

**CHEM 109, Organic Chemistry with Biological Applications**  
**EXAM 2A (250 points)**

**DO NOT BEGIN THE EXAM OR TURN THE PAGE UNTIL INSTRUCTED TO DO SO.**

**In the meantime, please read the instructions below.**

Page 1 (40)	
Page 2 (40)	
Page 3 (40)	
Page 4/5 (40)	
Page 6 (45)	
Page 7 (45)	
<b>Total</b>	

Use your knowledge of organic chemistry conventions to complete each problem in the proper manner. You have 1.5 hours to complete this exam. Point distributions are given throughout the exam so you can use your time wisely. **Be sure to read each question carefully. You are welcome to ask questions for clarification. Complete either page 4 or 5 (not both).** Write your last name and first initial on the top of pages 1-7. Check your exam for 7 pages of content.

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 <b>H</b> 1.008	2											13 <b>B</b> 10.81	14 <b>C</b> 12.011	15 <b>N</b> 14.007	16 <b>O</b> 15.999	17 <b>F</b> 18.998	18 <b>He</b> 4.0026
3 <b>Li</b> 6.94	4 <b>Be</b> 9.0122											5 <b>B</b> 10.81	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305											13 <b>Al</b> 26.982	14 <b>Si</b> 28.085	15 <b>P</b> 30.974	16 <b>S</b> 32.06	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.948
19 <b>K</b> 39.098	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.956	22 <b>Ti</b> 47.867	23 <b>V</b> 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.845	27 <b>Co</b> 58.933	28 <b>Ni</b> 58.693	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.38	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.630	33 <b>As</b> 74.922	34 <b>Se</b> 78.97	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.798
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.95	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.33	57-71 *	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.84	75 <b>Re</b> 186.21	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.97	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.38	82 <b>Pb</b> 207.2	83 <b>Bi</b> 208.98	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89-103 #	104 <b>Rf</b> (265)	105 <b>Db</b> (268)	106 <b>Sg</b> (271)	107 <b>Bh</b> (270)	108 <b>Hs</b> (277)	109 <b>Mt</b> (276)	110 <b>Ds</b> (281)	111 <b>Rg</b> (280)	112 <b>Cn</b> (285)	113 <b>Nh</b> (286)	114 <b>Fl</b> (289)	115 <b>Mc</b> (289)	116 <b>Lv</b> (293)	117 <b>Ts</b> (294)	118 <b>Og</b> (294)

\* Lanthanide series

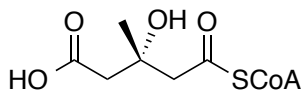
57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.96	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.93	70 <b>Yb</b> 173.05	71 <b>Lu</b> 174.97
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# Actinide series

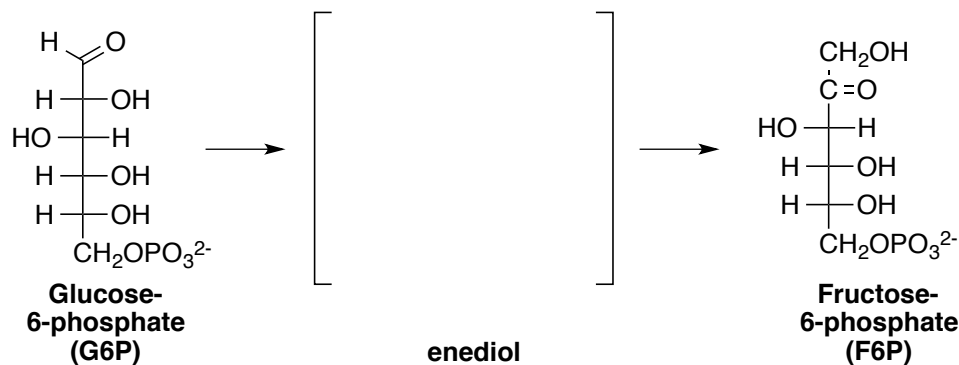
89 <b>Ac</b> (227)	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)
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## 1. Fundamentals

