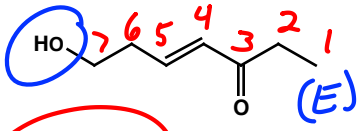
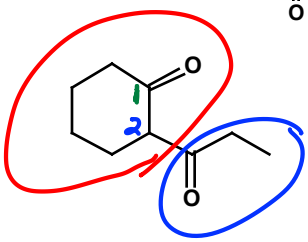
JASPERSE CHEM 360 TEST 3 VERSION 1
Ch 18 Ketones and Aldehydes
Ch 22 Additions and Conensations of Enols and Enolate Ions

1. Provide the Name for the Following (6 points)



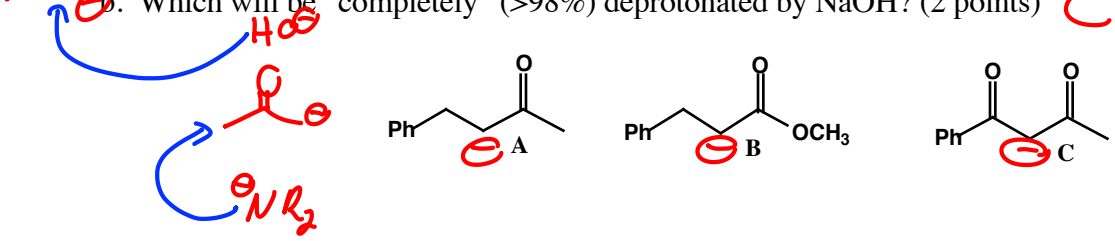
(E)-7-hydroxyhept-4-en-3-one



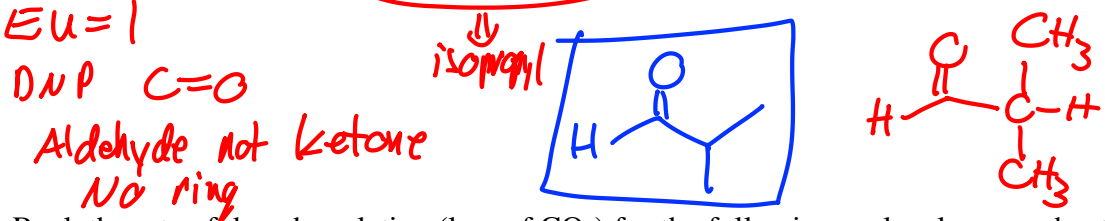
2-propanoylcyclohexanone

2. Of the following structures,
a. Which will be "completely" (>98%) deprotonated by LDA (LiN-iPr$_2$)? (2 points)
LDA deprotonates mono carbonyls
b. Which will be "completely" (>98%) deprotonated by NaOH? (2 points)

