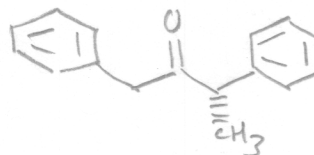
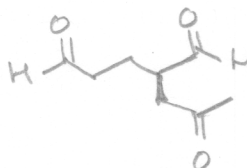


1. Draw the structure of the following compounds (don't forget stereochemistry). (30 points)

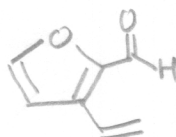
a. (S)-1-methyl-1,3-diphenylpropan-2-one



b. (R)-2-(2-oxopropyl)pentanedial

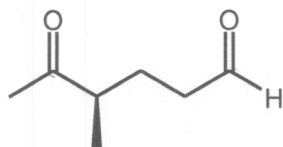


c. 2-vinyl-3-furancarbaldehyde



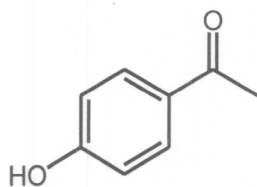
2. Provide IUPAC names for the following compounds (don't forget stereochemistry where appropriate). (30 points)

a.



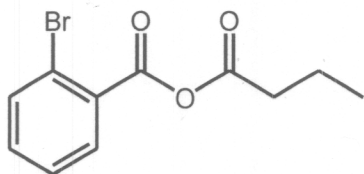
(R)-4-methyl-5-oxohexanal

b.



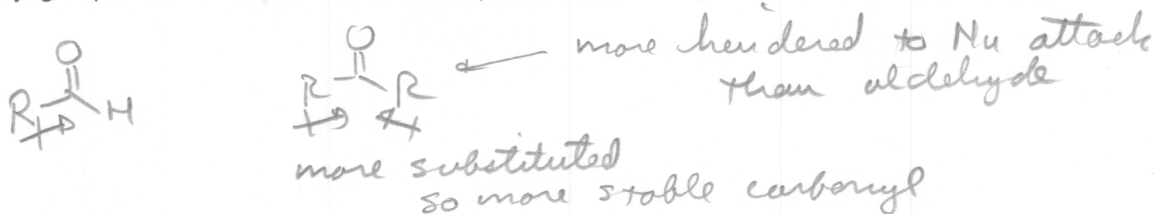
4-hydroxyacetophenone - not IUPAC, but OK
(4-hydroxyphenyl)-1-ethanone

c.

