Midterm Exam 2

Chem 3B, Fall 2016
Thursday, Nov. 3, 2016
7:00 – 9:00 pm

Name _____

Student ID _____
(Note: write the last 3 digits of your SID in the top right corner of each page)

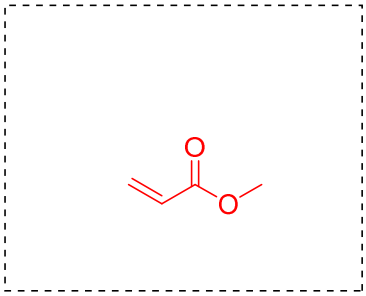
You have 120 minutes to complete this exam.

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.

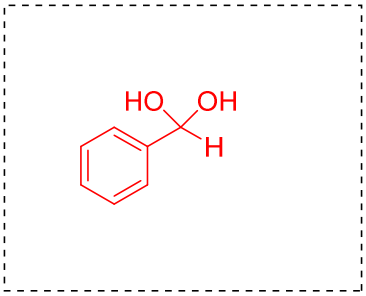
The last page of the exam is scratch paper. Please tear it off before you begin. It will not be collected, scanned, or graded, so make sure your answers are copied into the appropriate location on your exam.

Point values are listed within each question. The exam is worth 200 points total.

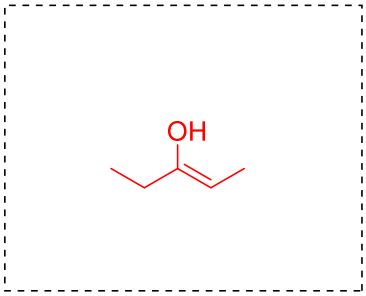
1. **Nomenclature and Functional Groups** (3x6 = 18 pt)
Draw a structure to match each prompt.



an α,β–unsaturated ester

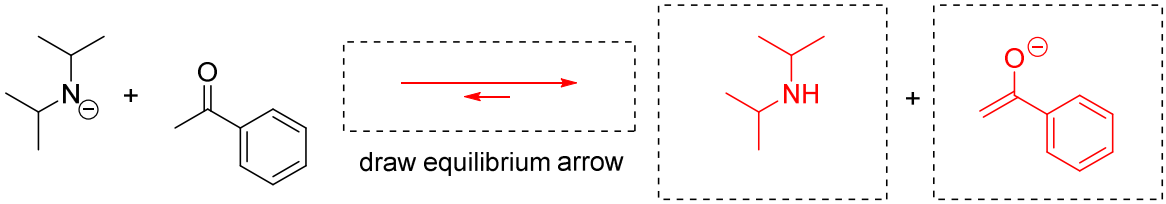


the hydrate derived from benzaldehyde



An enol tautomer of 3-pentanone

2. **Acid-Base Equilibrium.** (11 pt)
   a. Draw the products of the following acid-base reaction, and indicate the pKa under each acid in the scheme.

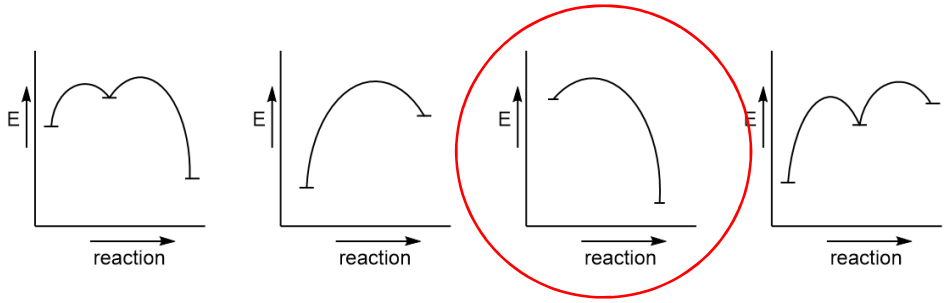


pKa of each acid: 20 35

   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)*

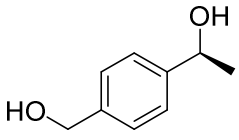
$K_{eq} = 10^{(35-20)} = 10^{(15)}$

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

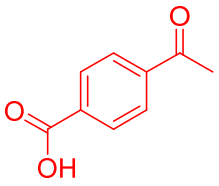


3. Predict the organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. (3x8 = 24 pt)

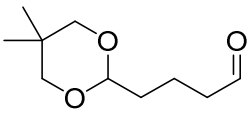
Reminder: no hydrates as predicted products