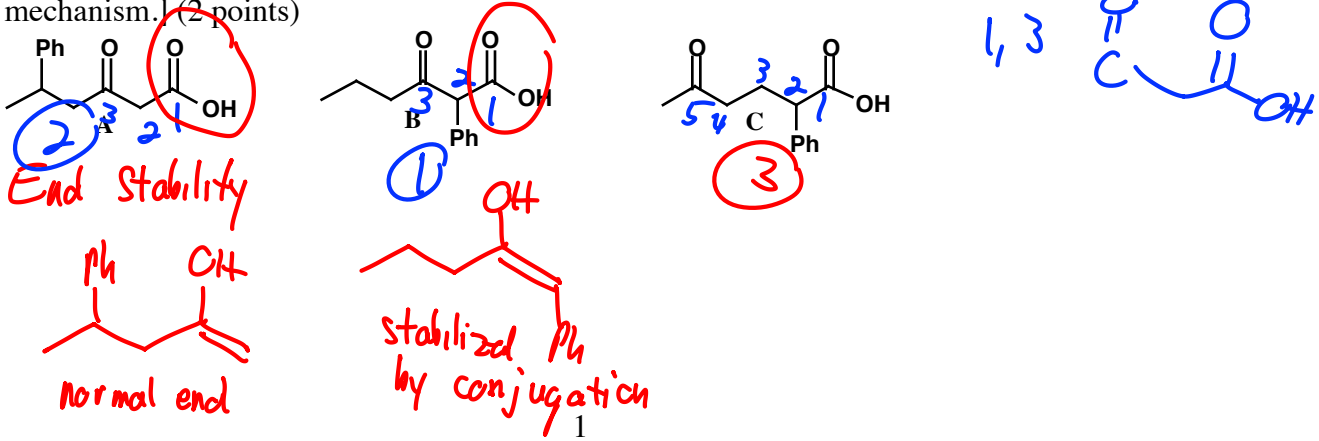
Oxyanion => dicarbonyls



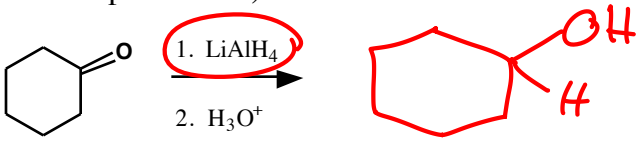
3. An unknown **X** has formula $C_4H_8O$. It gives 1) an orange precipitate upon treatment with 2,4-dinitrophenylhydrazine (2,4-DNP) and it gives 2) a silver mirror upon treatment with Tollen's reagent [$Ag(NH_3)_2^+OH^-$]. 3) It does not react with $Br_2$ in dichloromethane solvent. 4) Included in the $^1$H NMR (incomplete) is a 6H doublet at 1.2 ppm. What is **X**? (4 points)

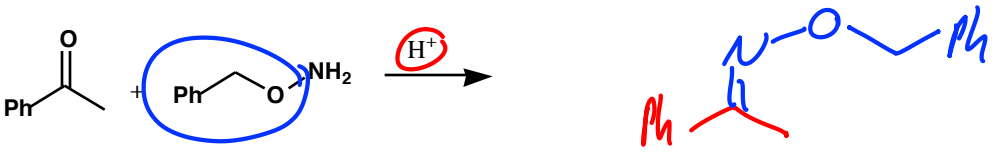


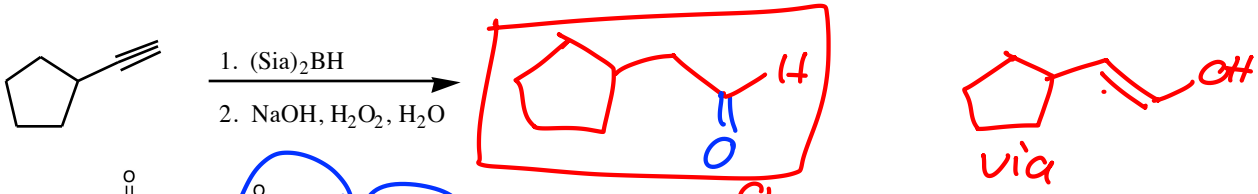
4. Rank the rate of decarboxylation (loss of $CO_2$) for the following molecules upon heating, with 1 being highest, 2 being next, and 3 being not at all. [Hint: Two out of the three will react, one will not, so you should be able to identify the unreactive isomer. To compare the reactivity of the two reactive isomers, the phenyl substituent impacts the relative stabilities in the key step of the mechanism.] (2 points)

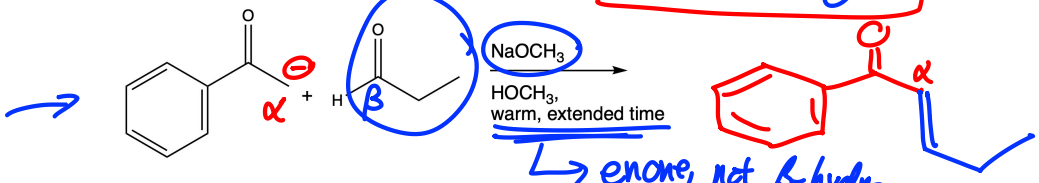


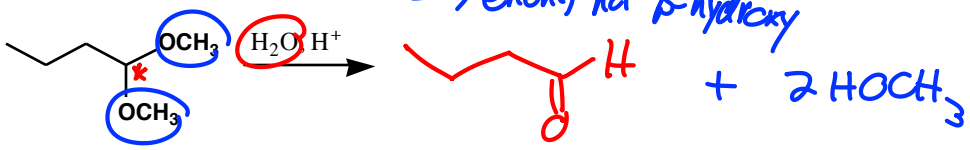
5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). NOTE: In every case, the product should be a stable, isolable **product**; an "intermediate" structure will not receive full credit. (2 or 3 points each; 1st 7 worth 2 points; last 5 worth 3 points each)