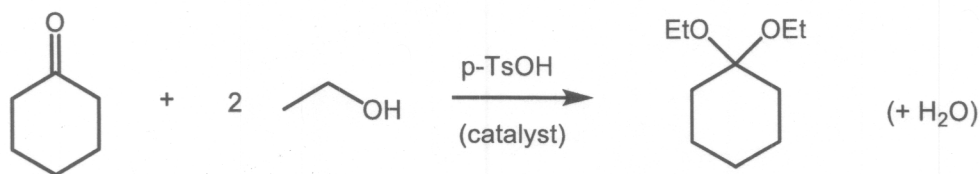


2-bromobenzoyl butanoate anhydride

3. Which carbonyl group is more reactive toward nucleophilic attack, aldehydes or ketones? Explain why. (10 points)

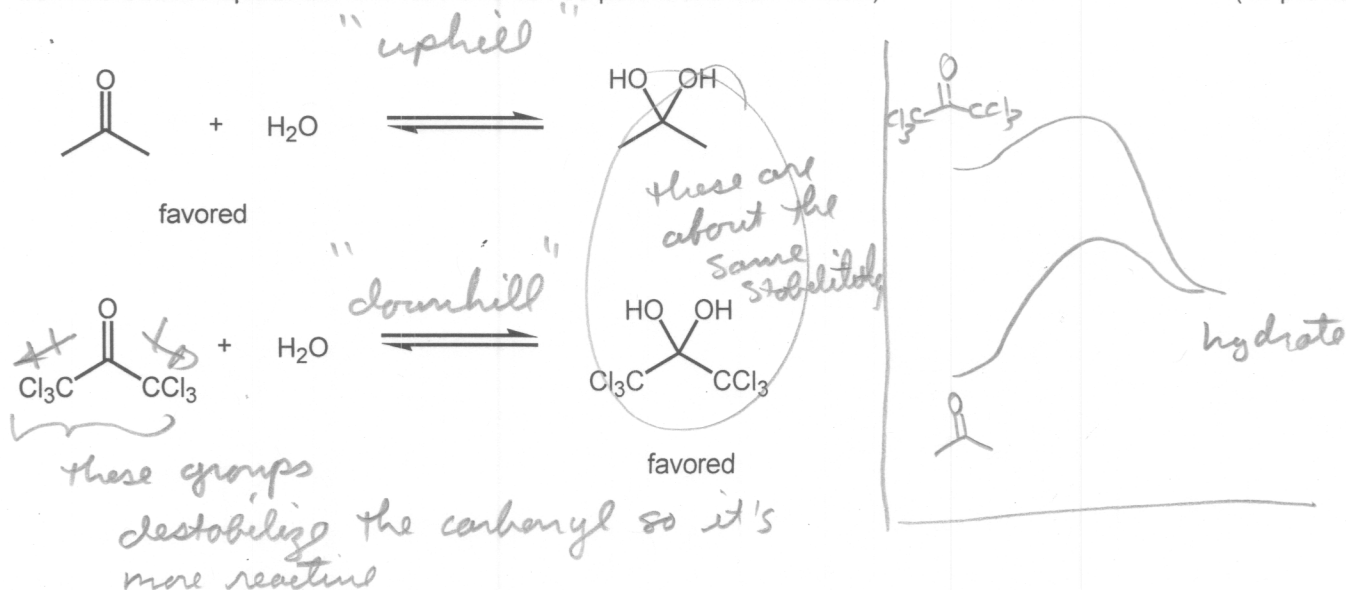


4. Show the complete mechanism for the following reaction. Label each step as slow or fast. (15 points)

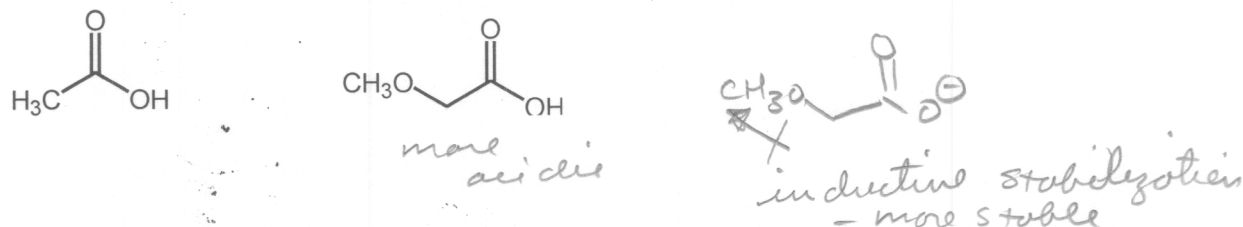


done in lecture!

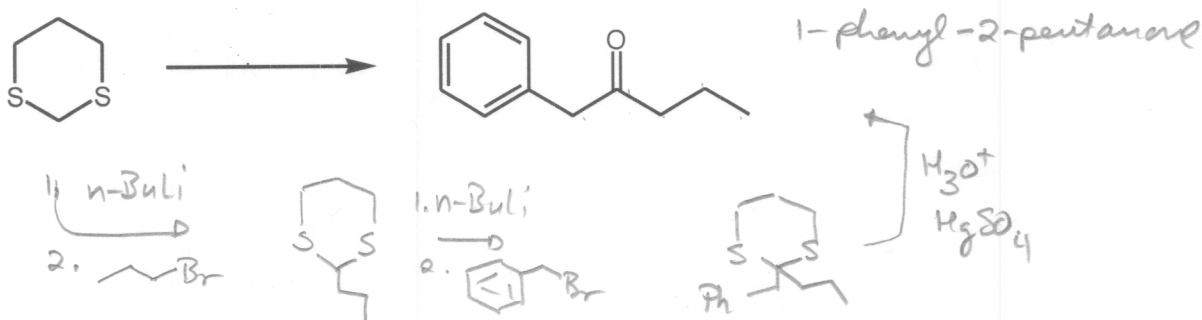
5. Explain why the top equilibrium favors the reactants and the bottom one favors the product. (In fact the product from the bottom equilibrium is a solid and can be purchased from Aldrich). (10 points)



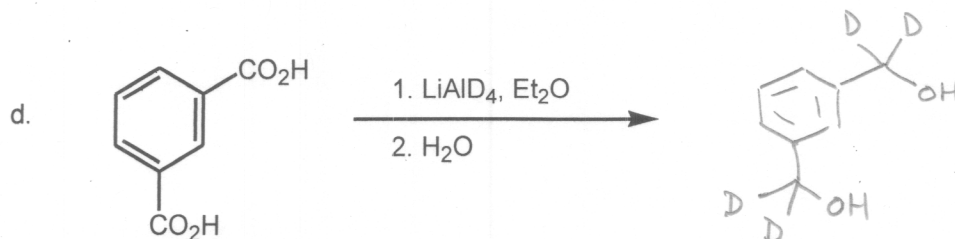
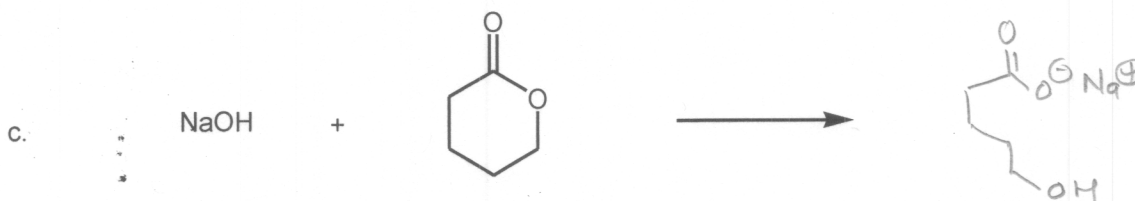
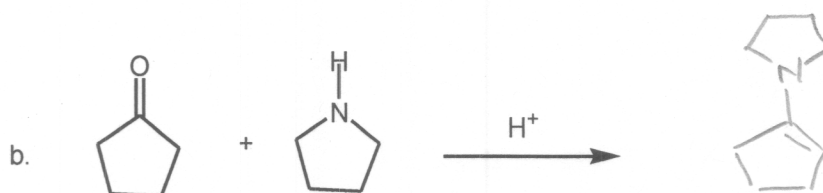
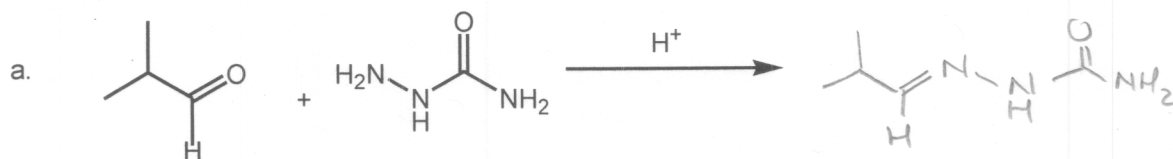
6. Which carboxylic acid shown below is more acidic? Clearly explain why. (10 points)



