CHEMISTRY 3331, Spring 2005
Professor Walba
Final Exam, May 3

scores:

1) 40

2) 40

3) 40

4) 20

5) 20

6) 40

200

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Name (printed): Key

Signature: _____

Recitation TA Name: _____

Recitation day and time: _____

This is a closed-book exam. The use of notes, models, calculators, scratch paper, or any other paraphernalia will not be allowed during the exam. Please put all your answers on the test. Use the backs of the pages for scratch.

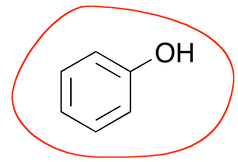
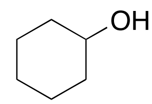
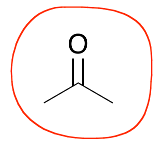
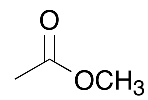
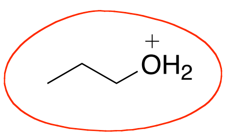
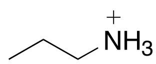
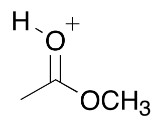
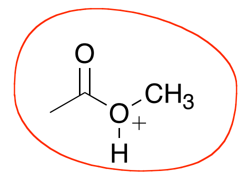
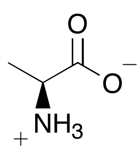
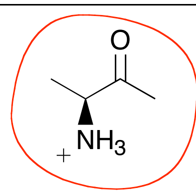
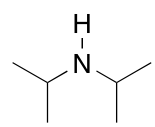
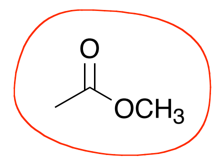
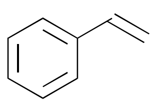
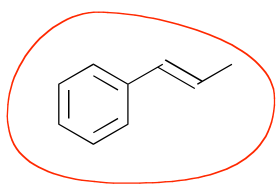
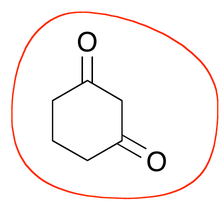
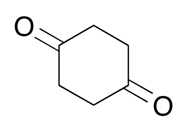
PLEASE read the questions very carefully!

Partial Periodic Table

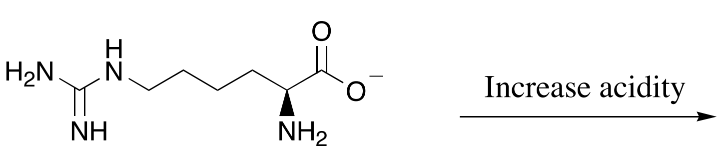
1A							8A
1 H	2A	3A	4A	5A	6A	7A	2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
						35 Br	
						53 I	

Name:____

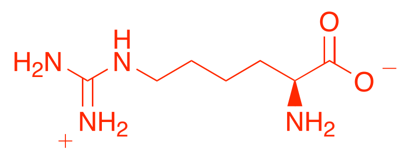
1) (40 pts) a) For each of the following pairs of compounds, circle the stronger Brønsted acid.

H_2O	H_3O^+		
HBr	H_3O^+		
			
			
			

b) The amino acid arginine (Arg) exists as a carboxylate anion (**1**) in strong aqueous base. Lowering the pH (increasing the Brønsted acidity) of the solution results in formation of a neutral zwitterion (a species with a positive and negative charge on the same molecule). Further increase of the acidity of the solution gives a cation, and eventually, at low pH (high acidity) a dication. Give the structure of the neutral zwitterion.



1



Neutral zwitterion

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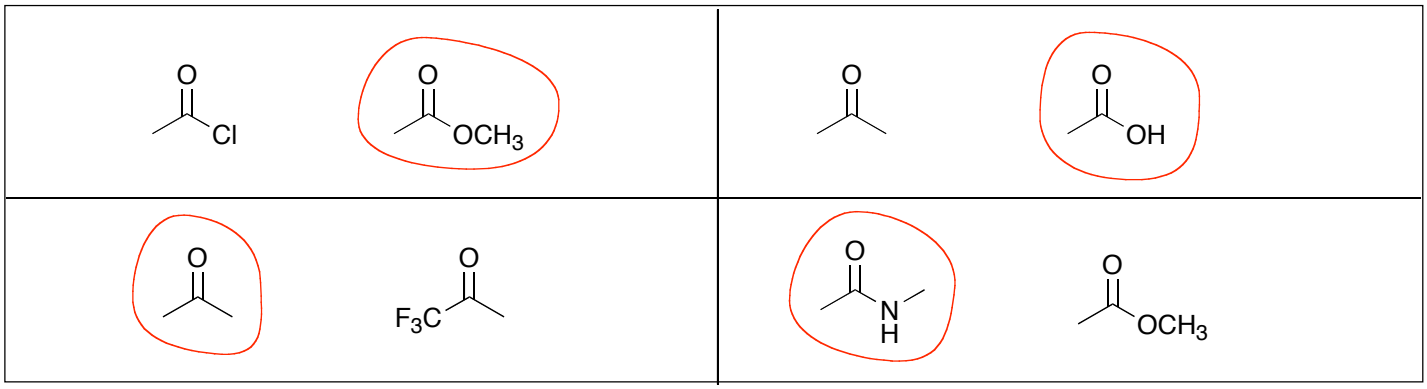
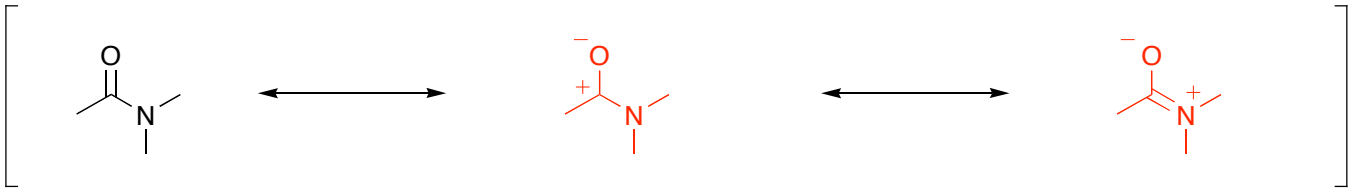
1) Continued

c) For each of the following pairs of compounds, circle the compound with the most stable carbonyl group.