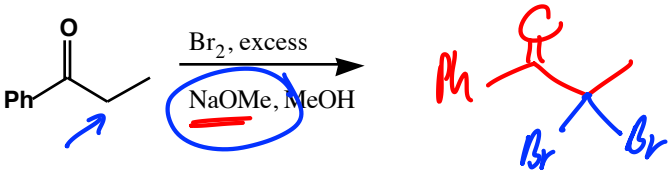


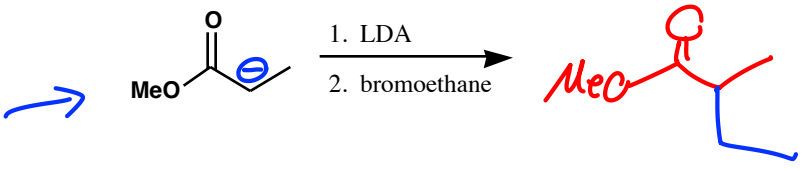



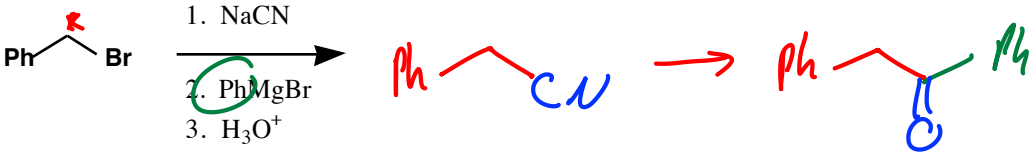



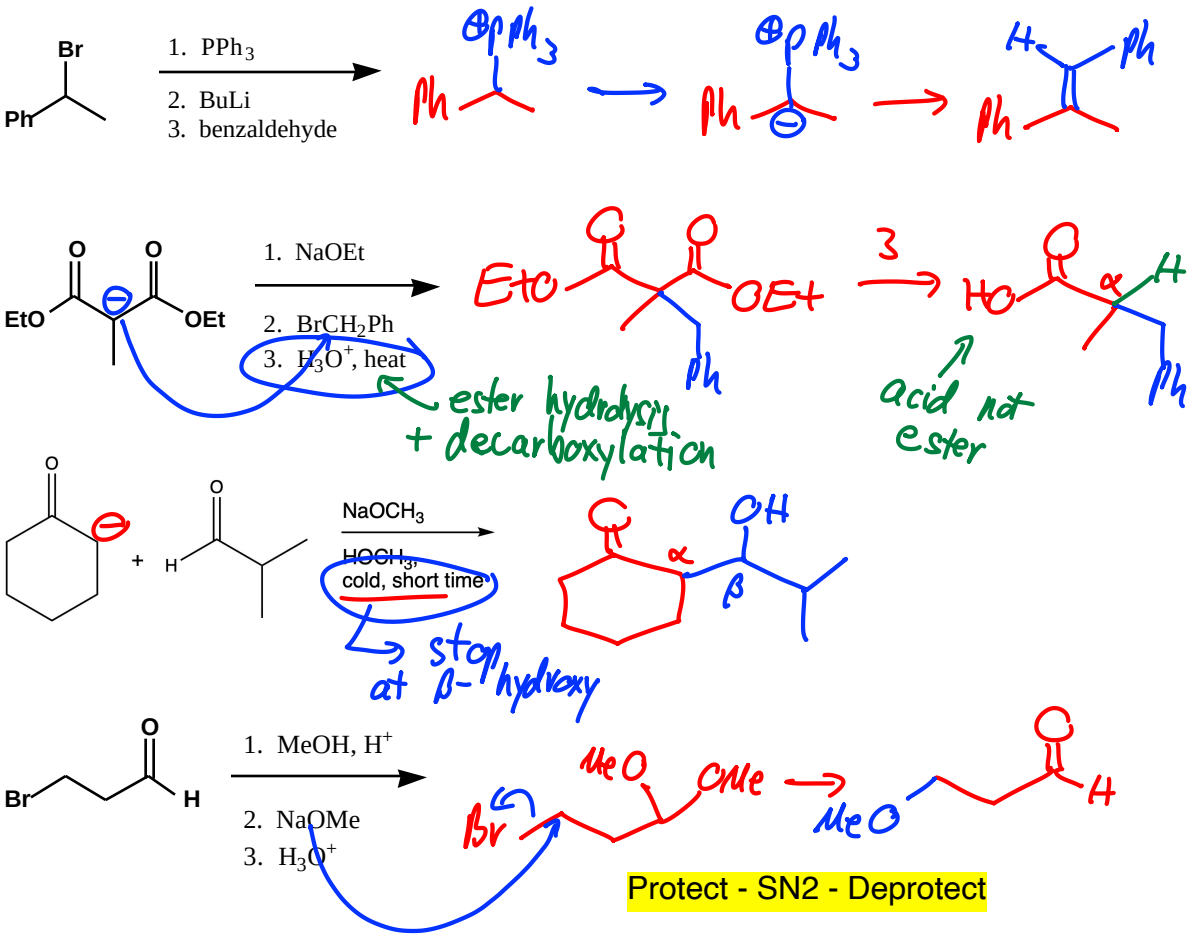



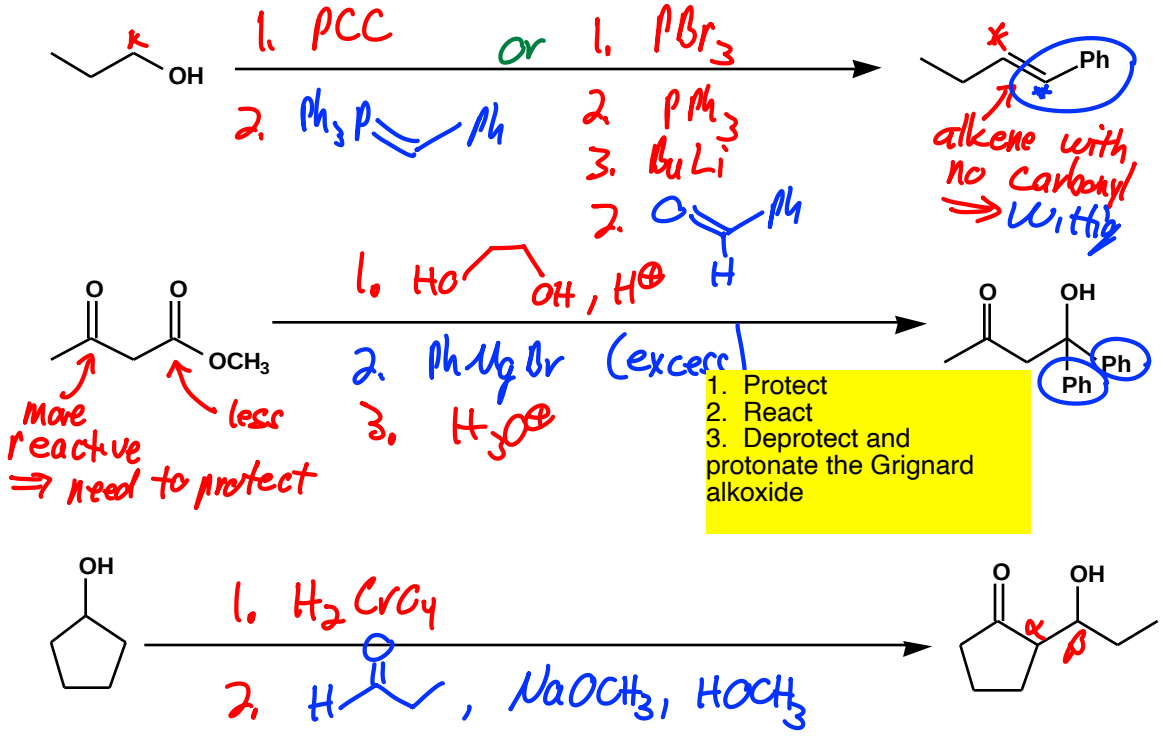



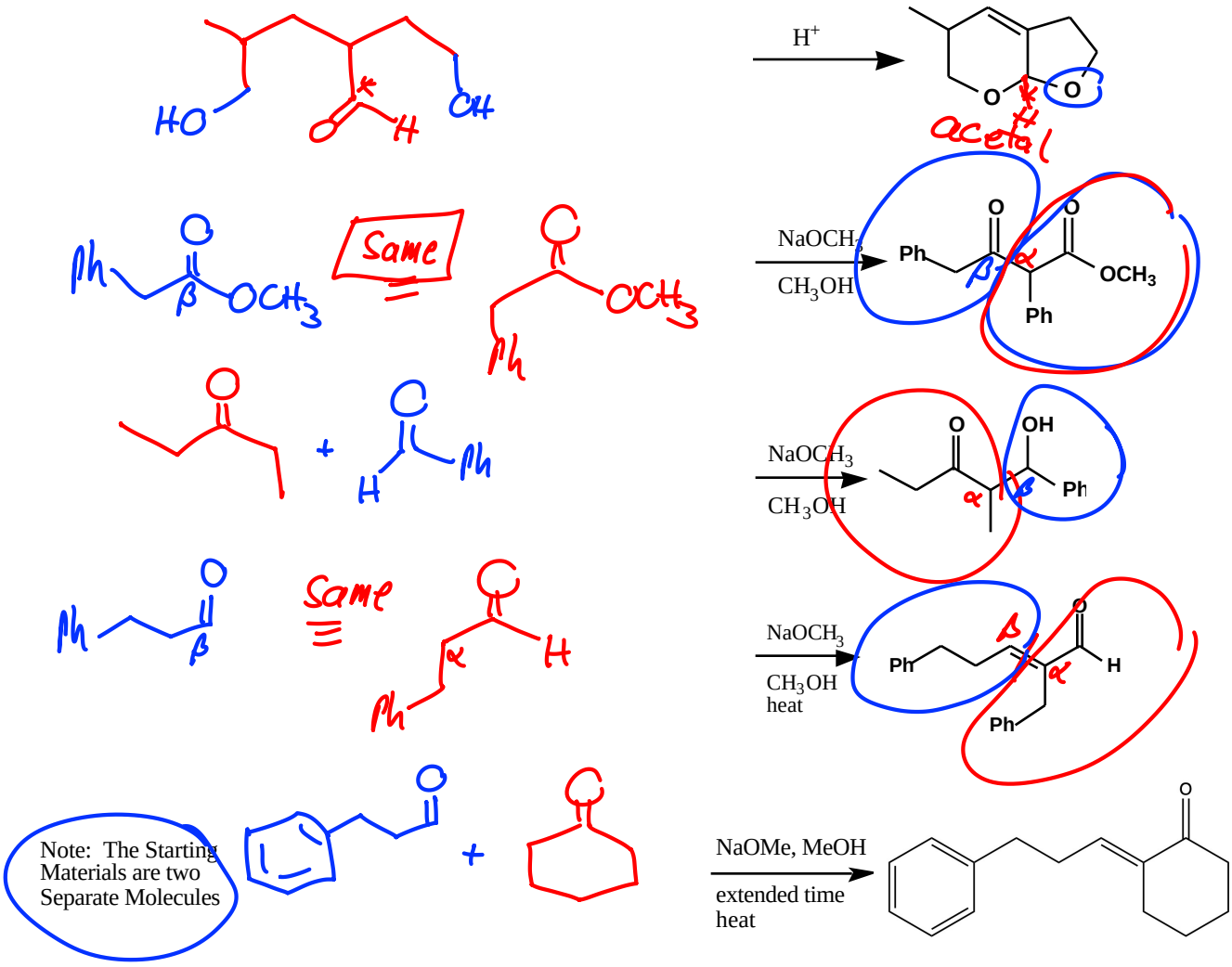





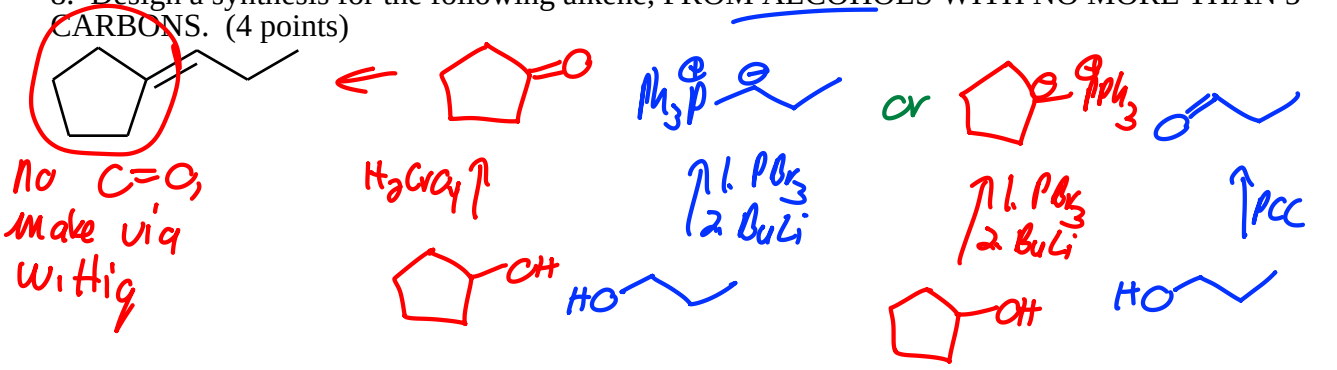

6. Provide Reagents for the Following Transformations: (4 points each)



