UCSC, Binder Name_____

Student ID # _____ Section Day/Time _____

Organic Chemistry
FINAL EXAM A (*250 points*)

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

Use your knowledge of organic chemistry conventions to answer the questions in the proper manner. You should be delighted to find that not every topic is included in the exam, otherwise we would be here all day! A representative portion of CHEM 109 material is presented to assess your cumulative knowledge of reaction mechanisms, biomolecules, and a bit of medicinal chemistry. **Be sure to read each question carefully.** *Before you start, make sure there are eight (8) exam problem/pages in your exam.* You have two hours to complete this exam. Point distributions are given throughout the exam so you can use your time wisely. **You may choose to skip either page 6, 7, or 8 without penalty.**

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.

Close your eyes, take ten slow breaths, and relax until we tell you to start…
Thanks for a great quarter and good luck to you all!!

Page 1 (40)	
Page 2 (40)	
Page 3 (40)	
Page 4 (30)	
Page 5 (30)	
Page 6 (30)	
Page 7 (30)	
Page 8 (30)	
Total	

1. Fundamentals/Nomenclature

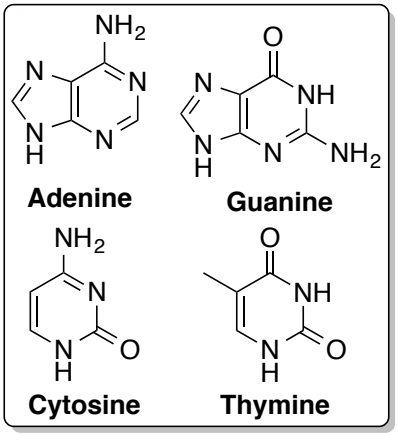
(a) (*10 points*) Draw the structures of **D-Glucose, β-D-glucopyranose,** and **pyruvate** below.

D-Glucose **β-D-glucopyranose (Haworth)** **Pyruvate**

(b) (*15 points*) Draw the full structures of **any three different common amino acids** below. Include the name and abbreviations above each structure.

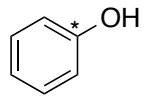
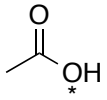
Name			
3-letter abbreviation			
1-letter abbreviation			
Structure			

(c) (*15 points*) Indicate the **nucleotide base pairs** in DNA. Redraw each structure to show the **H-bonding patterns** in the space provided.



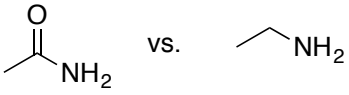
2. Acid-Base Chemistry

(a) (*10 points*) Provide the **pKa** of each compound below and indicate the **hybridization** of the starred atoms.

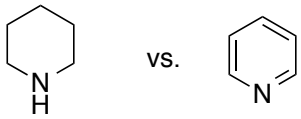
	*CH_4				*NH_3
pKa					
Hybridization (*)					

(b) (*14 points*) **Circle the <u>more basic</u> compound** in each pair.

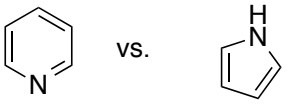
(i)



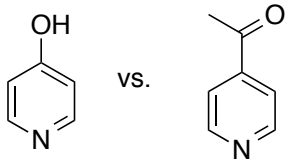
(ii)



(iii)



(iv)



(c) (*16 points*) Draw the dominant ionic forms of **L-Histidine** at the indicated pH ranges. Include and circle all formal charges and indicate the net charge of each structure in the boxes below.
pKa_1 1.77; pKa_2 9.18; pKa_R 6.10

L-Histidine (fully protonated)			
pH < 1.77	1.77 < pH < 6.10	6.10 < pH < 9.18	pH > 9.18
Charge:			

<u>SKIP EITHER PAGE 7 OR 8 (large X over entire page)</u>. No extra credit for doing both. 2_____

3. Medicinal Chemistry

(a) (*8 points*) Indicate whether each form of administration (dosage) is considered **enteral (E)** or **parenteral (P)**.

