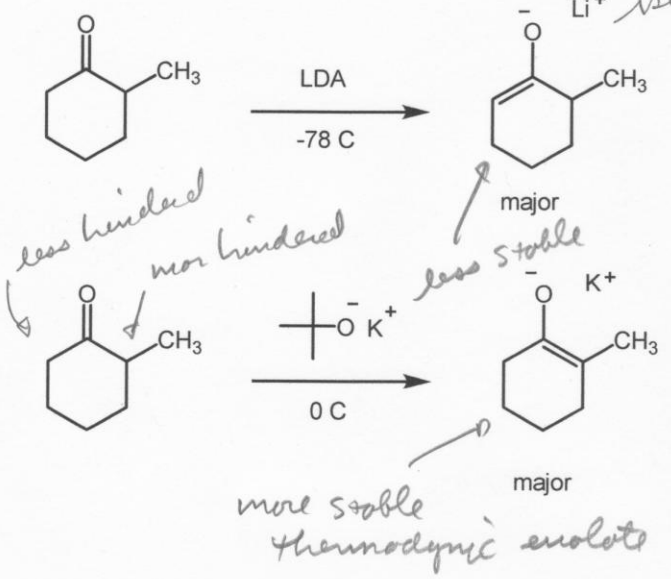
1. Explain the following results regarding the formation of the *enolates*, i.e., why are different *enolates* produced? Consider kinetics vs. thermodynamics. (10 points)

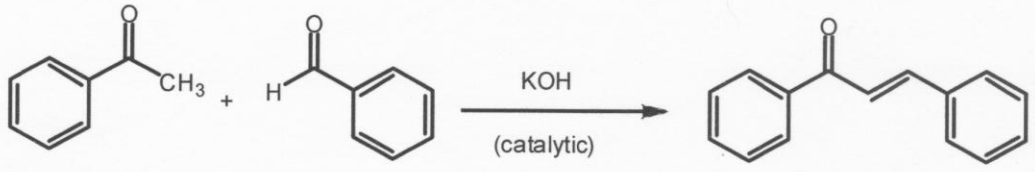


kinetic enolate

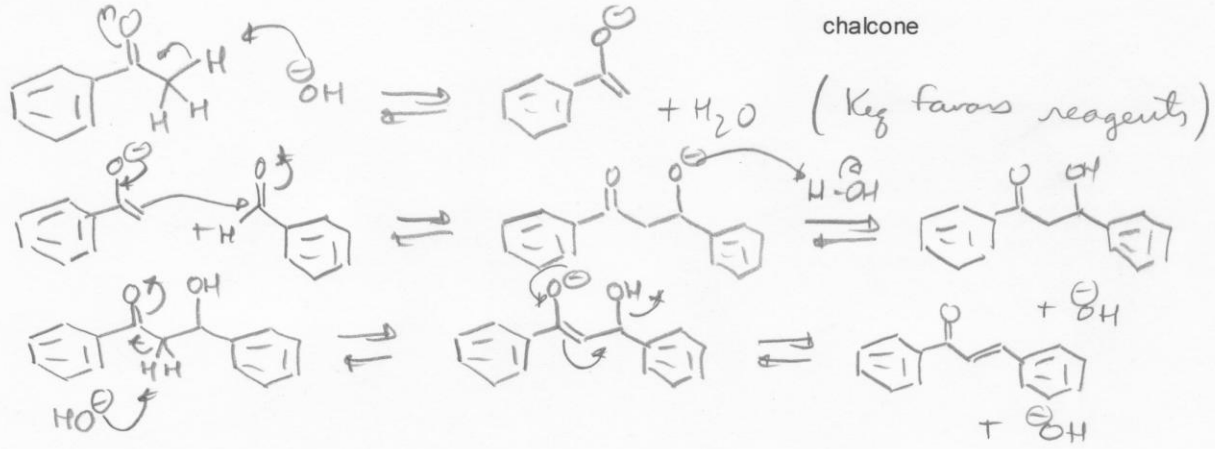
LDA is a super strong hindered base, and removes the more accessible proton faster – at low temp, the deprotonation is irreversible

t-O$^{\ominus}$ deprotonation still occurs at the less hindered faster, but undergoes equilibration to give the more stable, more substituted enolate

2. *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. (10 points)