7. Put in the starting materials from which the following structures would be produced. Depending on the product, the appropriate starting material may be either a single molecule, two of the same molecule, or two different molecules. For the last problem, you are required to start from two separate molecules. (2 points each)

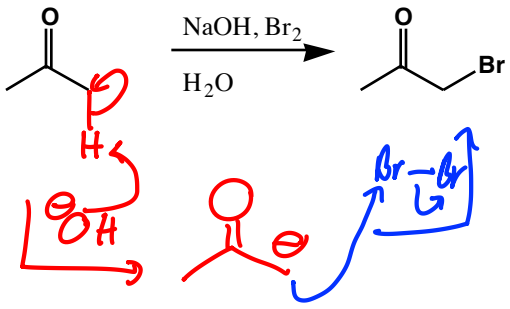



8. Design a synthesis for the following alkene, FROM ALCOHOLS WITH NO MORE THAN 5 CARBONS. (4 points)

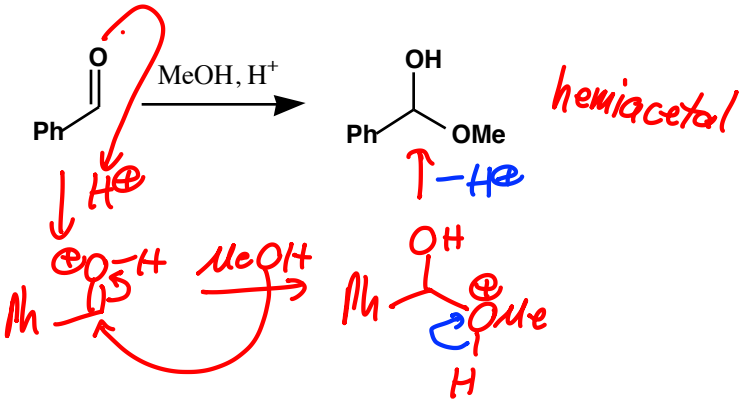


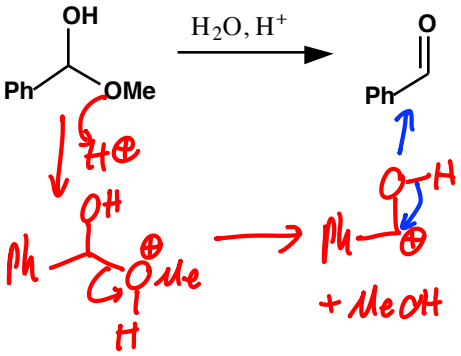

Either solution is fine, you'd not need to show both! :)

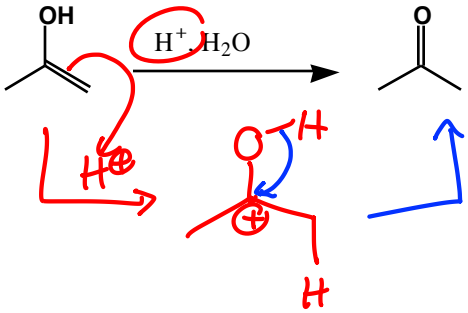
9. Provide Mechanisms for the Following Transformations. [Note: Some of these do not represent "clean" reactions; the product shown might go on to further reactions, or the reaction might be reversible, or the product might not be isolable. But that shouldn't prevent you from drawing the mechanism for the transformation indicated!] (3 points each)

