Aromaticity and Benzene #3: Identifying Directing Groups & Rxns with Benzene

Howdy, everybody! Welcome back ☺. Hopefully you've practiced those EAS mechanisms and have them down. We're going to move away from doing some mechanistic stuff, and we're going to dig deep into doing Complete the Reaction problems with Benzene and Benzene structures with one or more substituents attached. All of the chemistry is happening on a Benzene ring, so trust me when I say that this stuff isn't too bad.

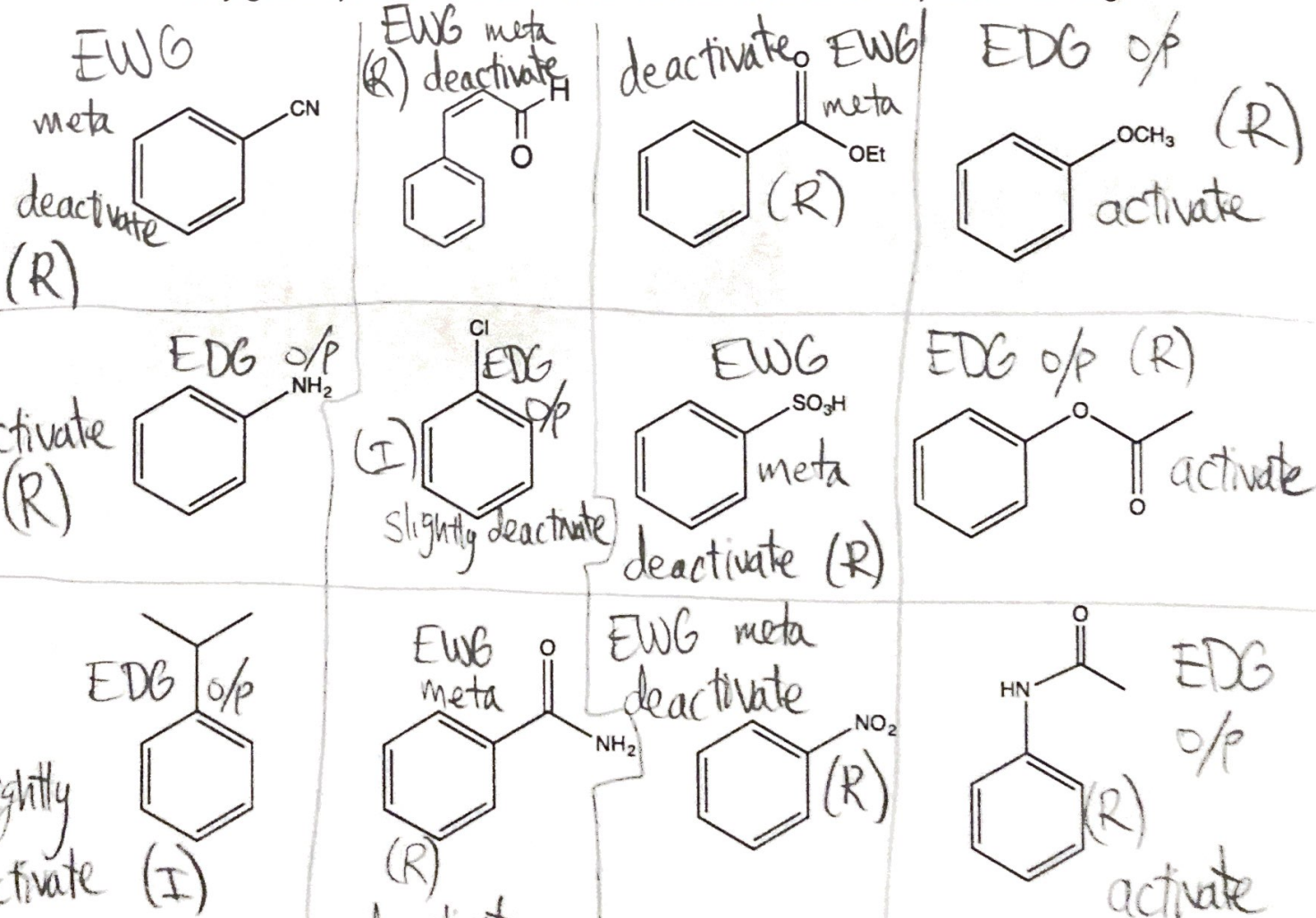
1.) Before we get down and dirty with some Complete the Reaction problems, let's do some practice with identifying Electron Donating Groups (EDG) and Electron Withdrawing Groups (EWG). **Label the group on each structure below as an EDG or EWG & specify whether it is a strong or weak activator/deactivator.**

