UCSC, Binder Name_____

Student ID # _____ Section Day/Time _____

Organic Chemistry
EXAM 1A (*250 points*)

DO NOT WRITE ON THE EXAM OR TURN THE PAGE UNTIL INSTRUCTED TO DO SO.
In the meantime, please read the instructions below.

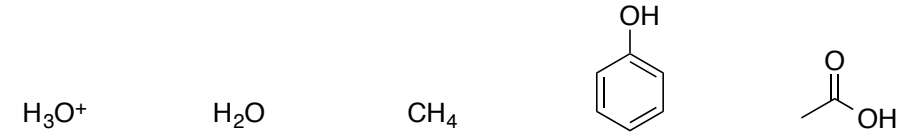
In each of the following problems, use your knowledge of organic chemistry conventions to answer the questions in the proper manner. **Be sure to read all instructions carefully.** You have one hour to complete this exam. Point distributions are given throughout the exam so you can use your time wisely. *Pencil is preferred, but blue or black ink is okay if you write neatly.* Do not use colorful (red, purple, etc.) pens as this interferes with grading. We are happy to answer questions, but please read instructions at least twice before asking. Make sure your belongings are in order now so that you can leave quietly when you are finished.

Keep your eyes on your own paper. Electronic devices of any kind are not allowed, including cell phones and calculators. Any student found using any of said devices, or found examining another student's exam, will be promptly removed from the exam room and at minimum will receive a zero on this exam. Such an incident may also be considered a form of academic dishonesty and reported to the UCSC Judiciary Affairs Committee.

1 (50)	
2 (50)	
3 (50)	
4 (30)	
5 (40)	
6 (30)	
Total	

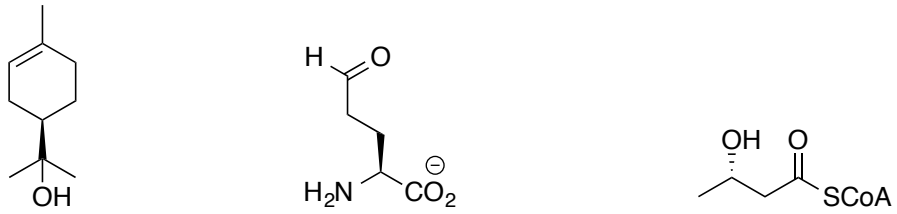
1. Fundamentals

(a) (*10 points*) **Provide the approximate pKa** of each of the following compounds on the lines provided.



_____ _____ _____ _____ _____

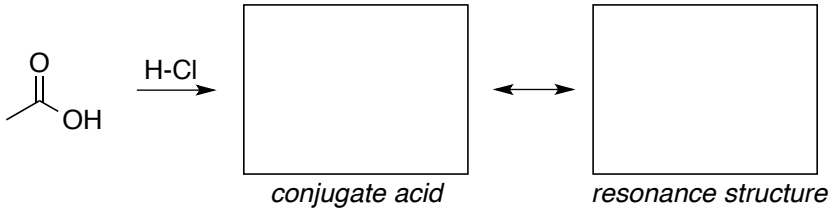
(b) (*14 points*) Each molecule below has multiple functional groups. **Circle and name each functional group**, then indicate whether it is likely to act as a **nucleophile (N)** or **electrophile (E).**



(c) (*20 points*) **Functional Groups** – Draw simple examples of molecules containing the functional groups below (*4 molecules, 1 functional group per molecule*).

Aldehyde **Ketone** **Ester** **Thiol**

(d) (*6 points*) **Draw the conjugate acid of acetic acid.** One oxygen atom is much more likely to be protonated in the reaction with HCl. Support your answer by drawing an equivalent **resonance structure** of the conjugate acid in the box provided.