d) The major resonance contributor to the structure of N,N-dimethyl acetamide is given below. Draw the two most important additional resonance contributors.



e) Is the hybridization of the nitrogen atom of N,N-dimethyl acetamide closer to sp^3, or sp^2?

sp^2

Total points for this page: ____

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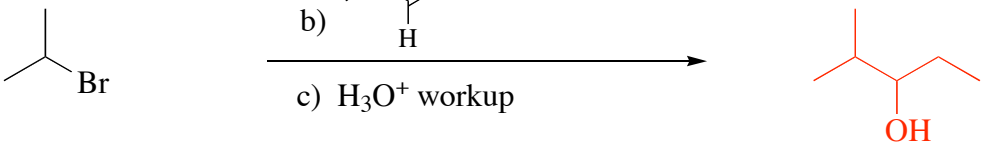
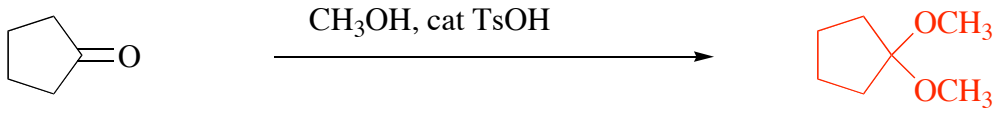
2) (40 pts) Give the single major organic product of each of the following reactions. Ignore stereochemistry for this question.

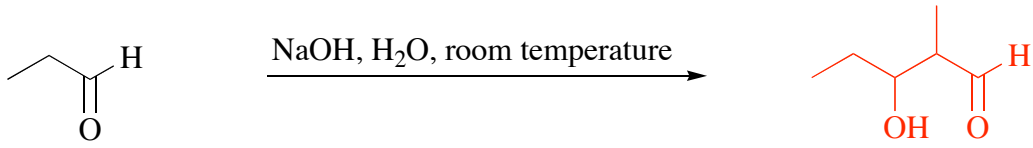
a)



b)

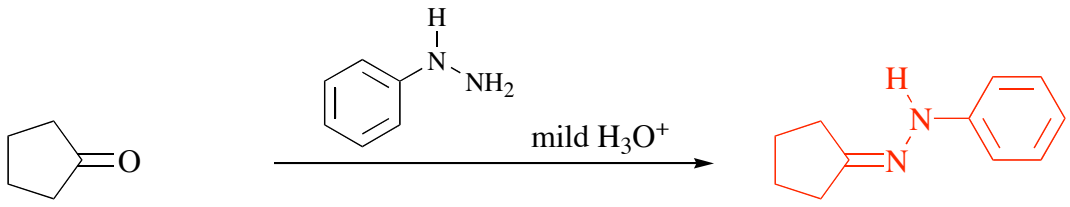


c)



$C_6H_{12}O_2$

d)



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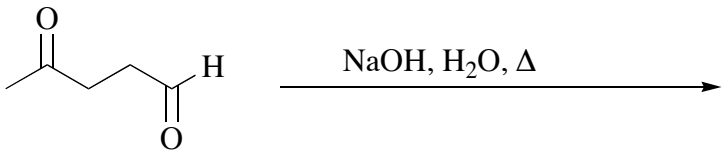
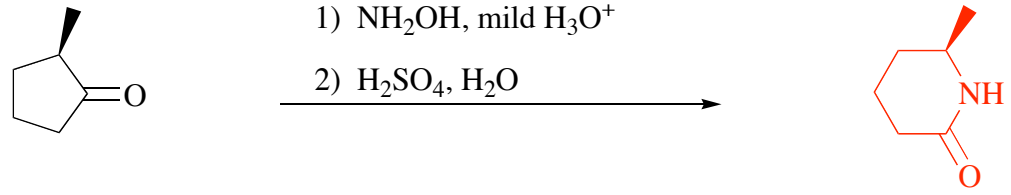
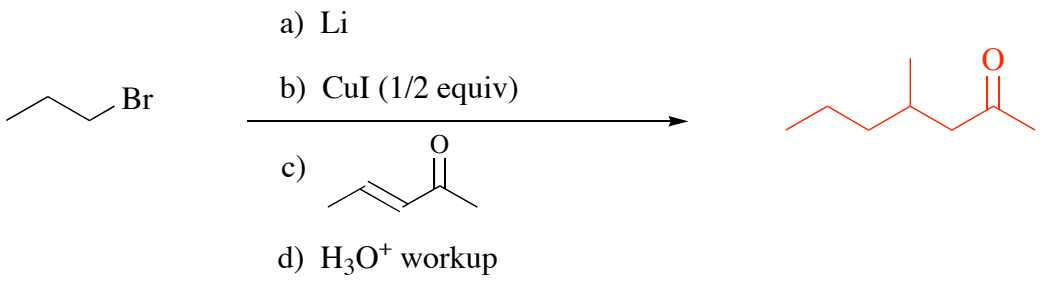
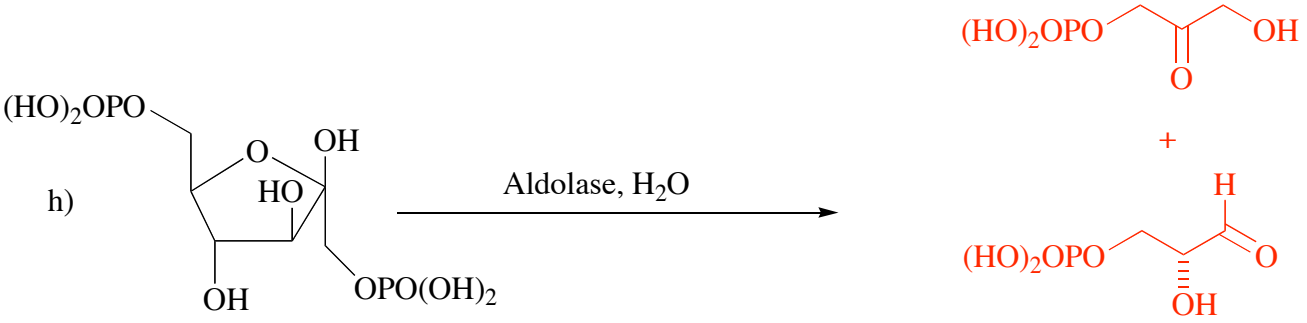
2) -Continued-

