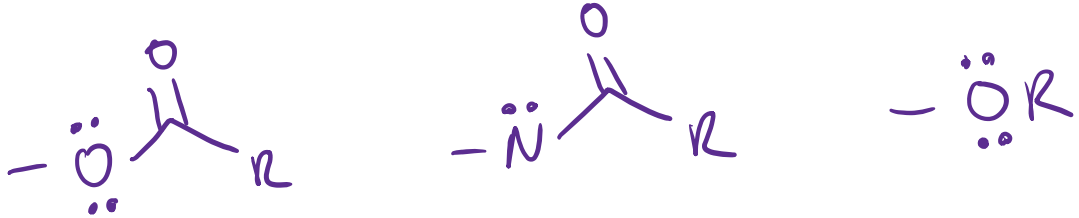
Strengths of Activating/Deactivating Groups

★ not compatible with Friedel-Crafts reactions ★

Activating Groups:

Strong:

Moderate:

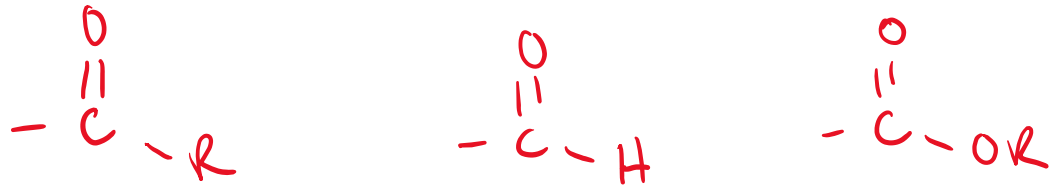


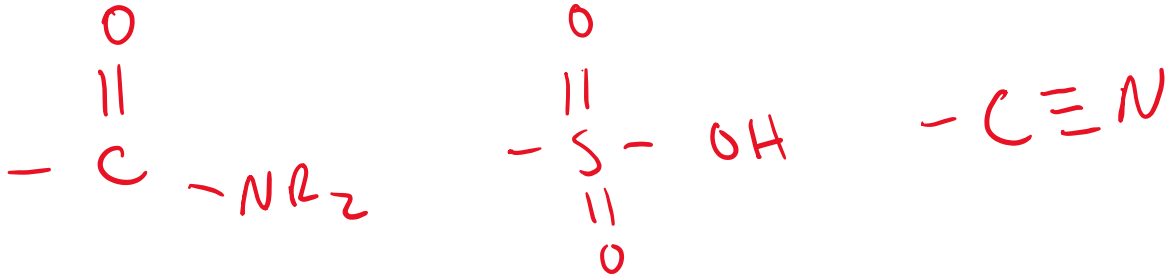
Weak:

Deactivating Groups:

Strong:

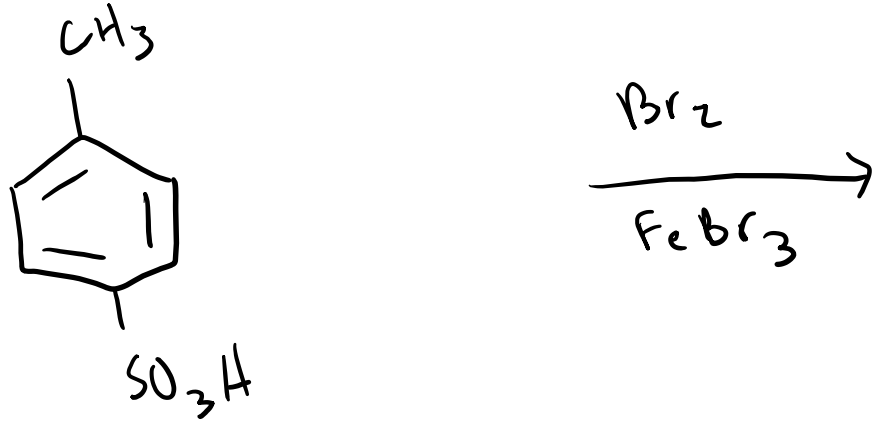
Moderate:



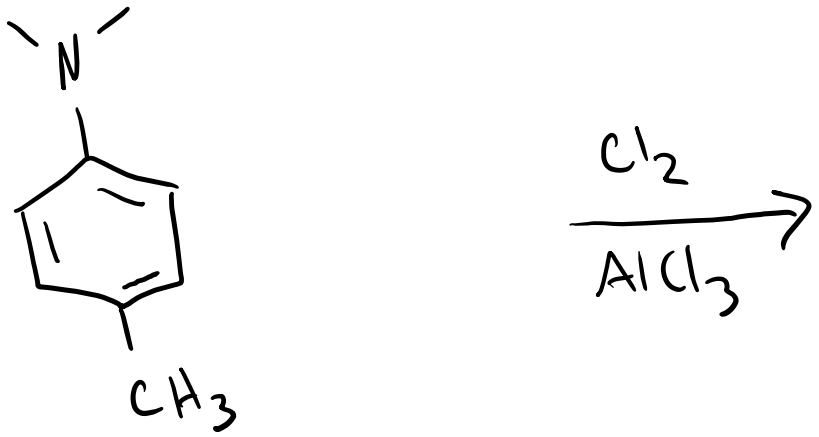


Multiple Substituents & Regioselectivity (18.11)

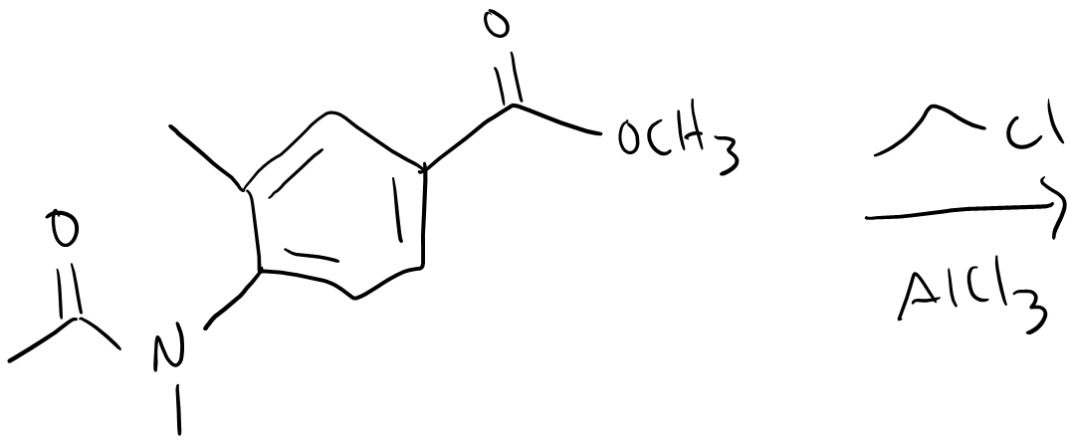
Case #1: Multiple directing effects "agree with" (or reinforce) each other



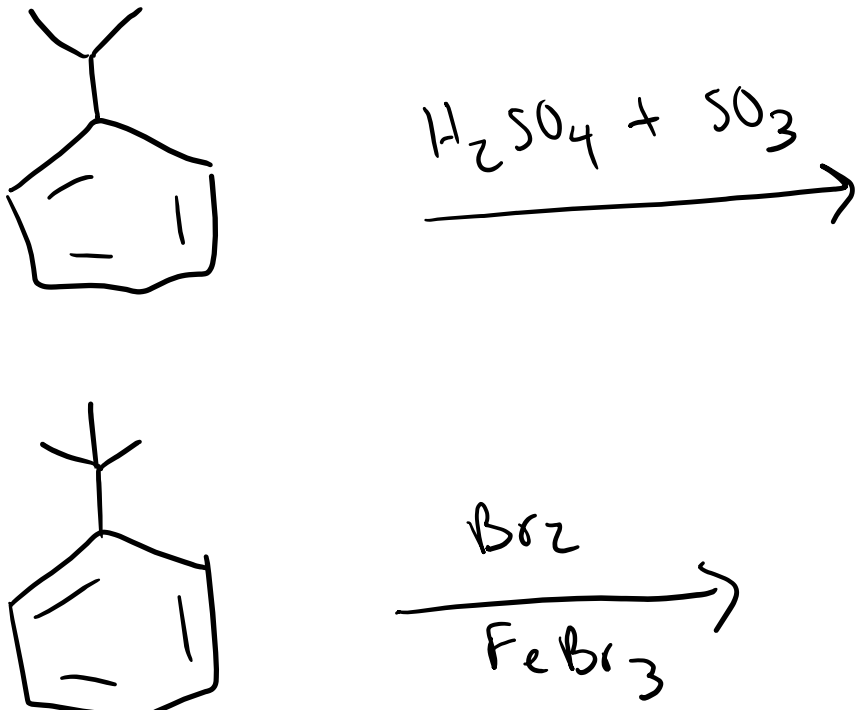
Case #2: Multiple directing effects compete.