conjugate acid *resonance structure*

2. Amino Acids & Peptides

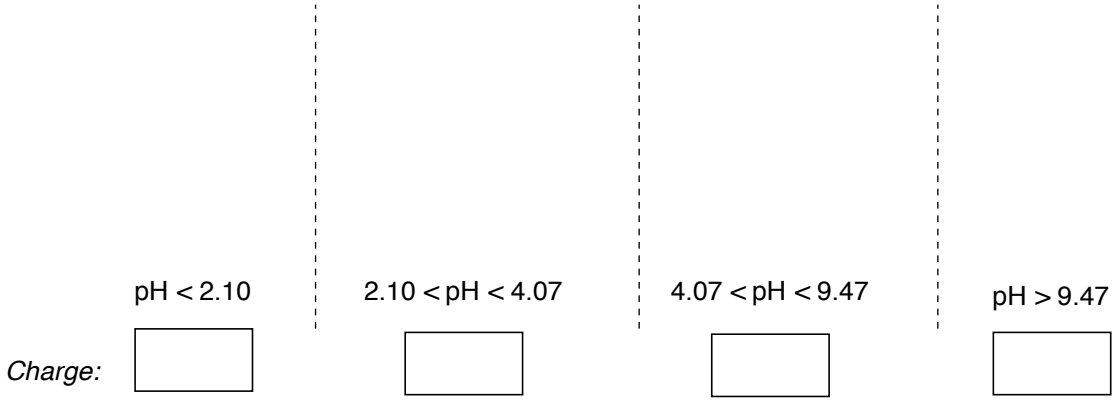
(a) (*20 points*) **Amino Acid Abbreviations – fill in the table**. The full name or abbreviation is given for an amino acid. Fill in the blank cells with the corresponding missing name or abbreviation.

Full Name	**Single-Letter Abbreviation**	**Three-Letter Abbreviation**
L-Serine		
	W	
		Phe
L-Arginine		
	Q	

(b) (*6 points*) **Fun question…**Which 6 letters of the alphabet are NOT used as abbreviations for the 20 common amino acids? It's only 6 points, so maybe come back to this one later!

(c) *Glutamic Acid* - pKa_1 2.10; pKa_2 9.47; pKa_R 4.07.

(i) (*16 points*) Draw the dominant ionic species of glutamic acid at the appropriate pH ranges based on the given pKa's. Indicate all charged atoms and circle the charges.

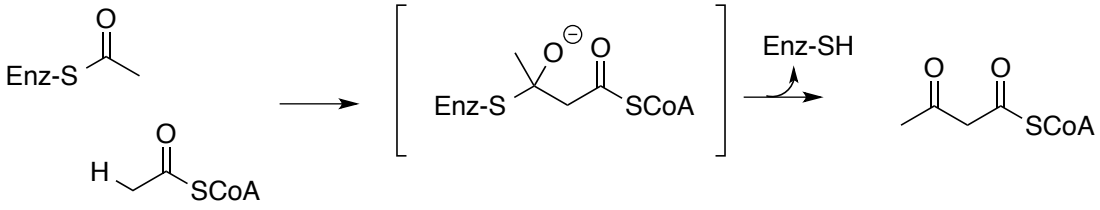


(ii) (*4 points*) **Why** is glutamic acid considered to be an acidic amino acid? Answer in 5 words or less!

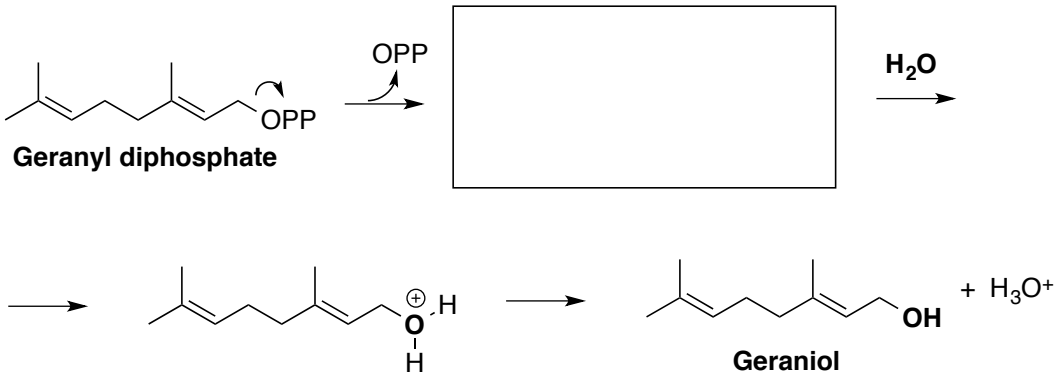
(iii) (*4 points*) At physiological pH (7.4), would the glutamate side chain act as an **acid** or a **base**?