(R)-resonance

(I)-induction

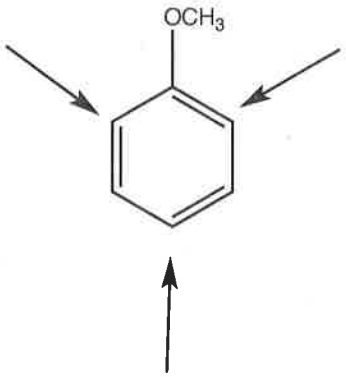
*Remember, you can pick out EDG's because they are electronegative atoms directly attached to the benzene ring and supply electrons to the conjugated system through resonance

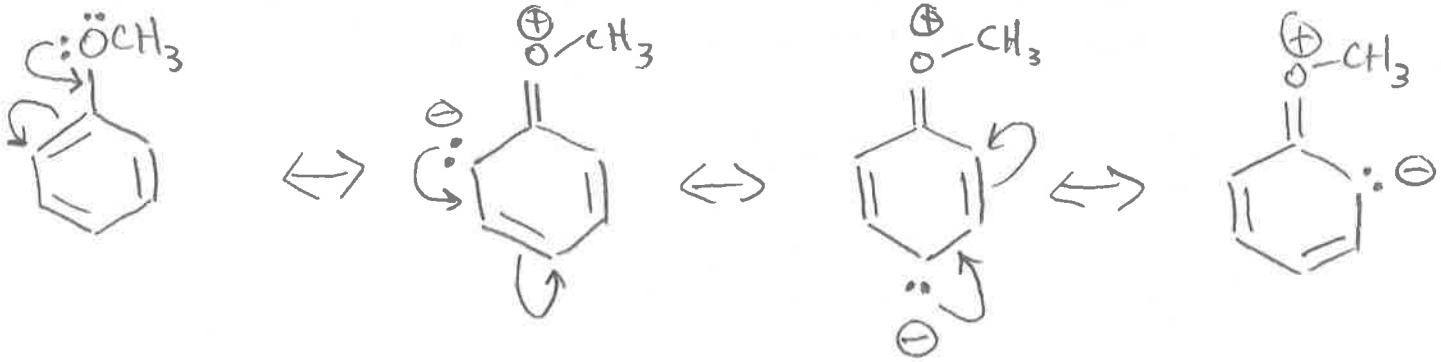
*On the other hand, you can spot EWG's because directly attached to the benzene ring will be a partially positive atom with **NO** electrons that it could donate to the conjugated system. This atom works to suck electron density out of the ring.

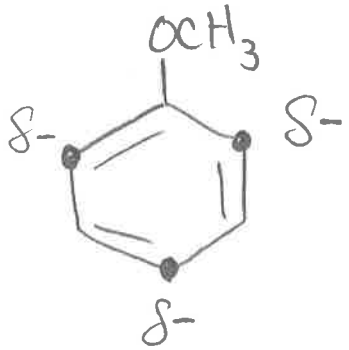


2.) Okay, awesome. Not too terrible deciding whether something is an EDG or an EWG, right? Alright, in the last video we established that EDG's are ortho/para directors while EWG's are meta, and I want to make sure you guys can prove why that's the case...

a.) In EAS reactions, methoxybenzene directs and attaches groups in the ortho and para positions. Illustrate why this is the case using structures (possibly redundant hint: resonance).

