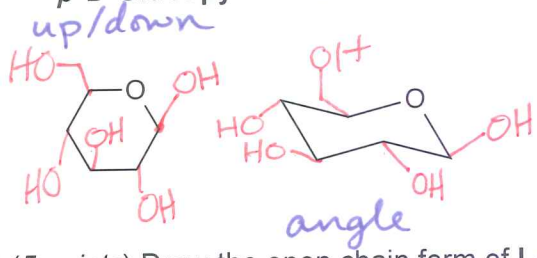
1. Nomenclature

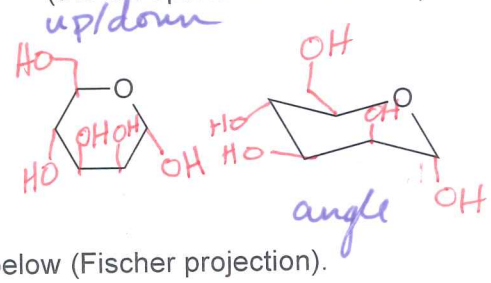
5pts/bond

(a) (*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.

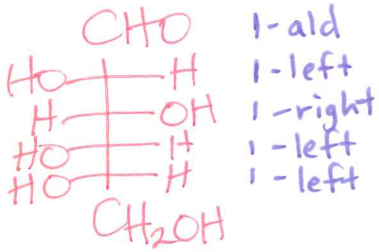
β-D-Glucopyranose



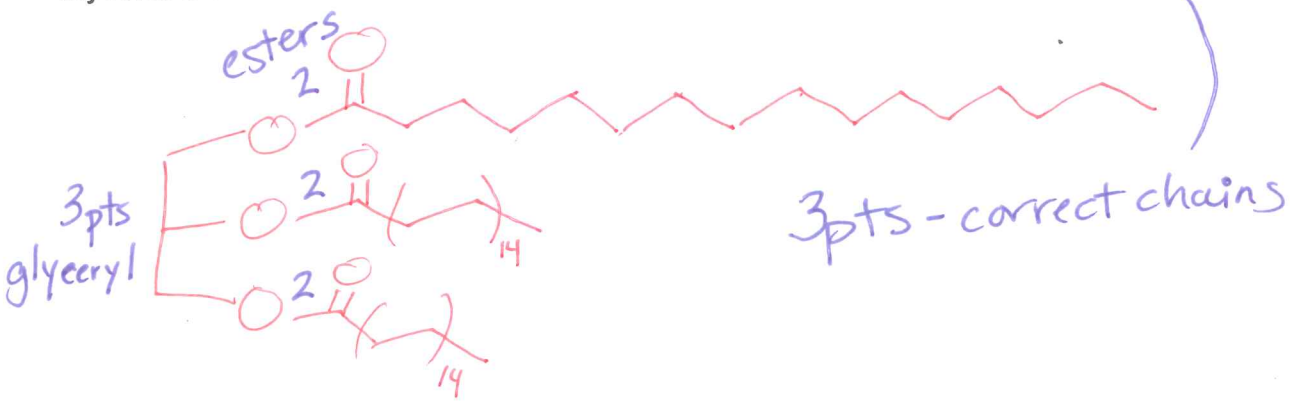
α-D-Mannopyranose
(the C2 epimer of D-Glucose)



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

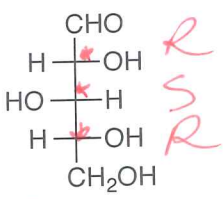


(c) (*12 points*) Draw the structure of a **glyceryl trilaurate**, the product of the triesterification of glycerol with three lauric acid units. **Lauric acid** is a saturated fatty acid containing 16 carbons. **Glycerol** is a three-carbon triol, where each alcohol is on different a carbon.

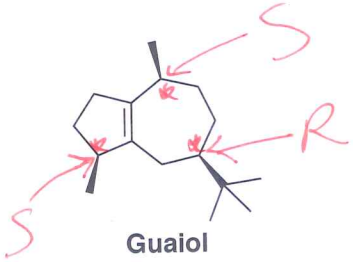


1pt/center

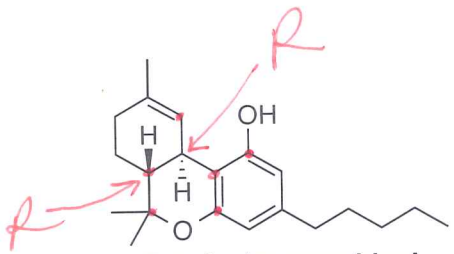
(d) (*8 points*) Draw an asterisk next to each chiral center on the molecules below and **clearly designate each chiral center as R or S**.



D-Xylose



Guaiol



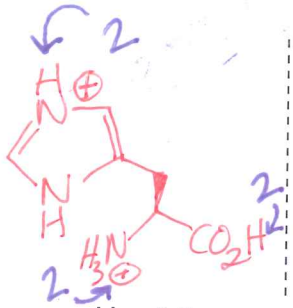
Tetrahydrocannabinol (THC)

-1 for each non-chiral atom starred/assigned

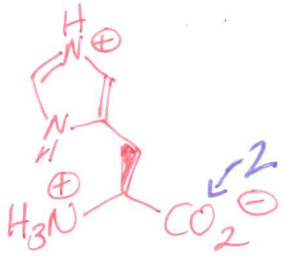
2. Acid-Base Chemistry 1 pt - protonated/deprotonated 1 pt - correct charge

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.

