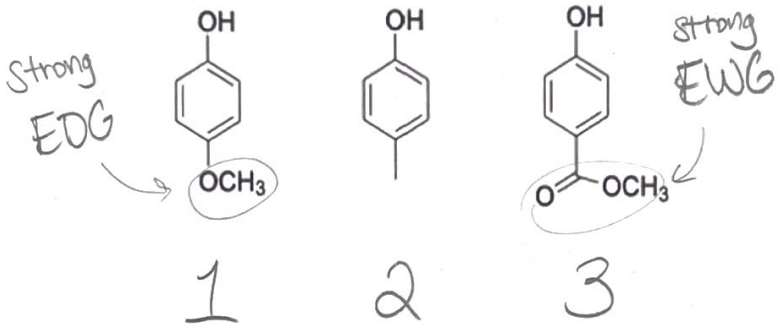
Benzene Substituents: Reactions, Concepts, and Synthesis Practice

Hey, gang! Welcome to the worksheet for the benzene substituent chemistry unit. Although there are a bunch of videos in this section, this one worksheet contains all the practice. It might be a lot, but I know you all are up to the task.

We'll cover everything from acid-base properties of phenols to cope rearrangements and back. If anything is confusing, check out the solutions and/or solutions walkthrough video ☺!

1.) To get this party started, let's hit some acid-base & concept questions:

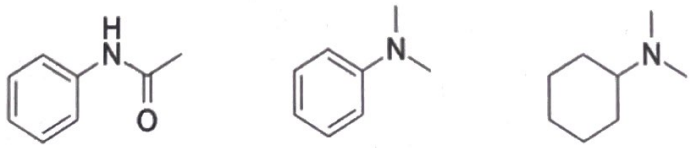
a.) Given the following three molecules, rank them 1 – 3 with 1 being the **weakest acid** and 3 being the **strongest acid**.



1 2 3

b.) Given the following three molecules, rank them 1 – 3 with 1 being the **weakest base** and 3 being the **strongest base**.

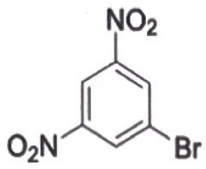
Resonance decreases the negativity on the N atom



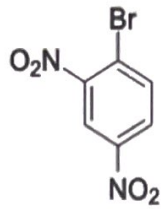
1 2 3

Having an EWG ortho/para to the leaving group increases ability to undergo NAS.

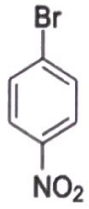
c.) Given the following three molecules, rank them 1 – 3 with 1 being the **least susceptible** and 3 being the **most susceptible** to nucleophilic aromatic substitution.



1



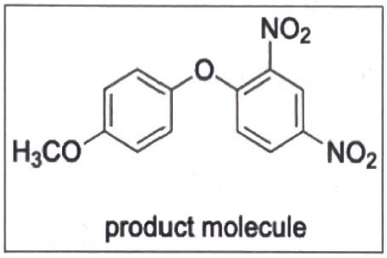
3



2

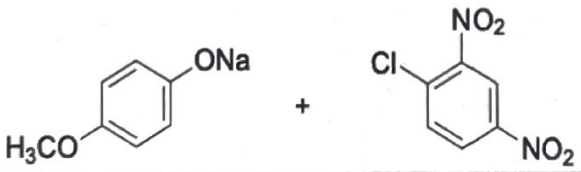
d.) Okay, let's shift away from ranking.

In this next problem, circle the reaction A, B, or C that will yield the product molecule (shown below) in the highest yield:



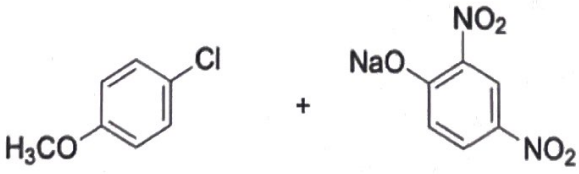
product molecule

A



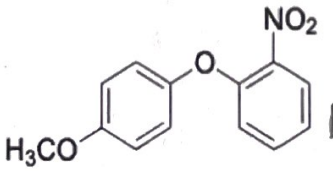
NAS works great with EAS groups ortho/para to L.G.