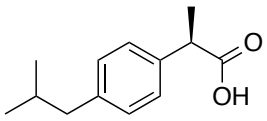
Oral _____ IV _____ Inhalation _____ Topical _____

(b) (*12 points*) Associate each one of the following terms with one of the three phases: **pharmaceutical (C), pharmacokinetic (K),** or **pharmacodynamics (D)**

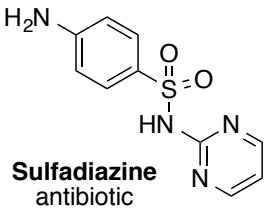
Absorption _____ Dosage Form _____ Receptor _____

Metabolism _____ Elimination _____ Excipient _____

(c) (*20 points*) For each of the compounds below, **list the functional groups** that contribute to solubility potential. Use this to **calculate solubility potential** and determine whether each structure as written is **likely to be water-soluble**.

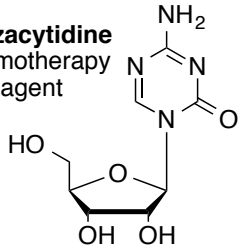


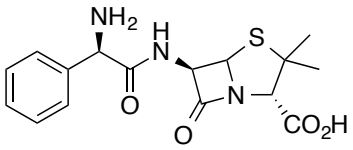
Ibuprofren
anti-inflammatory



Sulfadiazine
antibiotic

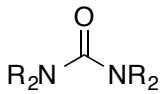
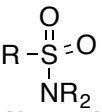
5-Azacytidine
chemotherapy agent





Ampicillin
antibiotic

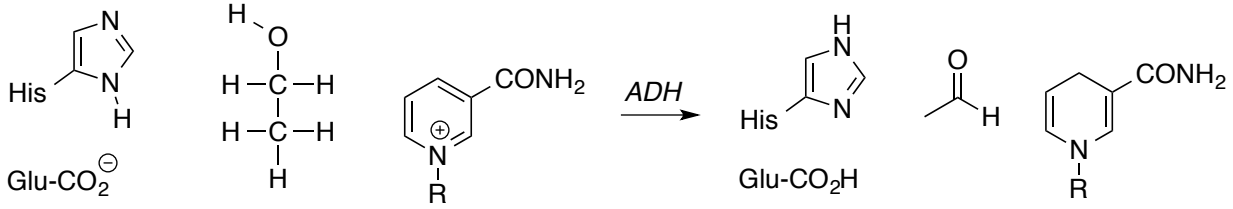
Compound	Functional Groups	Solubility Potential (# Carbons per FG)	Total Solubility Potential	Water-Soluble? (Yes or no)
Ibuprofen				
Sulfadiazine				
5-Azacytidine				
Ampicillin				

Functional Group	Solubility Potential	Lesser known FG's…
Alcohol	3-4 carbons	 **urea**
Amine / Carboxylic Acid	3 carbons	
Amide	2-3 carbons	 **sulfonamide**
Ether / Thioether / Urea	2 carbons	
Sulfonamide	20-30 carbons	

SKIP EITHER PAGE 7 OR 8 (large X over entire page). No extra credit for doing both. 3_____

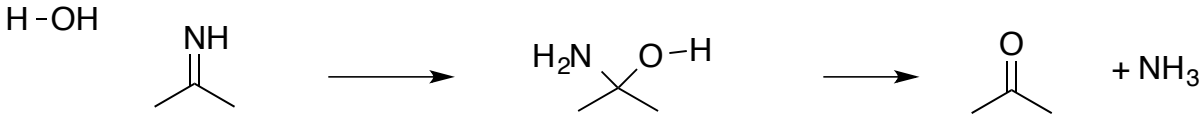
4. Mechanism Warm-up

(a) (*14 points*) During the metabolism of **ethanol** in humans, **alcohol dehydrogenase (ADH)** degrades ethanol to form **acetaldehyde** according to the following equation. **Add the mechanism arrows** to complete this reaction using each of the four components below.

