Homework Five

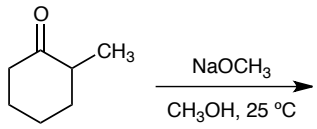
Organic Chemistry II (224) • Prof. Chad Landrie

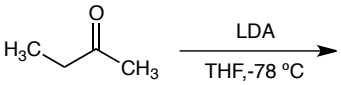
Spring 2013

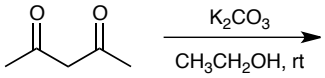
Completion (6 pts)		**Name**	
Random Sample(s) (4 pts)		**BID**	
Total (10 pts)		**Section-CRN**	

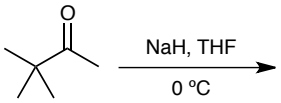
Additional Recommended Problems from McMurray (8th Ed.)	

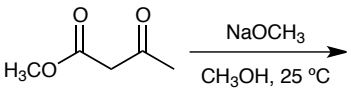
1. Draw the *major* enolate expected for each set of conditions.

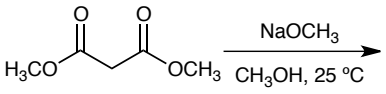
a. 

b. 

c. 

d. 

e. 

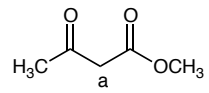
f. 

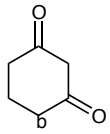
2. Draw the *major* product when each enolate above reacts with benzaldehyde. Assume all Aldols proceed to the α,β-unsaturated carbonyl.

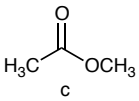
3. Draw the *major* product when each enolate above reacts with allyl bromide (3-bromo-1-propene).

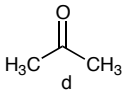
Homework Four Organic Chemistry II (224) Prof. Chad Landrie • Spring 2013	Name	
	OCC ID	
	Section CRN	

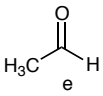
4. **First**, draw the conjugate acids and bases for each reaction. You must consider the *most* acidic proton in each acid. **Second**, use pK_a values found in your textbook (e.g., table 22.1) to calculate the K_{eq} for each reaction. It is not necessary to find exact pK_as (e.g, assume the pK_a for all B-ketoesters is 11.0).

A  + LDA ⟶ K_{eq}

B  + K_2CO_3 ⟶ K_{eq}

C  + $KOC(CH_3)_3$ ⟶ K_{eq}

D  + NaOH ⟶ K_{eq}

E  + NaOH ⟶ K_{eq}

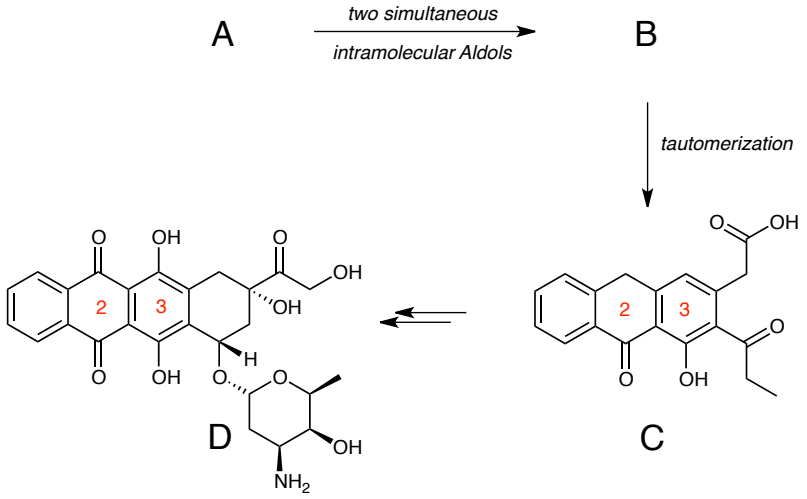
5. Based on pKa values, which is a stronger acid, a or b? Explain. Draw resonance structures to support your argument.

6. Based on pKa values, which is a stronger acid, c or d? Explain. Draw resonance structures to support your argument.

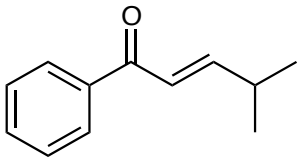
7. Based on pK_a values, which is a stronger acid, d or e? Explain.