B



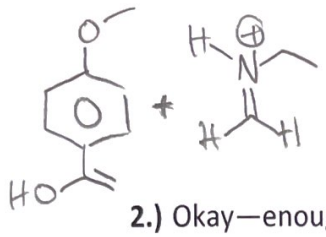
NAS isn't great since there is an EDG group para to L.G.

C

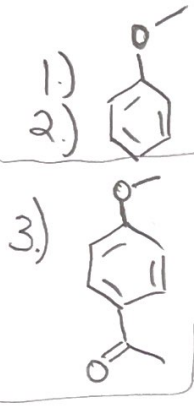


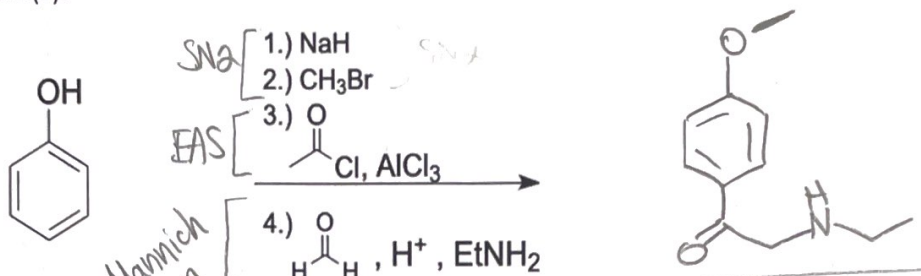
HNO_3, H_2SO_4

EAS rxn on benzene ring is slightly deactivated due to $-NO_2$ group

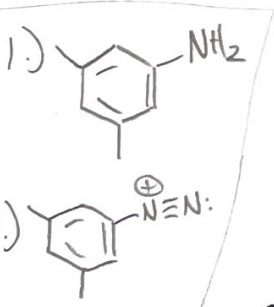
4.) 

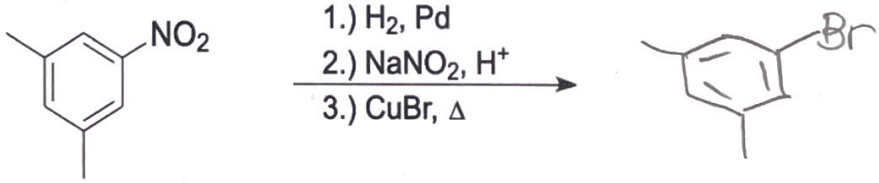
2.) Okay—enough of looking at and ranking reactions, let's complete some of our own! For the reactions below, you know the drill: either complete the reaction by predicting the major organic product, providing the reactant(s), or providing the reagent(s).

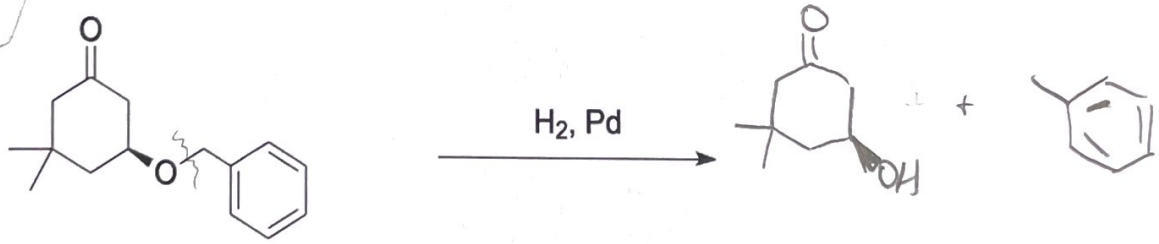
1.) 2.) 3.) 