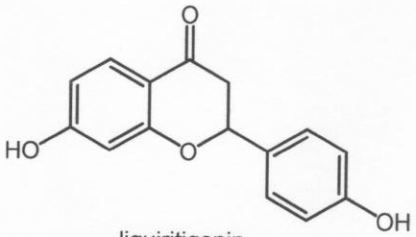


chalcone

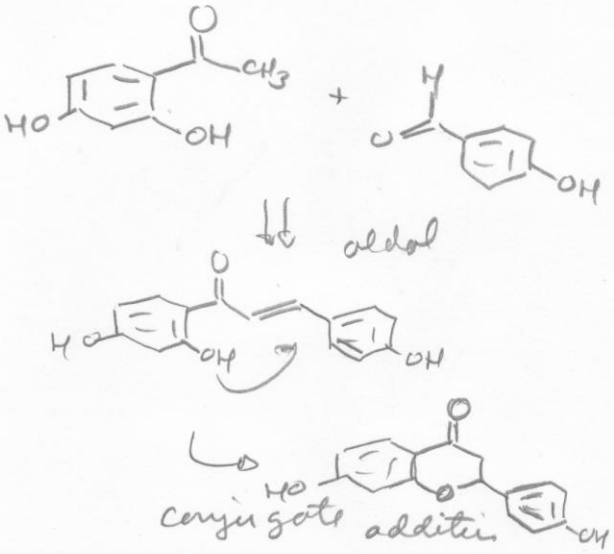


– $^{\ominus}$OH is used twice as a base, is regenerated once by proton exchange, and then through elimination in the last step

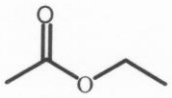
3. Suggest starting compounds that could be used in a synthesis of the natural product *liquiritigen*, found in licorice, shown below. (Hint: Nature uses an aldol and a conjugate addition reaction to do this) (10 points)



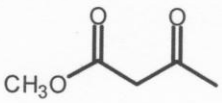
liquiritigenin
(a flavone)



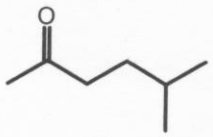
4. Place the following compounds (A-D) in order of acidity (*1 for most acidic, 4 for least acidic*) (8 points)



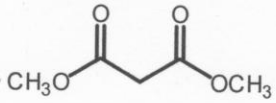
A



B



C

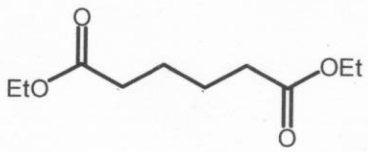


D

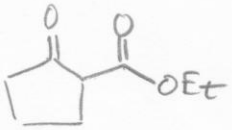
Order 4 1 3 2

5. Show the product (or products) for the following reactions. (10 points)

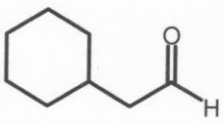
a.



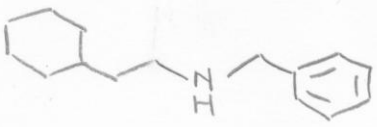
1. NaOEt (1equiv.)
2. H_3O^+ (1 equiv.)



b.

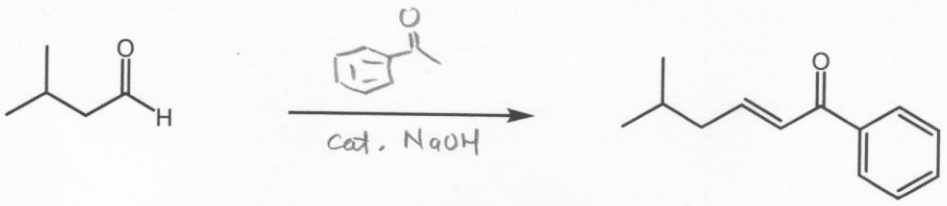


1. H_2N  , H^+
2. H_2, Pd/C

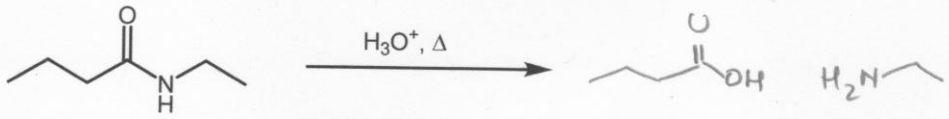


6. Show the reagents needed for question a. and the product (or products) for questions b. and c.. (15 points)
EXTRA CREDIT: What is the reason for adding exactly 1 equiv. of acid in question c., step 3? (5 EC points)

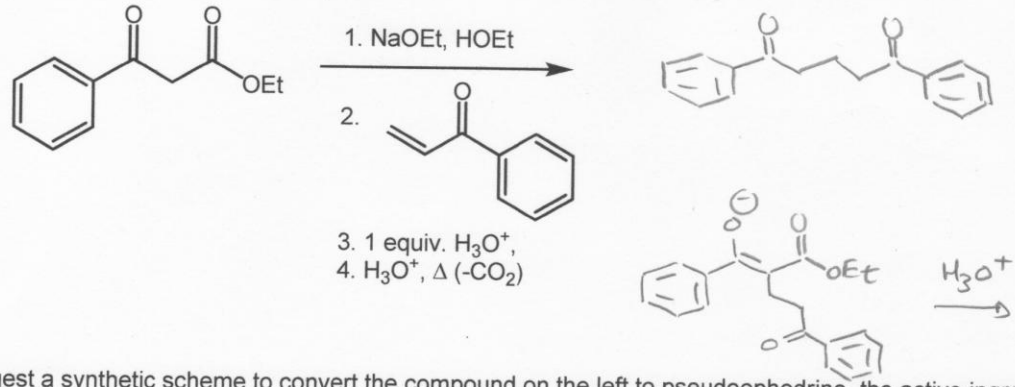
a.



