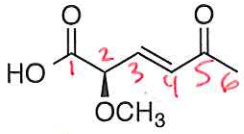
CHEM 108B, W16, Final Exam A Last Name, First Initial Key

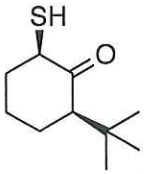
1. Nomenclature

5 pts each

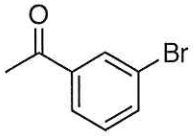
(a) (*20 points*) **Provide IUPAC names** for the following compounds. Suffixes for acyl derivatives can be found on the cover page.



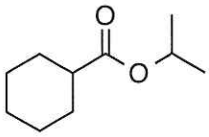
trans-R OR (3E, 2R) - 2 - Methoxy - 5 - oxohexanoic acid (2) (1) (1) (1)



(2R, 6R) - 2 - t - Butyl - 6 - mercaptocyclohexanone (2) (1) (1) (1)



meta - Bromoacetophenone (2) 3 OR (1) (2)

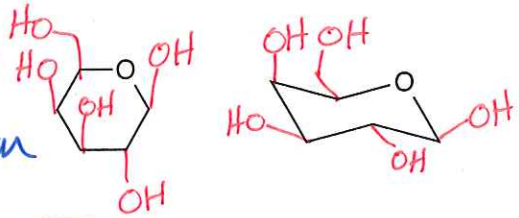


Isopropyl cyclohexane carboxylate (1) (2) (2)

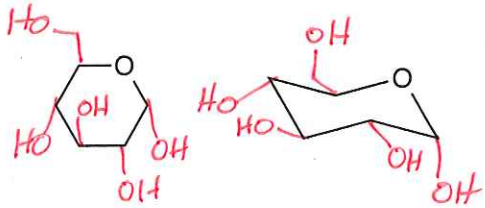
(b) (*20 points*) Complete the following Haworth projections and chair conformations…

5 each, 1 pt/ bond angle/ direction

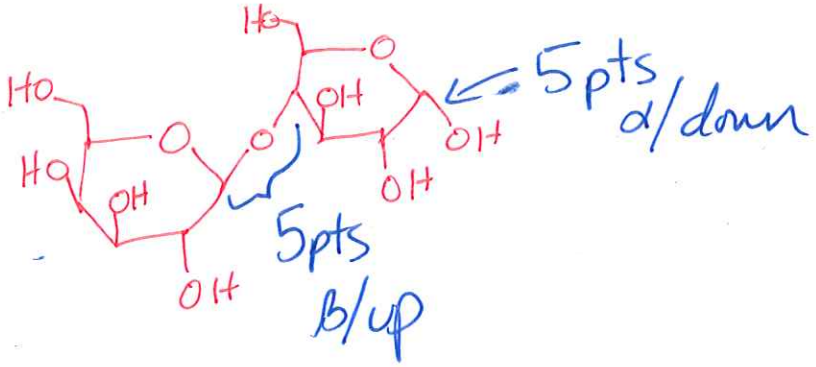
β-D-Galactopyranose
(the C4 epimer of D-Glucose)



α-D-Glucopyranose



(c) (*10 points*) Draw the Haworth projection of **lactose** as its **α-anomer**. Lactose contains a **β-1,4-glycosidic bond** between **D-Galactopyranose** and **D-Glucopyranose**.

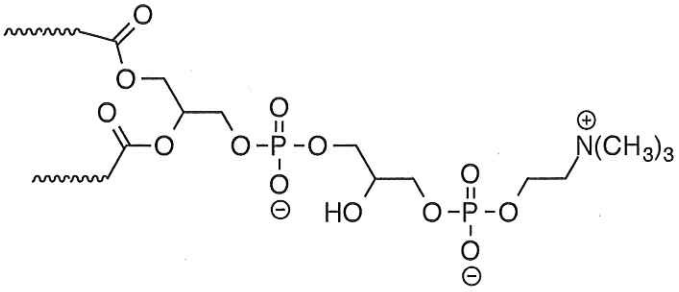


5 pts α/down

5 pts B/up

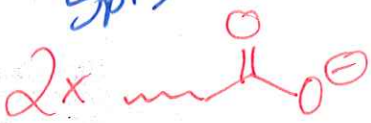
2. Biomolecules

(a) (*20 points*) The following **phospholipid** was subjected to **saponification** (basic hydrolysis). Draw the many **products of the reaction**.