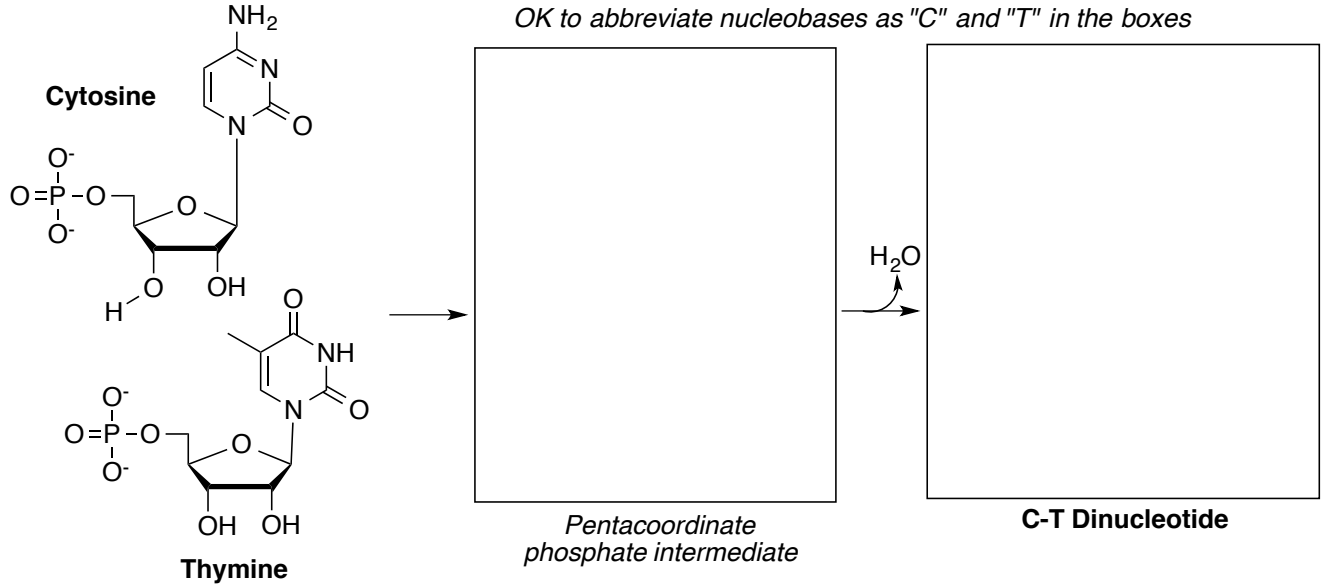


Add mechanism arrows

(b) (*8 points*) **Add arrows to complete the mechanism.** *Do not add more intermediates.* You will need to add an acid (H^+) and base (:B) to complete each step as written.

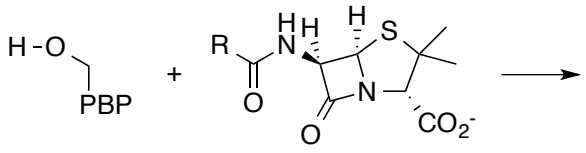


(c) (*18 points*) Complete the mechanism for the synthesis of a C-T dinucleotide below by **adding arrows** to each step and **drawing the intermediate and product**. Use acids (**H^+**) and bases (**:B**) when needed. You may abbreviate the nucleobases in the intermediate and product.



5. (*30 points*) **Fill in the box** (no mechanisms necessary) – **Skip one part on this page** by drawing a large "X" over the problem you do not want graded. Otherwise, **(a)** through **(c)** will be graded.

(a) Penicillin kills bacteria by reacting with a serine residue in the active site of an enzyme responsible for building murein, the polymer that holds together bacterial cells. This *nucleophilic acyl substitution* reaction occurs to alleviate ring strain in the electrophile. Draw the **product** of the reaction between the serine reside in **penicillin binding protein (PBP)** and **isopenicillin N**.



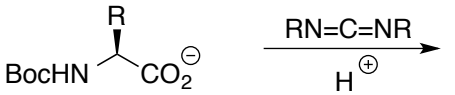
Enzyme **Isopenicillin N**

Covalently bound enzyme-isopenicillin N

(b) The first step in the mavelonate pathway is the **Claisen condensation of acetyl CoA**. Show the **product** of that reaction below.