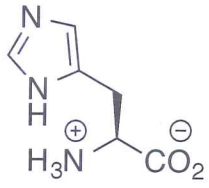
(a) (*10 points*) **Titration of Histidine** - pKa_1 1.8; pKa_2 9.2; pKa_R 6.0



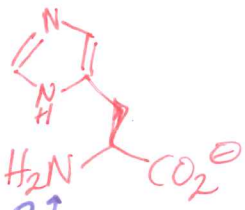
pH < 1.8



1.8 < pH < 6.0

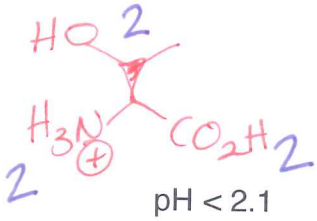


6.0 < pH < 9.2

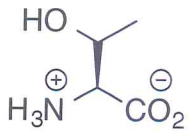


pH > 9.2

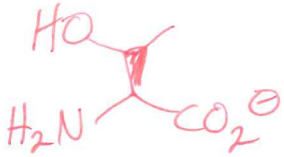
(b) (*8 points*) **Titration of Threonine** – pKa_1 2.1; pKa_2 9.4



pH < 2.1

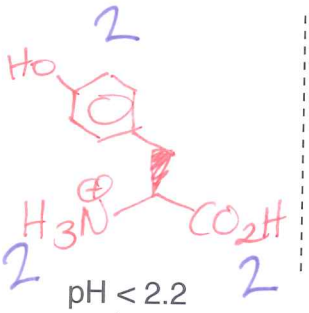


2.1 < pH < 9.4

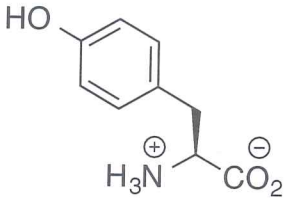


pH > 9.4

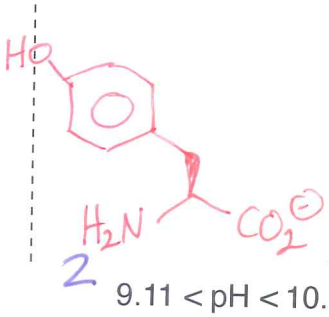
(c) (*10 points*) **Titration of Tyrosine** - pKa_1 2.2; pKa_2 9.11; pKa_R 10.1



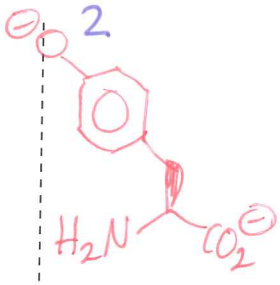
pH < 2.2



2.2 < pH < 9.11



9.11 < pH < 10.1



pH > 10.1

3. Amino Acids & Peptides
Use the structures from the previous page to answer the following.

1pt/box

(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 (pI)** of each in the table.

3 extra possible

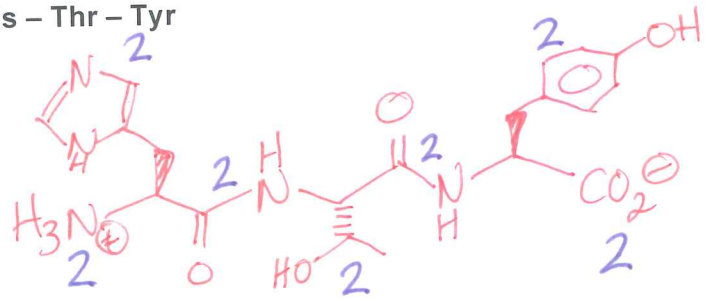
	pH 1	pH 4	pH 7.4	pH 11	pI (Isoelectric Point) Calculation Setup
Histidine	+2	+1	Ø	−1	$\frac{6+9.2}{2}$
Threonine	+1	Ø	Ø	−1	$\frac{2.1+9.4}{2}$
Tyrosine	+1	Ø	Ø	−2	$\frac{2.2+9.11}{2}$

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

Histidine is neutral (not charged) under basic pH / has basic pI

(c) (*14 points*) Draw the structure of a tripeptide containing Histidine, Threonine, and Tyrosine at **physiological pH (7.4)**.

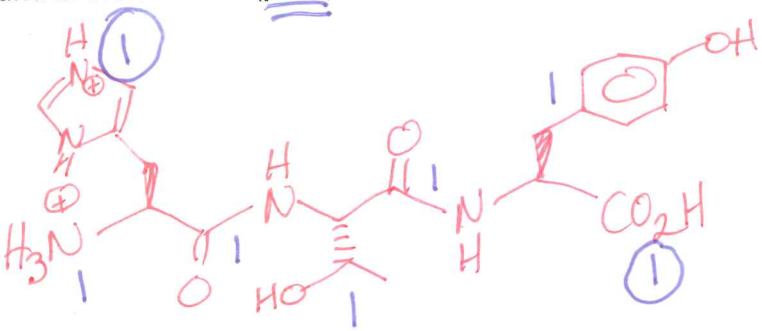
His – Thr – Tyr



sidechains −1
stereochem wrong/ not shown

- correctly (de)protonated
- charges shown

(c) (*7 points*) Draw the structure of the **His – Thr – Tyr** tripeptide under highly acidic conditions found in the stomach (**pH 1**).

