

1. _____

5. _____

2. _____

6. _____

3. _____

7. _____

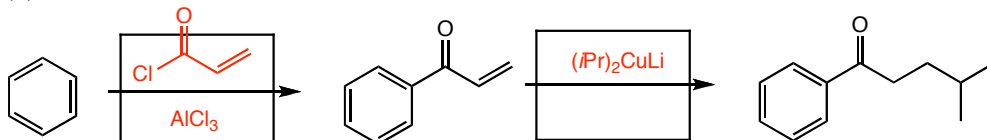
4. _____

8. _____

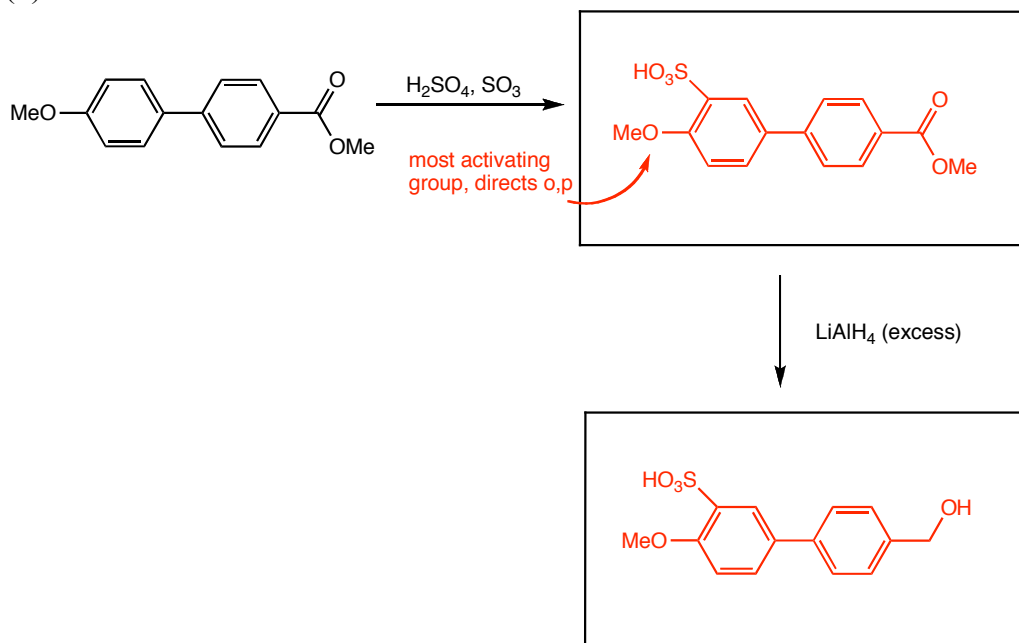


1. Fill in the boxes. Assume a single equivalent of reagent, unless otherwise noted, and that every reaction is quenched. (40 pts)

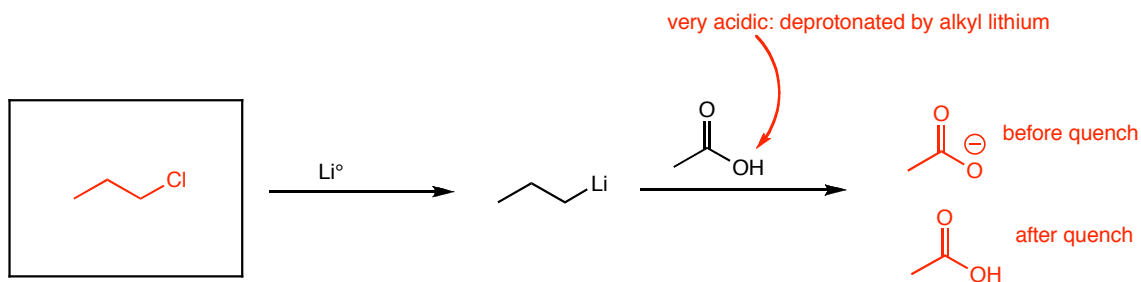
(a)



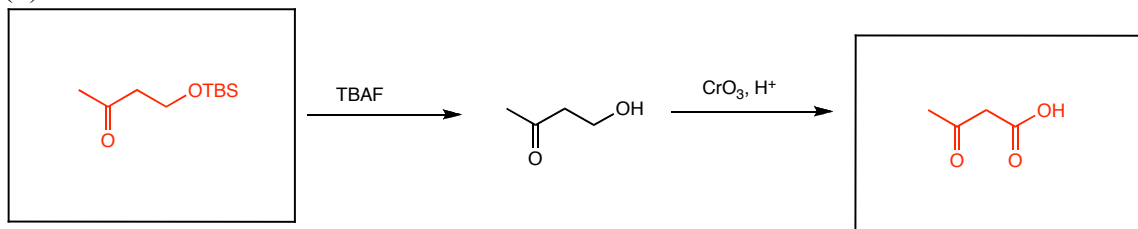
(b)