e) 

f) 

indicate stereochemistry for part f

g) 

h) 

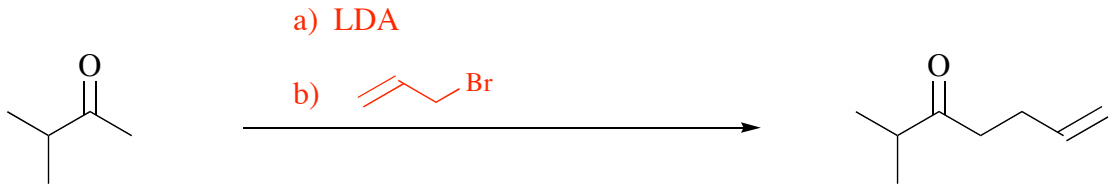
give two products for part h, showing stereochemistry

Total points for this page: ____

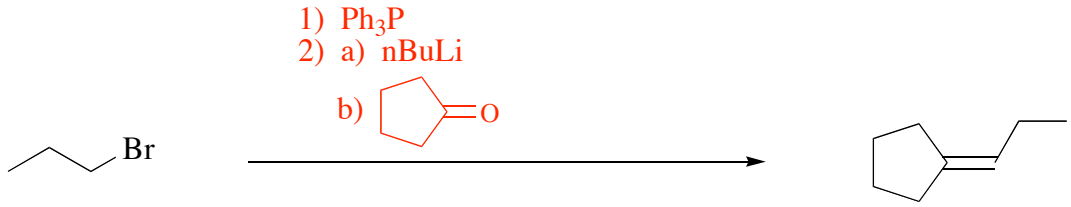
Name:_____

3) (40 pts) Propose reagents for accomplishing the following transformations. More than one step may be required.

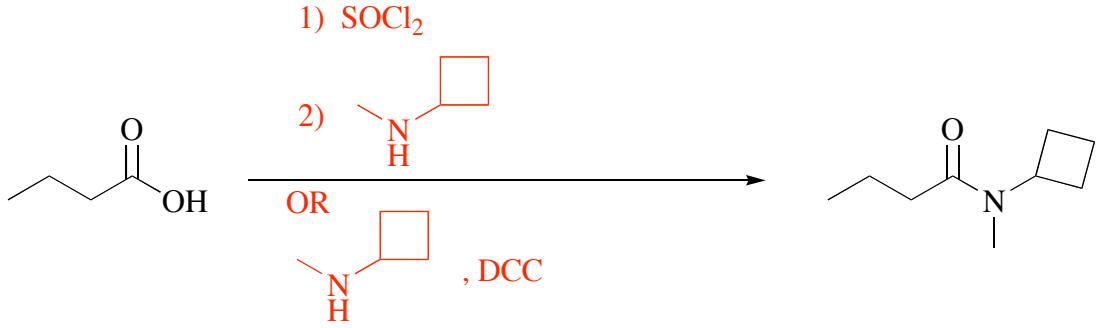
a)



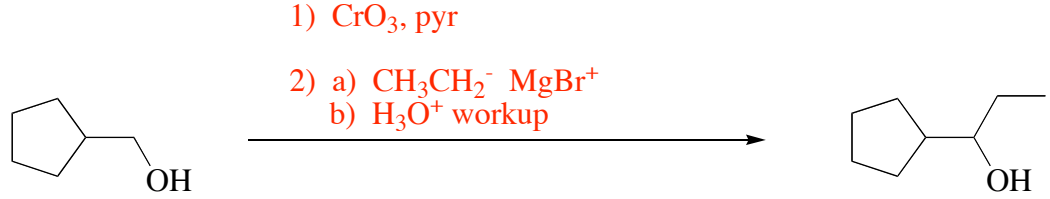
b)



c)



d)