Homework Four Organic Chemistry II (224) Prof. Chad Landrie • Spring 2013	Name	
	OCC ID	
	Section CRN	

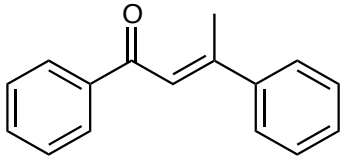
8. Doxyrubicin (trade: Doxil ®) is a chemotherapeutic agent used to treat cancers suchs a leukemia, Hodgkins, bladder and ovarian. It is biosynthesized by Streptomyces baceteria strains from polyketide precursors. Polyketide **A** underdgoes two simultaneous intramolecular Aldol condensations to form two a,b-unsaturated ketones. Tautomerization of the an α,β-unsaturated ketone to the enol provides the aromatic ring 3 in **C**. Draw the structures of **A** and **B**.



9. A junior chemist was attempting to make the α,β-unsaturated ketone **1** by a mixed Aldol condensation. He instead obtained a mixture of **1** and **2**, which made his boss very unhappy. When asked what conditions were employed, the chemist told his boss that he dissolved the starting materials in ethanol and then added sodium ethoxide at 25 ºC. The boss shook her head disappointingly and told the junior chemist that he had two days to figure it out or he was fired. Help him out! **First**, determine what carbonyl compounds he started with. **Second**, propose four changes that should be made to obtain **1** as the major product. **Third**, explain what effect each change is having on the reaction energy profile.



(*E*)-4-methyl-1-phenylpent-2-en-1-one (**1**)



(*E*)-1,3-diphenylbut-2-en-1-one (**2**)

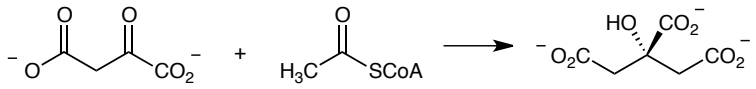
Homework Four Organic Chemistry II (224) Prof. Chad Landrie • Spring 2013	Name	
	OCC ID	
	Section CRN	

10. When optically active (R)-2-methylcyclohexanone is treated with either aqueous acid or base, raceminzation occurs. **First**, state the meaning of racemization. **Second**, explain why this occurs. **Third**, draw a mechanism that supports your argument.

11. Optically active (S)-3-methylcylclohexanone does not undergo racemization like above? Why?

12. (R)-2-phenylpropanoic acid is treated with PBr3 and Br2 to give the a-bromoacid (Hell-Volhardt-Zelinski reaction). Is the product optically active? Why or why not?

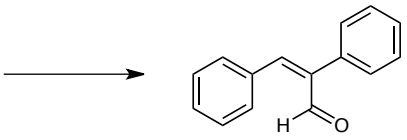
13. The first step in the citric acid cycle (Kreb's cycle) of metabolism is the reaction of oxaloacetate with acetyl CoA to give citrate. Propose a mechanism using base or acid catalysis as needed.

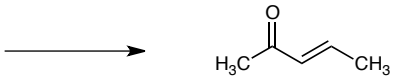


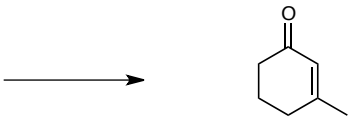
oxaloacetate acetyl CoA citrate

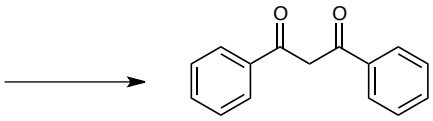
Homework Four Organic Chemistry II (224) Prof. Chad Landrie • Spring 2013	Name	
	OCC ID	
	Section CRN	

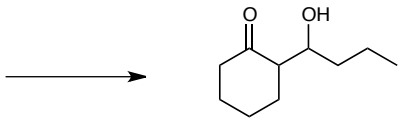
14. Draw the reactants required to make each Aldol or Claisen product.