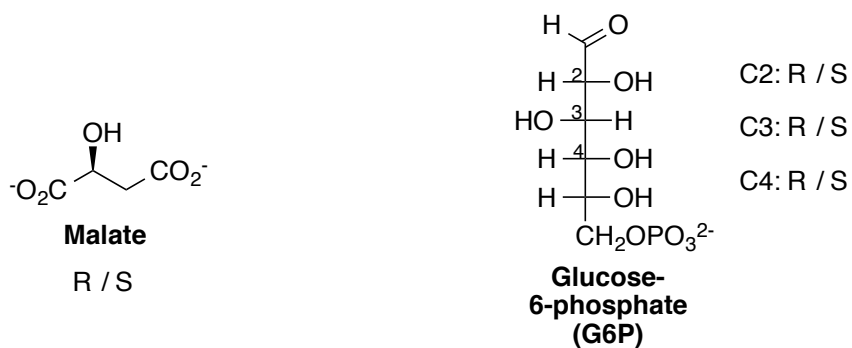
(a) (15 points) **Functional Groups** – Circle and name the three functional groups in the metabolic intermediate below.



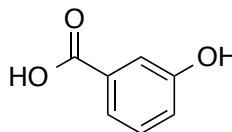
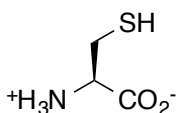
(b) (7 points) **Isomers** – Draw the **enediol** intermediate involved in the isomerization of **G6P** to **F6P** in glycolysis. No mechanism!



(c) (8 points) **Chirality** – Assign the R/S configuration to the compounds below. Circle your answer.



(d) (10 points) **Indicate (circle) the most acidic proton** on each compound and give the **approximate pKa** on the line provided.



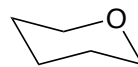
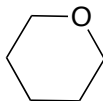
**2. Carbohydrates**

(a) (15 points) Draw the structure of D-Glucose as a **Fischer projection** and of  **$\alpha$ -D-Glucopyranose** in a **Haworth projection** as well as a **chair conformation**. Stereochemistry is important!!

FISCHER

HAWORTH

CHAIR



(b) (10 points) Lactose, or milk sugar, is a disaccharide composed of one D-galactose unit linked through a  $\beta$ -1,4-glycosidic bond to one  $\alpha$ -D-glucose unit (the glucose unit has the free anomeric OH). *Galactose is the C4 epimer of glucose.*

- Draw the structure of  **$\beta$ -D-Galactopyranose** as a Haworth projection.
- Draw the **full structure of lactose** below using **Haworth projections**.

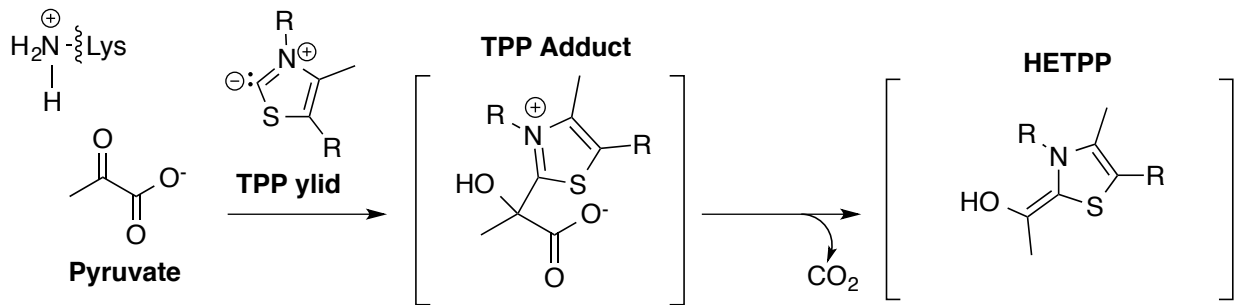
 $\beta$ -D-GalactopyranoseLactose:

(c) (15 points) Draw one example of each type of carbohydrate listed below. There may be several correct answers possible. No abbreviations such as R groups.