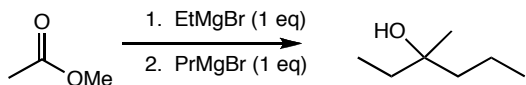
(c)



(d)

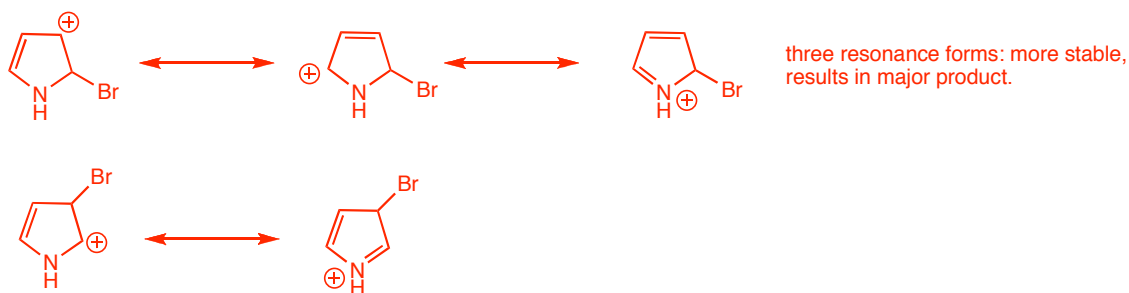
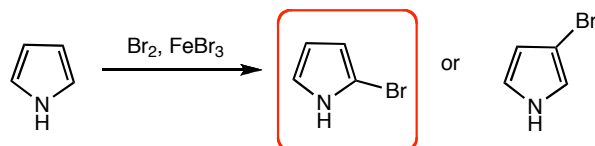


2. Explain why the following does not work. (6 pts)

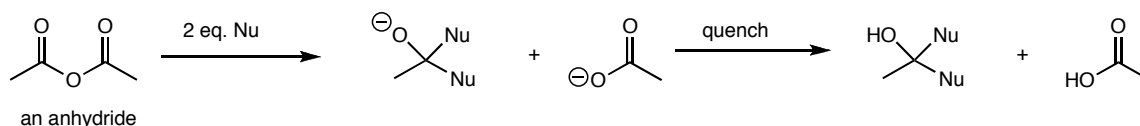


Addition of ethyl Grignard to the ester gives a ketone, which is more reactive than the initial ester, and goes on to react with ethyl Grignard before reacting with ester. After the first addition, the product would be a mixture of ester, ketone, and alcohol resulting from double addition.

3. Pyrrole can also react with electrophiles in an EAS reaction. Two possible products can be formed. Using resonance forms, predict which is the major product. (8 pts)

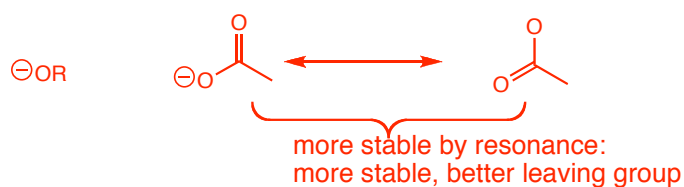


4. Anhydrides react with two equivalents of a nucleophile as shown below.



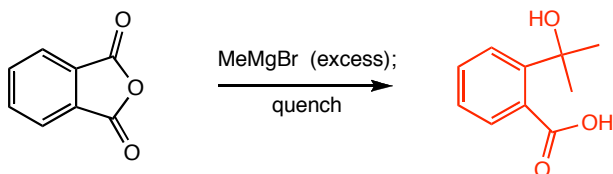
(a) Do you expect anhydrides to be more or less reactive than esters? Why? (6 pts)
 Extra credit: more or less reactive than acid chlorides? Why?

The reactivity of carboxylic acid derivatives is determined by the relative stability of the leaving group. From class: Cl^- is a better leaving group than ^-OR , so acid chlorides are more reactive than esters. In this case, we are comparing the following leaving groups:

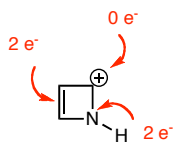


Extra credit: anhydrides are less reactive than acid chlorides, because chloride is a better leaving group. In order to determine which is a better leaving group, think of the conjugate acids: HCl is more acidic than acetic acid, so Cl^- is more stable than acetate.

