Midterm Exam 2

Chem 3B, Spring 2016
Monday, April 11, 2016
7:00 – 9:00 pm

Name _____

Student ID _____

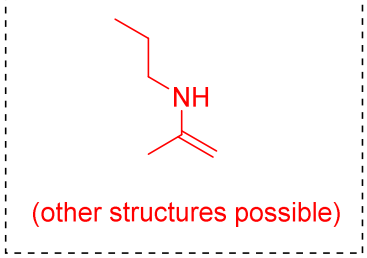
You have 120 minutes to complete this exam.

Please provide all answers in the space provided. Work drawn in the margins may not be picked up by the scanner and therefore will not be graded.

The last page of the exam is scratch paper. Please tear it off before you begin. It will not be collected, scanned, or graded, so make sure your answers are copied into the appropriate location on your exam.

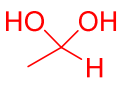
Point values are listed within each question. The exam is worth 250 points total.

1. Nomenclature and Functional Groups
   a. Draw a structure to match each prompt. (3x7 = 21 pt)



(other structures possible)

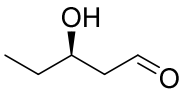
an enamine with an N-propyl group



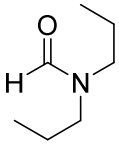
the hydrate derived from acetaldehyde

an aldotetrose in open chain (acyclic) form

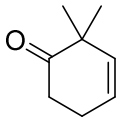
   b. Provide systematic name for each of the following structures. (3x6 = 18 pt)



(R)-3-hydroxypentanal



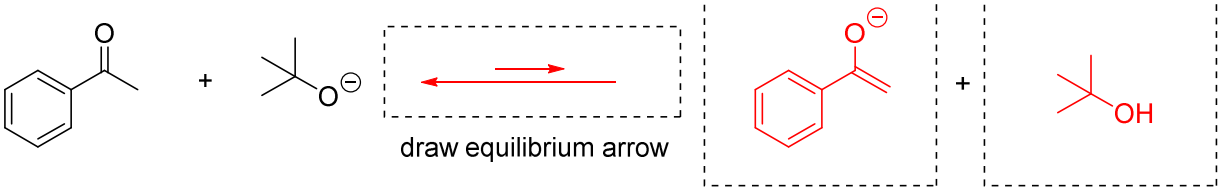
N,N-dipropylformamide



2,2-dimethyl-3-cyclohexenone

or 2,2-dimethyl cyclohex-3-en-1-one

2. Acid-Base Equilibrium. (16 pt)
   a. Draw the products of the following acid-base reaction.

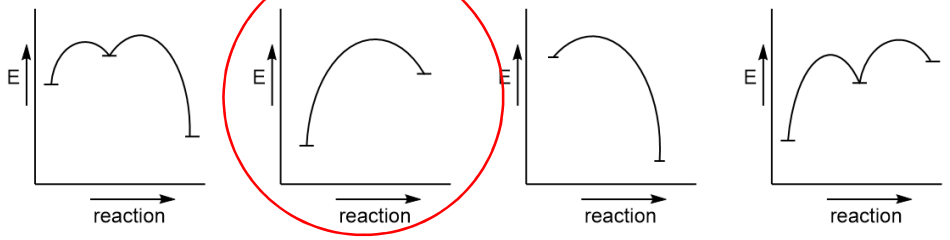


   b. Calculate the equilibrium constant (Keq) for the reaction in part a. Show your work and **circle the final answer**. Add the corresponding equilibrium arrow to the scheme above. *(no credit if work is not shown)*

pKa of ketone = 20
pKa of alcohol = 15

$K_{eq} = 10^{(pka\ alcohol - pKa\ ketone)} = 10^{(15-20)} = 10^{-5}$

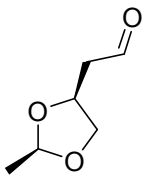
   c. Which reaction coordinate diagram below best corresponds to the reaction from part a? (circle one)



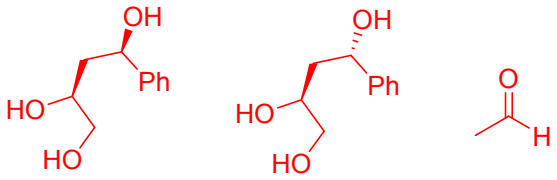
3. Predict the major organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. (3x10 = 30 pt)

Reminder 1: H_3O^+ always means excess strong acid in excess water as a solvent

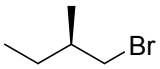
Reminder 2: No hydrates as predicted products