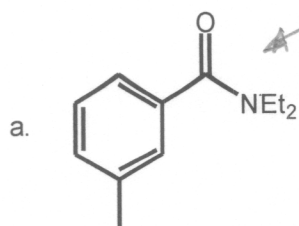
7. Show how to convert 1,3-dithiane to the product shown. Also, provide an IUPAC name for the product. (15 points)



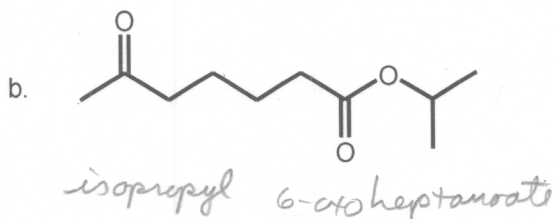
8. Show the product (or products) produced or the reagents needed for the following synthetic transformations. (20 points)



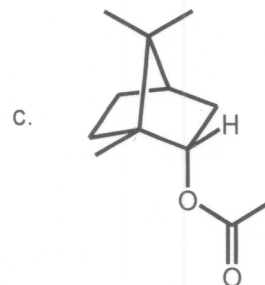
1. Provide IUPAC names for the following compounds. (30 points)



N,N-diethyl-m-toluamide
N,N-diethyl-3-methylbenzamide



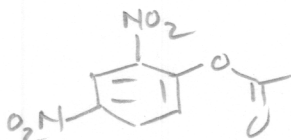
isopropyl 6-oxoheptanoate



1,5,7-trimethylbicyclo[2.2.1]-
heptan-2-yl acetate

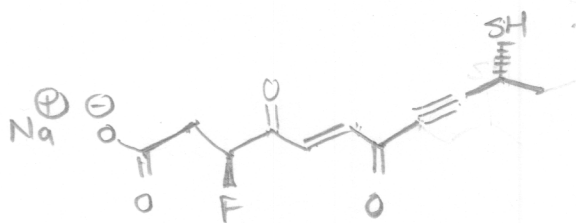
2. Draw the structure of the following compounds (don't forget stereochemistry). (30 points)

- a. 2,4-dinitrophenyl acetate



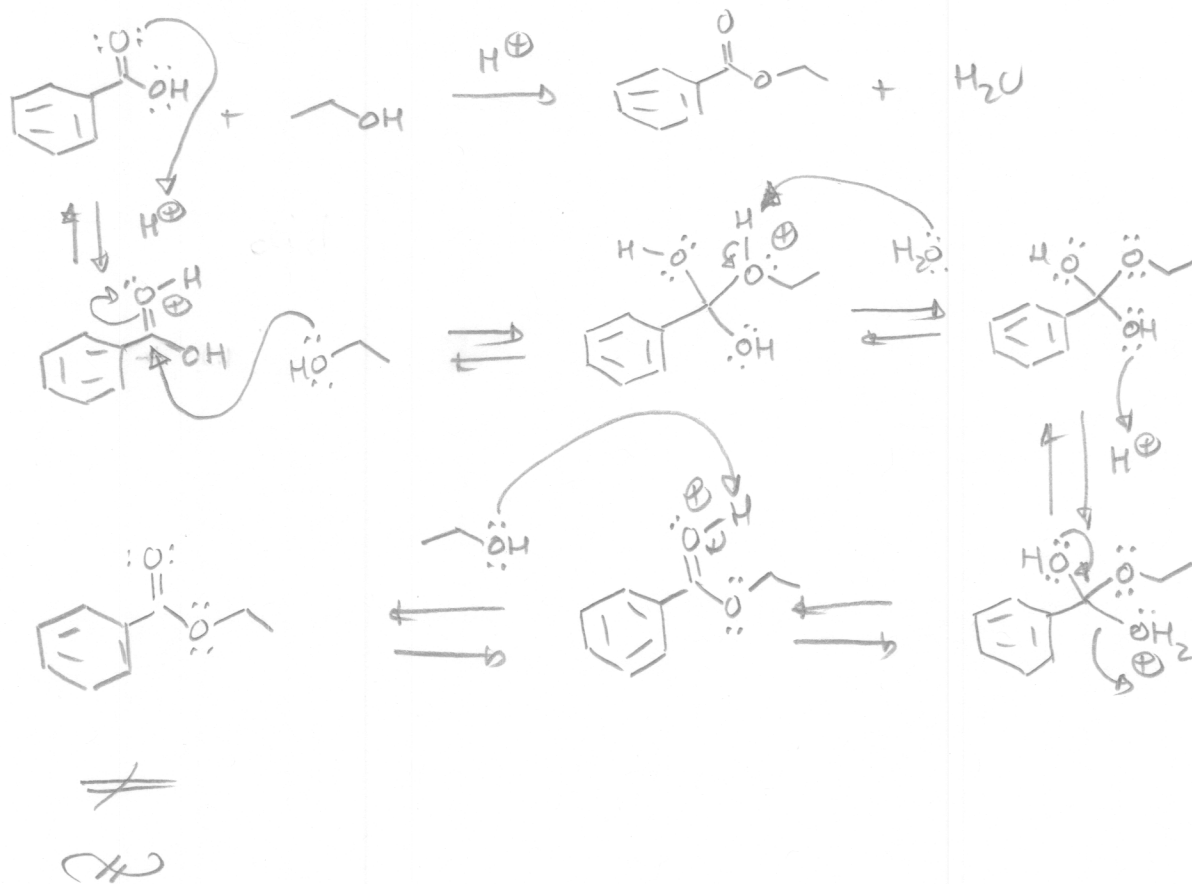
- b. (R)-N,1-dimethyl-2-cyclopentenecarboxamide