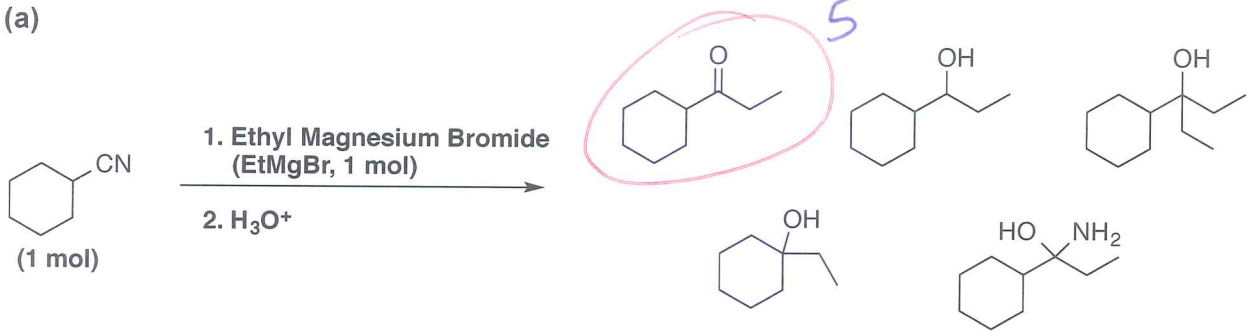


protonated grps (circled)

4. (*20 points*) **Single Step Reactions – Multiple Choice** 5 pts each

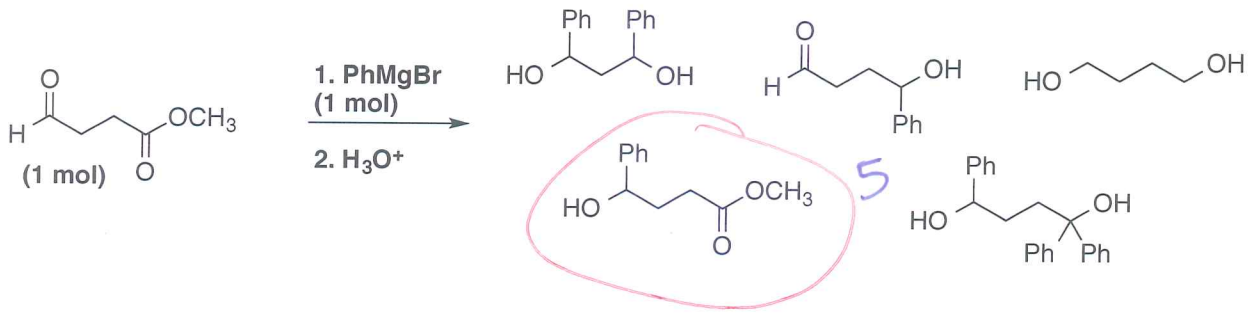
For parts (a) & (b) below, circle the correct product in each reaction. Only one answer is correct for each.

(a)



5

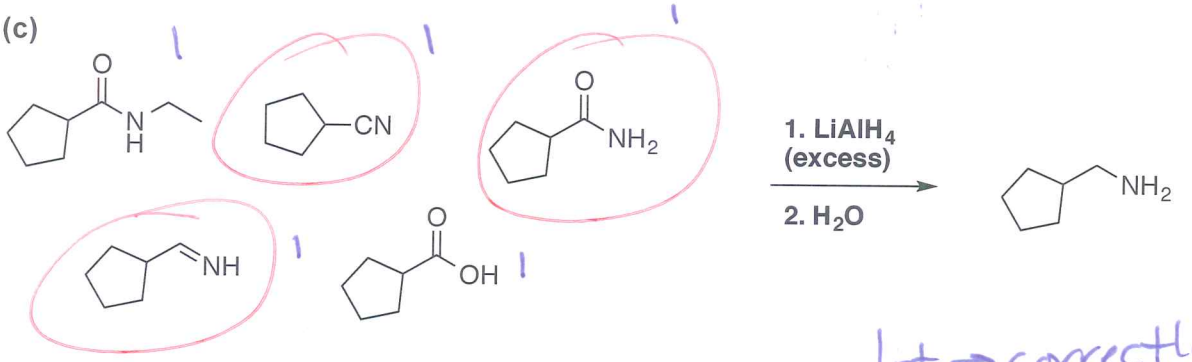
(b)



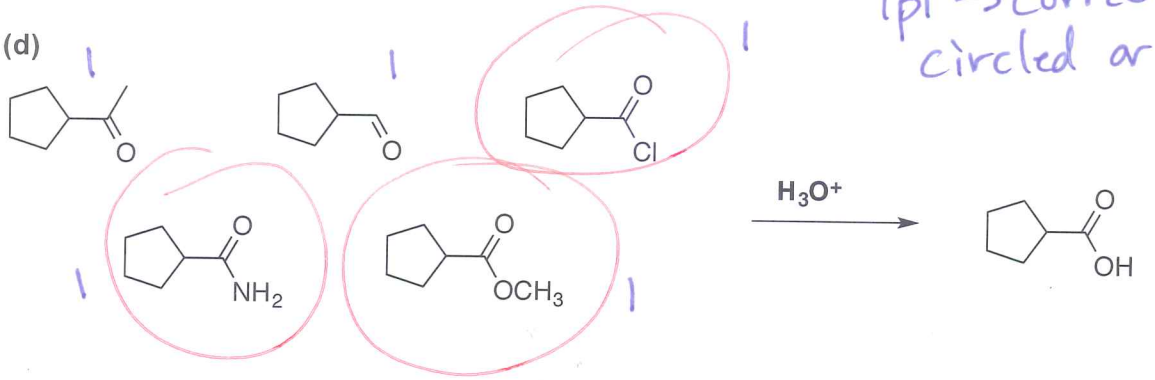
5

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

(c)



(d)