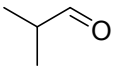


1. PhMgBr
2. H_3O^+ workup

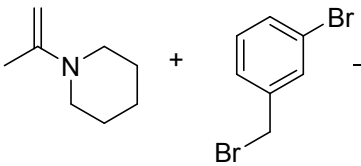


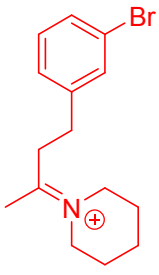
three structures, two of them are stereoisomers and the other one is an aldehyde



1. PPh_3
2. KH
3. 

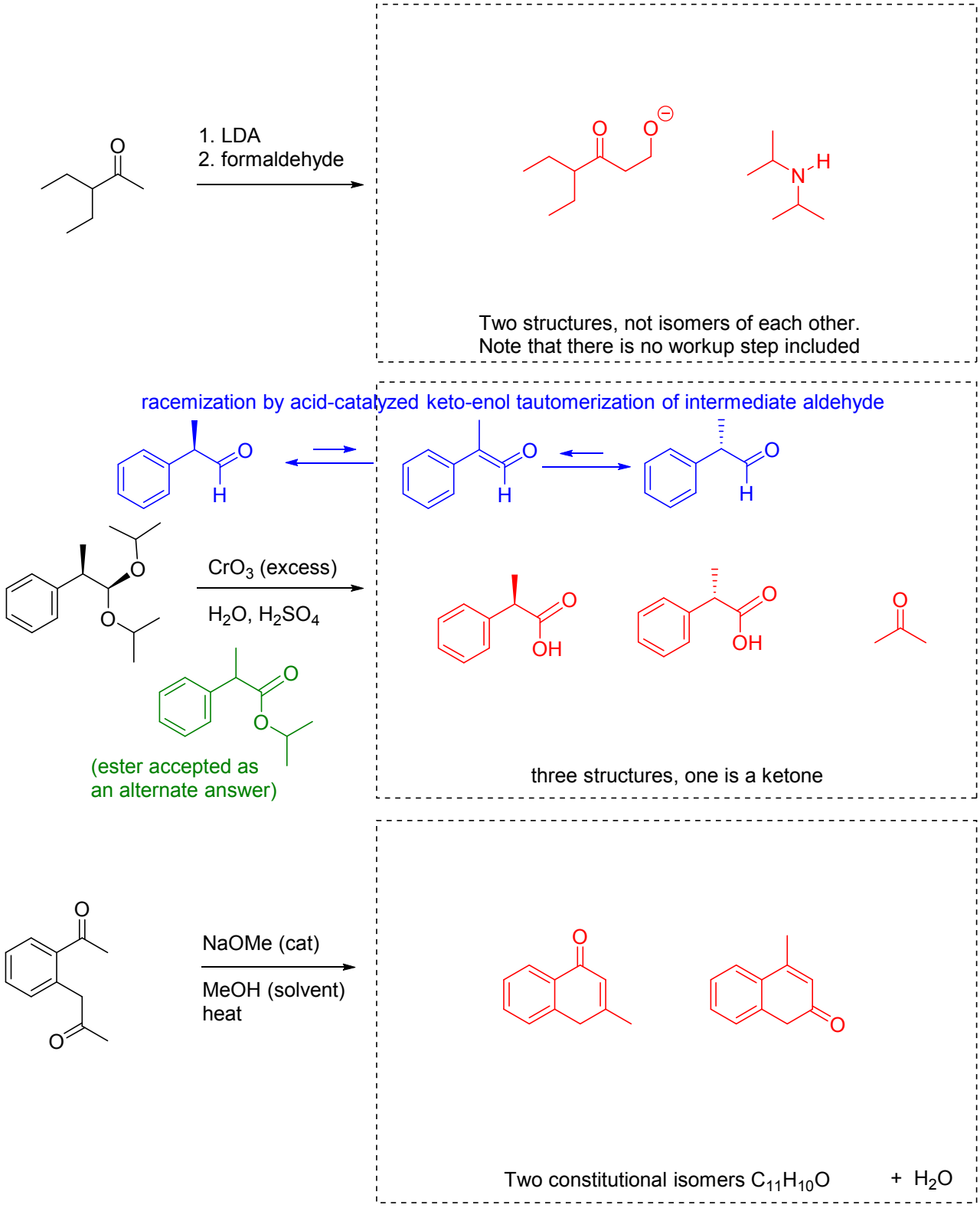
Two stereoisomers + KBr + $OPPh_3$



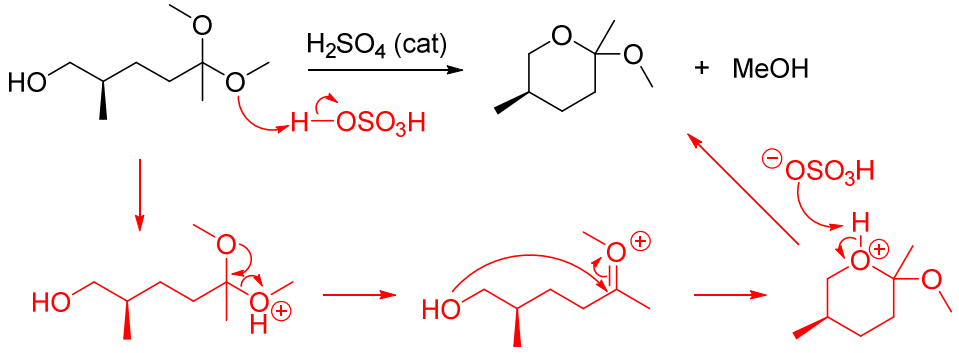


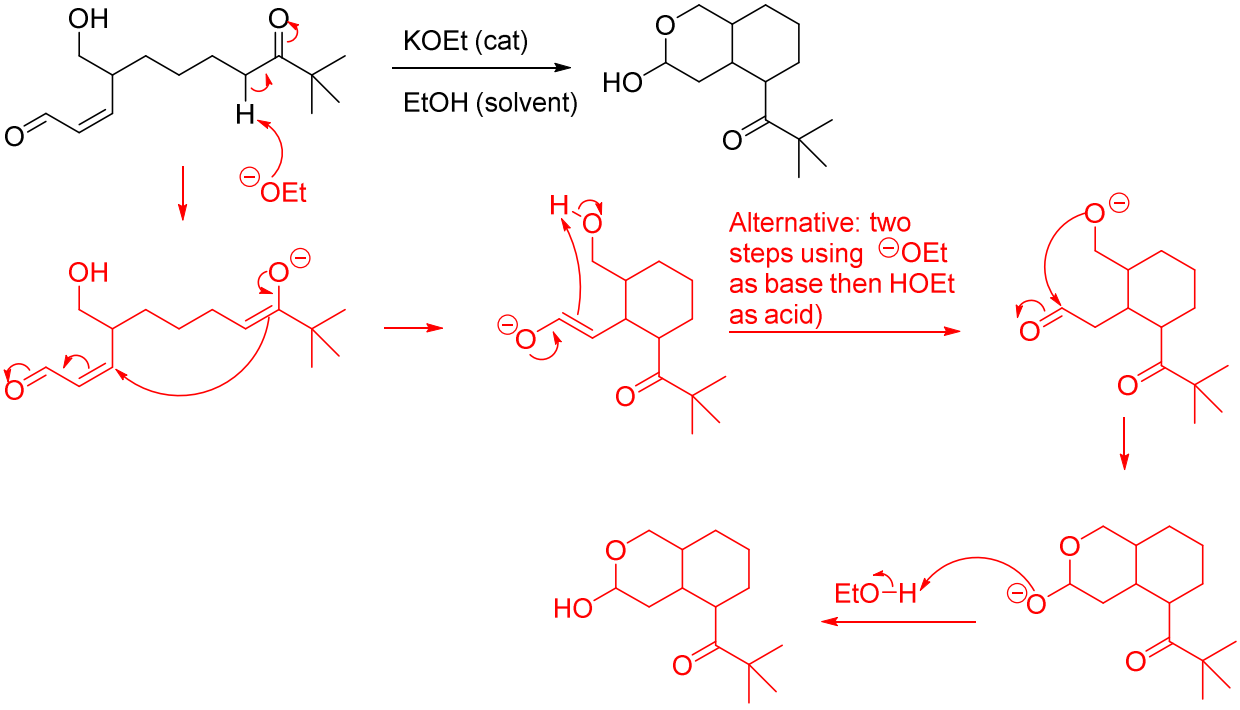
one structure; $C_{15}H_{21}BrN^+$ $Br^{\ominus}$

4. Predict the major organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. (3x10 = 30 pt)



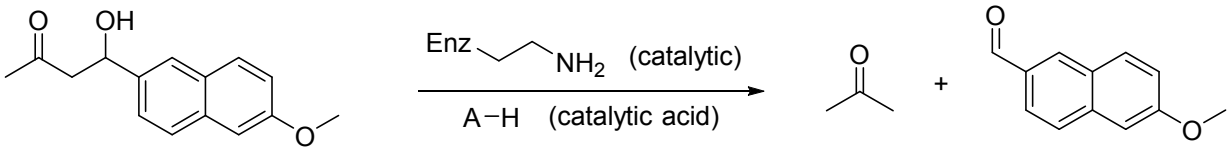
5. Draw a curved arrow mechanism for each reaction shown below. Your mechanism must account for all product(s) shown. (Note: For some of these reactions, there may be other possible products that are not shown. You only need to explain the product(s) pictured in the scheme) (2x10 = 20 pt)