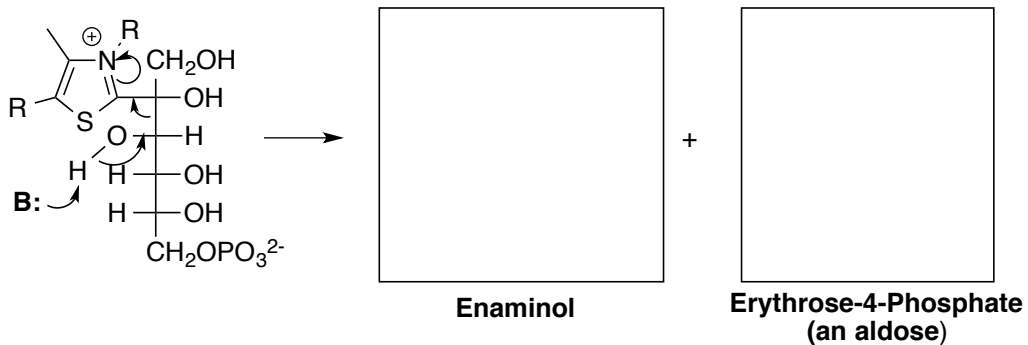
**D-Aldotetrose****L-Ketopentose****D-Ketohexose**

**3. Mechanism Warm-up – pay special attention to the start and end points of arrows**

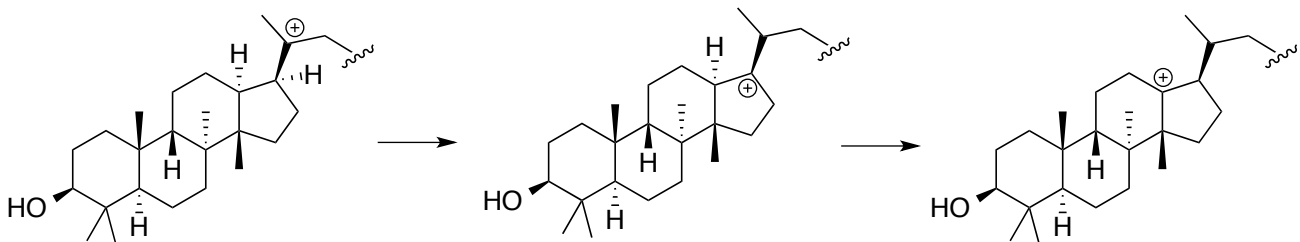
(a) (18 points) **Add the arrows** to complete both steps in the mechanism below, part of the anaerobic metabolism of pyruvate.



(b) (24 points) Follow the arrows and **draw the products** of the retro-aldol-like reaction in gluconeogenesis.