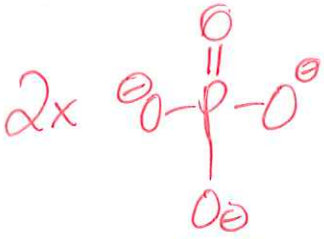


Excess NaOH

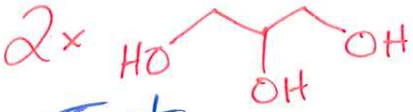
5pts

2x 

5pts

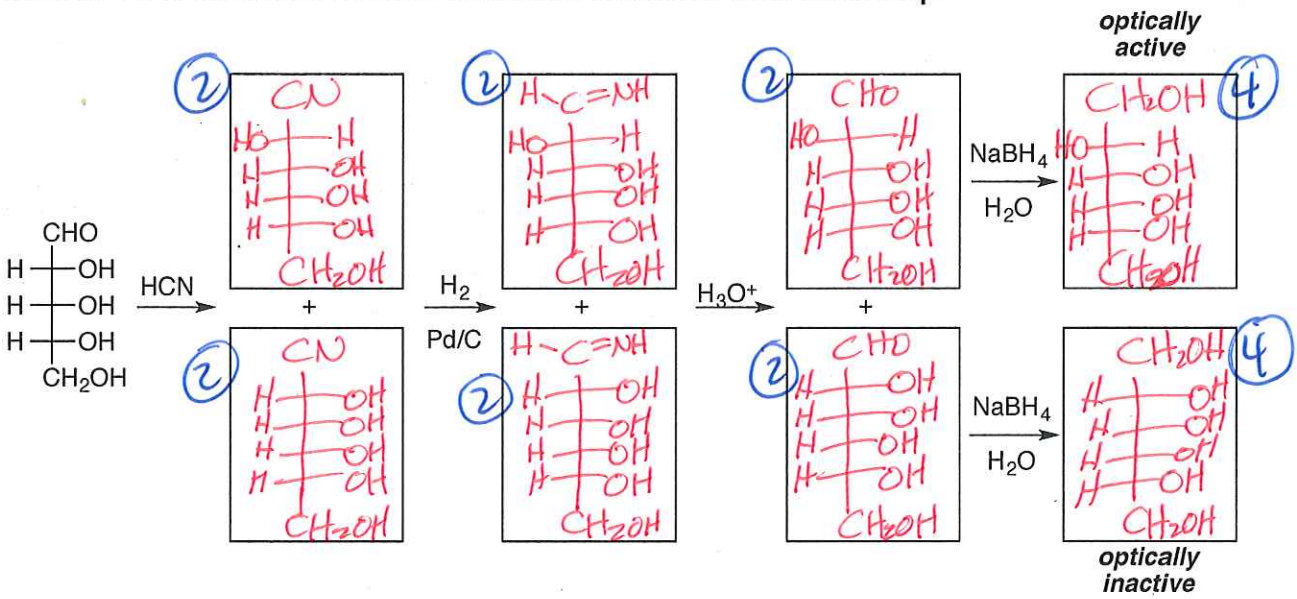


5pts

2x 

5pts

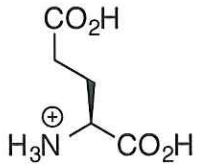
(b) (*20 points*) The D-aldopentose below was subjected to **Kiliani-Fischer synthesis** followed by **reduction** to afford two **epimers**, one of which is optically active and the other optically inactive. Fill in the boxes below to **show the structures after each step**.



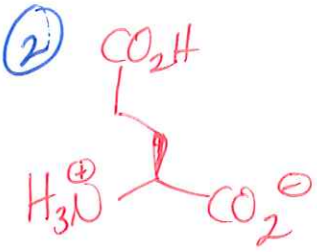
3. Amino Acids

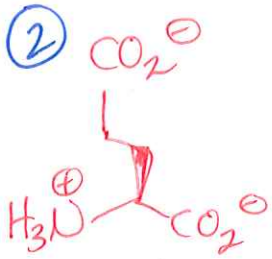
Draw the dominant ionic species of the amino acids at each of the indicated pH ranges based on the given pKa's. Indicate all charged atoms. Circle the charges as shown below.

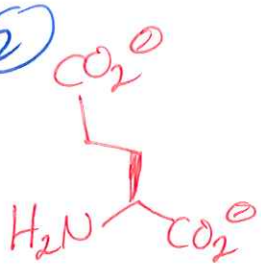
(a) *(10 points)* **Titration of Glutamic Acid** - pKa_1 2.10; pKa_2 9.47; pKa_R 4.07



L-Glutamic Acid
(fully protonated)

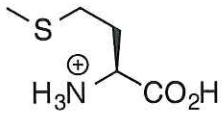




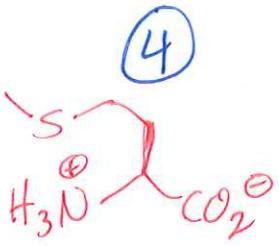


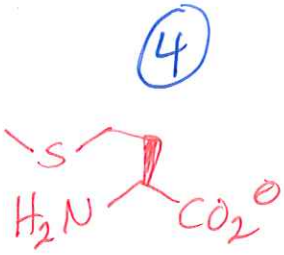
	pH < 2.10	2.10 < pH < 4.07	4.07 < pH < 9.47	pH > 9.47
Charge:	+1 (1)	∅ (1)	−1 (1)	−2 (1)