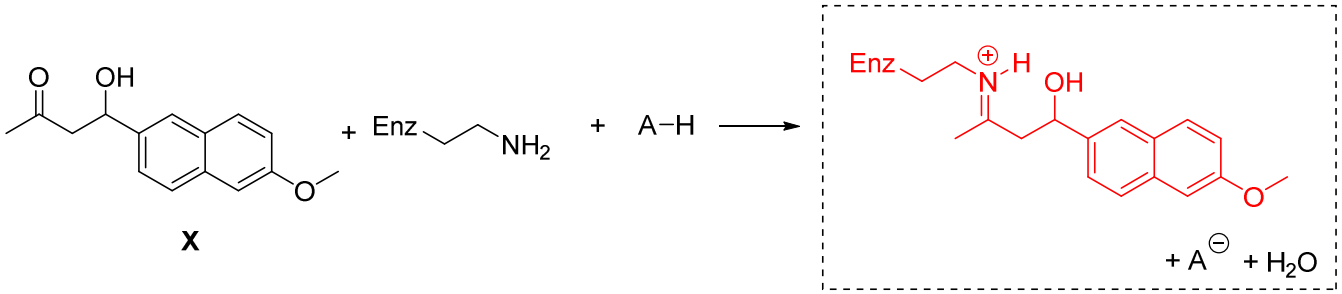
6. **An Artificial Retro-Aldol Enzyme**[1]

In 2008, a research team reported the computational design of an artificial enzyme for the **retro-aldol** reaction pictured below, which does not naturally occur in biological systems. The artificial enzyme uses an active site **lysine sidechain (abbreviated EnzCH$_2$CH$_2$NH$_2$)** along with appropriately positioned **acidic sidechains (abbreviated AH)** to catalyze the reaction via an **iminium ion intermediate**, similar to the aldolase enzyme that was discussed in lecture.



X **Z**

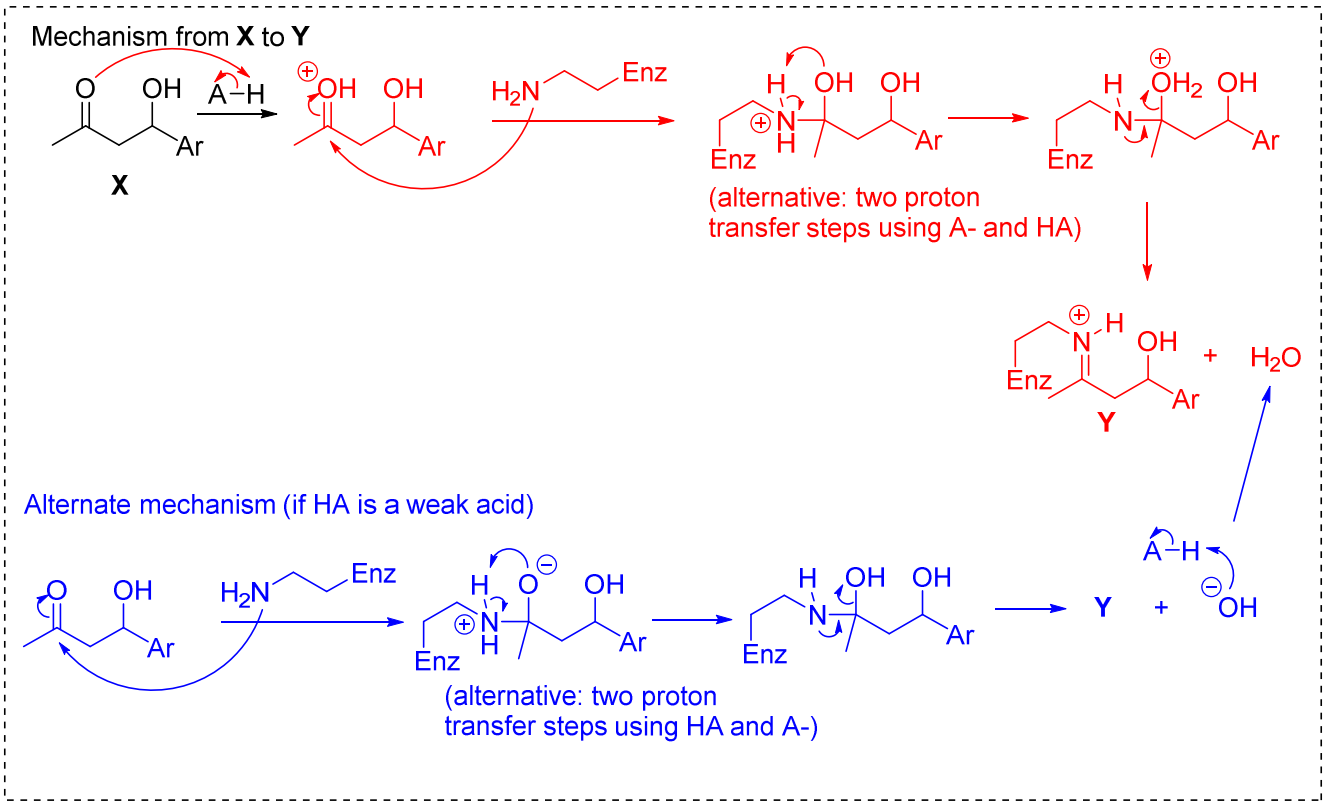
A. Draw the structure of the iminium ion intermediate **Y**. (5 pt)