3. Mechanism Warm-up

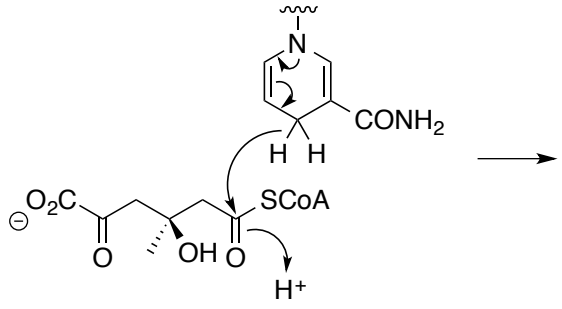
(a) (*10 points*) **Add arrows to complete the mechanism.** *Do not add more intermediates.* Add any acids (**H**$^+$) and bases (**:B**) needed to complete each step as written.



(b) (*15 points*) Add the missing elements in the hydration reaction below – **draw the missing intermediate** in the box provided, then add the **missing arrows** in the next steps. Add any acids (**H**$^+$) and bases (**:B**) needed to complete each step as written.



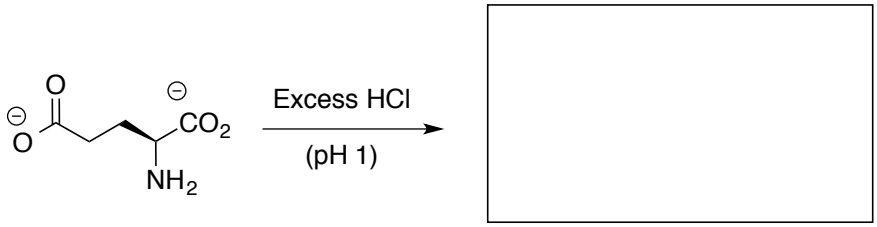
(c) (*15 points*) Follow the arrows and **draw the products.**



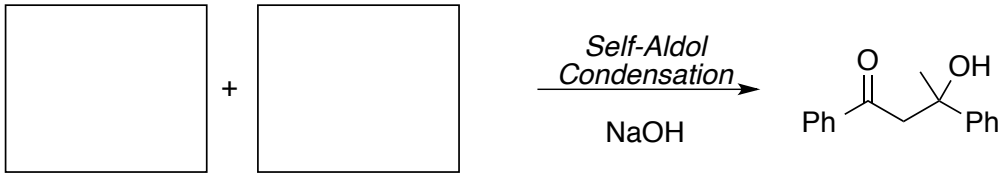
4. Fill in the Box

(*6 points per box*) Each reaction below is missing a component (reactant or product). There is ample information/clues given to reasonably complete the reaction scheme. Be sure to balance reaction if needed. *No arrows necessary!*

(a)

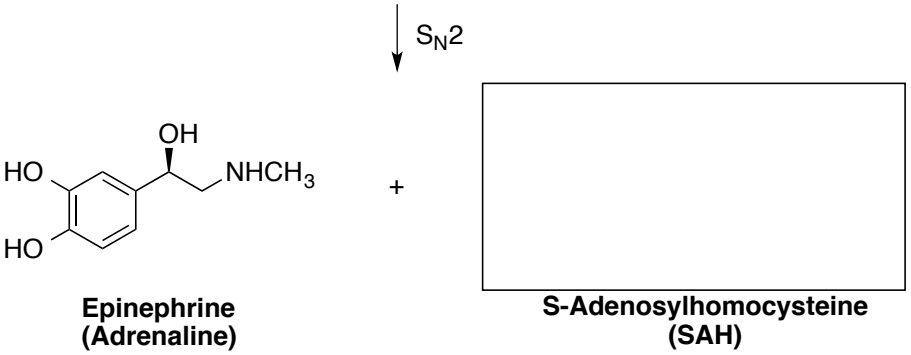


(b)



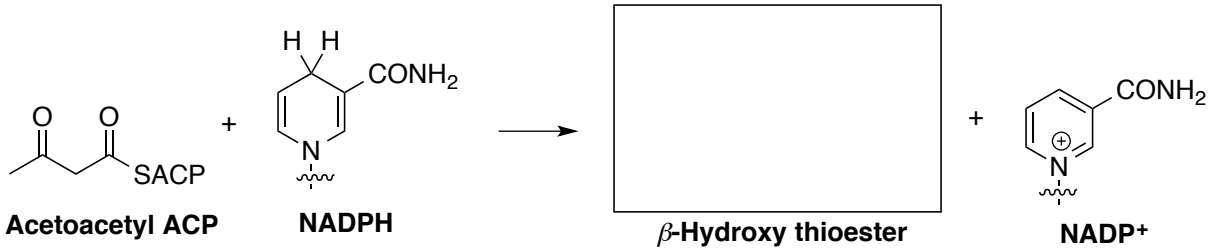
(c)