(b) *(10 points)* **Titration of Methionine** – pKa_1 2.28; pKa_2 9.21



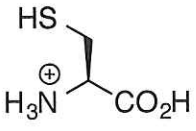
L-Methionine
(fully protonated)



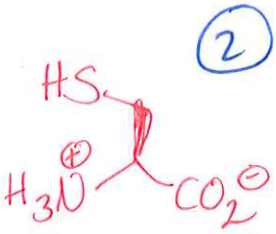


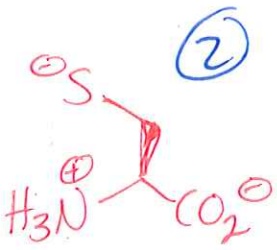
	pH < 2.28	2.28 < pH < 9.21	pH > 9.21
Charge:	+1 (1)	∅ (1)	−1

(c) *(10 points)* **Titration of Cysteine** - pKa_1 2.05; pKa_2 10.25; pKa_R 8.00



D-Cysteine
(fully protonated)



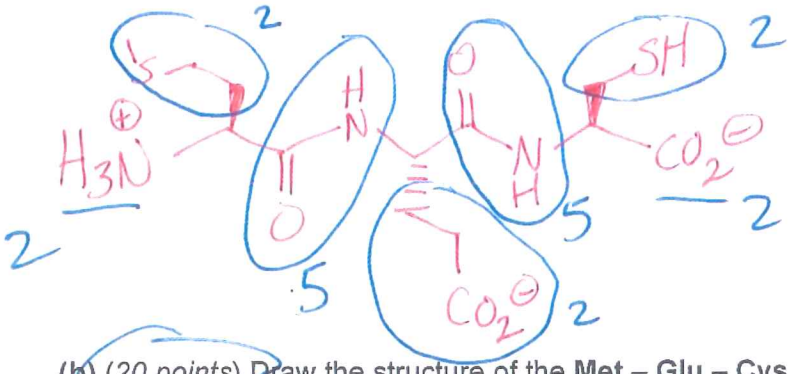


	pH < 2.05	2.05 < pH < 8.00	8.00 < pH < 10.25	pH > 10.25
Charge:	+1 (1)	∅ (1)	−1 (1)	−2 (1)

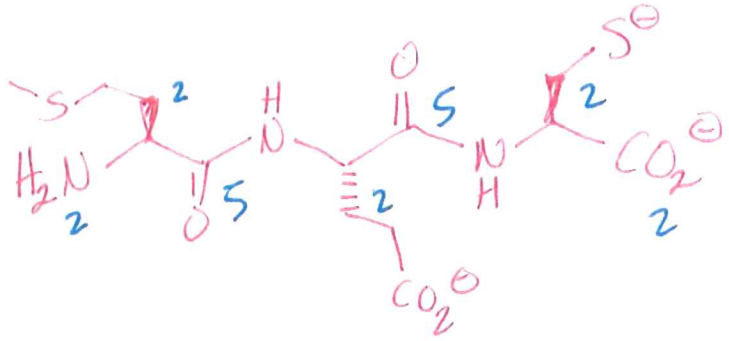
4. Peptide Primary Structure

(a) (*20 points*) Draw the structure of a tripeptide containing L-Methionine, L-Glutamic Acid, and D-Cysteine at **physiological pH (7.4)** using the structures from page 3.

Met – Glu – Cys



(b) (*20 points*) Draw the structure of the **Met – Glu – Cys** tripeptide at **pH 10** using the structures from page 3.



(c) (*10 points*) Suppose Met-Glu-Cys was **hydrolyzed** into its constituent **amino acids** with HCl and subjected to two separate **electrophoresis** experiments in buffered solution. **Indicate the results (relative positions) of each amino acid on the "gels" below.**

pI 2-9 Met +1 pI 2-4 Glu +1 pI 2-8 Cys +1

Electrophoresis at **pH 2**

(+) [Glu Cys Met] (-)

4 pts - order 3 pts - near (-)