X

iminium ion intermediate **Y**

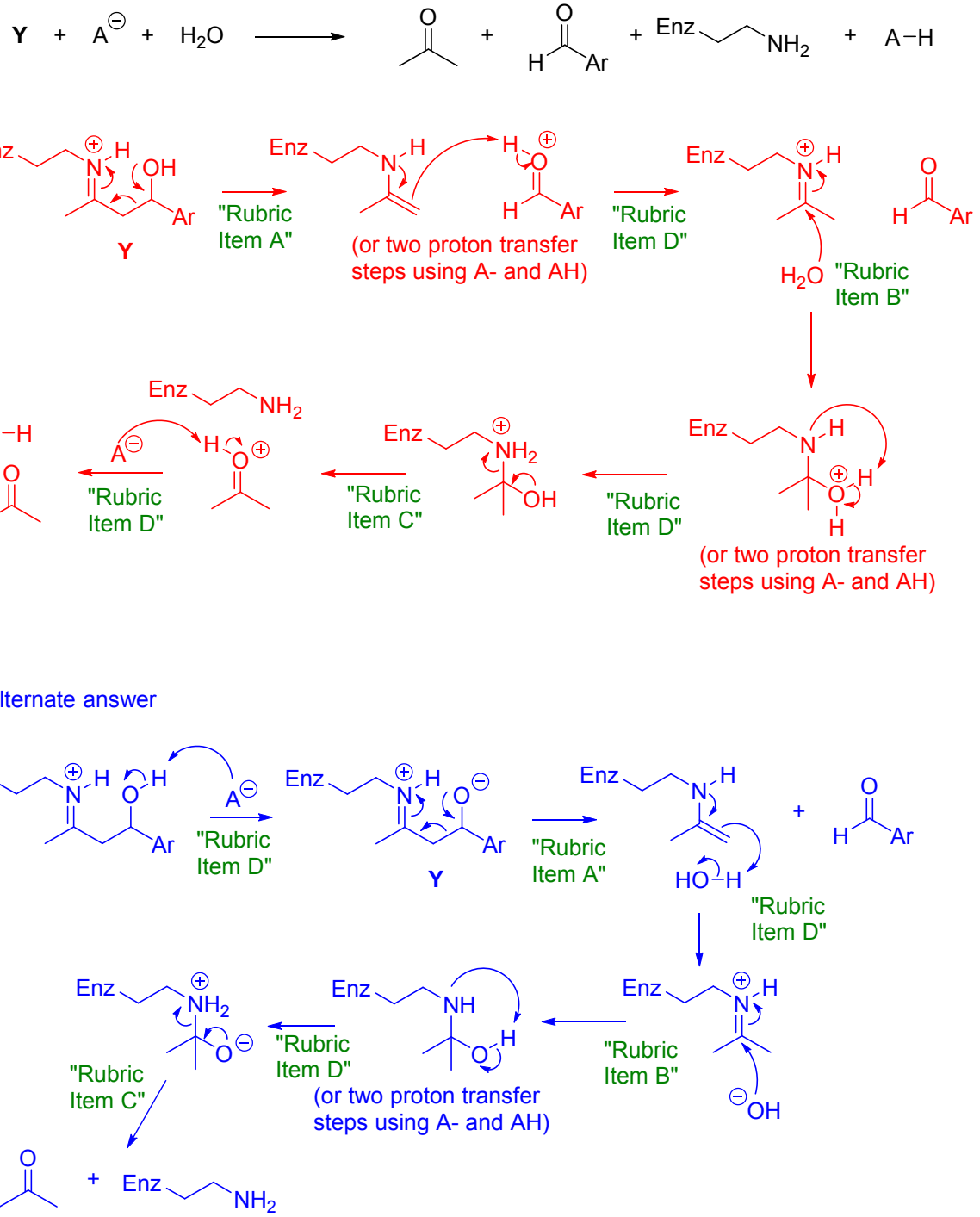
B. Draw a curved arrow mechanism for the reaction in part A (from **X** to iminium ion **Y**). Abbreviate the aromatic portion of the molecule as "Ar" throughout your mechanism. (10 pt)