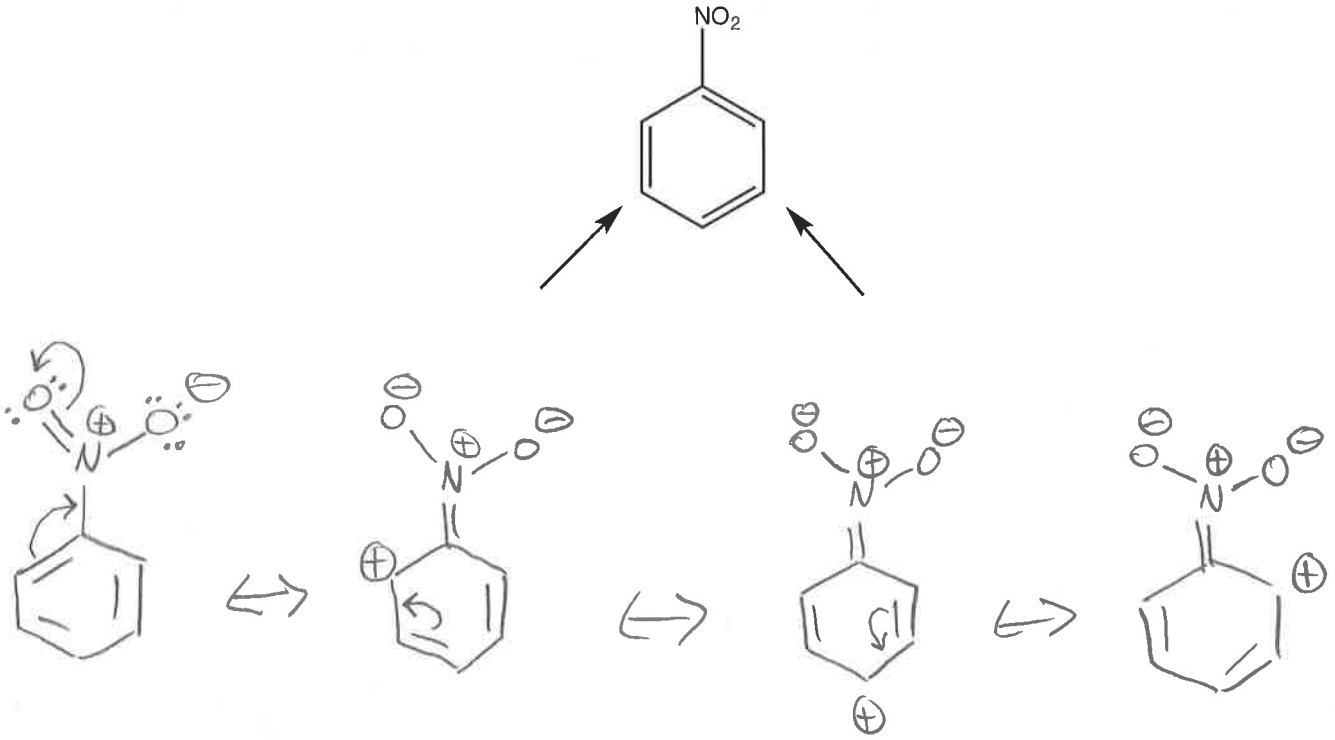


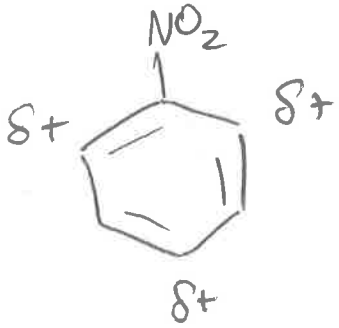




* Adding electrophiles will occur at the δ- (2) ortho and para positions.

b.) Okay, same drill here, but with a different compound and a little twist. In EAS reactions, nitrobenzene directs and attaches groups in the meta positions. Illustrate why this is the case using structures (possibly redundant hint: resonance).