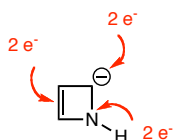
(b) Predict the product(s) of the following reaction. (5 pts)



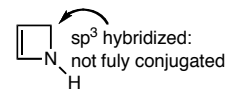
5. Determine if the following are non-aromatic, aromatic, or anti-aromatic. Assume fully conjugated species are planar. (9 pts)



4 e⁻ = antiaromatic

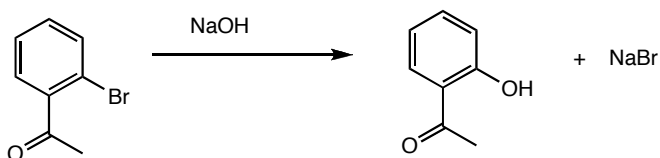


6 e⁻ = aromatic

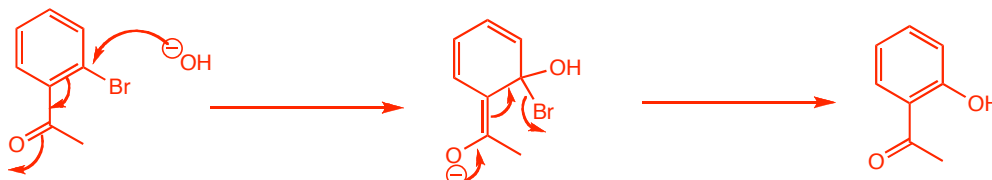


non-aromatic

6. Aromatic compounds that contain a leaving group ortho or para to an electron withdrawing group can undergo *nucleophilic aromatic substitution*, as shown below. Propose a mechanism for this transformation (hint: the reaction does not work without the carbonyl). (8 pts)

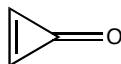


As one of you pointed out, this is more like carbonyl chemistry than aromatic chemistry:



this step is basically a 1,4-addition of hydroxide

7. Cyclopropenone is much more stable than expected, given its ring strain and unsaturation. Explain why. (6 pts)



See problem 17.53 for similar problem.

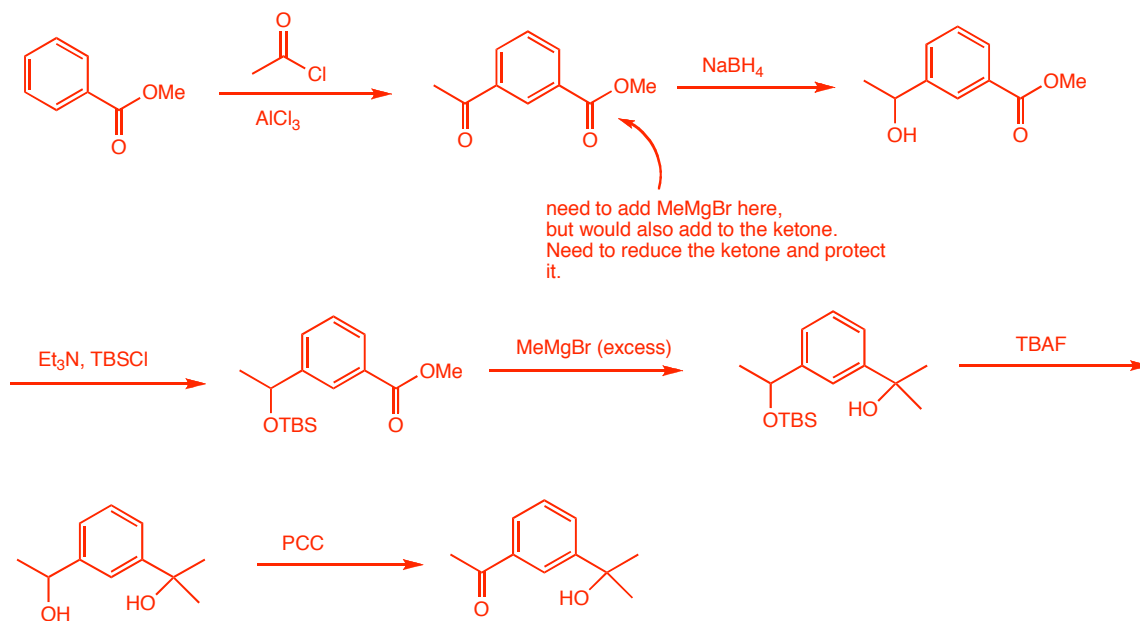
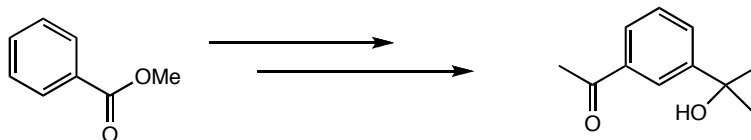
Whenever you see the words more stable than expected for a cyclic molecule, think aromaticity.

A resonance form of the ketone has positive charge on the ring:



This compound is cyclic, planar, and fully conjugated. It contains $2e^-$, and fulfills Hückel's law with $4n+2$ electrons, making it aromatic.

8. Propose a synthesis of the target molecule, using the starting material given, and any other organic or inorganic reagent you may need. No mechanisms are necessary. (12 pts)



Even better...proposed by two of you:

