UCSC, Binder

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#### CHEM 8B Organic Chemistry II FINAL EXAM, Version B (*300 points*)

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 each question carefully. You have 3 hours to complete the exam, but hopefully you won't need it! You are welcome to use pre-built models. Complete every problem on Pages 1-6. You are instructed to skip parts of problems on Pages 7-9. Be sure to clearly indicate which parts you DO and DO NOT want graded, otherwise you may lose points.

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 "cheat sheets," 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. Nomenclature (45)	
<b>2</b> . Acid-Base (28)	
<b>3.</b> Amino Acids & Peptides (37)	
4. Single Step, MC (20)	
5. Single Step, MC (30)	
6. Mini Puzzles (40)	
7. Reaction Puzzle (40)	
8. Mechanisms (30)	
9. Multi-Step (30)	
Total	

## 1. Nomenclature

(a) (5 points) Draw the open chain form of L-Glucose below (Fischer projection).

(b) (20 points) Complete the following **Haworth projections** and **chair conformations**, being careful to clearly indicate proper directions (up or down) in the Haworth projections and bond angles in the chair conformations.

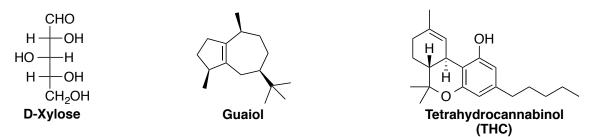
 $\beta$ -D-Glucopyranose

 $\alpha$ -D-Mannopyranose (the C2 epimer of D-Glucose)

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(c) (8 *points*) Draw an asterisk next to each chiral center on the molecules below and **clearly** designate each chiral center as R or S.

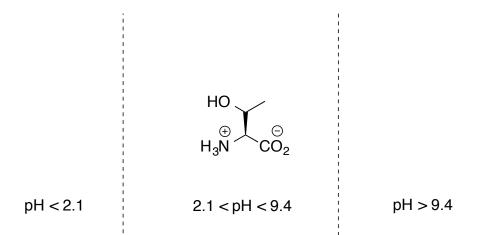


(d) (*12 points*) Draw the structure of a **glyceryl trilaurate**, the product of the triesterification of glycerol with three lauric acid units. **Lauric acid** is a saturated fatty acid containing 16 carbons. **Glycerol** is a three-carbon triol, where each alcohol is on different a carbon.

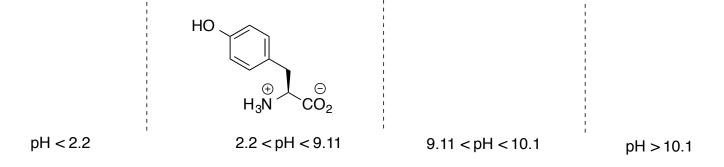
## 2. Acid-Base Chemistry

The physiological form of each amino acid is given below. Draw the dominant ionic species of the amino acids at each of remaining indicated pH ranges based on the given pKa's. Indicate all charged atoms. Circle the charges as shown below.

(a) (8 points) Titration of Threonine – pKa<sub>1</sub> 2.1; pKa<sub>2</sub> 9.4



(b) (10 points) Titration of Tyrosine -  $pKa_1 2.2$ ;  $pKa_2 9.11$ ;  $pKa_R 10.1$ 



(c) (10 points) Titration of Histidine - pKa1 1.8; pKa2 9.2; pKaR 6.0

pH < 1.8 
$$1.8 < pH < 6.0$$
  $6.0 < pH < 9.2$   $pH > 9.2$ 

## 3. Amino Acids & Peptides

Use the structures from the previous page to answer the following.

(a) (*12 points*) Indicate the charge of the dominant form of each amino acid at the indicated pH. Show the setup for calculation of the isoelectric point (pl) of each in the table.

	рН 1	рН 4	рН 7.4	рН 11	pl (Isoelectric Point) Calculation Setup
Threonine					
Tyrosine					
Histidine					

(b) (4 points) Why is histidine considered to be a basic amino acid? "It can act as a base" is <u>not</u> a sufficient answer!

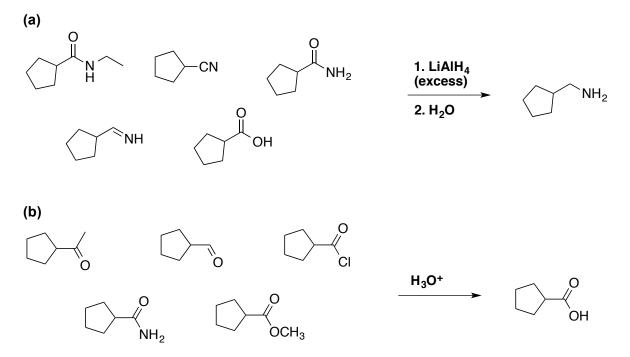
(c) (*14 points*) Draw the structure of a tripeptide containing threonine, tyrosine, and histidine at **physiological pH (7.4)**.

Thr – Tyr – His

(c) (7 *points*) Draw the structure of the Thr – Tyr – His tripeptide under highly basic conditions found in the intestines (pH 11).

4. (20 points) Single Step Reactions – Multiple Choice

For parts (a) & (b) below, circle the starting material(s) that would give the indicated product. More than one answer is possible for each.



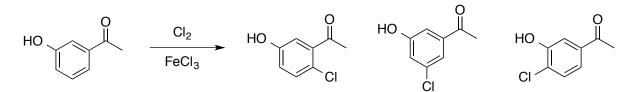
For parts (c) & (d) below, circle the correct product in each reaction. Only one answer is correct for each. (c)

OH OH 1. Ethyl Magnesium Bromide CN (EtMgBr, 1 mol) OH 2. H<sub>3</sub>O+ HO NH<sub>2</sub> (1 mol) (d) Ph Ph OH OH 1. PhMgBr (1 mol) HO ОН H HO Ph OCH<sub>3</sub> н 2. H<sub>3</sub>O+ Ph Ph 0 (1 mol) .OCH<sub>3</sub> OH HO ΗΟ Ö Ph Ρh

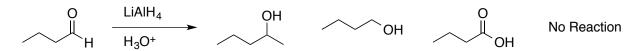
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# 5. (30 points) Single Step Reactions, Multiple Choice

(a) Circle the major products in the reaction below.

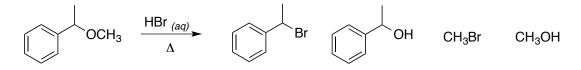


(b) Circle the product in the following reaction or circle "No Reaction" if the aldehyde does not react as written.

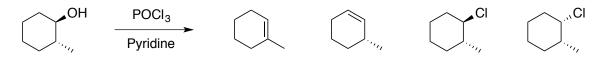


If "No Reaction", briefly explain:

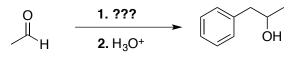
(c) Circle the two major products in the reaction below.



(d) Circle the product in the following reaction (only one is formed).



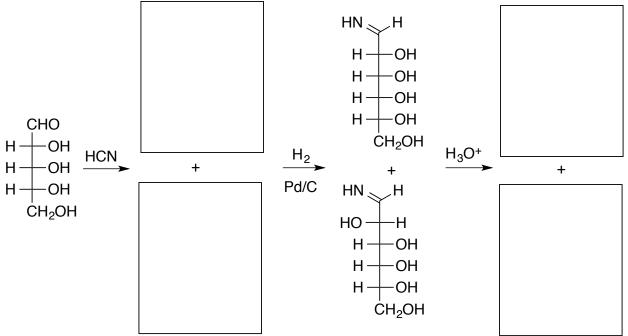
(e) Circle the appropriate reagent to complete the transformation below (what is ???).



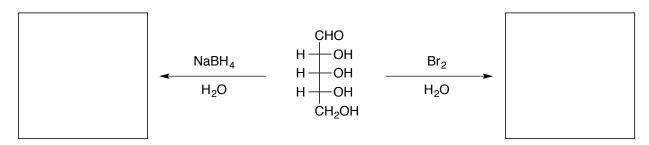
Benzyl magnesium bromide Phenyl magnesium bromide

# 6. (40 points) Mini-Puzzles with Biomolecules

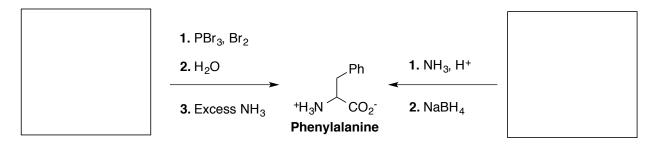
(a) Indicate the products in the first and last steps of the Kiliani-Fischer synthesis outlined below.



(b) Show the products of two different reactions of the following D-aldopentose.



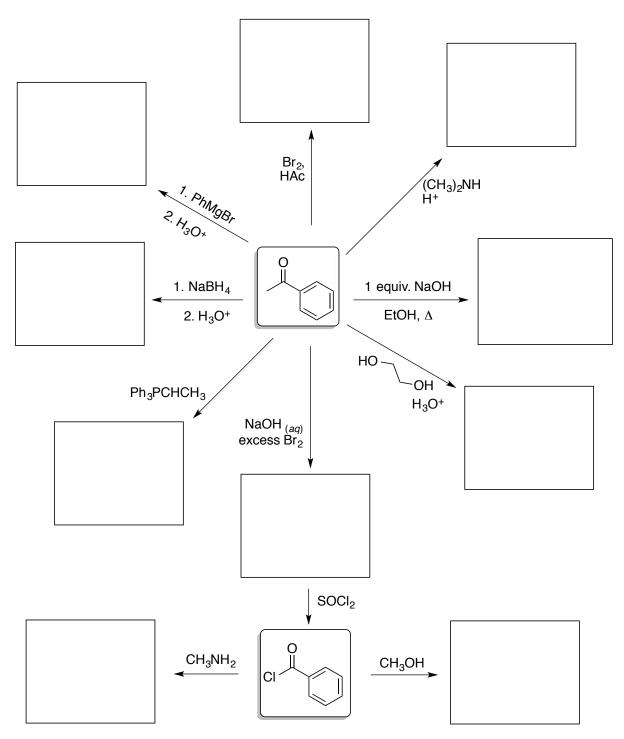
(c) Show the starting materials for two different methods for synthesizing phenylalanine.



#### 7. (40 points) Reaction Puzzle / Starburst

Aldehydes and ketones were major focal points of this course. Over the past 10 weeks, you learned over 10 reactions of aldehydes and ketones. Acid chlorides were also found to be a useful synthetic tool, opening up possibilities of making any acyl derivative.

Convey your knowledge of ketone and acid chloride chemistry by **drawing the products of the reactions in the boxes** below. It's not uncommon to forget a few things on an exam so please <u>SKIP ANY TWO by drawing a LARGE X over the boxes to skip</u>, otherwise the top eight reactions in the starburst will be graded.

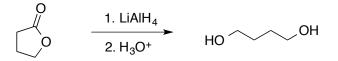


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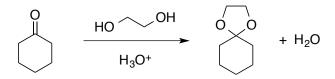
**8.** (*30 points*) **Mechanisms –** Draw the full arrow-pushing mechanism for <u>one of the reactions</u> below, including all arrows for acid-base reactions (no "PT"). Include all intermediates with proper charges circled for each step.

# CIRCLE THE REACTION TO BE GRADED. DRAW A LARGE "X" OVER THE REACTION YOU DO NOT WANT GRADED, OTHERWISE (a) WILL BE GRADED.

(a) Draw the full arrow-pushing mechanism for the reduction of the **lactone** (cyclic ester) below with **lithium aluminum hydride**, followed by quenching with **acid** in a separate second step.



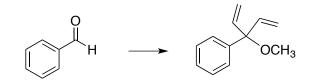
(b) The following **acetal** is synthesized from **cyclohexanone** and **1,2-ethanediol** under acidic condition. This mechanism takes places *via* two nucleophilic addition reactions, one of which results in dehydration (loss of water). Draw the full arrow-pushing mechanism for this reaction.



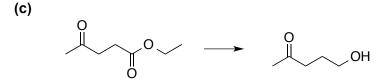
# 9. (30 points) Multi-Step Synthesis – CHOOSE TWO

Carry out the syntheses of the indicated target molecules using the starting material provided and any other reagents or carbon sources needed. Draw the **product after each synthetic step. No mechanisms.** 

(a)







### PUT A LARGE "X" OVER THE ENTIRE REACTION & SPACE YOU ARE SKIPPING. OTHERWISE THE TOP TWO REACTIONS WILL BE GRADED, EVEN IF THEY ARE BLANK!

9\_\_\_\_

## Extra Reaction = Extra Credit

Is there one reaction you studied particularly hard that didn't show up on this exam? Or did you otherwise notice a reaction that wasn't covered here (there are many!)?

Draw the **full reaction scheme for any <u>one</u> reaction not covered on this final** (no abbreviations such as R groups) including starting material, reagent(s), and product(s). It must be 100% correct and not included anywhere else on this exam (including the multi-step reactions you used)! Write <u>only one reaction or no credit</u> (don't write multiple reactions hoping we'll choose the correct one). *No mechanisms, but thanks anyway*.