- c. sodium (3S,5Z,10R)-3-fluoro-4,7-dioxo-10-sulfanylundec-5-en-8-ynoate



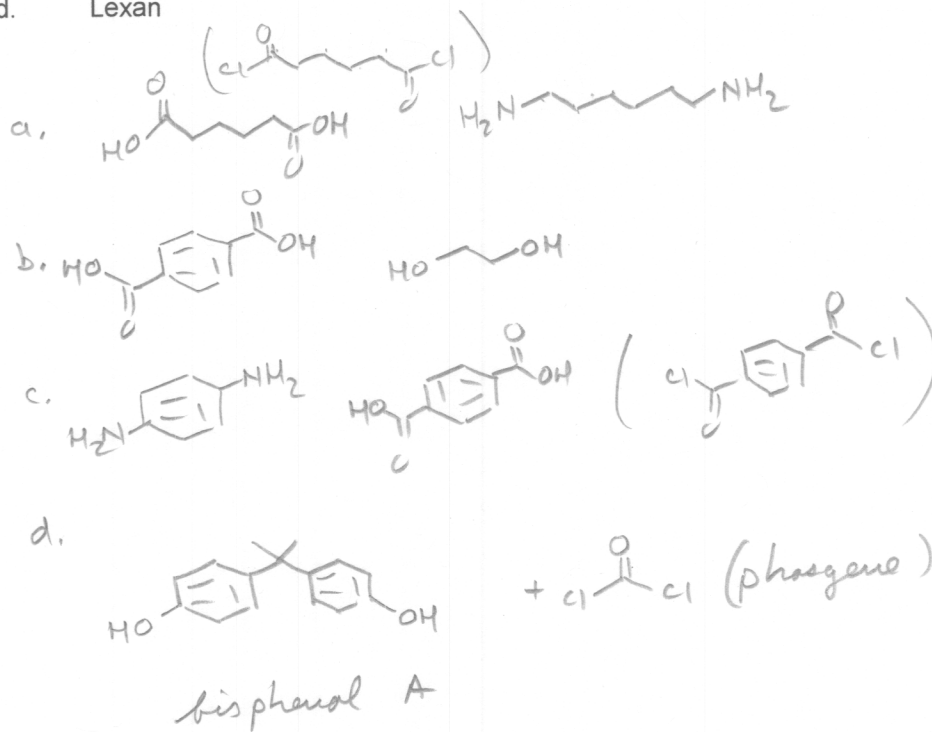
3. On the Internet, go to the KEGG website (<http://www.genome.jp/kegg/>) and find examples of the following reactions. Show the reaction and cite the reaction number (e.g., R00619) and the give the enzyme name and number (e.g., thiamine diphosphokinase, 2.7.6.2). (20 points)
- a. conversion of an ester to a carboxylic acid
 - b. hydrolysis of an amide
 - c. oxidation of ethanol to give acetaldehyde

4. Show the *complete* mechanism of the Fischer esterification of benzoic acid with ethanol (using a catalytic amount of H_2SO_4). For each step of the reaction, indicate whether the step is a *proton transfer*, *nucleophilic attack*, or *loss of a leaving group*. Also, show which steps are fast and which ones are slow. (40 points)

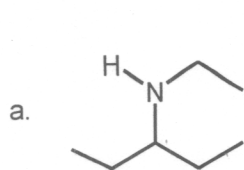


5. Many polymers contain repeating carboxylic acid derivatives. For the following four examples, show what the starting materials (monomers) are in each case and describe the most common uses for of each type of polymer. (40 points)