EAS with Multiple Substituents: Example

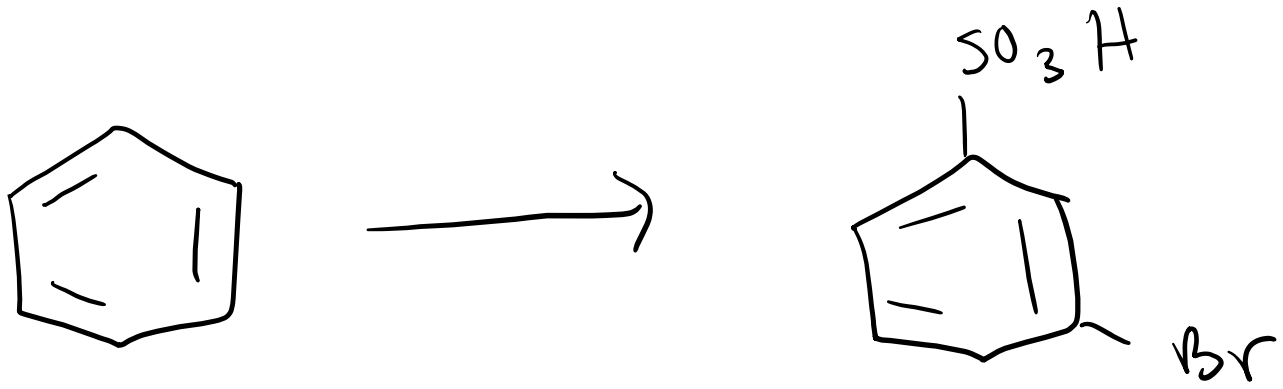


Steric Effects and “Blocking” Groups (18.11)



EAS Synthesis Strategies

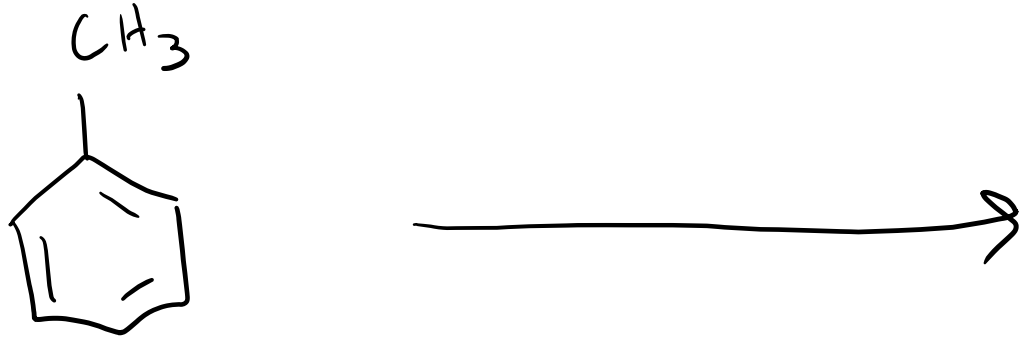
(18.12)

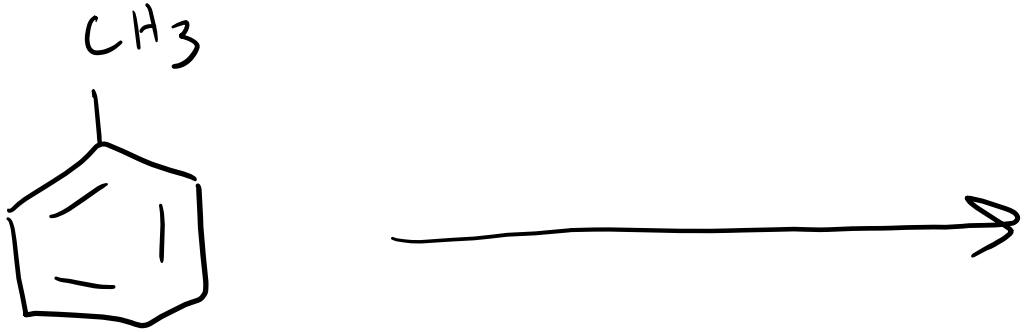


propose a synthesis!

Some Useful Transformations

KNOW THESE RECIPES





EAS Synthesis Strategies

(18.12)