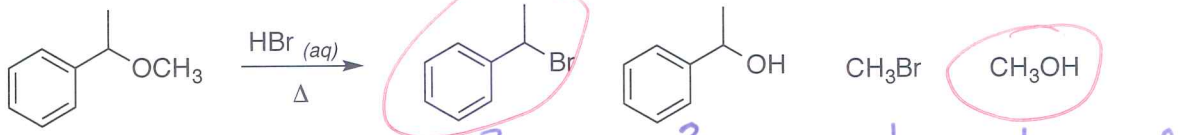
1 pt → correctly circled or not

5. (*30 points*) **Single Step Reactions, Multiple Choice** 6 pts each

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

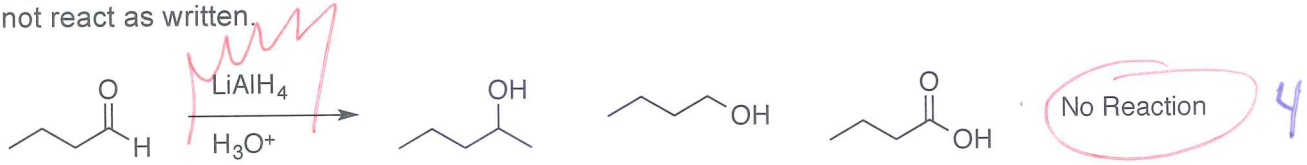
6

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



2 circled 2 not 1 not 1 circled

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

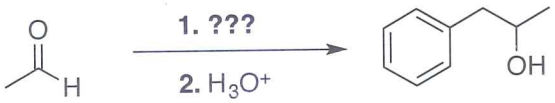


4

If "No Reaction", briefly explain:

2 LAH & $H^{\oplus}$ not in separate steps
↑ violently quenched, maybe even fireballs ∞

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



6

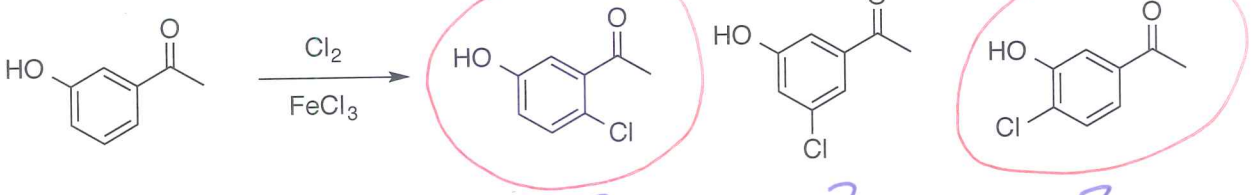
Benzyl magnesium bromide

Phenyl magnesium bromide

Methyl magnesium bromide

Bromobenzene

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

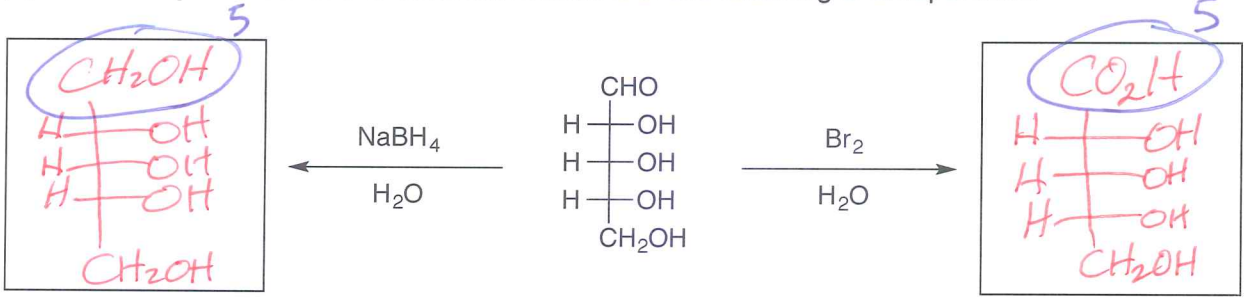


2 circled 2 not 2 circled

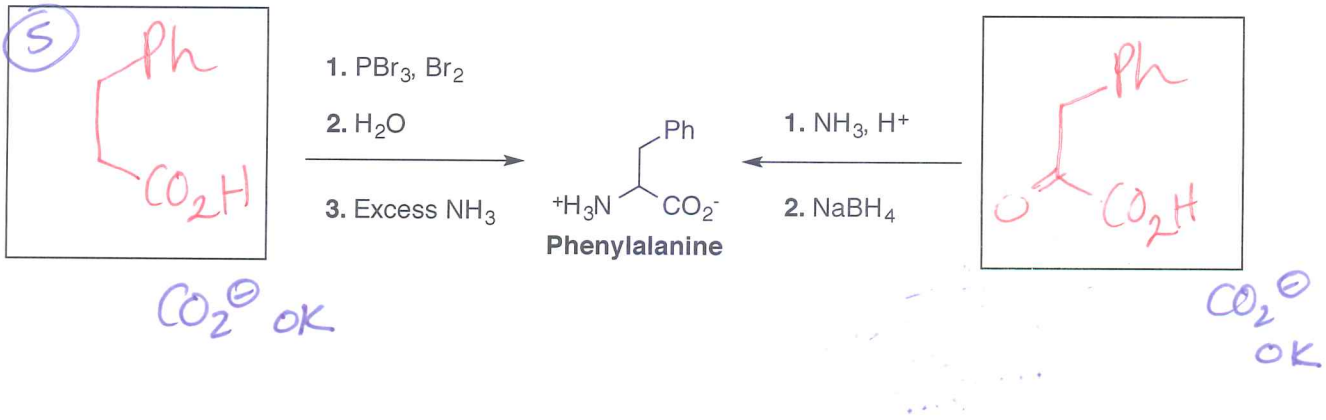
5 pts/box

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

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

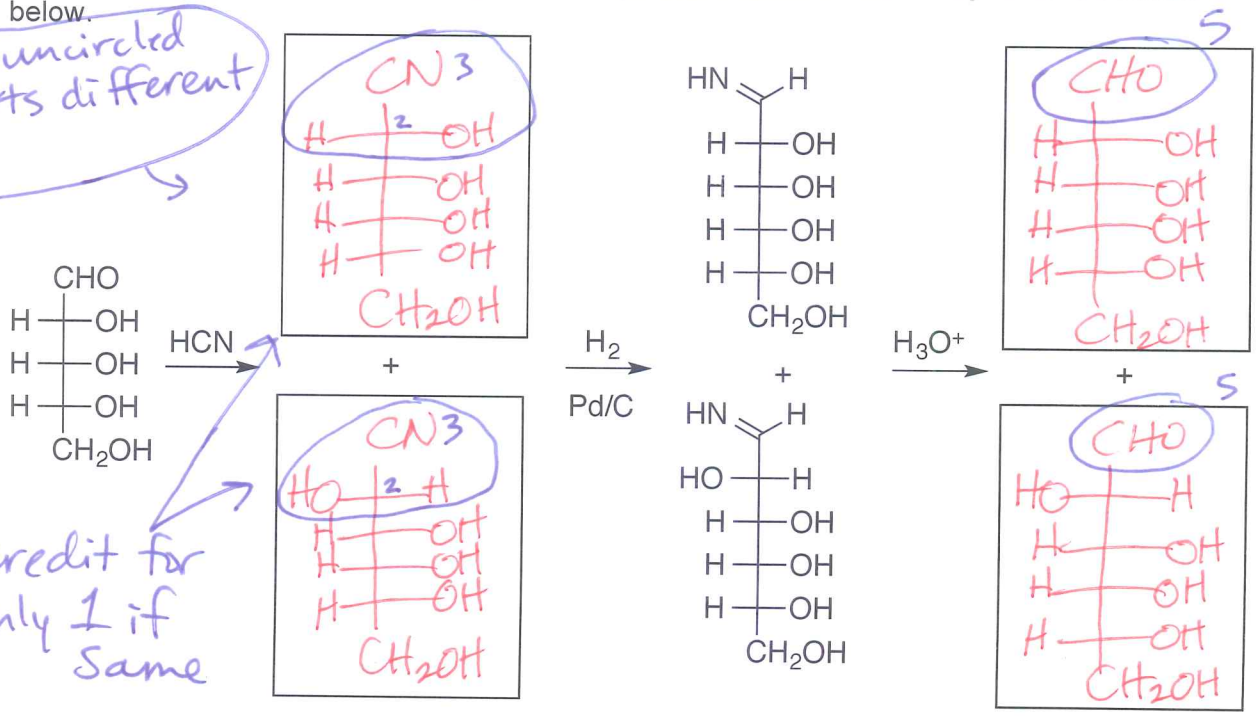


(b) Show the **starting materials** for two different methods for synthesizing **phenylalanine.**