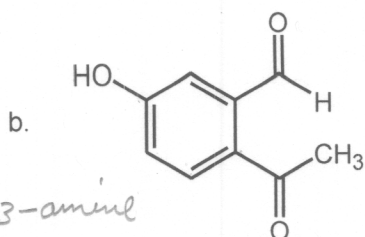
- a. Nylon-6,6
b. Polyethylene terephthalate (PET)
c. Kevlar™
d. Lexan



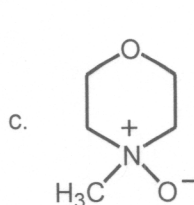
1. Provide IUPAC names for the following compounds (don't forget stereochemistry where appropriate). (25 points)



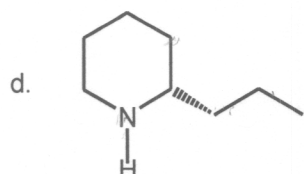
N-ethylpentan-3-amine



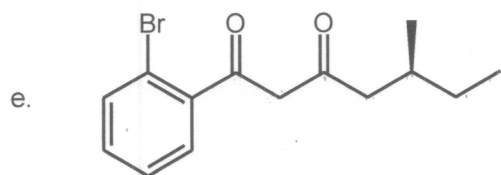
2-acetyl-5-hydroxybenzaldehyde



*N-methylmorpholine
N-oxide*



(S)-2-propylpiperidine

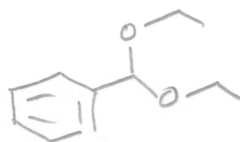


(S)-1-(2-bromophenyl)-5-methylheptane-1,3-dione

2. Draw the structure of the following compounds (don't forget stereochemistry). (30 points)

a. ~~(R)-2-(2-oxopropyl)pentanal~~

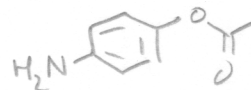
b. benzaldehyde diethyl acetal



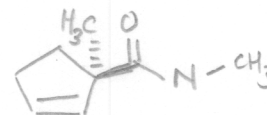
c. N-(1-ethylethenyl)pyrrolidine



d. 4-aminophenylmethyl acetate



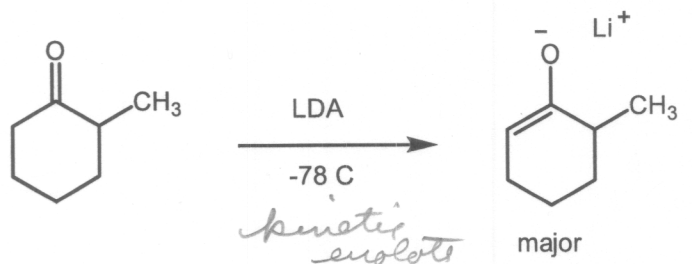
e. (R)-N,1-dimethyl-2-cyclopentenecarboxamide



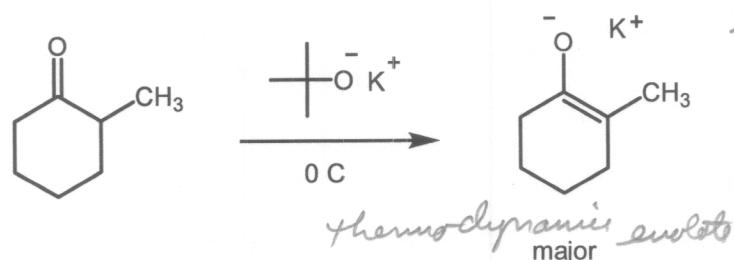
f. (Z)-1-fluoro-11-sulfanylundec-8-en-6-yne-2,3,10-trione



3. Explain the following results regarding the formation of the enolates, i.e., why are different enolates produced? Consider kinetics vs. thermodynamics. (10 points)