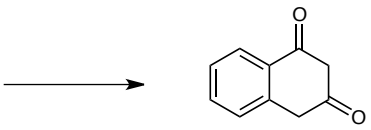


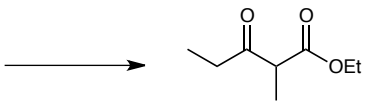


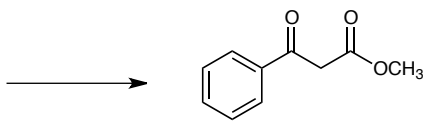




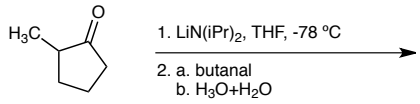


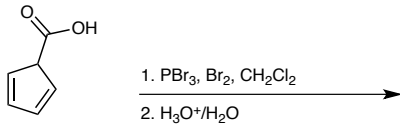


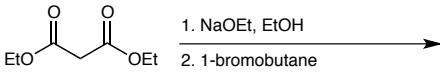


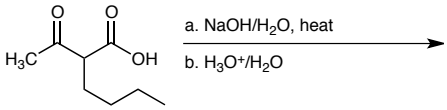


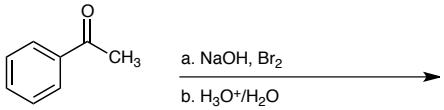
15. Draw the *major* product for each transformation.

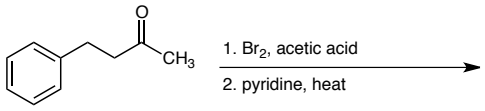


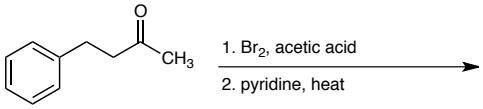


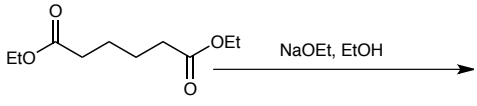


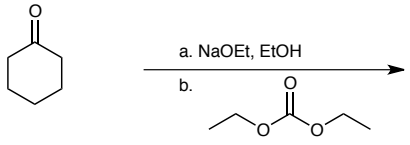






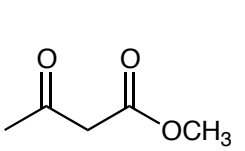
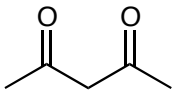
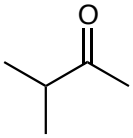
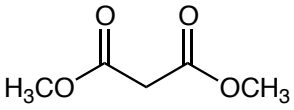
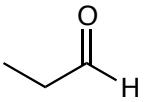






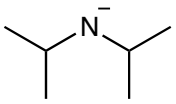
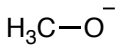
Homework Four Organic Chemistry II (224) Prof. Chad Landrie • Spring 2013	Name	
	OCC ID	
	Section CRN	

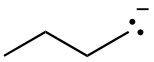
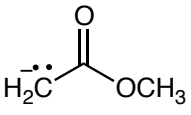
16. Rank in order of increasing acidity (1 = weakest acid, largest pKa; 5 = strongest acid, smallest pKa).

What was your reasoning?:

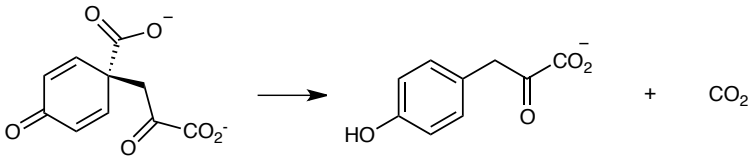
17. Rank in order of increasing basicity. (1 = weakest base; 5 = strongest base).

What was your reasoning?:

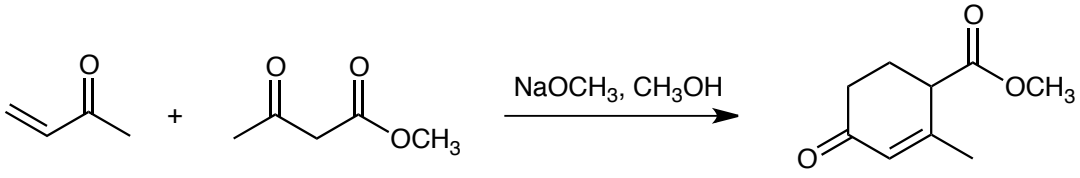
18. Using curved arrows, propose a mechanism for the following reaction, one of the steps in the biosynthesis of the amino acid tyrosine.



Homework Four Organic Chemistry II (224) Prof. Chad Landrie • Spring 2013	Name	
	OCC ID	
	Section CRN	

19. Draw the complete mechanism for each transformation.

A. Robinson-Annulation



B. Acetoacetic Ester Synthesis