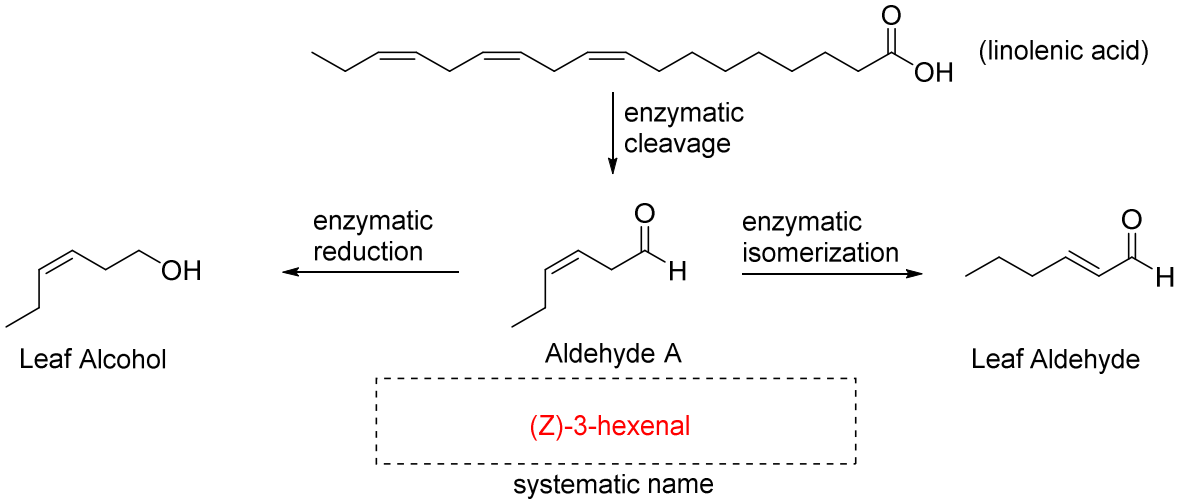
[1] Jiang, L. et. al. De Novo Computational Design of Retro-Aldol Enzymes. *Science*, **2008**, *319(5868)*, 1387.

C. Draw a curved arrow mechanism for the reaction of intermediate **Y** (from the previous page) to the final products (acetone, **Z**, and regenerated catalysts) (10 pt)

Mechanism:



7. **Green Leaf Odors**: The "green odor" of green leaves arises from a series of 6-carbon aldehydes and alcohols.[2] The biosynthesis of these compounds occurs via enzymatic cleavage of fatty acids to make "Aldehyde A", which is the main compound that gives fresh-cut grass its characteristic smell. Aldehyde A can either isomerize to form "leaf aldehyde", or be reduced to form "leaf alcohol".



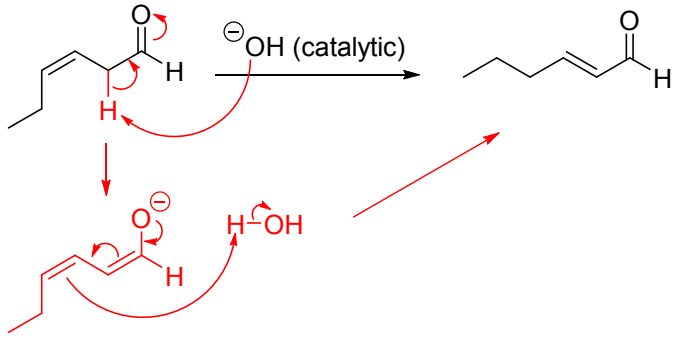
A. Provide a systematic name for "aldehyde A" in the scheme above. (5 pt)

B. List two reasons why "Leaf Aldehyde" is more thermodynamically stable than Aldehyde A. (up to 5 words per reason, one reason per box) (10 pt)

trans geometry

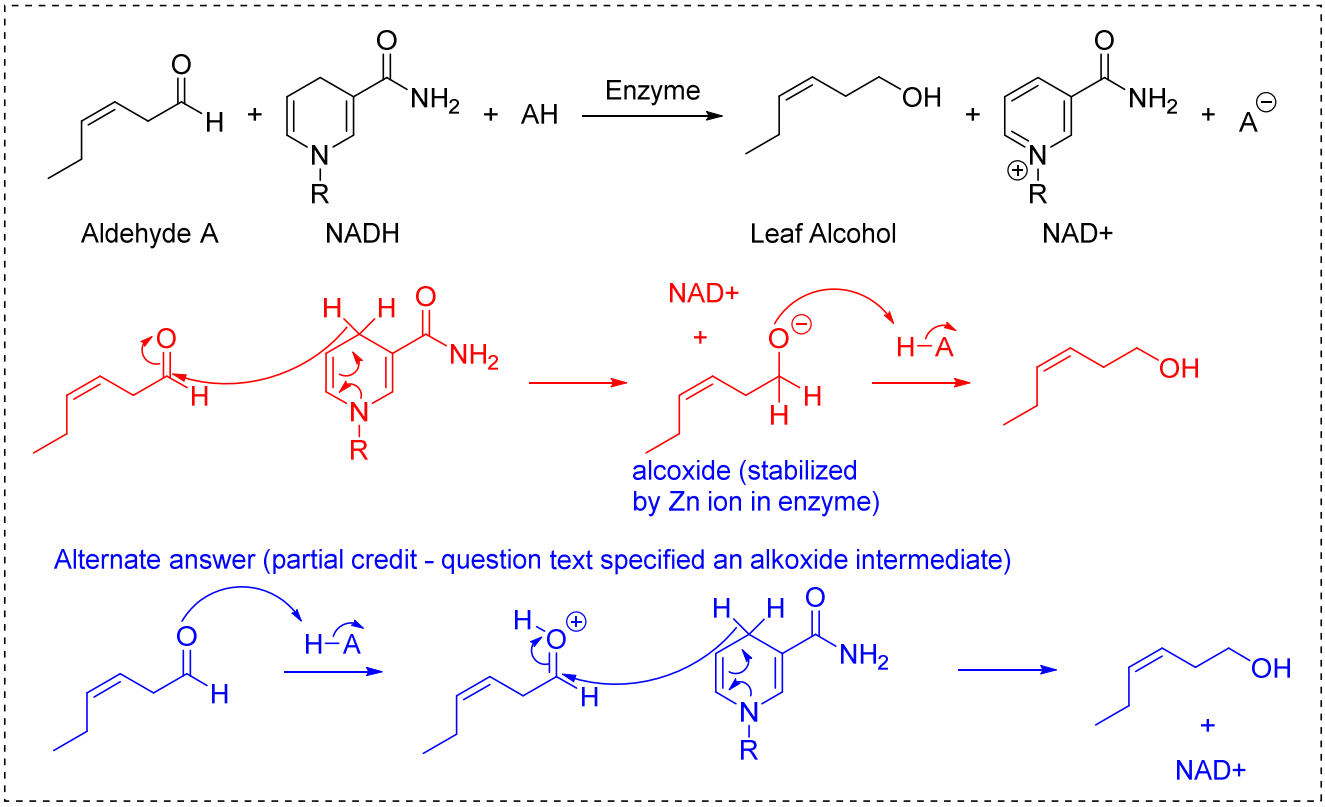
conjugated

C. Propose a mechanism for the isomerization reaction using hydroxide as a catalyst. (10 pt)

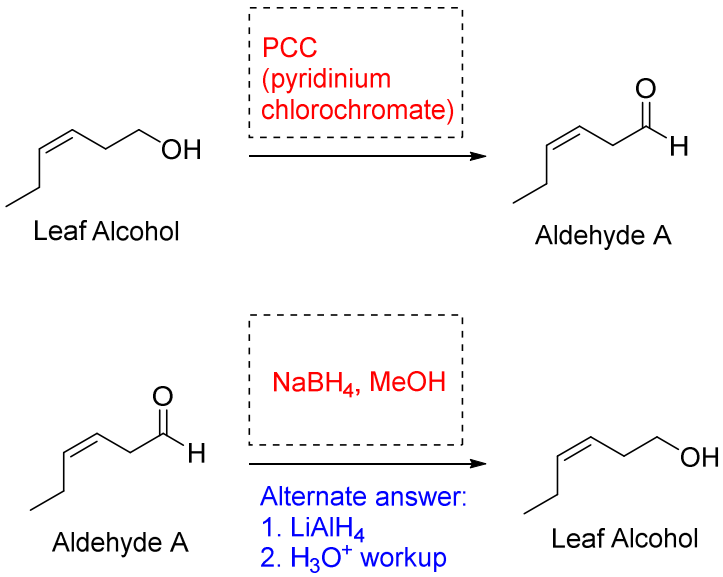


[2] Hatanaka, A. The biogeneration of green odor by green leaves. *Phytochemistry*, **1993**, *34(5)*, 1201.