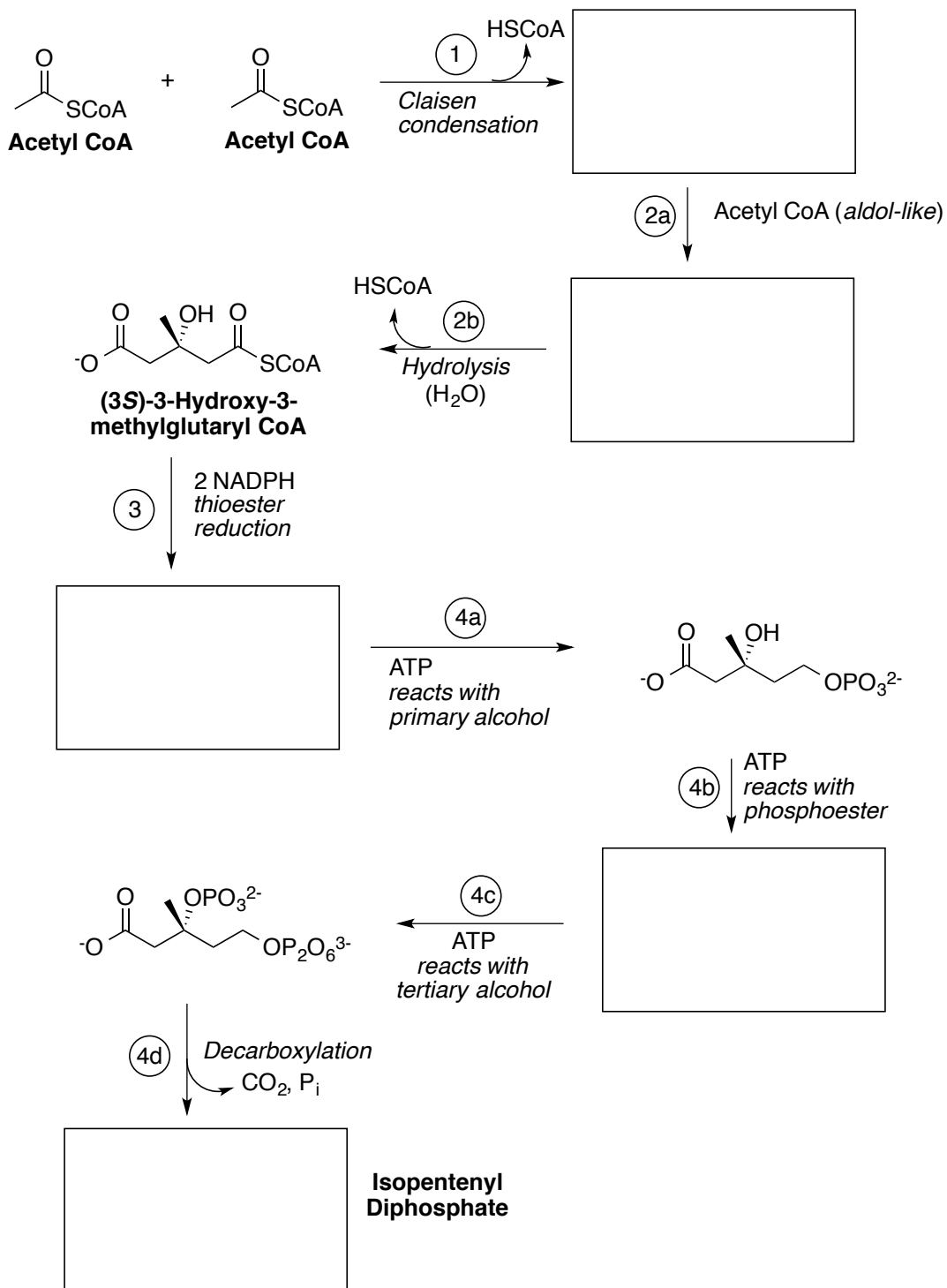


(c) (6 points) **Add the arrow** in each step to lead to the next product in the steps below, part of the biosynthesis of cholesterol.



4. (40 points) Fill in the Boxes on *either* Page 4 or 5. Draw a large X over the problem to skip, otherwise page 4 will be graded, even if it's blank!

Draw each intermediate in the synthesis of **isopentenyl diphosphate (IPP)**.  
No arrow pushing is necessary.