Met -1 Glu -2 Cys -1

Electrophoresis at **pH 10**

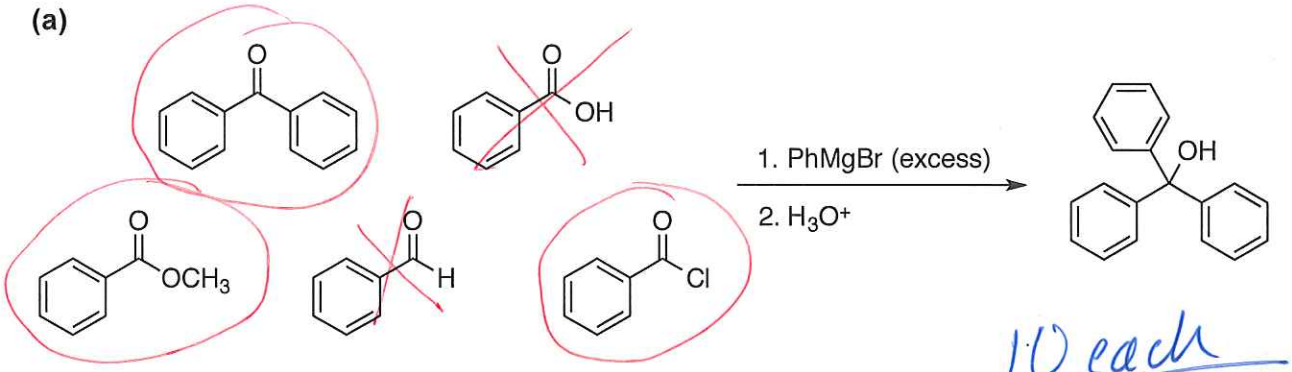
(+) [Glu Cys Met] (-)

3 pts - near (+)

5. (*40 points*) **Single Step Reactions – Multiple Choice**

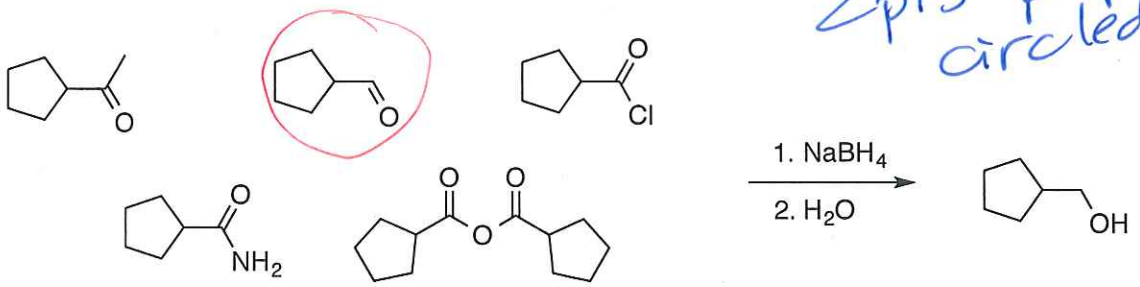
Circle the starting material(s) that would give the indicated product. More than one answer may be possible for each.

(a)



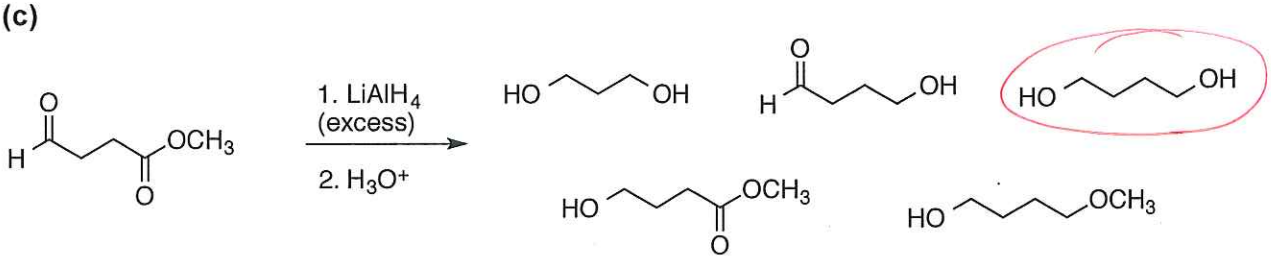
10 each
2pts - properly circled or not

(b)