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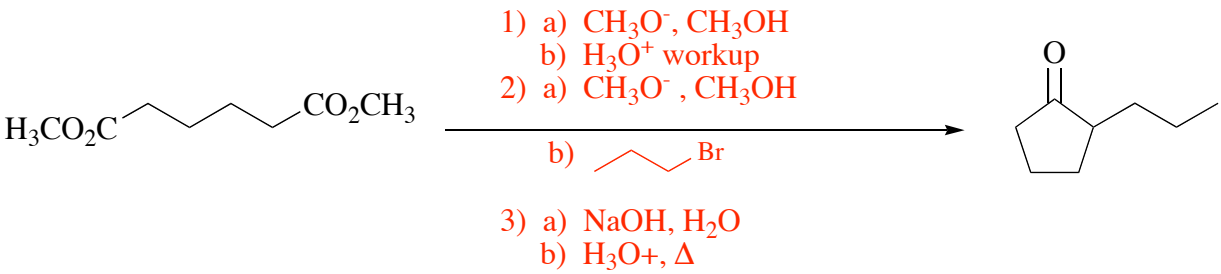
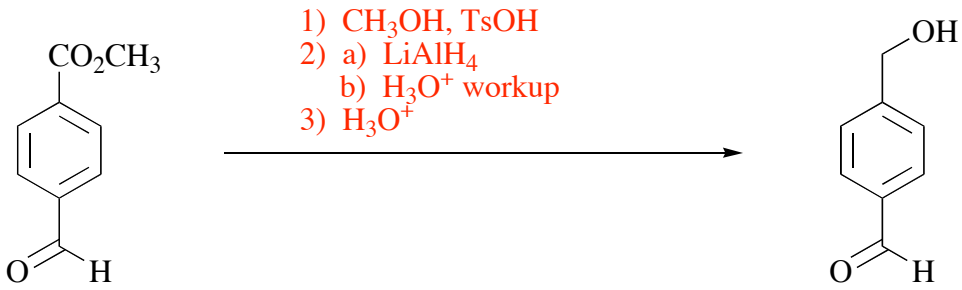
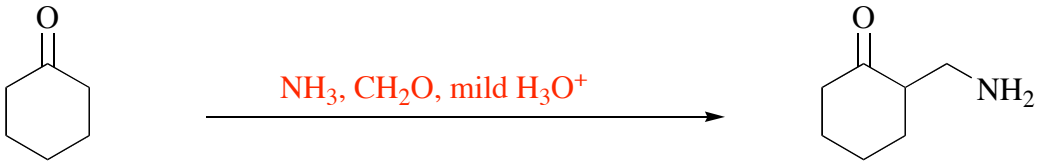
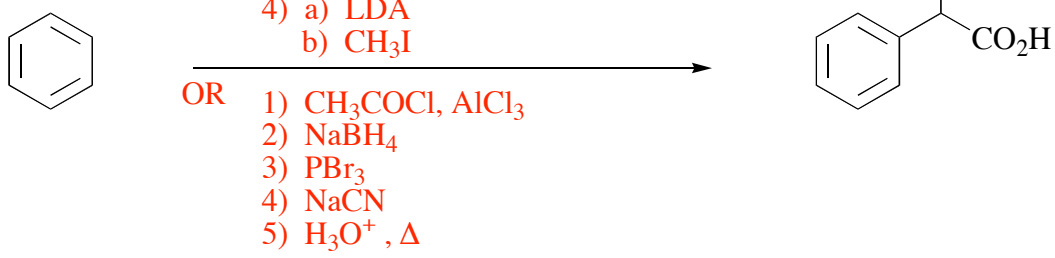
3) -Continued-

e) 

f) 

g) 

h) 

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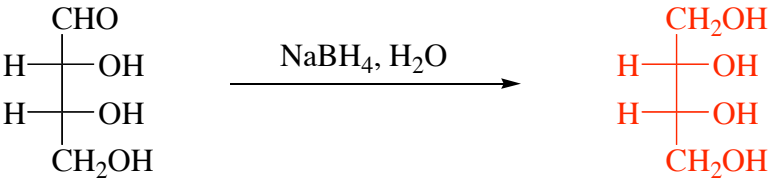
4) (20 pts) a) D-Erythrose is an enantiomerically pure optically active natural aldo-tetrose. A Fischer projection of the open-chain form of D-erythrose is given below. Give a Fischer projection of the product of reaction of D-erythrose with sodium borohydride.

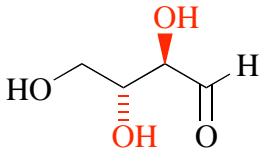


D-Erythrose

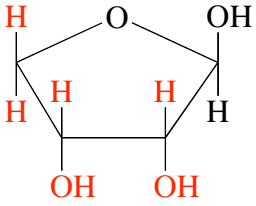
b) Is the product from part (a) optically active, or not optically active.

NOT optically active

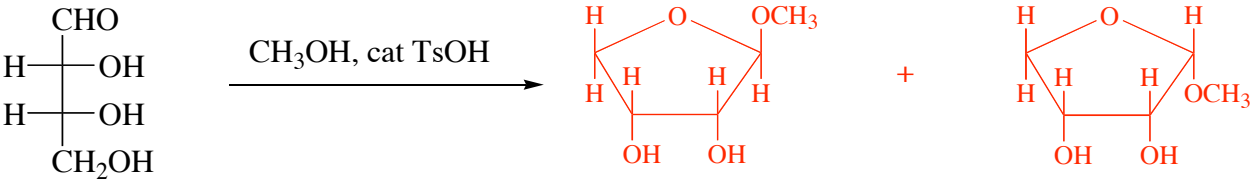
c) Carefully complete the wedges-and-dashes structure of D-erythrose open-chain aldehyde below.



d) Carefully complete the Haworth projection of β-D-erythrofuranose below.



e) Two products are formed when D-erythrose is treated with methanol and catalytic TsOH. Give Haworth projections for both products.