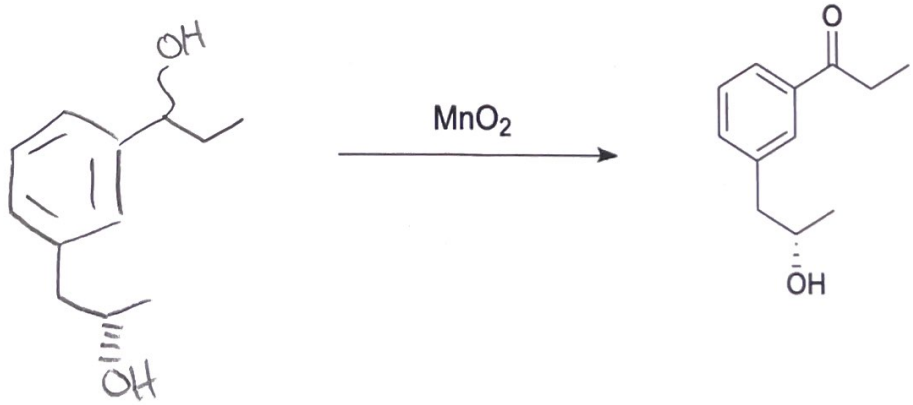


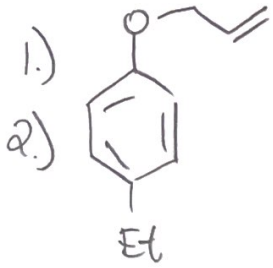
Benzylic radical bromination

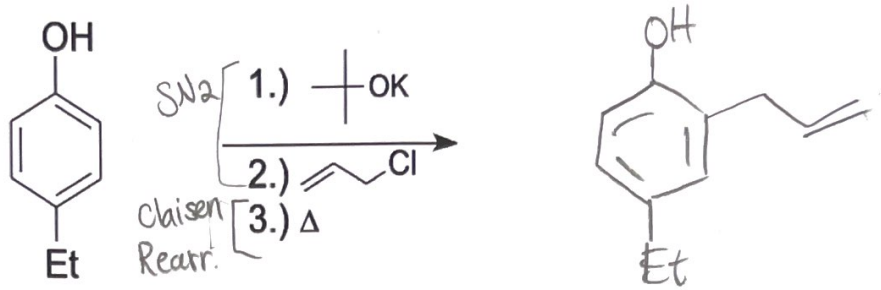
1.) 