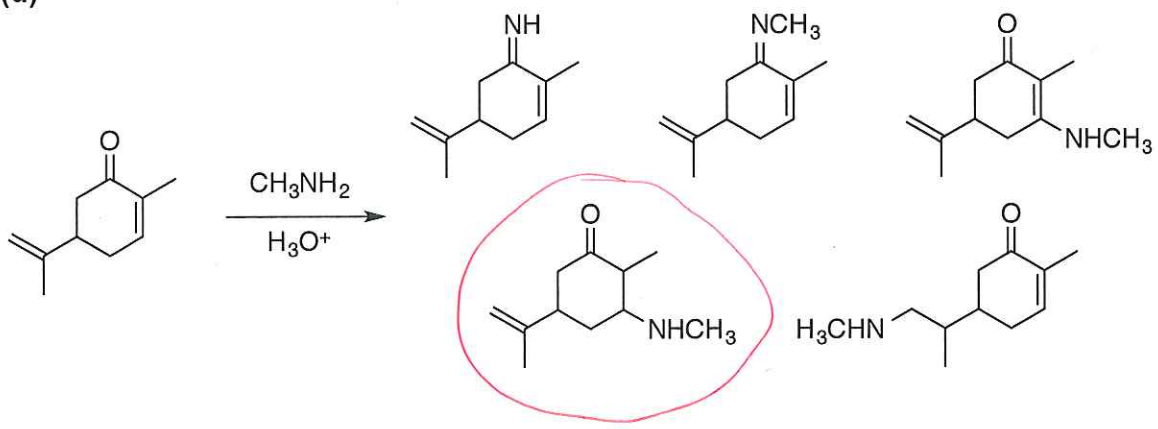


Circle the correct product in each reaction.

(c)

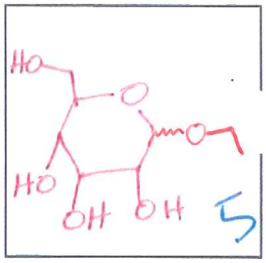


(d)

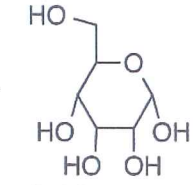


6. (*40 points*) **Mini-Puzzles** 10/part

(a) Show the **products** of two different reactions of **α–D-allopyranose.**

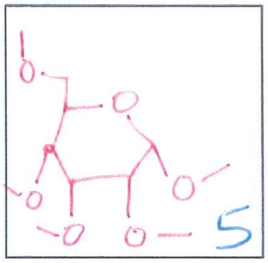


CH_3CH_2OH, H_3O^+



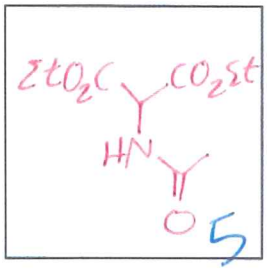
α-D-Allopyranose

CH_3I (excess), Ag_2O



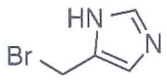
5 5

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

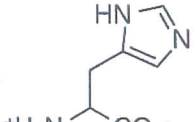


1. NaOEt

2.



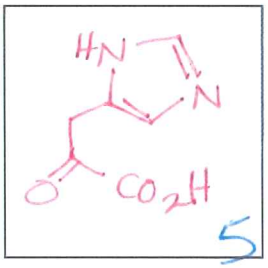
3. H_3O^+



Histidine

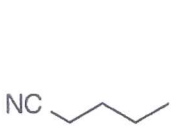
1. NH_3, H^+

2. $NaBH_4$



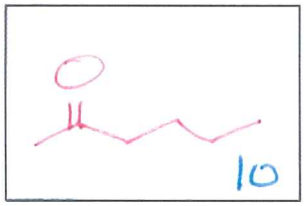
5 5

(c) The two reactions below give the same product. Draw that **product**.



1. CH3MgBr

2. H_3O^+



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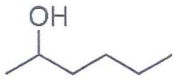
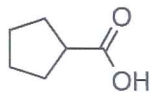
Dess-Martin Periodinane



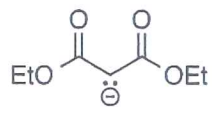
(d) Indicate the single **starting material** can be used to make two very different rings.



+ CO_2 + 2 EtOH

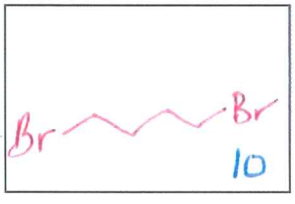
+ 2 HBr

1.



2. NaOEt

3. H_3O^+



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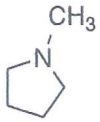
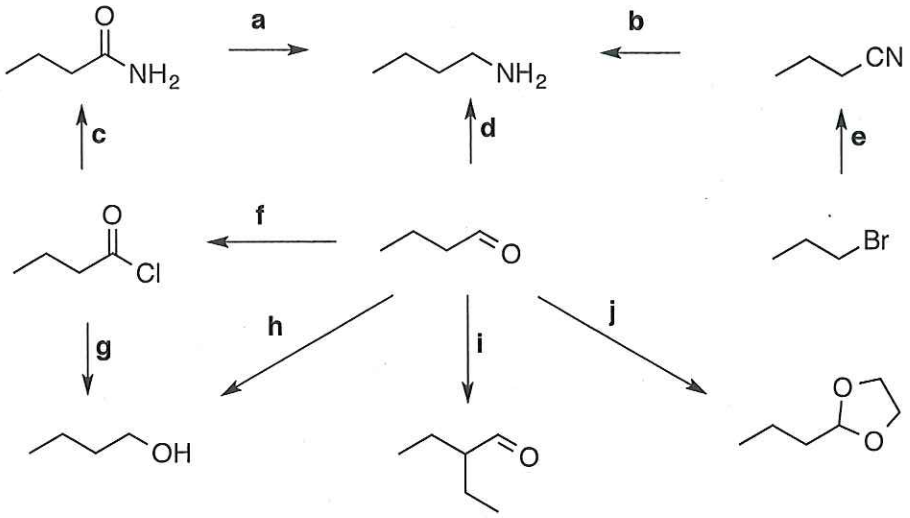
CH_3NH_2 (1 equiv.), NaOH



+ 2 HBr

7. (*50 points*) **Reaction Puzzle**

(a) Fill in the missing reagents. More than one set of reagents may be required in each step (letter). *Pro-tip: try not to get overwhelmed, take it one reaction at a time!*



5pts each

(a) 3 1. LAH 2 2. H_3O^+

(b) 3 1. LAH 2 2. H_3O^+

(c) 5 NH_3, H^+

(d) 3 1. NH_3 2 2. $NaBH_4$

(e) 5 NaCN

(f) 3 1. CrO_3, H_3O^+ 2 2. $SOCl_2$

(g) 3 1. LAH 2 2. H_3O^+

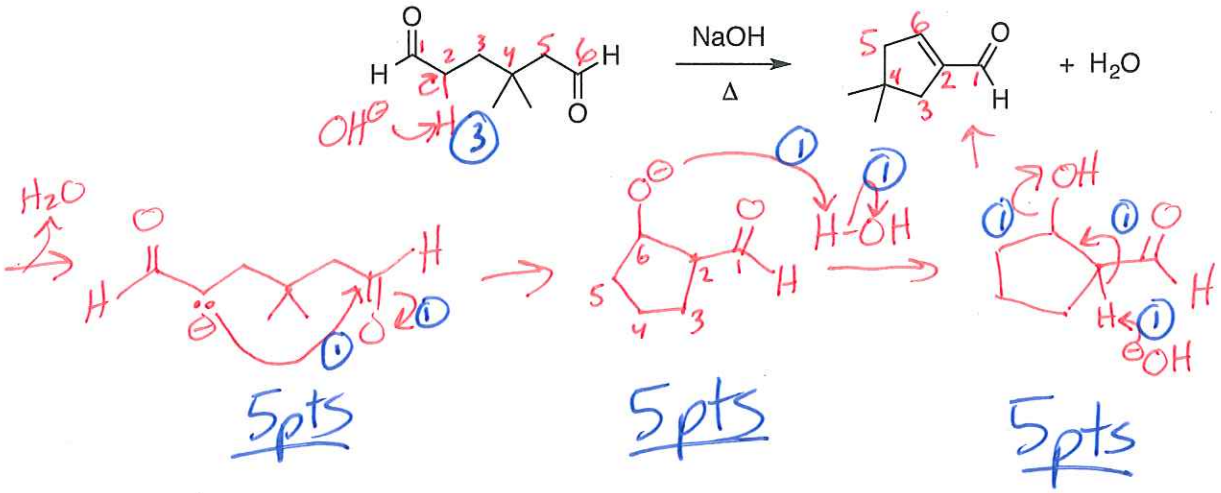
(h) 3 LAH or 1. $NaBH_4$ 2 2. H_3O^+

(i) 3 1. LDA 2 2. 