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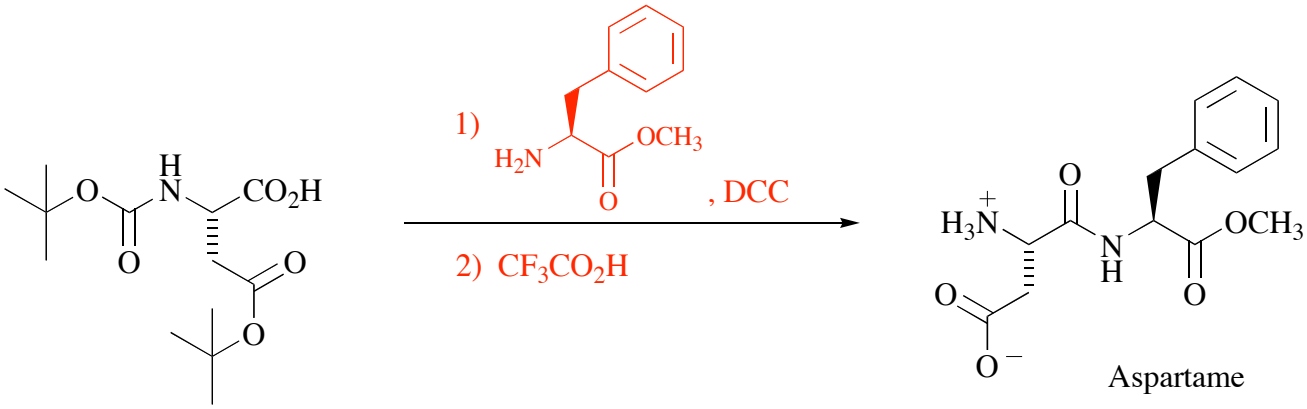
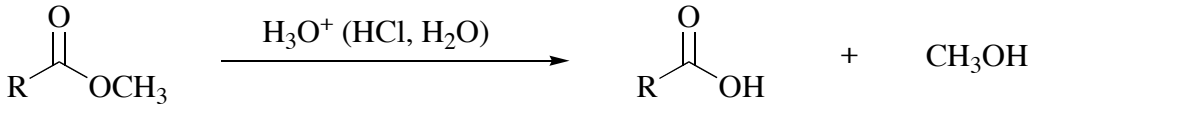
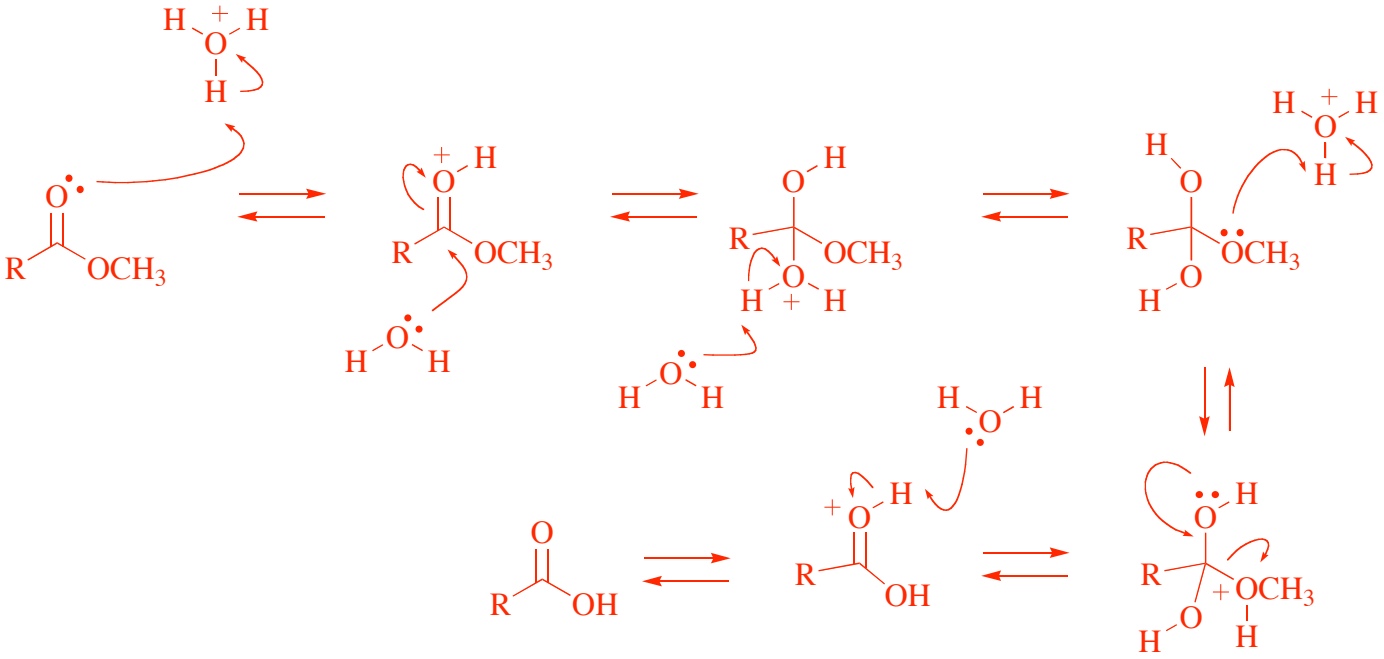
Name:_____

5) (20 points) a) Propose reagents for accomplishing the following transformation. More than one step may be necessary.



b) In aqueous HCl aspartame is hydrolyzed to the dipeptide H_3N^+-Asp-Phe-CO_2^- plus methanol. Give an arrow-pushing mechanism for this transformation using the abbreviated aspartame structure shown below.