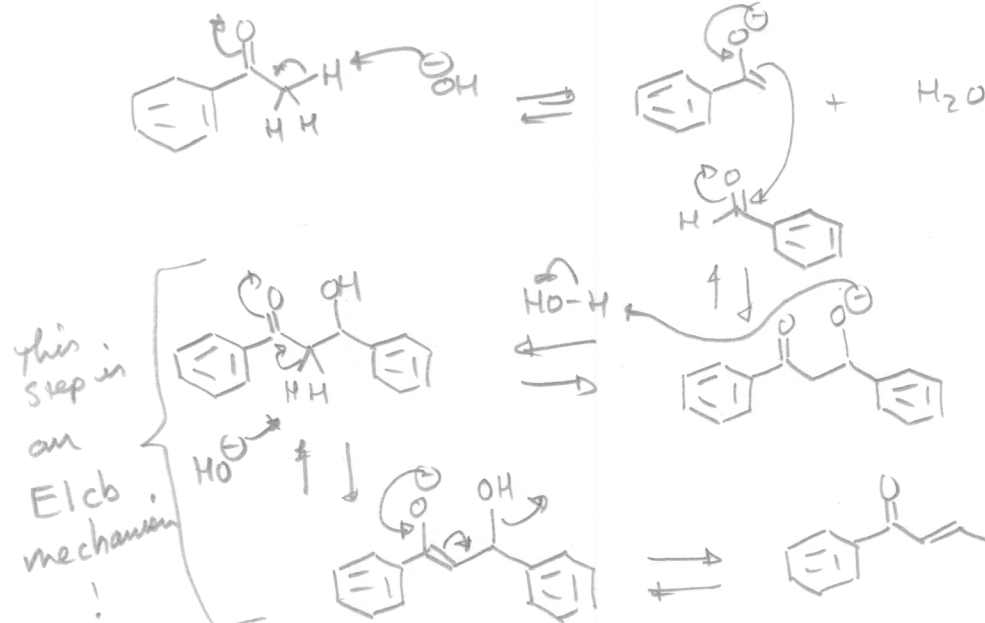
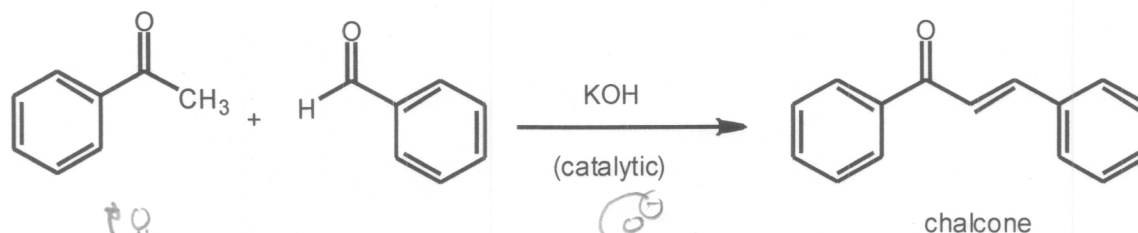


This enolate is formed faster since the less substituted carbon is more accessible. Also, the LDA is at least 10^{20} times more basic than the formed enolate so deprotonation is $\sim 100\%$ and irreversible.

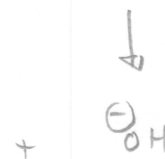


The more substituted enolate is more stable. Using a weaker base, such as *t*-butoxide, allows for equilibration of the kinetic enolate with the thermodynamic one. The base used is close to the basicity of the formed enolate.

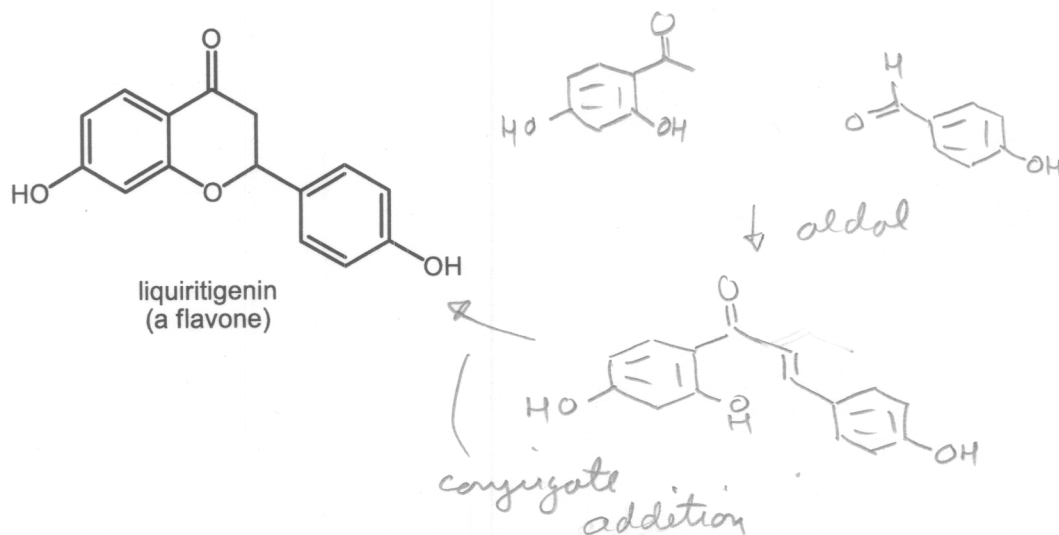
4. Show the complete mechanism for the reaction shown below and provide an IUPAC name for the product, whose common name is chalcone. Explain why only a catalytic amount of KOH is needed for the reaction.



hydroxide is regenerated in the last step so only a catalytic amount is needed



5. Suggest starting compounds that could be used in a synthesis of the natural product *liquiritigenin*, found in licorice, shown below. (Hint: Nature uses an aldol and a conjugate addition reaction to do this)



6. Place the following compounds (A-D) in order of acidity (1 for most acidic, 4 for least acidic)

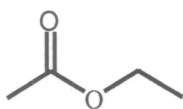
(8 points)