CrO_3 (excess)
H_2SO_4, H_2O

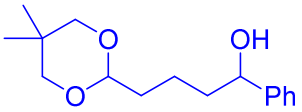


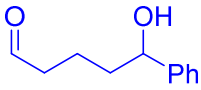
(include stereoisomer(s) if relevant)

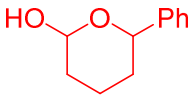


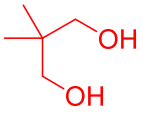
1. PhMgBr

2. excess HCl, H_2O





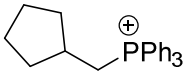




a cyclic hemiacetal

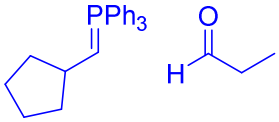
a diol

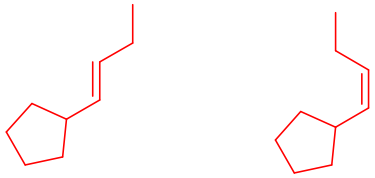
(do not include steroisomers)



1. KH

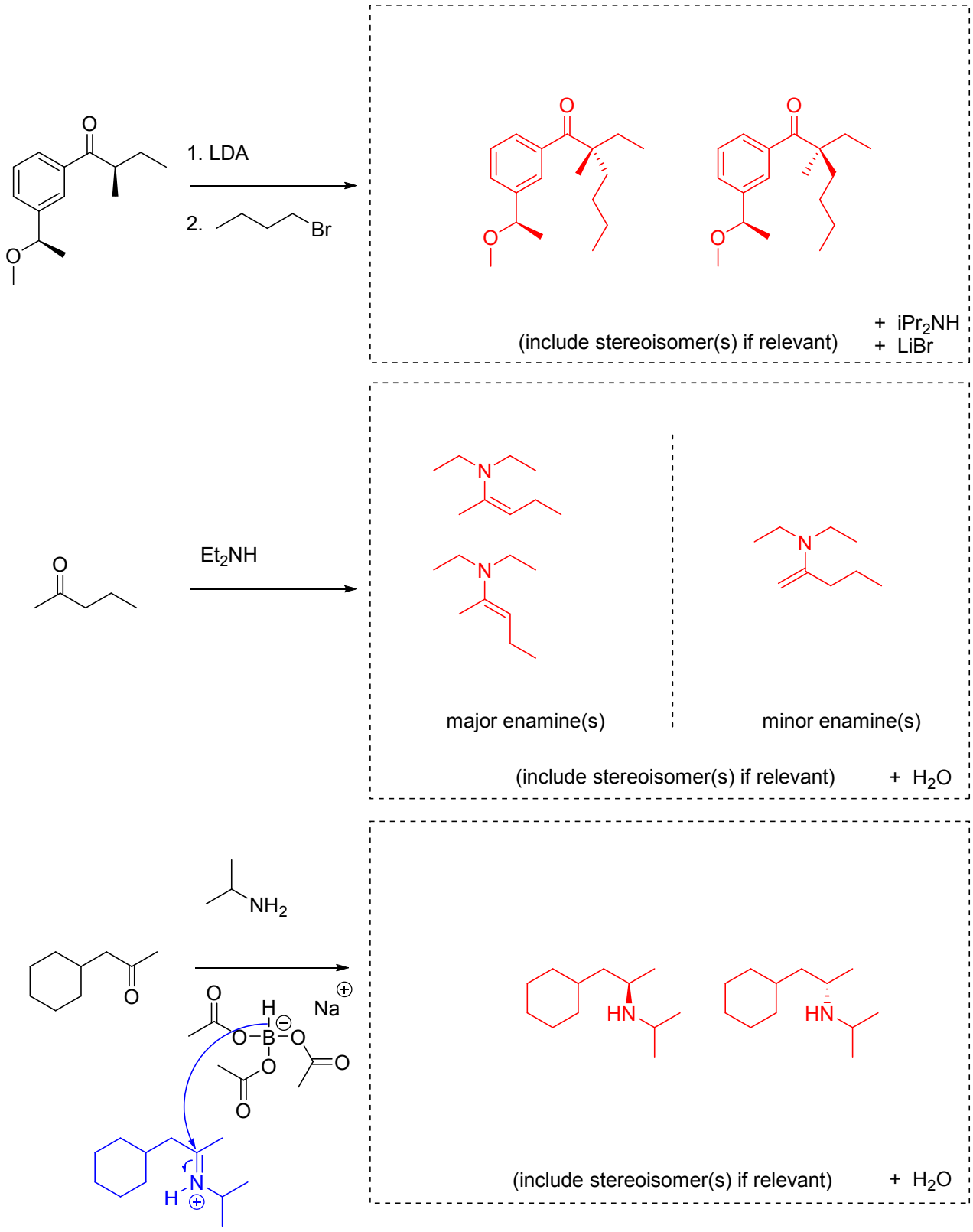
2. propanal





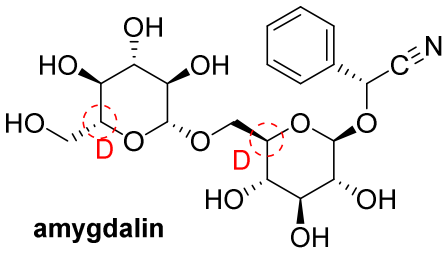
(include stereoisomer(s) if relevant) + $OPPh_3$

4. Predict the organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. (3x8 = 24 pt)



5. **Amygdalin** is a poisonous compound found in the pits of apricots and some other fruit.

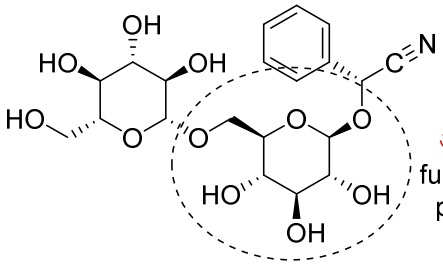
   a. Circle the carbons in the amygdalin structure below that allow each sugar to be classified as D or L. **Add a D or L label** to each circle. (4 pt)



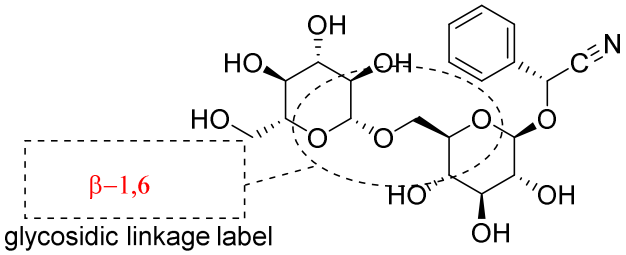
amygdalin

(circle and label the carbons that allow D or L classification)

   b. Classify the circled portion of the structure below (left side) by circling the **appropriate term out of each pair** of choices. Name the **glycosidic linkage** that is circled in the structure below (right side) (α or β, and the corresponding numbers) (5 x 3 = 15 pt)



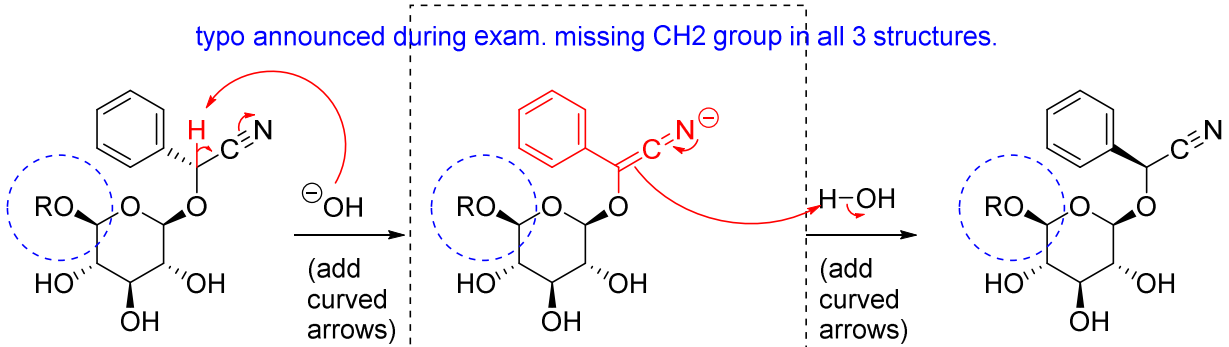
α or β
aldose or ketose
furanose or pyranose
pentose or hexose



glycosidic linkage label

   c. A hydrogen adjacent to a cyano group is much more acidic than a "normal" CH, due to resonance stabilization of the conjugate base. Add curved arrows and finish drawing the MAJOR resonance contributor of the intermediate to complete the base-catalyzed mechanism below. (5 pt)

typo announced during exam. missing CH2 group in all 3 structures.



amygdalin (abbreviated structure)

major resonance contributor (finish the structure)

Compound X

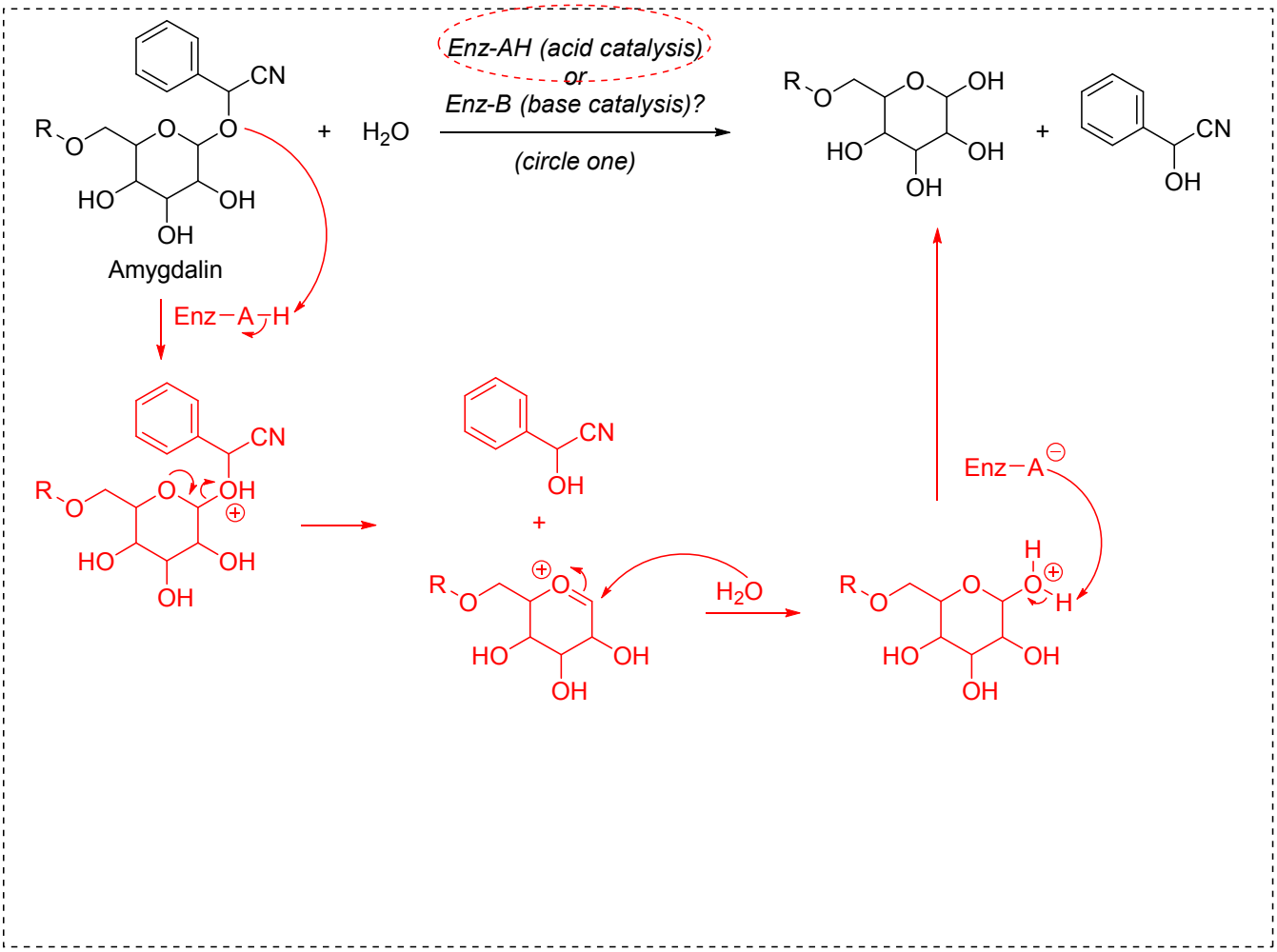
   d. Under the same "catalytic base" conditions (hydroxide in water) used in the previous scheme, would the stereochemical configuration of any other carbons in amygdalin also change? (circle one option below) (3 pt)

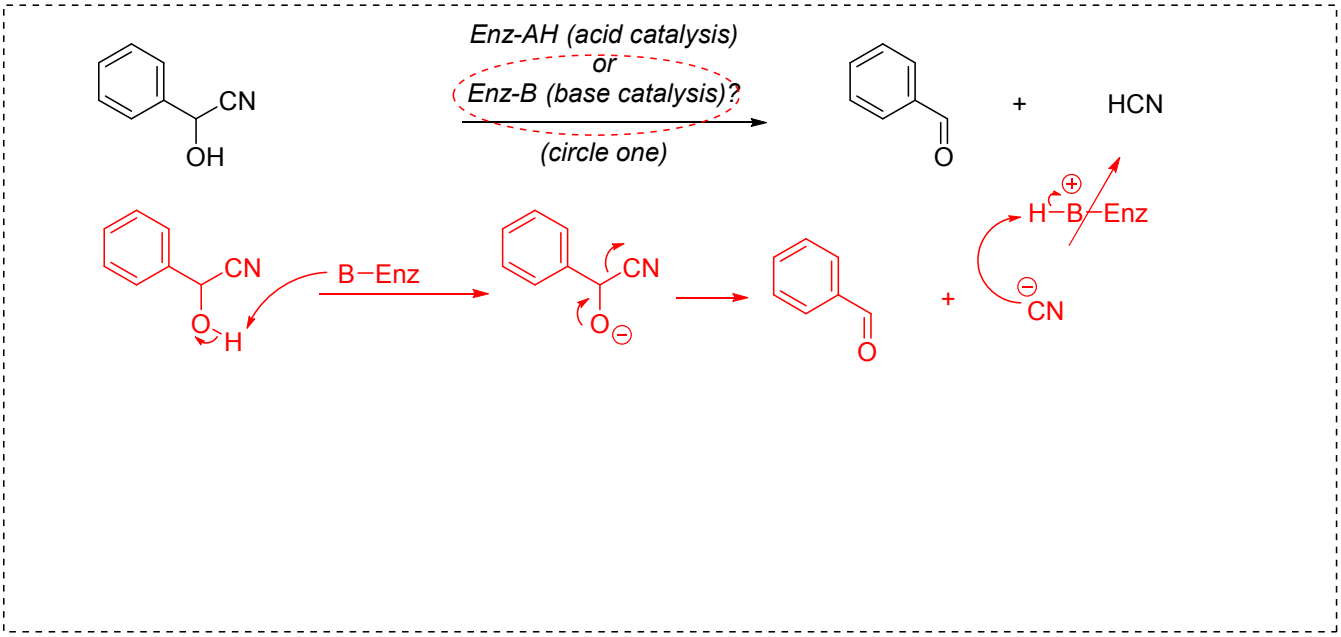
- Yes (many sterocenters can change configuration)
- Yes (both anomeric carbons can change configuration)
- Yes (one anomeric carbon can change configuration)
- No (none of the other stereocenters can change configuration)

   e. Which of the following terms best describes the relationship between amygdalin and compound X? (circle one) (3 pt)

Enantiomers Diasteromers Regioisomers Tautomers

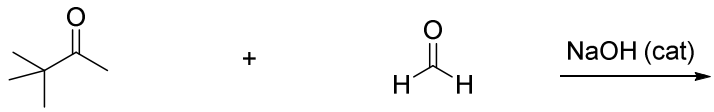
f. The multistep enzymatic hydrolysis of amygdalin releases HCN, which causes cyanide poisoning if ingested in sufficient quantities. For each reaction below, decide whether **acid or base catalysis** is more likely, circle the corresponding catalyst, then draw the corresponding **curved arrow mechanism**. *(Note: stereochemistry is omitted and a portion of the amygdalin structure is abbreviated for your convenience)* (2x10 = 20 pt)





6. **The Aldol and Mannich reactions**

a. Provide either a **systematic or common name** for each reactant below, and predict the major product of the aldol reaction. (3x6 = 18 pt)



3,3-dimethyl-2-butanone
or tert-butyl methyl ketone

formaldehyde
or
methanal

major aldol product ($C_7H_{14}O_2$)

b. Aldol reactions between two different carbonyl compounds can sometimes be complicated by selectivity issues (formation of multiple competing products). Explain how selectivity for the roles of nucleophile and electrophile are obtained in the reaction above (2x3 = 6 pt)