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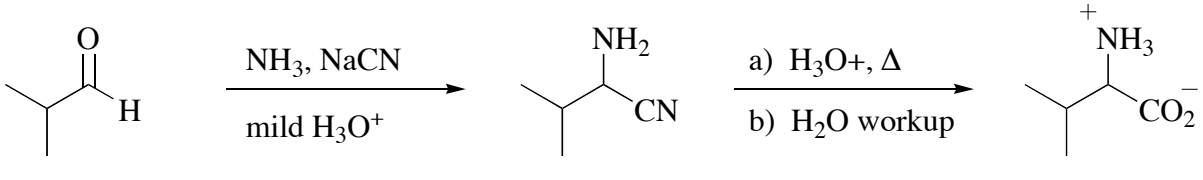
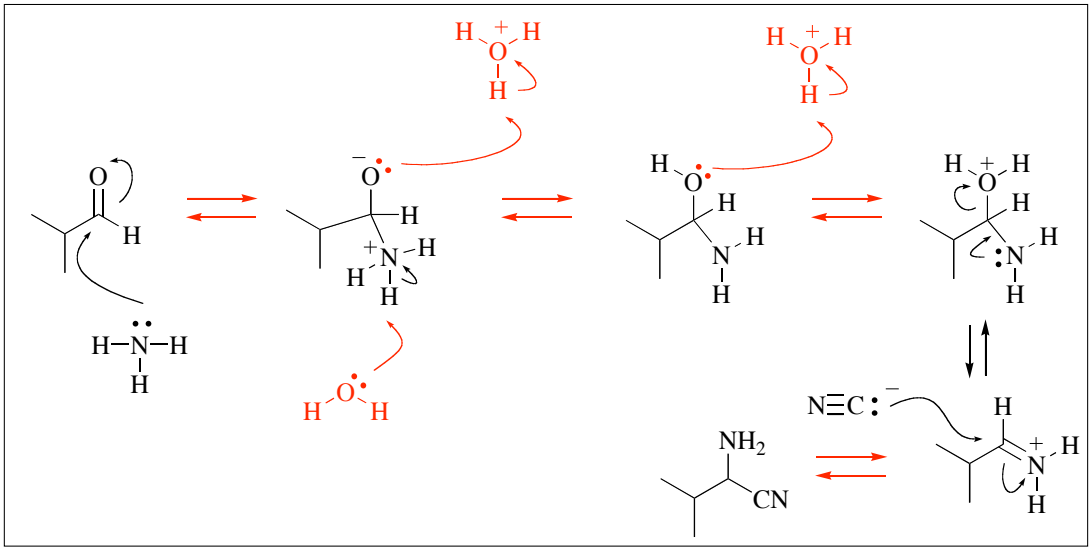
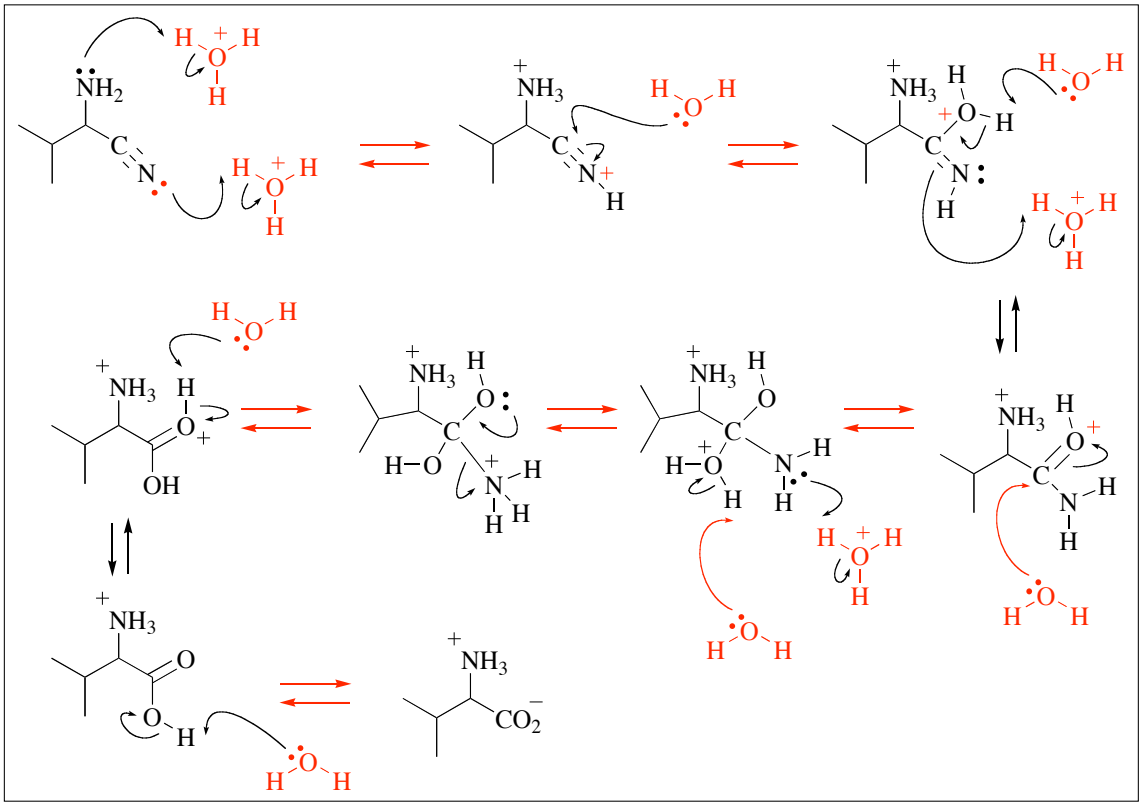
5) -Continued-

c) The Strecker synthesis is the classic amino acid synthesis. Propose a mechanism for both steps of the Strecker synthesis of racemic valine, shown below.



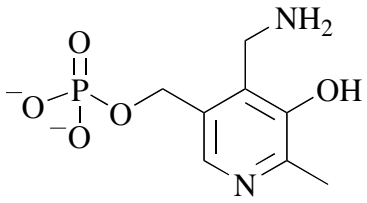




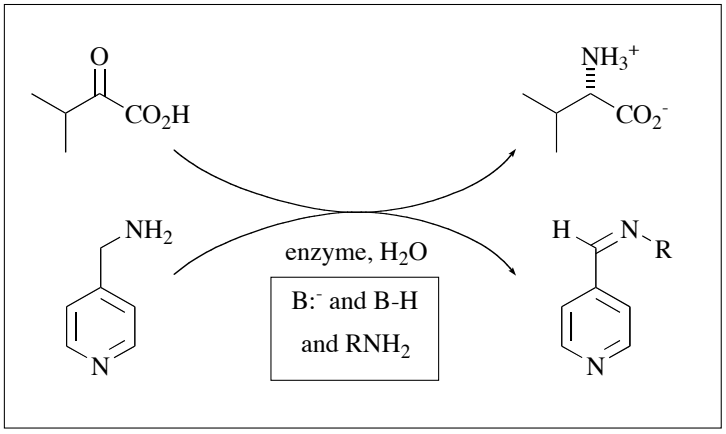
Page 10 of 13 Total points for this page:

Name:_____

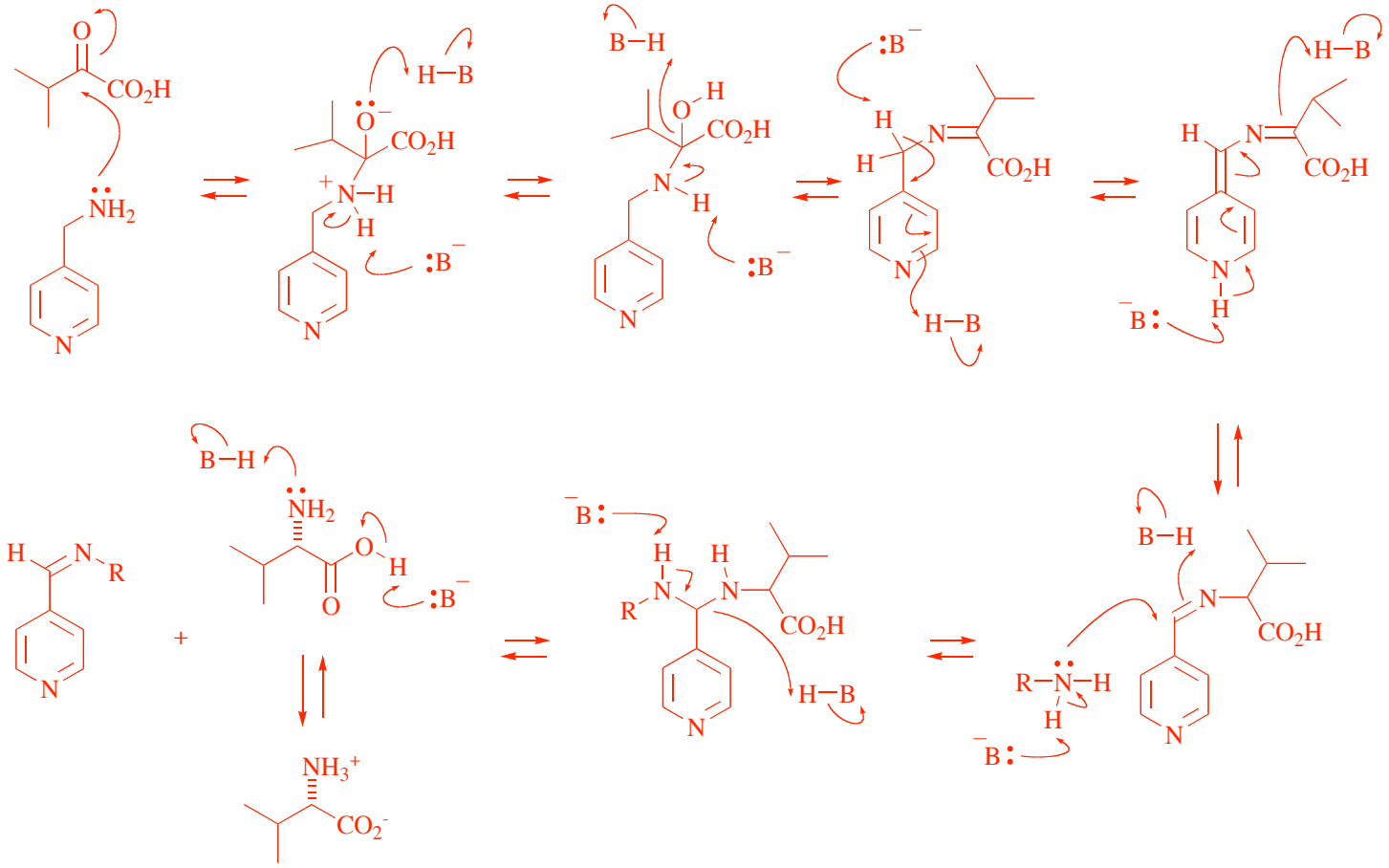
6) (40 pts) a) The cofactor pyridoxamine phosphate (from vitamine B_6), is involved in the enzymatic transformation of α-ketoacids to amino acids.



pyridoxamine phosphate



For example, the biosynthesis of valine might be accomplished as indicated in the box above. In this equation, the structure of the pyridoxamine phosphate is abbreviated. Also, the enzyme provides base (B:⁻), acid (B-H), and an amine (RNH_2), as reagents. Propose a mechanism for the transformation indicated in the box. For this type of enzyme-mediated mechanism, it is customary to allow protonation by acid and proton abstraction by base in the same step. Please work out your mechanism on a scratch page, and neatly put your answer below.