$pK_a \approx 23$

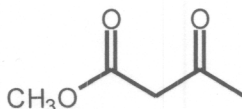
≈ 11

≈ 20

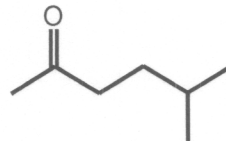
≈ 13



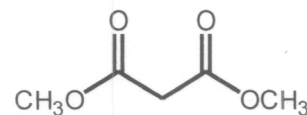
A 4



B 1



C 3

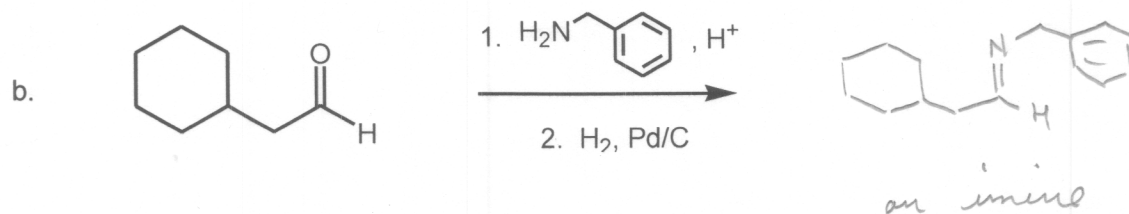
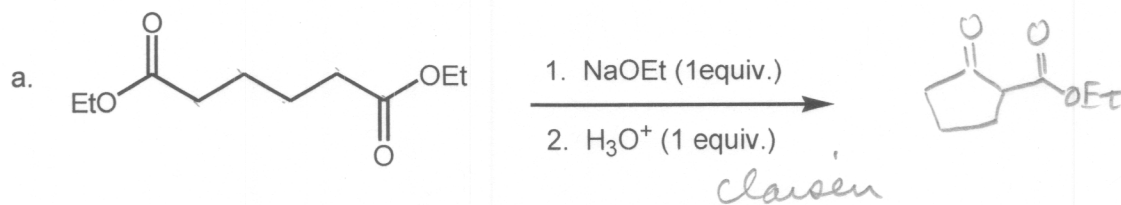


D 2

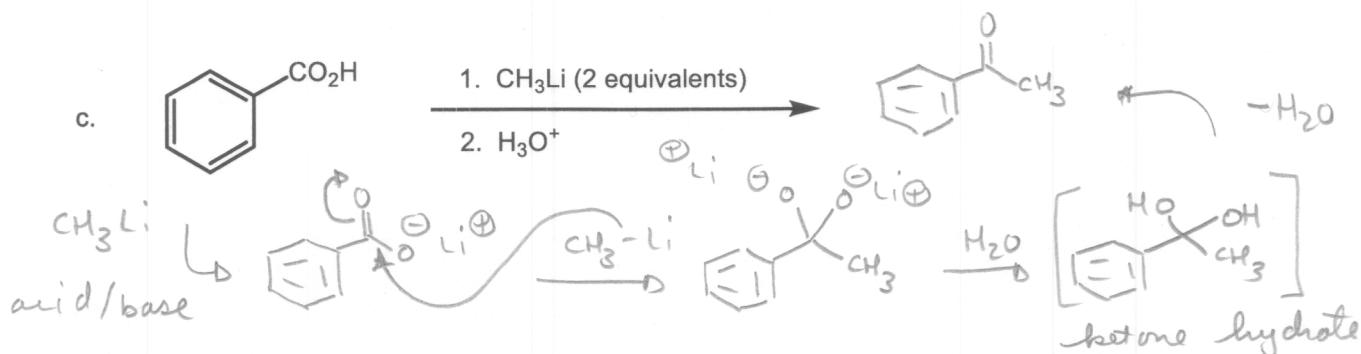
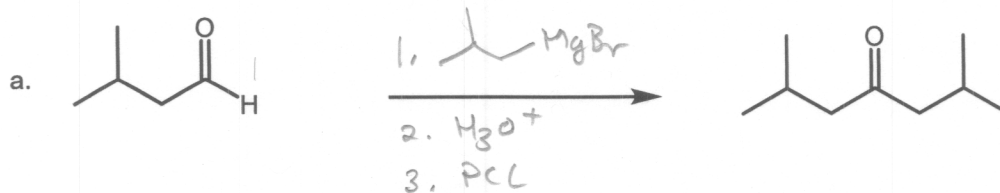
Order ____

7. Show the product (or products) for the following reactions.

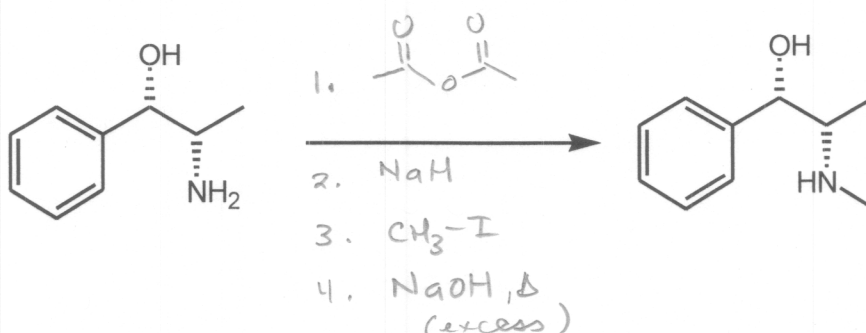
(10 points)