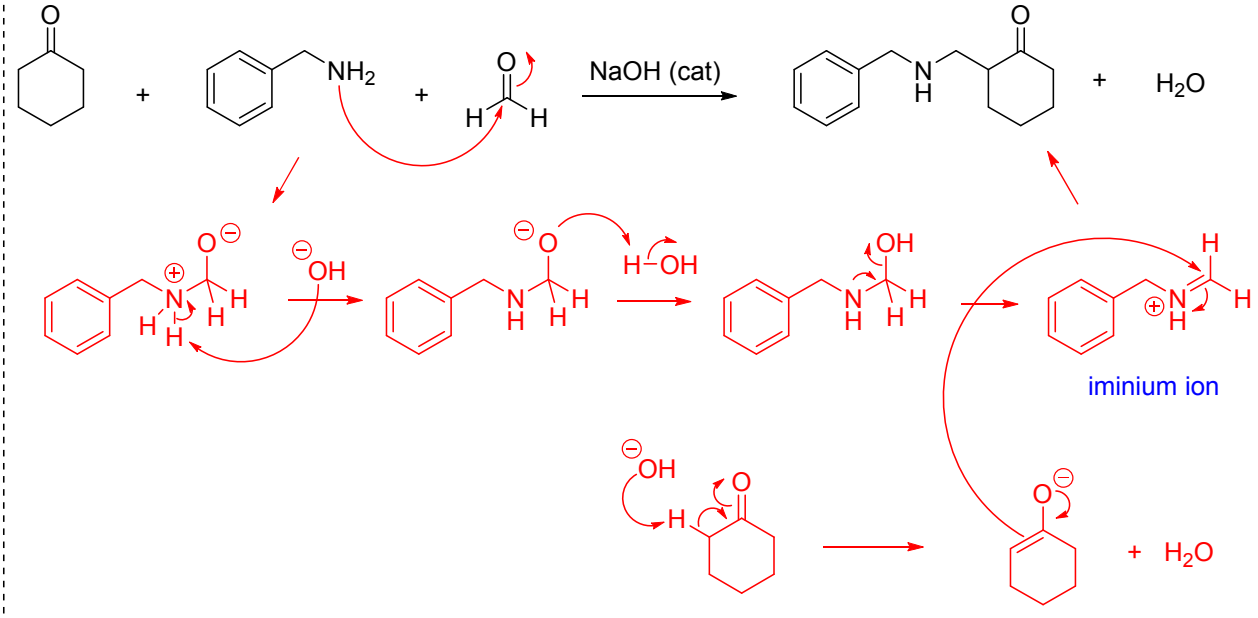
Nucleophile selectivity

Formaldehyde does not have any α hydrogens, so it cannot become an enolate nucleophile

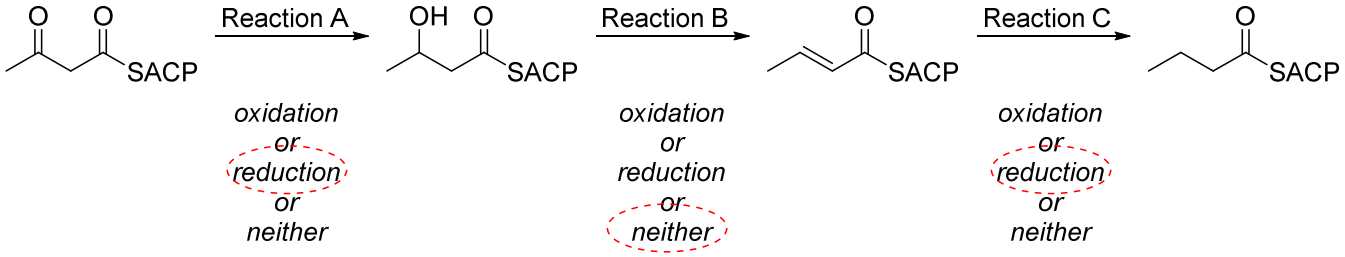
Electrophile selectivity

aldehydes are more electrophilic (more reactive electrophiles) than ketones
or
the aldol reaction with aldehyde electrophiles is favorable but with ketone electrophiles is unfavorable

c. The Mannich reaction is a variation of the aldol reaction, in which an **iminium ion** acts as the electrophile for the carbon-carbon bond forming step. Draw a curved arrow mechanism. (10 pt)

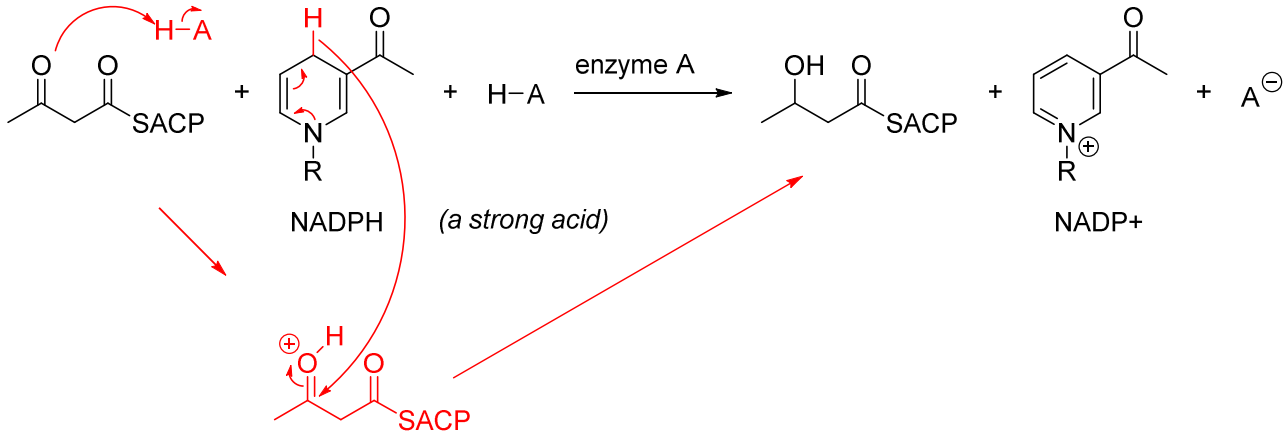


7. **Biosynthesis of fatty acids**
The series of reactions shown below is a portion of the biosynthetic pathway leading to fatty acids. *(Note: "SACP" is an abbreviation for a large portion of the molecule. Treat it as a generic "R" group throughout this question)*