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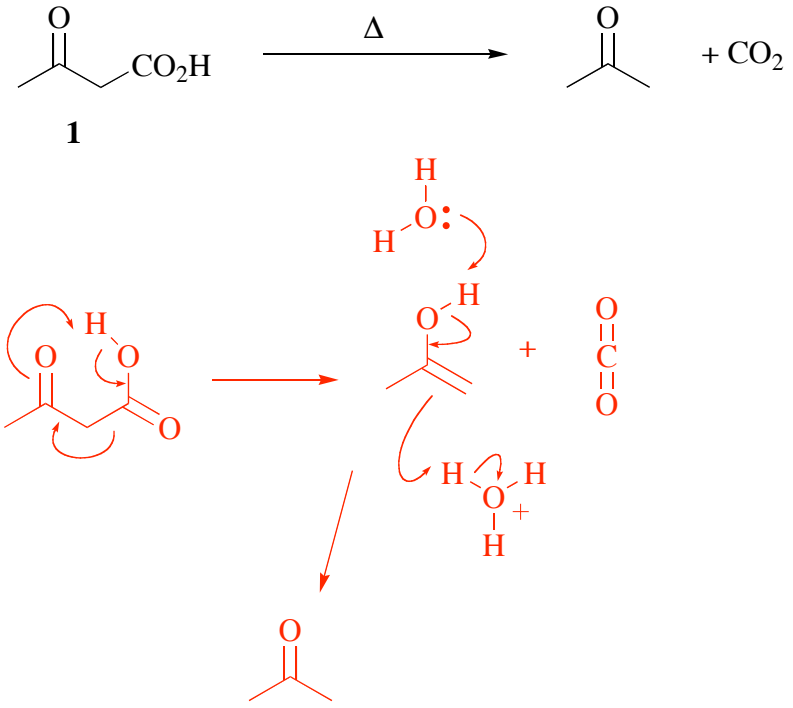
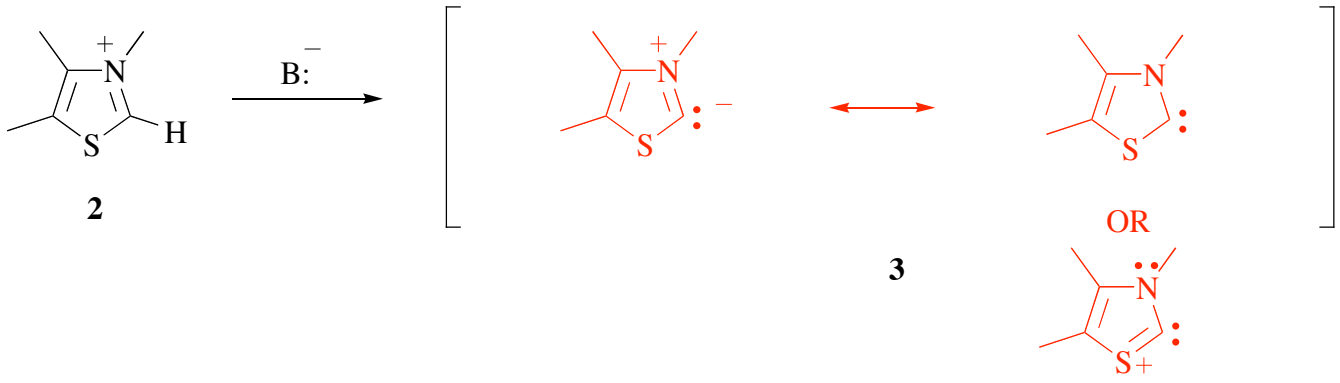
(6) -Continued-

b) Decarboxylation of β-ketoacids such as acetoacetic acid (**1**), occurs spontaneously upon heating. Propose an arrow pushing mechanism for this transformation.



1

c) Decarboxylation of α-ketoacids is much more difficult in the lab than decarboxylation of β-ketoacids. Biological systems accomplish this reaction with the cofactors thiamine (vitamine B_1) and lipoic acid. The key structural features of thiamine are captured in the heterocyclic structure **2**. Reaction of **2** with an enzyme-bound base ($B:^-$) gives a neutral species **3** with two major resonance contributors, one of which is a zwitterion. Write the structure of the two major contributors to the structure of intermediate **3**.



2

3

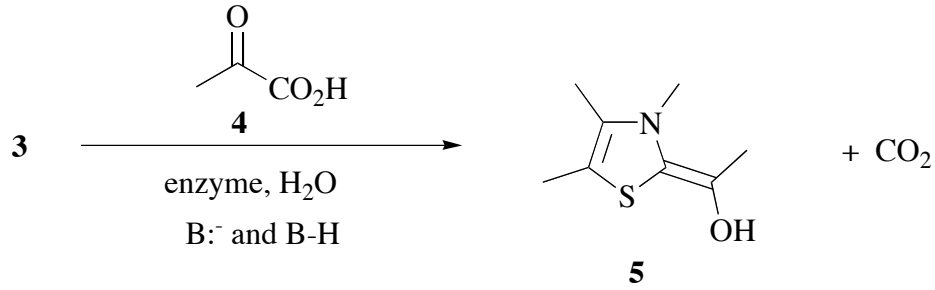
OR

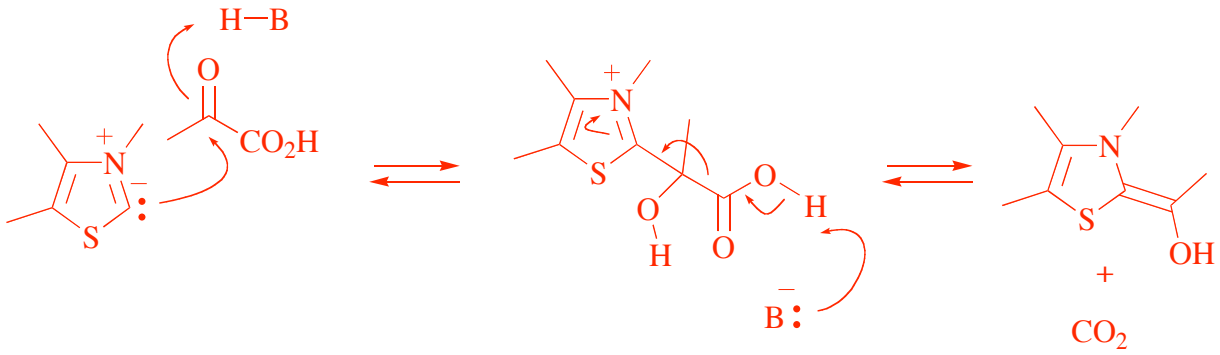
Total points for this page: ____

Name:_____

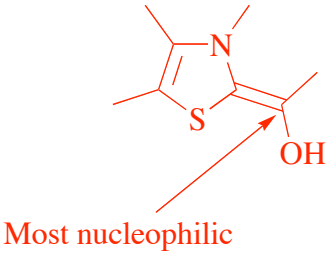
(6) -Continued some more-

d) Intermediate **3** reacts with an α-ketoacid such as **4** to give the intermediate **5** plus CO_2 (some structures are abbreviated to show the key features). Propose an arrow-pushing mechanism for this transformation.





e) Intermediate **5** has two nucleophilic carbon atoms. Re-draw the structure of **5** below, indicating which carbon is the most nucleophilic.



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