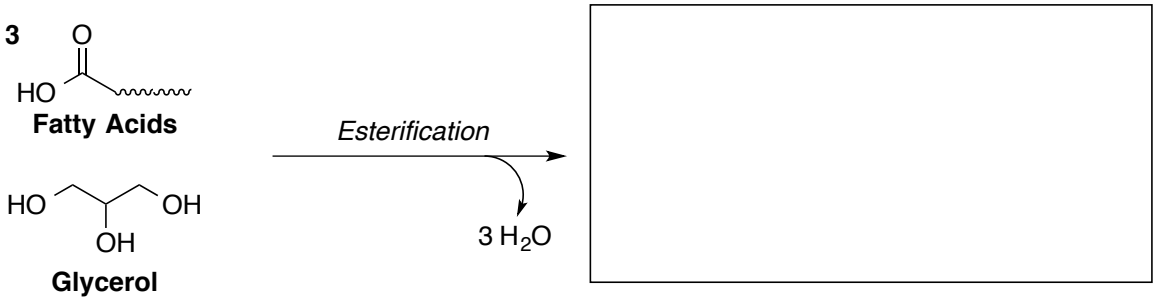
Acetyl CoA

(c) Activation of the carboxylate end of an N-protected amino acid occurs with a **carbodiimide** reagent under **mildly acidic conditions**. Show the structure of the activated acid in the reaction below.



Activated Acid

(d) Provide the structure of a **triacylglycerol**, formed through three esterification reactions between **glycerol** and **three fatty acids**.



Fatty Acids

Glycerol

Triacylglycerol

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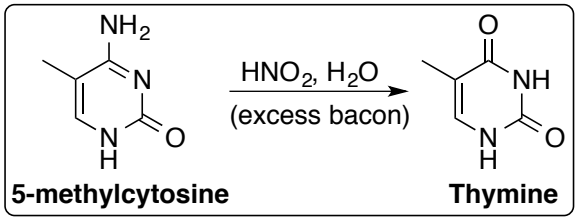
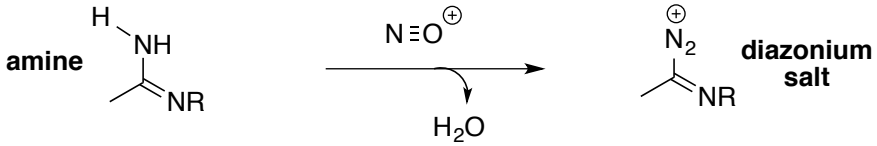
6. Show that mechanism! Excessive consumption of cured meats, while delicious, has been shown to cause mutations in nucleobases, like the such as the example shown below. This process is broken down into three steps, outlined below with simplified molecules.

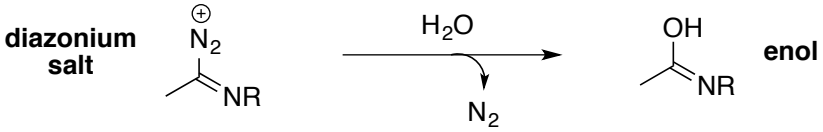
In each step, use water (H_2O), acids (H^+), and/or bases (:B) as needed to complete the transformation. Carry out the mechanism in the indicated number of steps or within the range of steps provided. Structures are given in such a way that you do not have to redraw the starting materials.



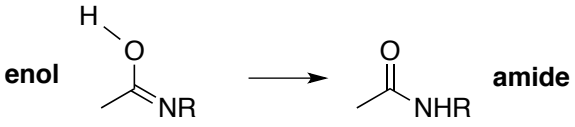
(a) (*16 points*) Show the mechanism for conversion of the **amine** into a **diazonium salt** in two to three (2-3) steps. Believe it or not, this mechanism is analogous to imine formation.



(b) (*10 points*) Show the mechanism for hydrolysis (a type of nucleophilic acyl substitution) of the **diazonium salt** into the **enol** in two to three (2-3) steps.



(c) (*5 points*) Show the mechanism for *tautomerization* in one step (no intermediate).