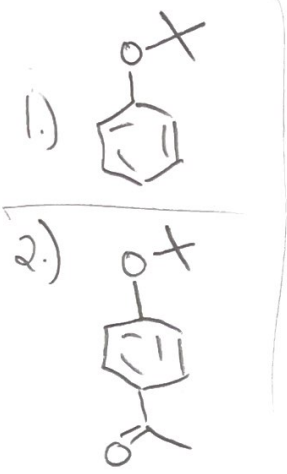


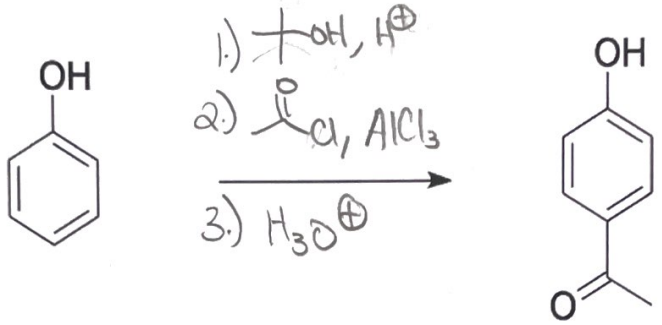




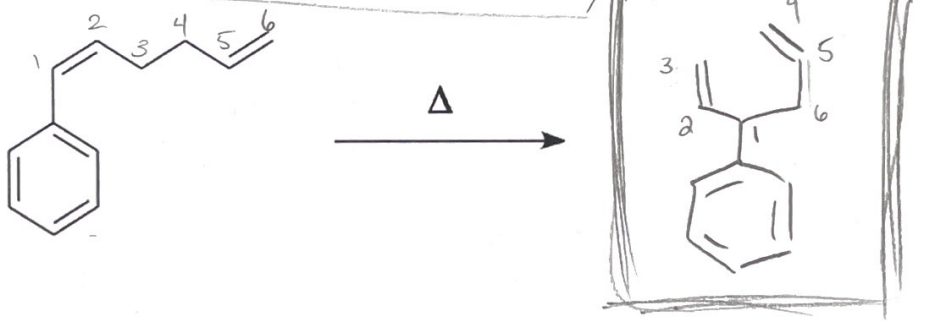




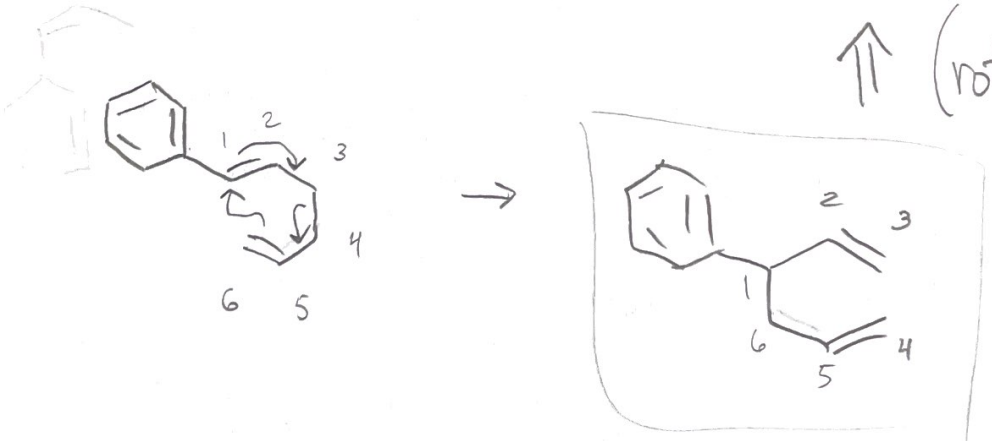




Cope rearrangement



redraw & rotate ring

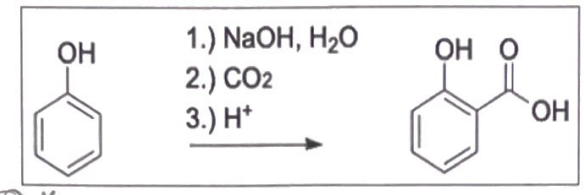


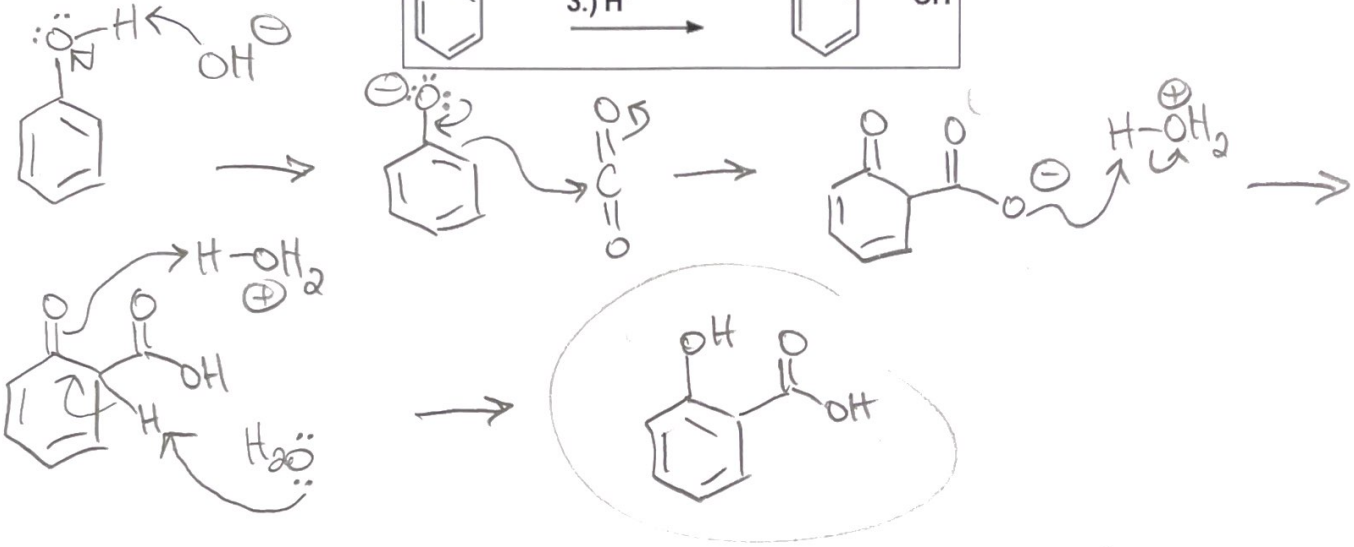
⇑ (rotating back)