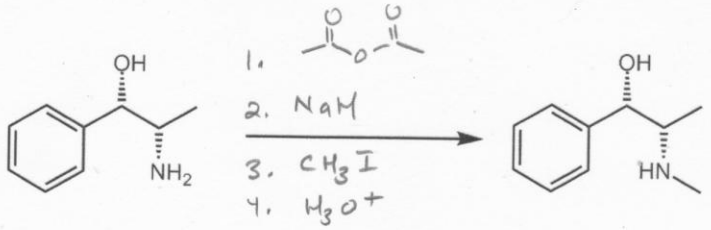
b.



c.

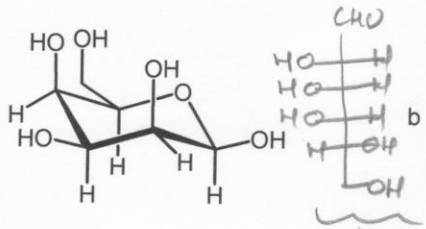


7. Suggest a synthetic scheme to convert the compound on the left to pseudoephedrine, the active ingredient in the decongestant SUDAFED. (10 points)
EXTRA CREDIT Provide IUPAC names for the starting material and the product. (10 EC points)



8. Provide the *complete* name for the following sugars (see Figures 24.5 and 24.6 in Klein) (10 points)

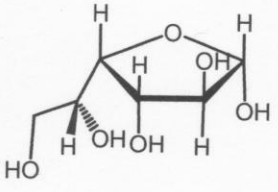
a



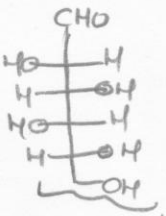
β-D-talopyranose

b

D-talose



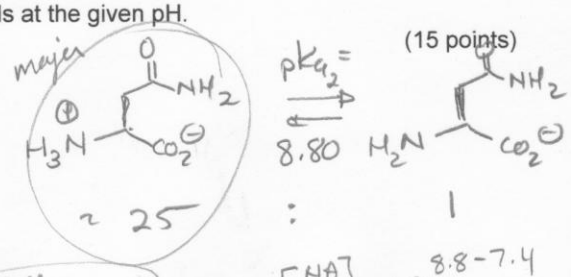
β-D-Idofuranose



D-Idose

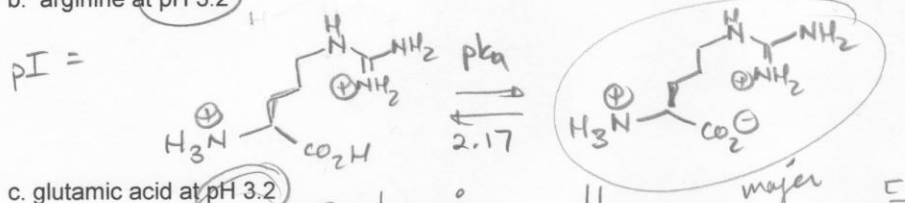
9. Show the predominant acid/base form of the following amino acids at the given pH. (you might need data from Table 25.2) (15 points)

a. asparagine at pH 7.4 (physiological, or "blood" pH)



→ pI = 5.41
(calculated from Table 25.2)

b. arginine at pH 3.2



$\frac{[HA]}{[A^-]} = 10^{8.8-7.4} = 10^{1.4} \cong 25$

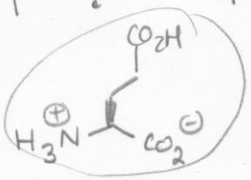
c. glutamic acid at pH 3.2

≈ 1 : 11

$\frac{[HA]}{[A^-]} = 10^{2.17-3.2} = 10^{-1.03} \cong \frac{1}{11}$

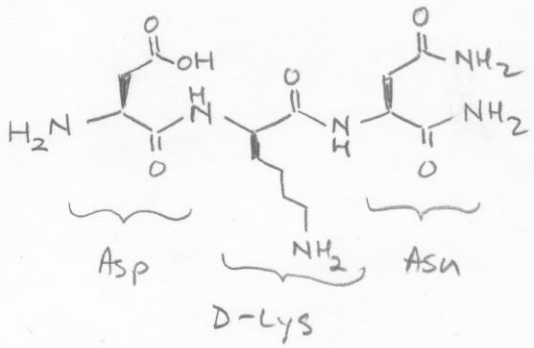
pI = 3.2

if pI = pH then the zwitterionic form is present



← zwitterionic form

10. Provide the complete structure for the peptide H-Asp-*D*-Lys-Asn-NH_2 and show all relevant stereochemistry. (See Table 25.1 in Klein, and note the notations and descriptors used in the name of the peptide) (10 points)



note this means the C-terminus is in the form of an amide