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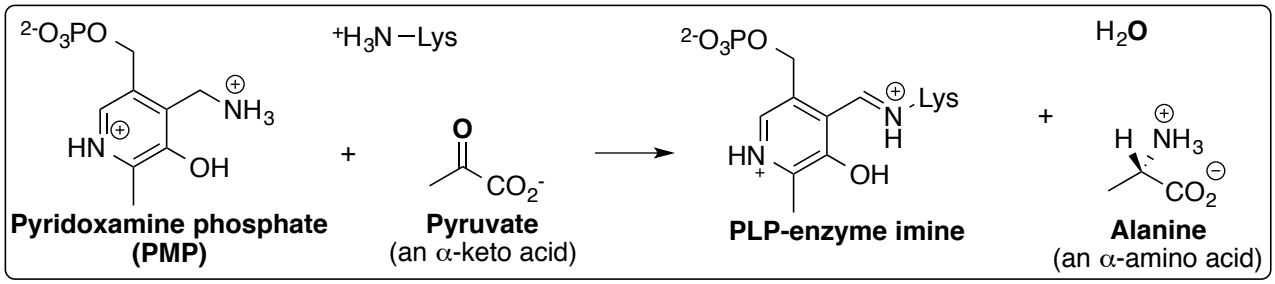
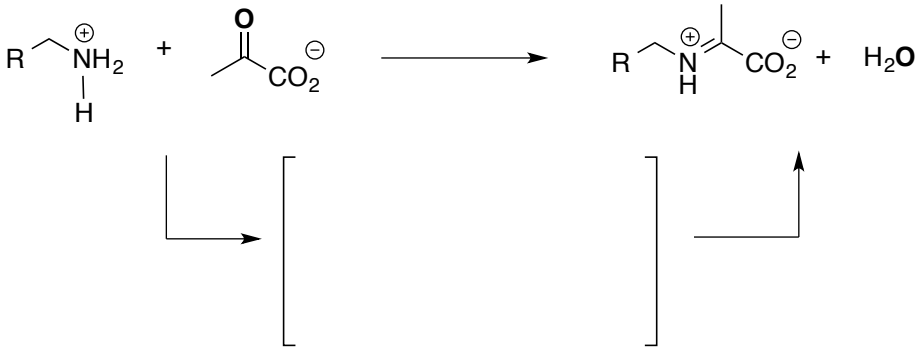
7. Amino Acid Biosynthesis – Do either this page or page 8, not both. Big "X" on the page to skip.
The metabolism and catabolism of amino acids involves the co-factor **PLP**, which requires regeneration for it to be recycled in another process. The overall scheme for PLP regeneration is shown below along with the conversion of **pyruvate** into **alanine**. This process is broken down into three steps, outlined below with simplified molecules.



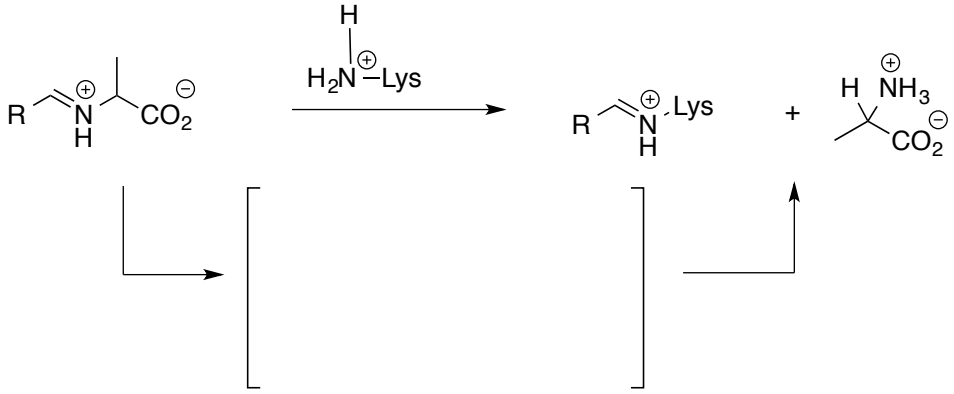
In each step, use amino acid residues as acids and bases as needed to complete the transformation. Carry out the mechanism in the indicated number of steps. Structures are given in such a way that you do not have to redraw the starting materials.

(a) (*13 points*) Show the mechanism for iminium formation in two steps (one intermediate).



(b) (*5 points*) Show the mechanism for *isomerization* in one step (no intermediate).

(c) (*13 points*) Show the mechanism for *trans-imination* and release of **alanine** in two steps (one intermediate). You do not need to account for stereochemistry.