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

-2 if uncircled parts different



-1 per missing/extra C

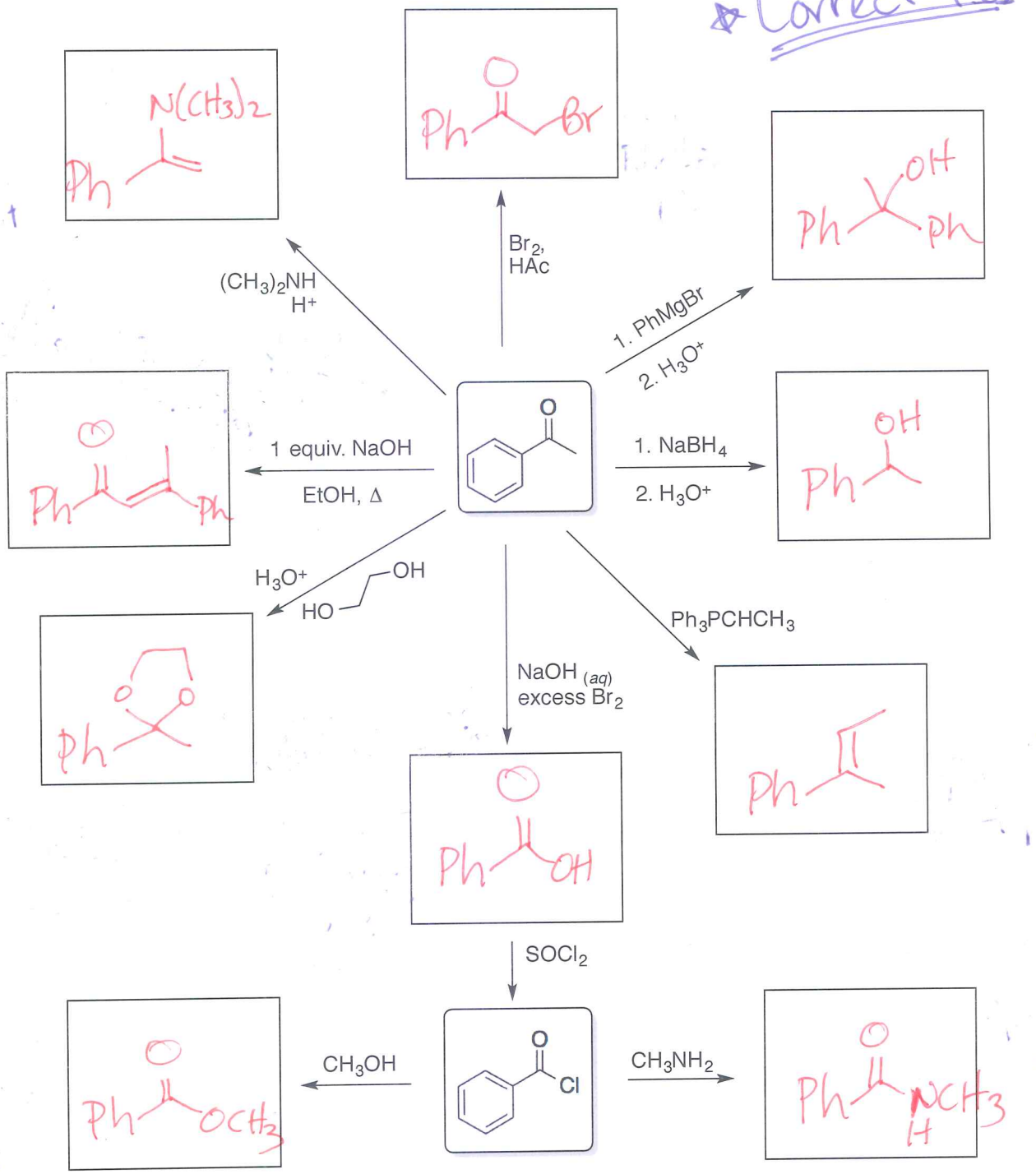
 5pts/box

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 **SKIP ANY TWO by drawing a LARGE X over the boxes to skip, otherwise the top eight reactions in the starburst will be graded.**

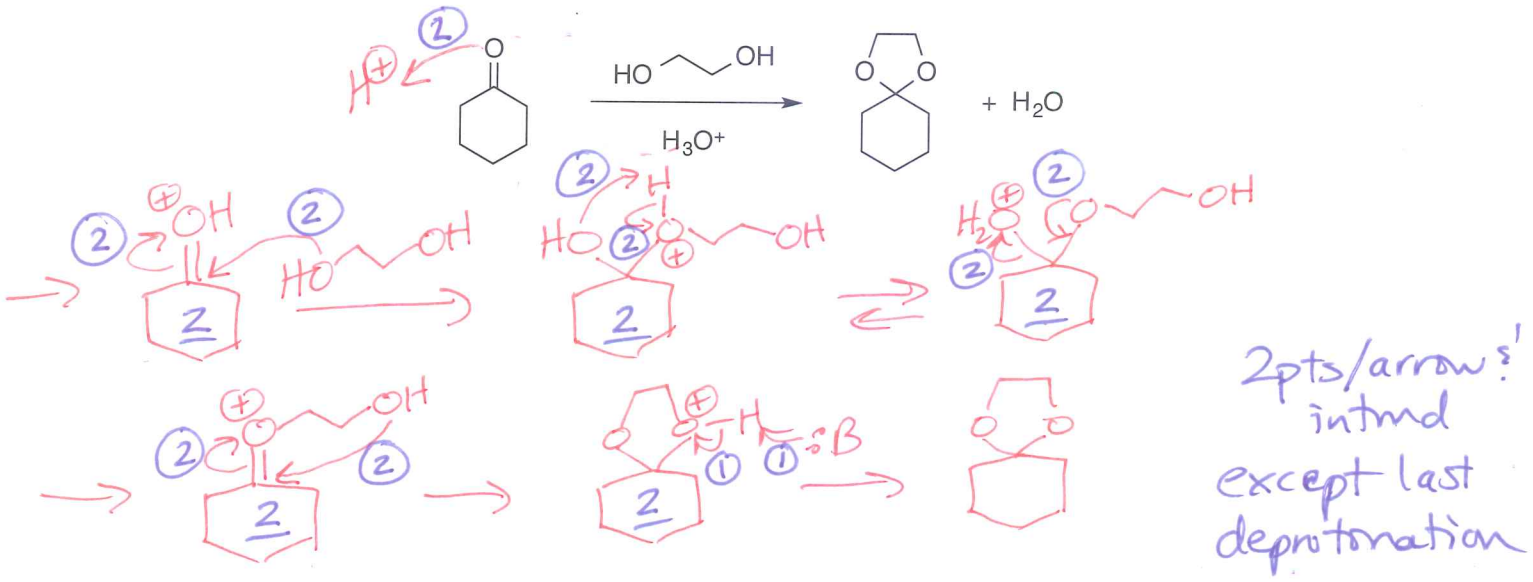
* Correct FG *



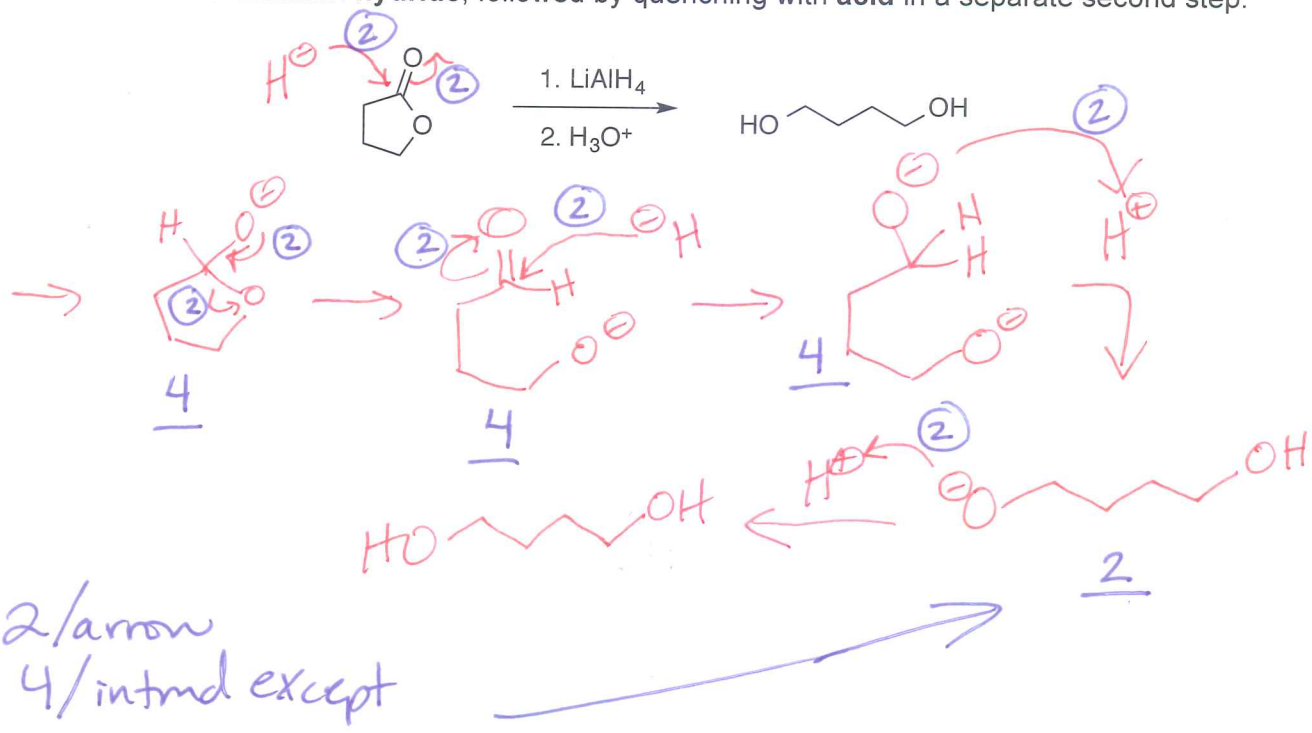
8. (*30 points*) **Mechanisms** – Draw the full arrow-pushing mechanism for **one of the reactions** below, including all arrows for acid-base reactions (no "PT"). Include all intermediates with proper charges circled for each step.

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

(a) 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.



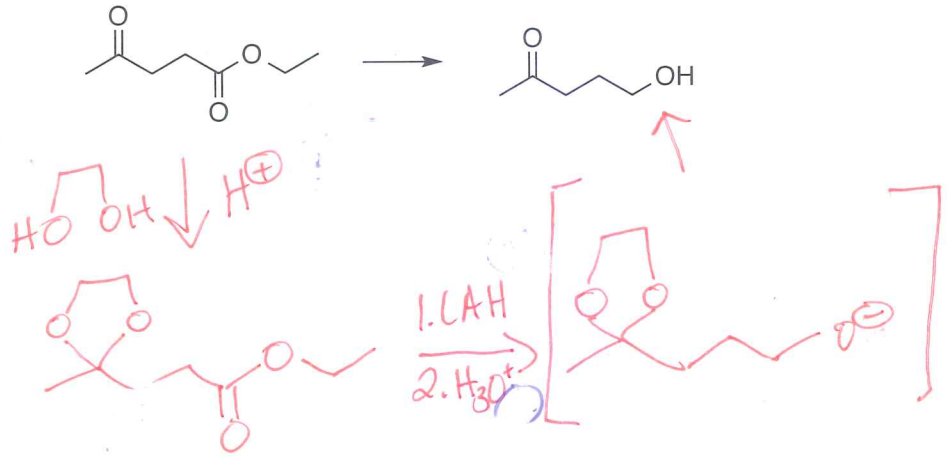
(b) Draw the full arrow-pushing mechanism for the reduction of the **lactone** (cyclic ester) below with **lithium aluminum hydride**, followed by quenching with **acid** in a separate second step.