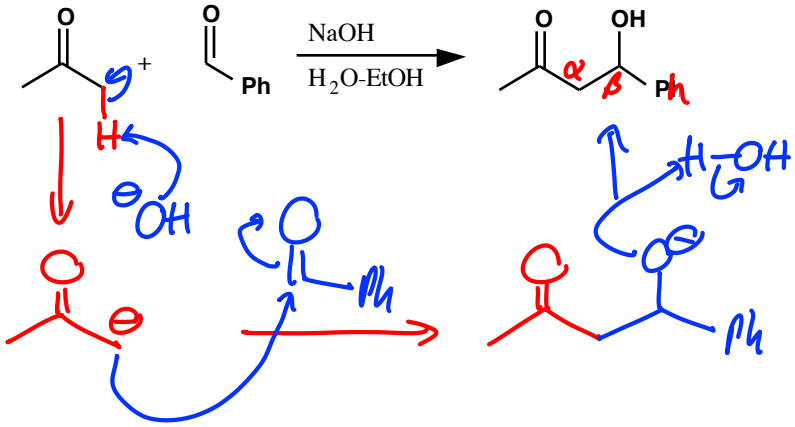



1. Deprotonate
2. React with Br2 electrophile

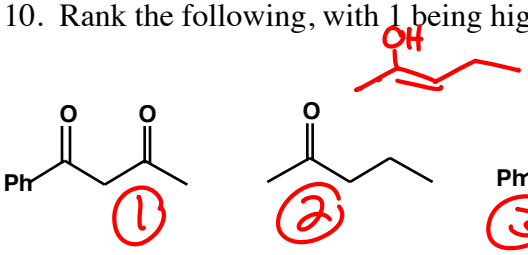


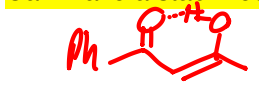
10. Rank the following, with 1 being highest, or most. (2 points each)

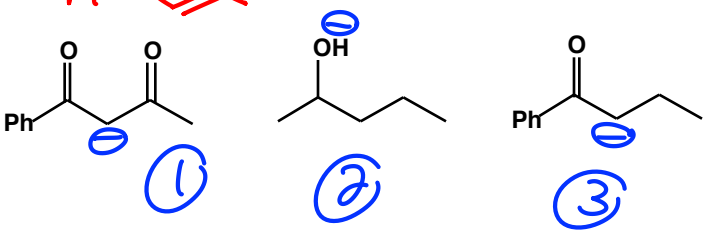


Relative amount in the "enol" form at equilibrium

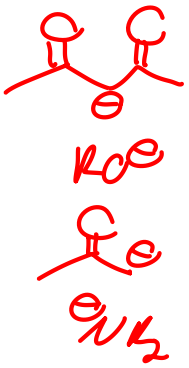
Can make a stabilized enol

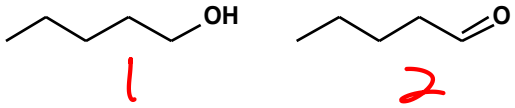
No alpha-H, no enol possible



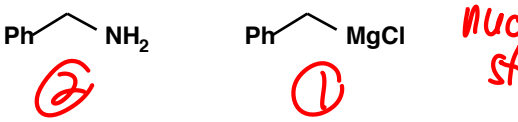


Acidity





Boiling Point

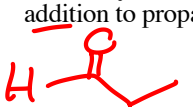


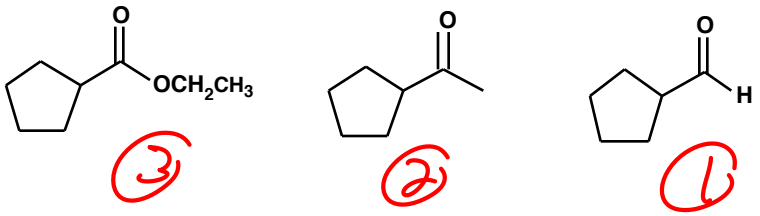




Nucleophile strength

Reactivity toward addition to propanal





Reactivity toward either MeOH/$H^+$ or PhLi (pattern is the same with either one)

Aldehyde > ketone > ester