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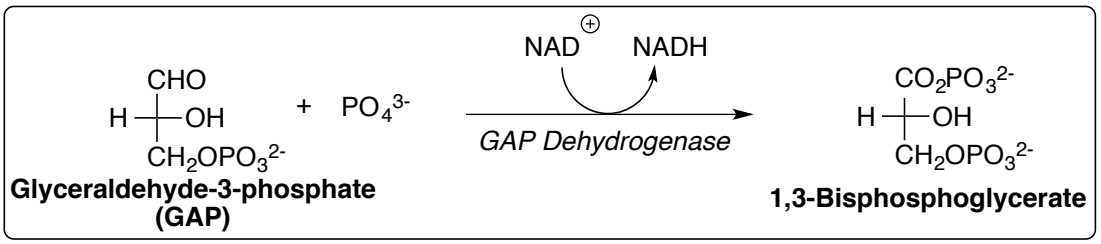
8. Glycolysis – Do either this page or page 7, not both. Big "X" on the page to skip.
The second phase of glycolysis begins with the oxidative phosphorylation of GAP to produce the mixed carboxylic-phosphoric anhydride in 1,3-bisphosphoglycerate. This process involves covalent binding to the enzyme GAP dehydrogenase and can be broken down into three steps, outlined below with simplified molecules.



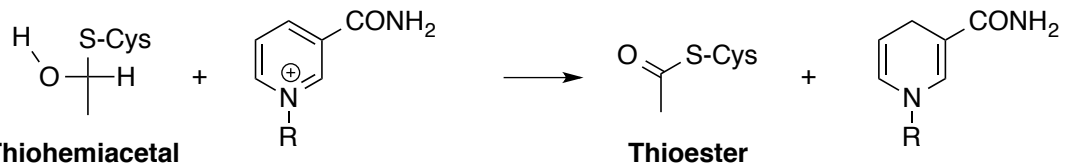
Glyceraldehyde-3-phosphate (GAP)

1,3-Bisphosphoglycerate

Use amino acid residues as acids and bases as needed to complete each transformation. Carry out the mechanism in the indicated number of steps. Structures are given in such a way that you do not have to redraw the starting materials, unless otherwise stated.

(a) (*6 points*) Show the mechanism for the covalent binding of a cysteine residue to an aldehyde in one step (no intermediate).

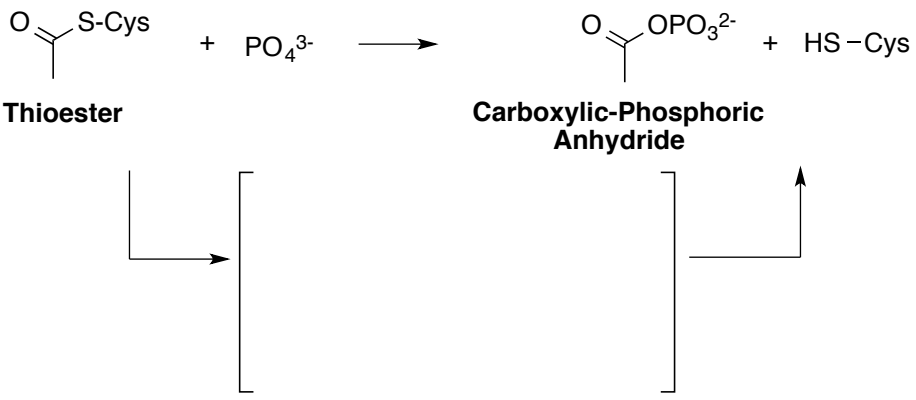
(b) (*6 points*) Show the mechanism for oxidation of the **thiohemiacetal** into a **thioester** using NAD^+ in one step (no intermediate).



Thiohemiacetal

Thioester

(c) (*18 points*) Show the mechanism for conversion of a **thioester** into a **carboxylic-phosphoric anhydride** in two steps (one intermediate). Begin by drawing the Lewis structure of a phosphate ion.



Thioester

Carboxylic-Phosphoric Anhydride

SKIP EITHER PAGE 7 OR 8 (large X over entire page). No extra credit for doing both. 8_____

Have a great summer!