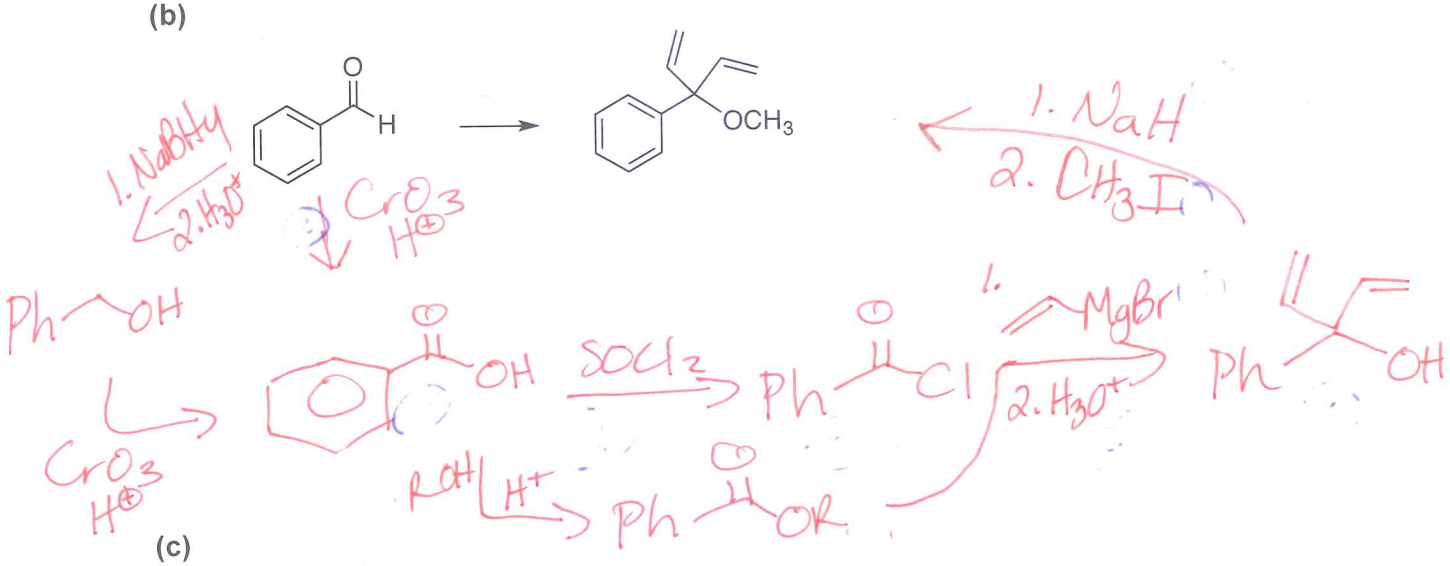
15pts each

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.**

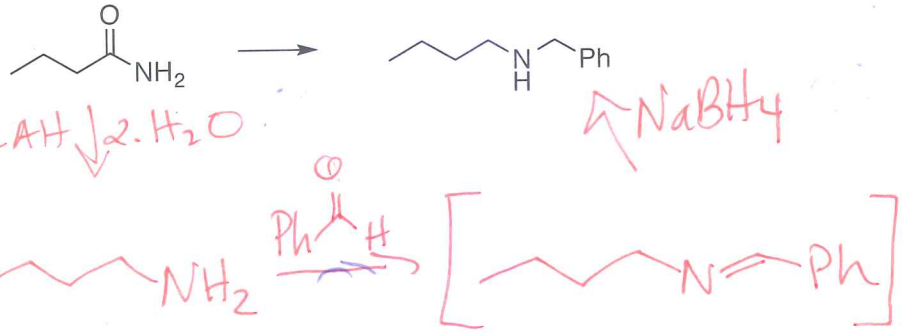
(a)



(b)



(c)



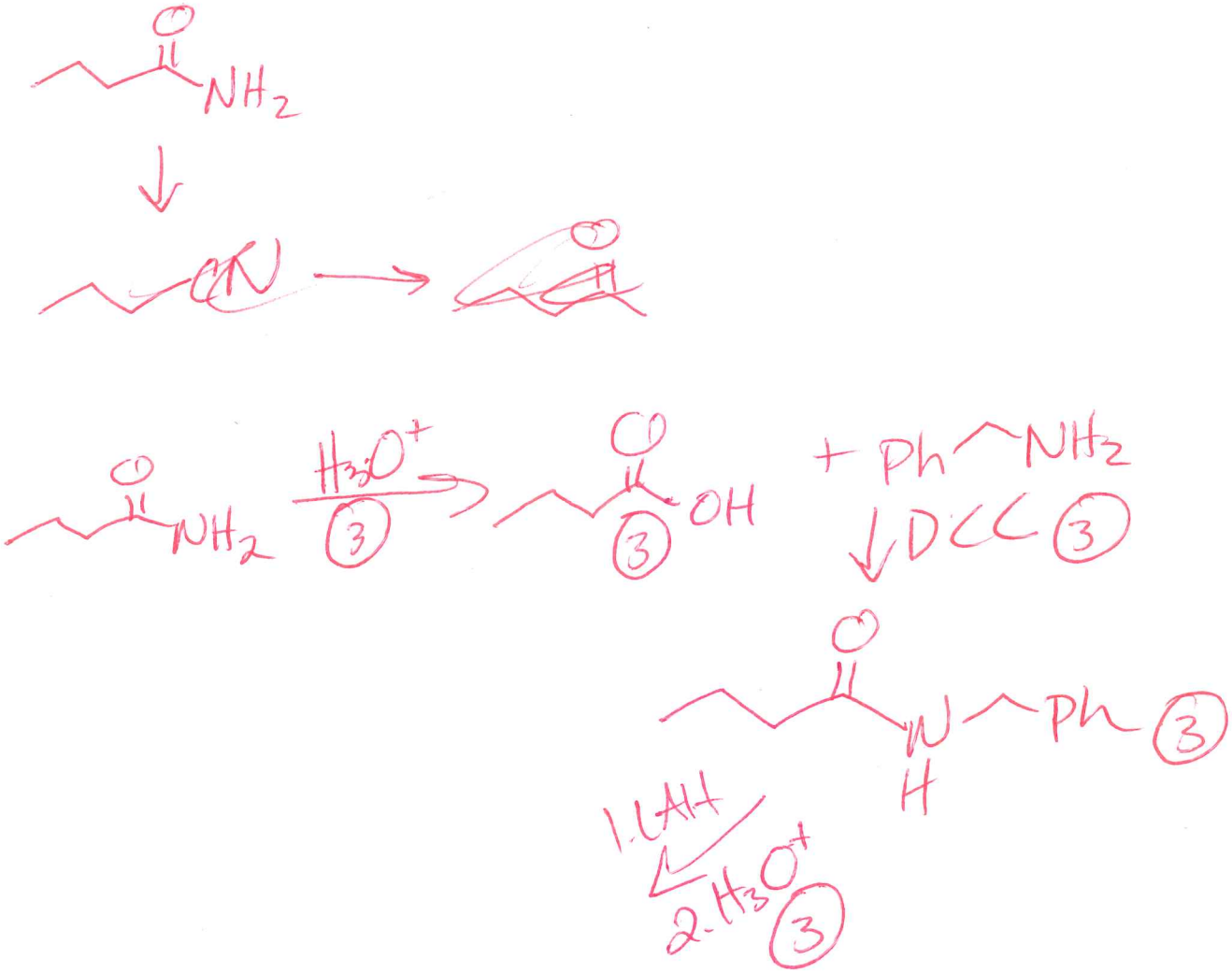
OR excess 

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!

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 one 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 ***only one reaction or no credit*** (don't write multiple reactions hoping we'll choose the correct one). *No mechanisms, but thanks anyway.*



Thanks for a great class and have a fantastic break!
Sincerely,
Dr. B