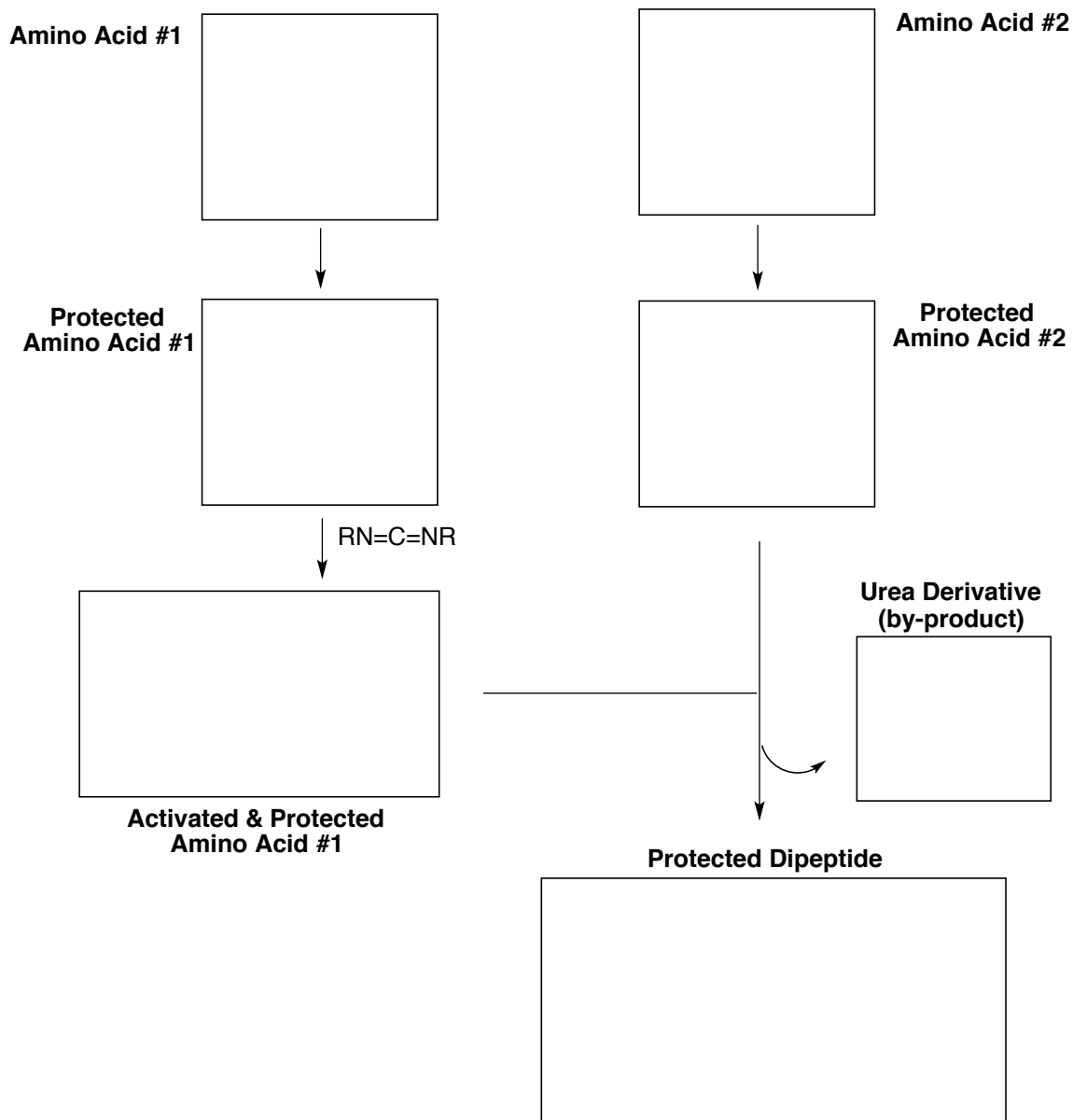


CHOOSE EITHER PAGE 4 OR 5

5. (40 points) Fill in the boxes on either Page 4 or 5. Draw a large X over the problem to skip, otherwise page 4 will be graded, even if it's blank! No arrow-pushing necessary, only structures in boxes graded.

Outline the steps for the laboratory synthesis of "your" protected dipeptide. Begin by drawing the full structure of **Amino Acid #1** (with the same single letter abbreviation as your first initial) and **Amino Acid #2** (last initial). If either of your initials is of the 6 letters without an amino acid abbreviation, move to the next letter in the alphabet.

**Protect** each amino acid appropriately (reagents not necessary), then **activate the acid** of one with the carbodiimide coupling agent ( $\text{RN}=\text{C}=\text{NR}$ ). Include stereochemistry at each step. Protect amino acid side chains with "PG" if necessary. Finally, draw the structure of the **dipeptide** with protecting groups still attached as well as the by-product of the coupling reaction, a **urea derivative**.