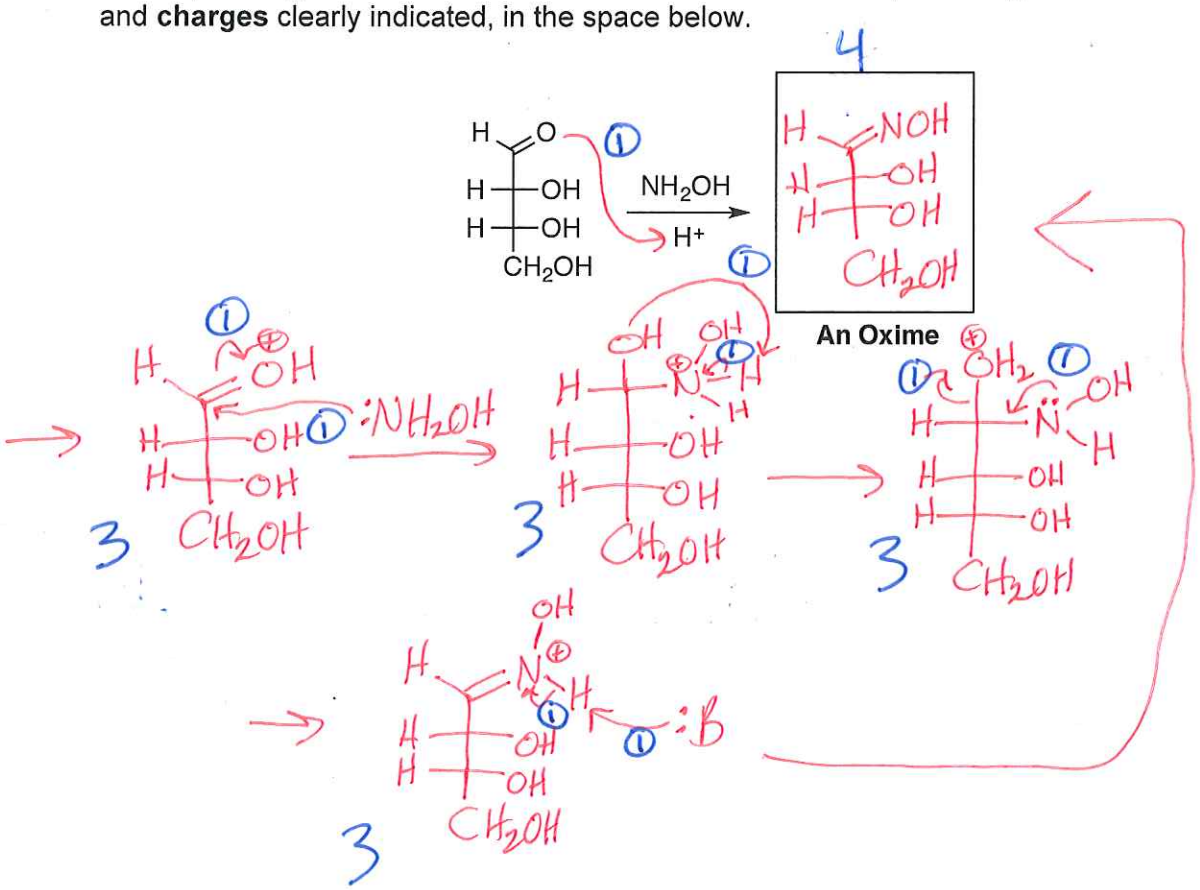
(j) 3  2 H^+

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

(a) (*25 points*) 4,4-Dimethyl-1-cyclopentene carbaldehyde is made through a **base-promoted intramolecular aldol cyclization** of the dialdehyde below. Show this mechanism. Yes, this is the same mechanism from the second exam.
Pro tip: consistently number the carbons in the starting material & product.

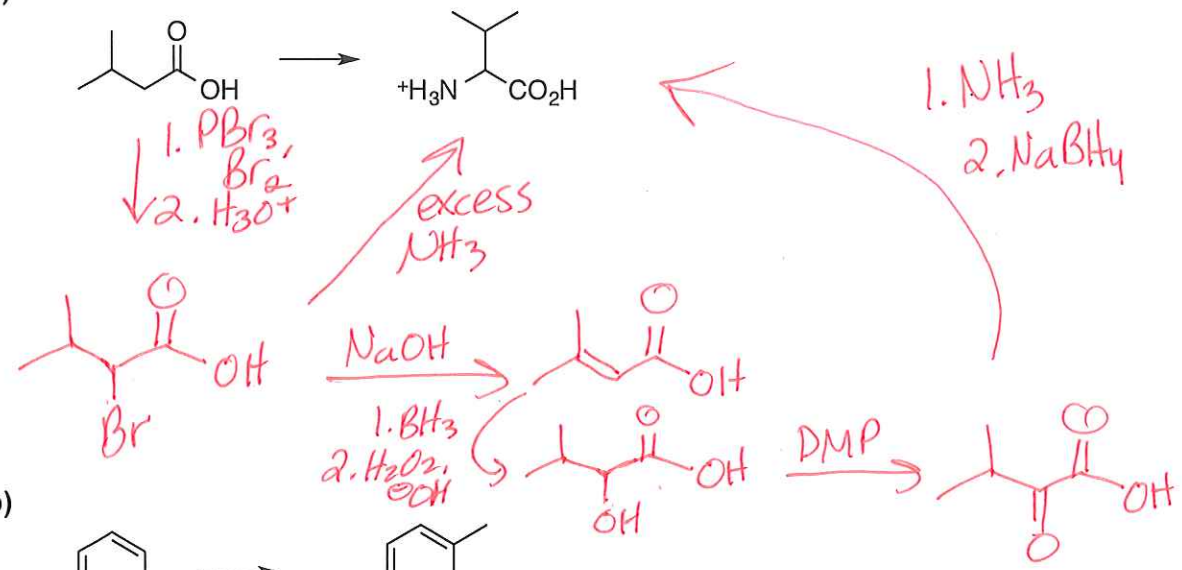


(b) (*25 points*) The first step in the **Wohl degradation** is the reaction of an aldopentose with **hydroxylamine** to form an **oxime**, which is closely related to an imine. **Draw the structure of the oxime** that would be formed in the reaction of the D-aldotetrose below. Also draw the **full arrow-pushing mechanism** for the formation of the oxime, including reaction **intermediates** and **charges** clearly indicated, in the space below.