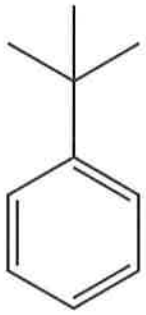




Adding electrophiles will occur away from the δ+ ortho and para positions ⇒ meta *

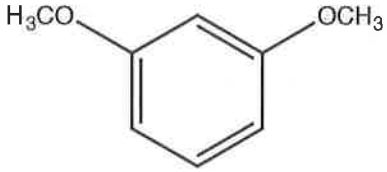
(2)

3.) Good job. Okay, so I can only imagine you guys are **dying** to predict some products (maybe not, but act excited for me). These questions are going to test your ability to correctly identify ortho/para and meta directing groups and your knowledge of the EAS reactions we talked about (the ones with and without mechanisms). Give them a go, and if something went wrong, take a sneak peak at the answers, learn from your mistake, and eventually give that problem another go. Let's complete some reactions ☺.



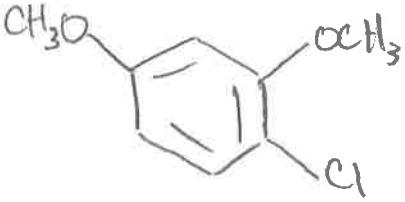
SO_3

H_2SO_4

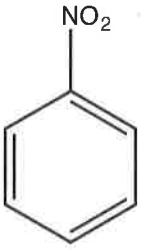


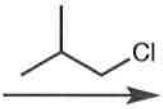
Cl_2

$AlCl_3$

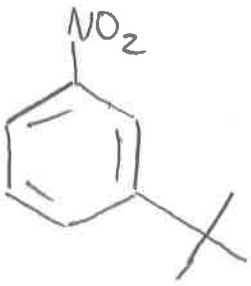


Hydride Shift!