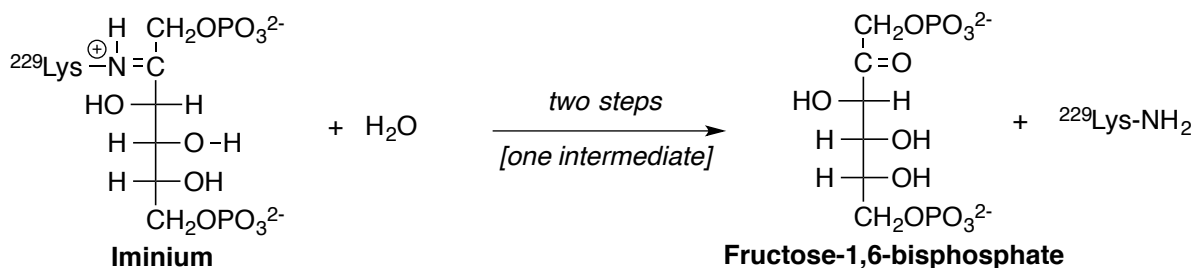
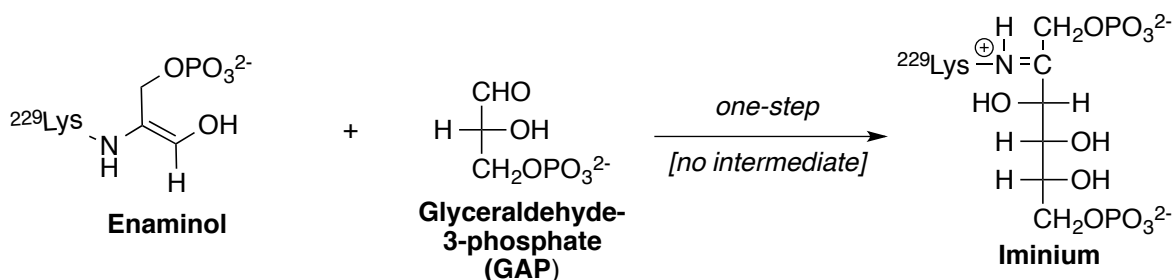
CHOOSE EITHER PAGE 4 OR 5

## 6. (45 points) Reaction Mechanisms

In gluconeogenesis, the reverse of glycolysis, Dihydroxyacetone phosphate (DHAP) is covalently bound to the active site through a lysine residue to form the **enaminol** shown below. **Glyceraldehyde-3-phosphate (GAP)** joins to this **enaminol** by an aldol-like reaction to form an **iminium** intermediate followed by hydrolysis to give **fructose 1,6-bisphosphate**.

Use the materials below along with **amino acid residues as acids and bases** to propose the full arrow-pushing mechanism of the formation of the product below within the enzyme active site. **No stabilizing factors such as hydrogen bonds are necessary on this page.** Carry out each mechanism in the number of steps indicated over the arrow. Feel free to abbreviate parts of structures not directly involved in the mechanism.

**Redraw the components – please do not draw any arrows to or from the structures provided!**



## 7. (45 points) Active Site Design

The reaction of a **fatty acyl CoA** with a **2-monoacylglycerol** to give a **1,2-diacylglycerol** is catalyzed by *monoacylglycerol acyltransferase* and proceeds by two nucleophilic acyl substitution mechanisms. **Fatty acyl CoA** first undergoes a reaction with a cysteine –SH group on the enzyme to give an enzyme-bound fatty acyl intermediate, which then reacts with **2-monoacylglycerol** and the product is released by the enzyme.

**Design the active sites** for both steps below with the following criteria in addition to standard mechanistic arrow-pushing to complete each transformation:

- The substrate and intermediate must each be held in place by **one H-bond to the peptide backbone**.
- **Amino acid residues must be used as acids and bases.**
  - o These residues must start in their natural **physiological state**.
  - o You must **re-use the same residues in both steps**.
- **Redraw the given components within the active site.** Please DO NOT draw the active sites around the structures provided!
- Complete each transformation in two steps with one intermediate.