D. The reduction of aldehyde A to leaf alcohol is catalyzed by an enzyme (an alcohol dehydrogenase) and uses **NADH as a reducing agent**. The enzyme active site contains a zinc ion (Zn^{2+}) which acts as a Lewis Acid to stabilize the **alkoxide ion intermediate** in this reaction. Draw a curved arrow mechanism, using the generic weak acid AH to protonate the alkoxide ion intermediate. *Note: You do not need to show the Zn ion in your mechanism.* (10 pt)

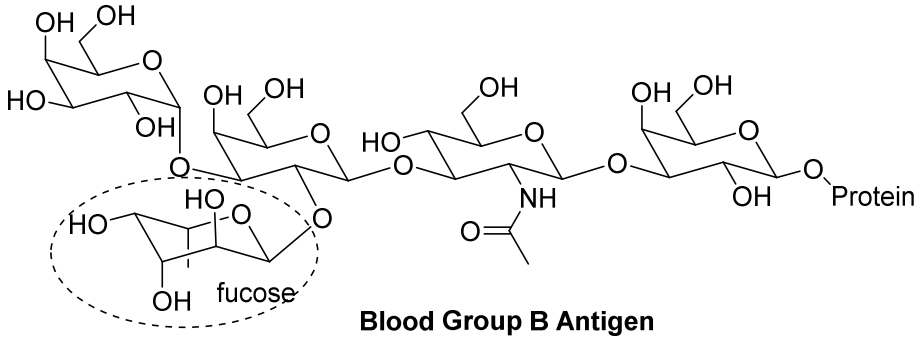


E. Propose reagents to carry out the corresponding oxidation and reduction reactions in the chemistry lab. (10 pt)



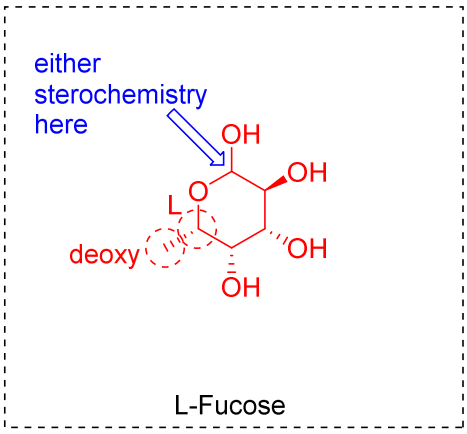
8. Blood types (A, B, AB, and O) are defined by the "Blood Group Antigens" which are polysaccharides that are present of the surface of the red blood cells. (45 pt)

A. Circle each of the anomeric carbons in the structure of the "B Antigen" below.



Blood Group B Antigen

B. One of the monosaccharides that would be obtained if the "B antigen" (above) was hydrolyzed in aqueous HCl is L-fucose, which can be classified as a 6-deoxy sugar (circled above).



L-Fucose

a. Draw a **flat ring representation** (with wedges/dashes) of L-fucose in the box to the left. (*Only draw one anomer. It does not matter which anomer you draw*)

b. On your drawing, circle the site that allows fucose to be classified as a "deoxy sugar" and label it "**deoxy**"

c. On your drawing, circle the site that allows fucose to be classified as an L sugar and label it "**L**"

d. Which two words below can be used to describe fucose in the B antigen structure? (**circle two**)

(Pyranose) (Furanose) (Pentose) (Hexose)

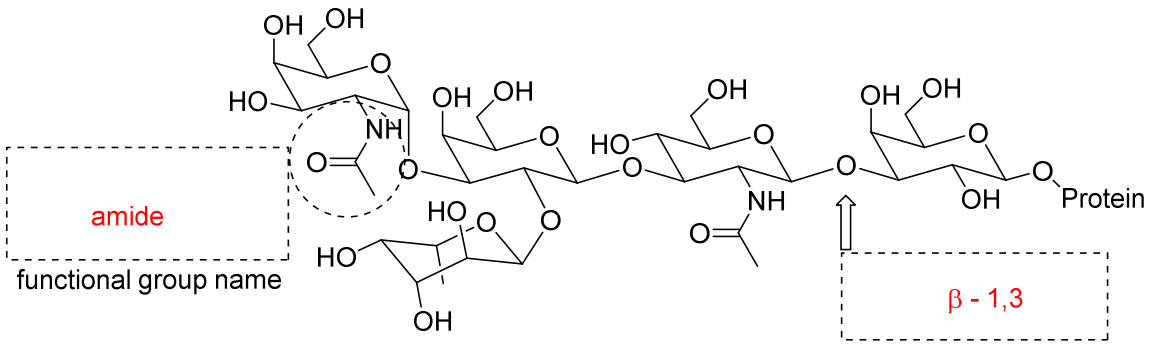
C. How many **DIFFERENT monosaccharides** (including fucose) would be observed if the "Blood Group B Antigen" (above) is hydrolyzed in aqueous HCl?

3 (three of the five monosaccharides match each other)

D. The "A Antigen" differs from the "B Antigen" by the replacement of just one hydroxyl group with a different functional group.

a. Fill in the box on the left (below) to indicate the name of **the circled functional group**.

b. Fill in the box on the lower right (below) to **name the indicated glycosidic linkage** (α or β, and the corresponding numbers)



Blood Group A Antigen

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