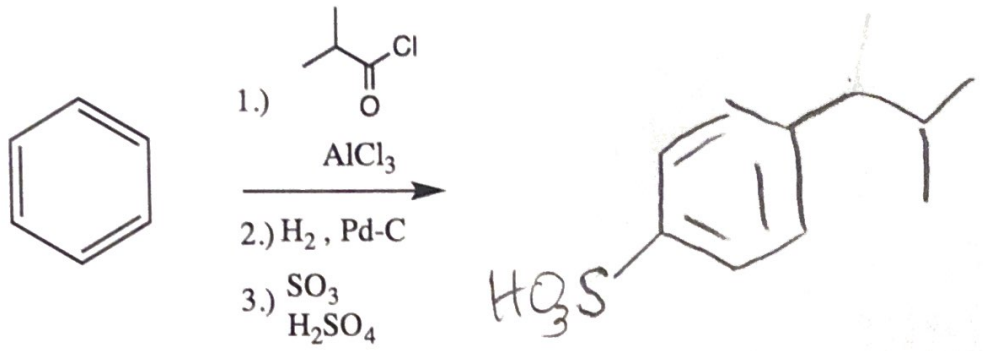


$AlCl_3$

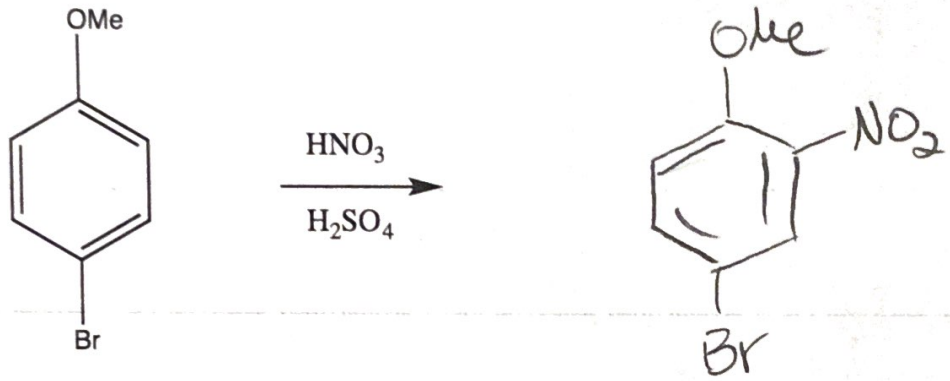


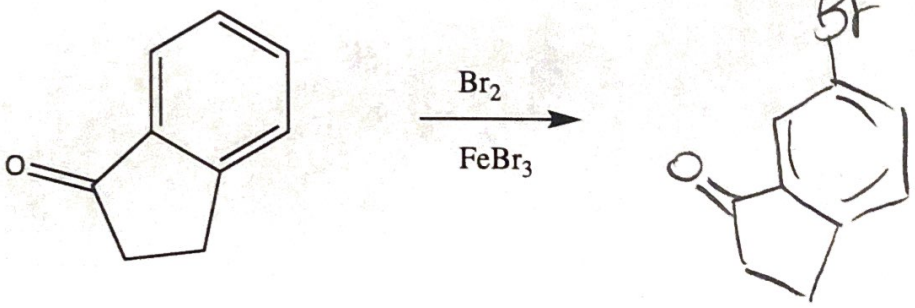
$H_3O^{\oplus}$

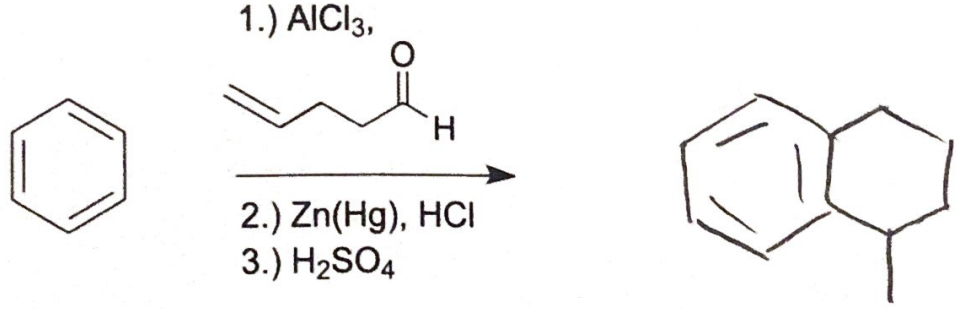
Δ



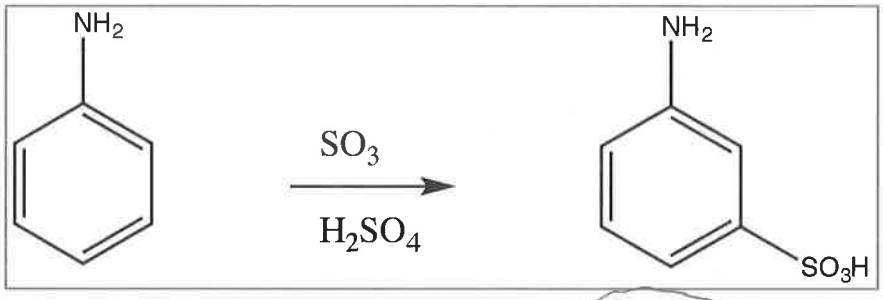
go w/ stronger director







4.) Okay, last problem, and then this worksheet is history. The following reaction below is observed. We know amines to be strong EDG's (aka ortho/para directors), so how does the bromine end up in the meta position? Draw the curved arrow mechanism and show how this occurs. (Hint: remember that amines are also very basic. You got this)



- In acid, amines are protonated to $\oplus NH_3$ and become an EWG