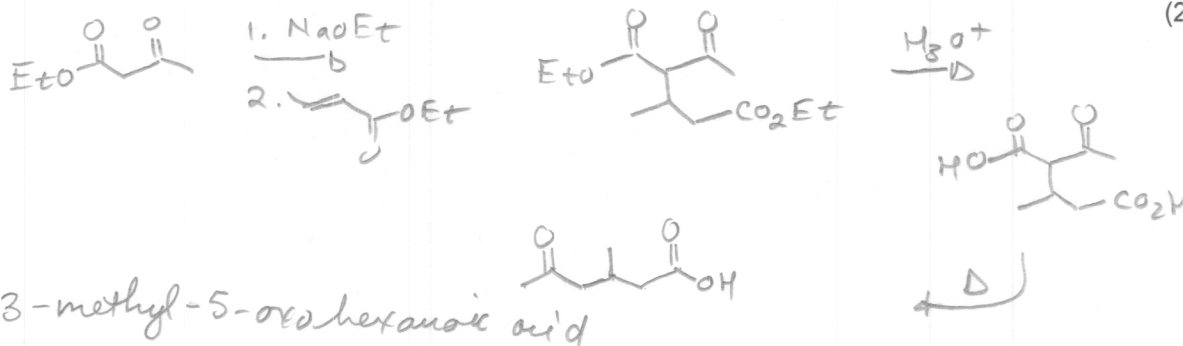
8. Show the product (or products) produced or the reagents needed for the following synthetic transformations. (15 points)



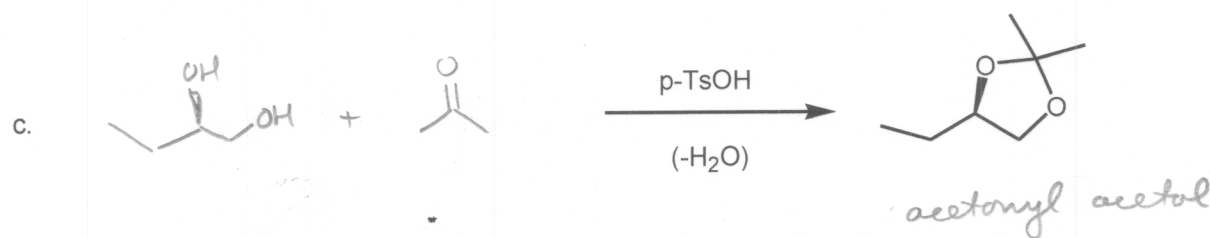
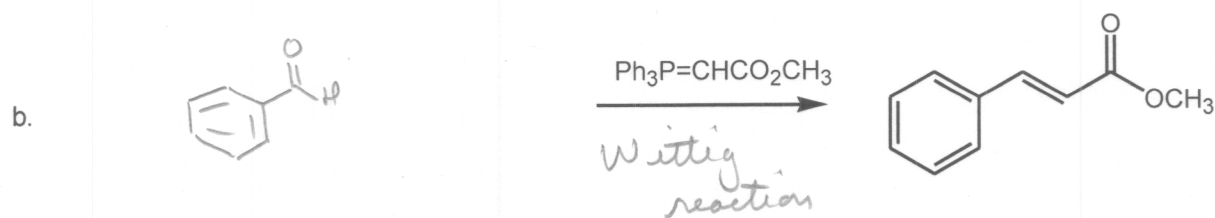
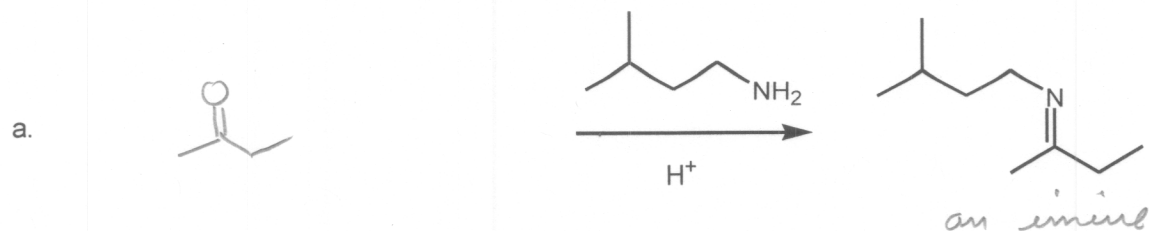
9. Suggest a synthetic scheme to convert the compound on the left to pseudoephedrine, the active ingredient in the decongestant SUDAFED. (10 points)
EXTRA CREDIT Provide IUPAC names for the starting material and the product. (10 EC points)



10. Challenge synthesis question Show the Michael addition reaction of ethyl acetoacetate with ethyl crotonate, followed by aqueous hydrolysis and decarboxylation. Finally, provide the IUPAC name of the product. (25 points)



9. Show the starting materials for the following products from the following reactions. (20 points)



(show both starting materials for c.)

10. Avermectin, shown below, is a naturally occurring antiparasitic and insecticidal compound used in veterinary medicine for the treatment of fur mites (e.g., *Ornithonyssus bacoti*, the Tropical rat mite).

Circle all *acetals* and *lactones* indicate if any of the acetals are *hemi-acetals*?

(10 points)