Kolbe Rxn

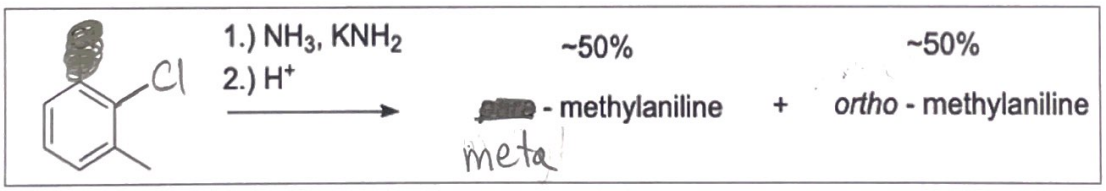
3.) Now that we've completed *plenty* of reactions, let's transition to mechanism mode.

a.) Draw the full arrow pushing mechanism for the reaction displayed below



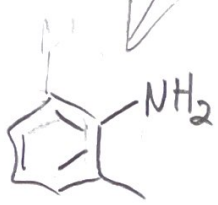


b.) Justify the observed reaction below with a mechanism



attack can & will occur @ both alkynl positions

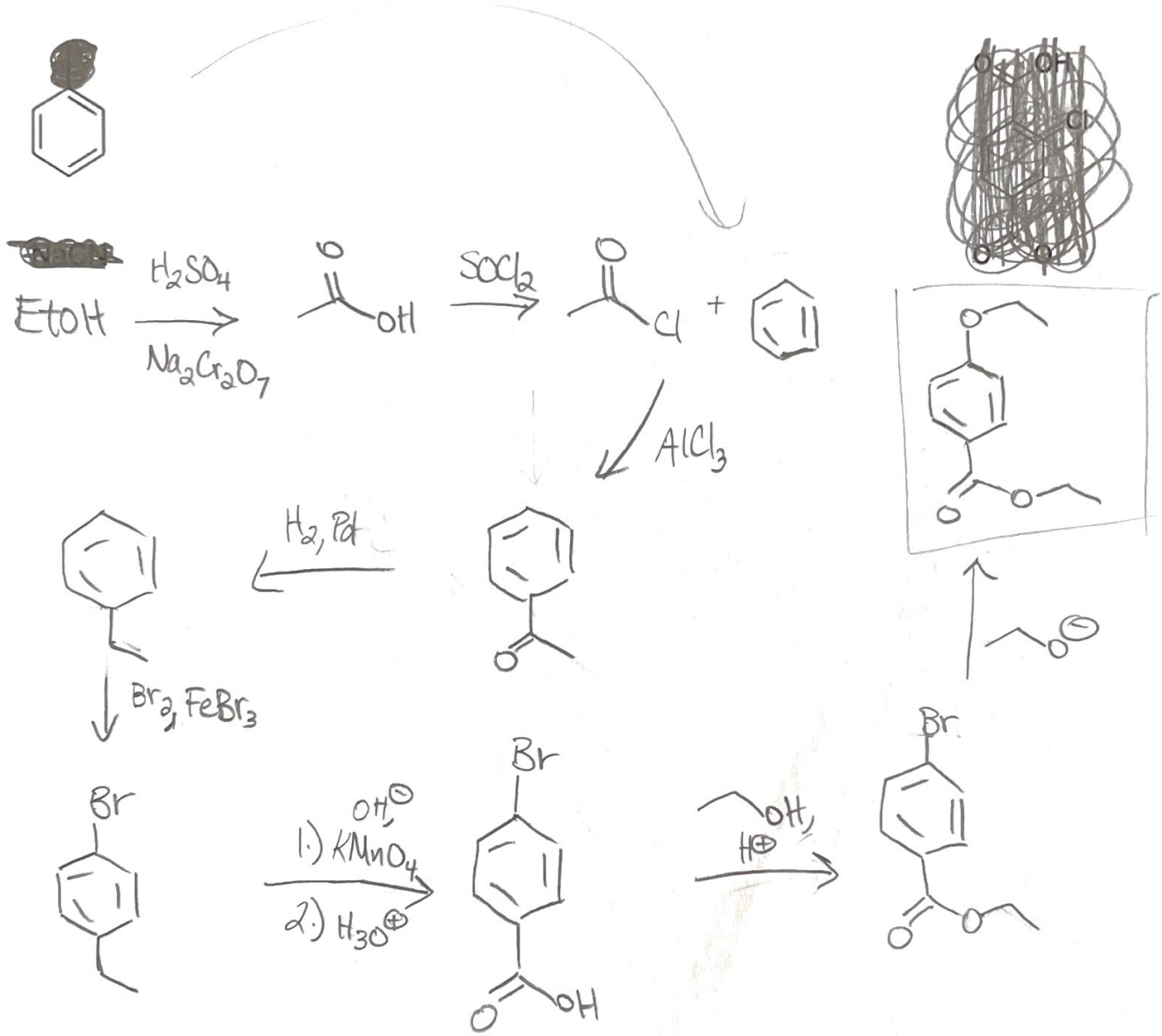
meta



Okay, gang, we're close to the end. After this synthesis question below there's one more question, which is more of a bonus.