Norepinephrine **S-Adenosylmethionine (SAM)**



Epinephrine (Adrenaline) **S-Adenosylhomocysteine (SAH)**

(d)

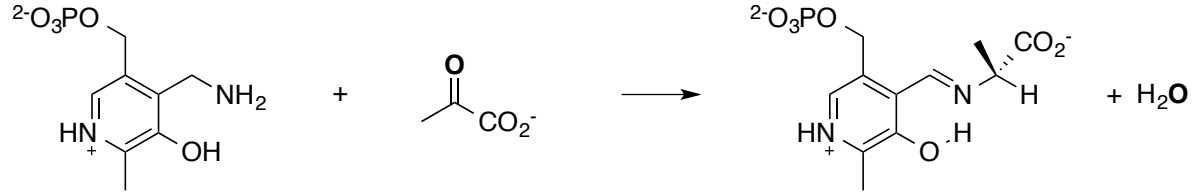


Acetoacetyl ACP **NADPH** **β-Hydroxy thioester** **NADP+**

5. Reaction Mechanisms

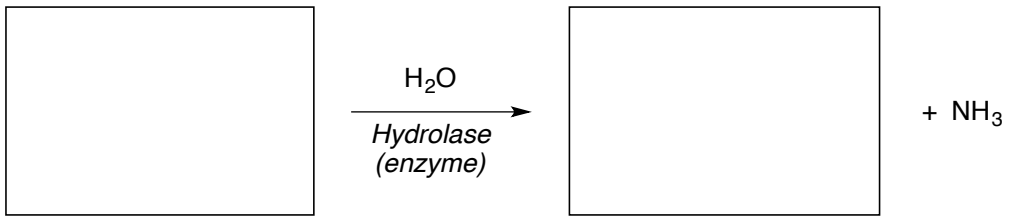
Bring in acids ($\mathbf{H^+}$) and bases (**:B**) where necessary. You may define abbreviations (R) to simplify structures, but be sure to draw out the bonds needed to draw the complete mechanism. *A minimum of one reaction intermediate is required for each. No lazy mechanisms!*

(a) (*20 points*) The first step in the regeneration of cofactor **PLP** from **PMP** in the biosynthesis of **alanine** is imine formation between **PMP** and **pyruvate**. Draw the arrow-pushing mechanism and intermediate(s) involved in this transformation.



Pyridoxamine phosphate (PMP) | **Pyruvate** (an α-keto acid) | **PLP-amino acid imine**

(a) (*20 points*) It's a good thing you memorized amino acid structures! Begin by drawing the full structures of **aspartate** and **asparagine**, then draw the arrow-pushing mechanism and intermediate(s) involved in this hydrolysis reaction.

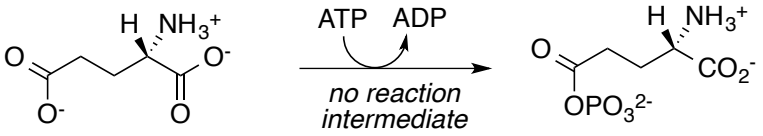


Asparagine | **Aspartate**

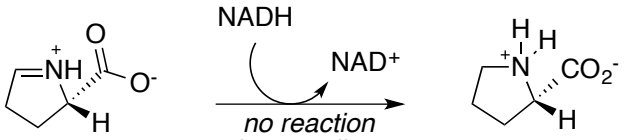
6. (*40 points*) **Active Site Design**
L-Proline is an essential amino acid that is synthesized by plants and bacteria but humans must obtain it through the diet. **Proline** is synthesized from **glutamate**. The first and last steps in this process are highlighted below.

Propose arrow-pushing mechanisms for the steps below by **designing the enzyme active sites for each step.** Redraw all substrates, abbreviating only **ATP** & **NADH** while still including the bonds involved in the mechanism. Use appropriate **amino acid residues** as acids and bases when needed. Include **at least three additional stabilizing factors per reaction** that keep the substrates and cofactors in place in the enzyme active sites. There are many ways to do this. Try to have fun with it!

READ INSTRUCTIONS CAREFULLY BEFORE YOU BEGIN!



Glutamate



Proline