a. Classify each of the reactions in the scheme above by circling one answer choice under each arrow. (3x2 = 6 pt)

b. Draw a curved arrow mechanism for reaction A, using the generic strong acid HA. (10 pt)

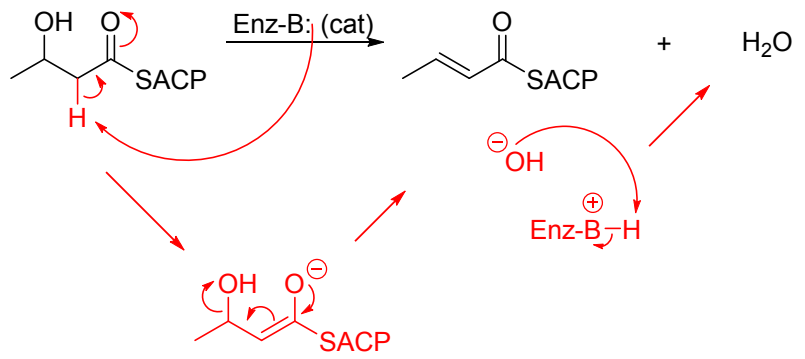


c. The reaction scheme above specifies that HA is a strong acid. Explain in one sentence how your mechanism would be different if HA was a weak acid (for example pKa = 13) instead. (3 pt)

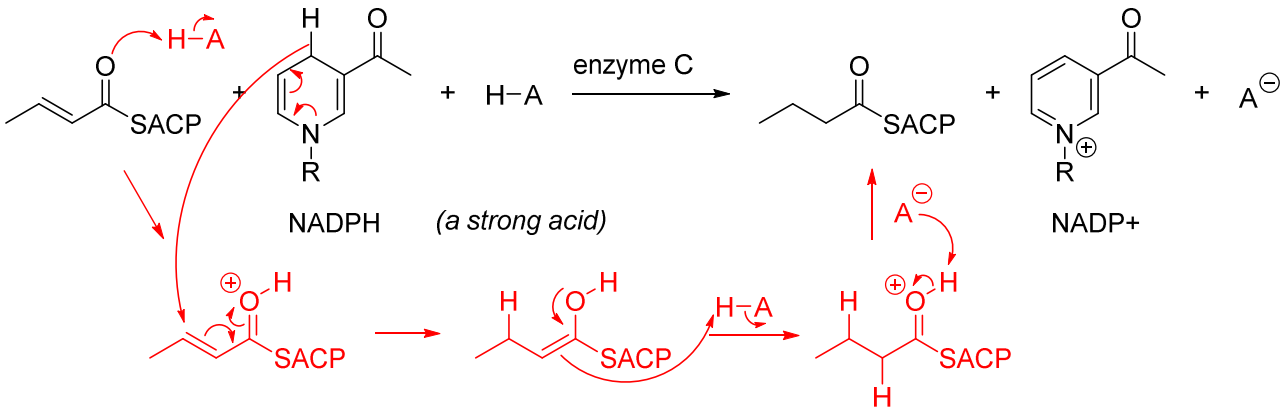
The order of the two steps (protonation vs hydride attack) would be reversed.

Longer explanation (these details not required for grading): a weak acid would not be reactive enough to protonate a carbonyl oxygen. By switching the order of the two steps, the weak acid will react with an alcoxide ion instead, which is a much stronger base than a carbonyl oxygen.

d. Draw a curved arrow mechanism for reaction B, using the catalytic base Enz-B: (10 pt)



e. Draw a curved arrow mechanism for reaction C, using the generic strong acid HA. (10 pt)



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