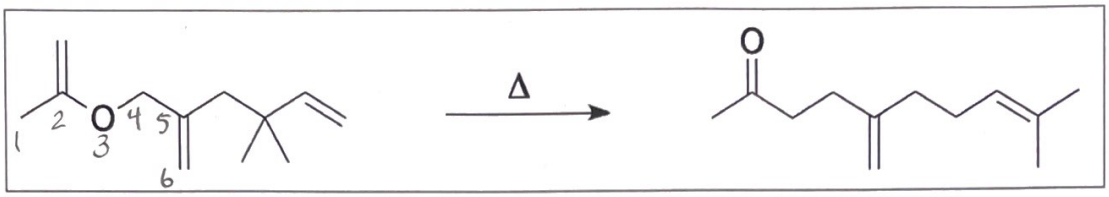
benzene ethanol

4.) Using ~~toluene~~ and ~~cyanide~~ as your only carbon source, synthesize the target molecule shown below.

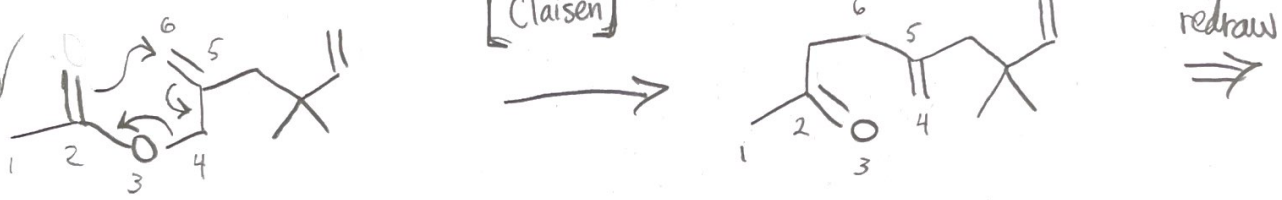


Claisen Rearrangement followed by a Cope Rearr.

5.) BONUS QUESTION: Draw a mechanism to illustrate the reaction displayed below.



- Step 1.) redraw for convenience ahead of Claisen
- Step 2.) perform Claisen
- Step 3.) redraw for convenience ahead of Cope
- Step 4.) perform Cope



(redrawn reactant)