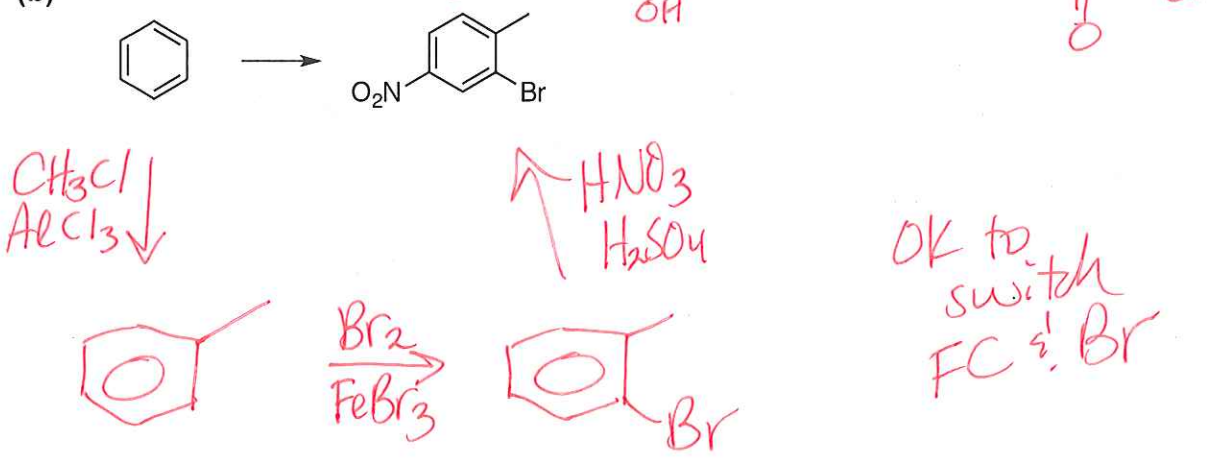


9. (*30 points*) **Multi-Step Synthesis – CHOOSE TWO** 15 pts each
Carry out the syntheses of the indicated target molecules using the starting material provided and any other reagents or carbon sources needed. Draw the **product after each synthetic step. No mechanisms.**

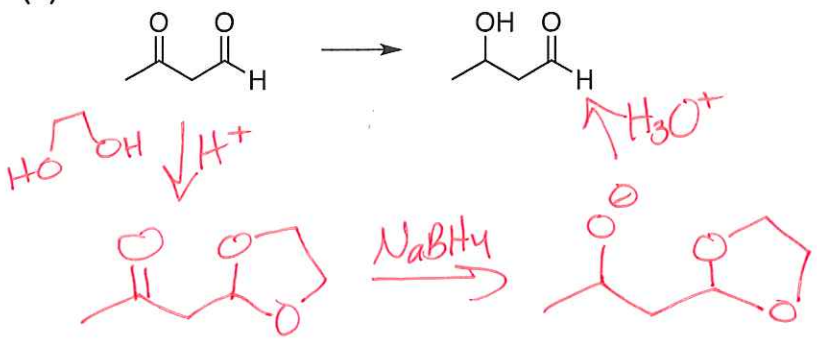
(a)



(b)



(c)

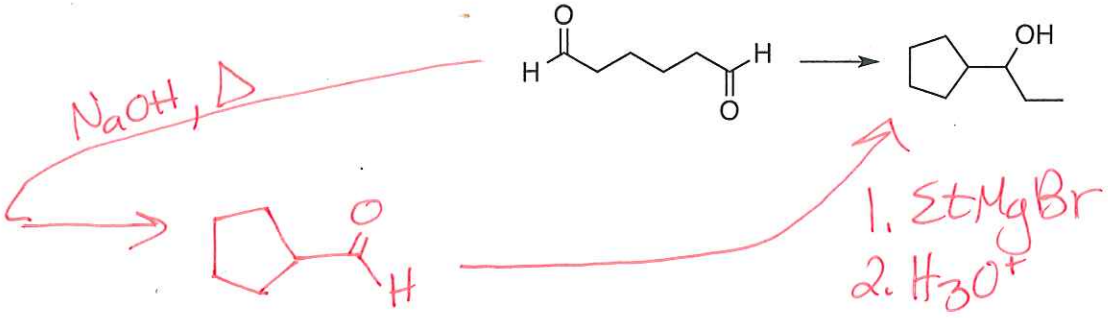


PUT A LARGE "X" OVER THE ENTIRE REACTION & SPACE YOU ARE SKIPPING AND DO NOT WANT GRADED.
OTHERWISE THE TOP TWO REACTIONS WILL BE GRADED, EVEN IF THEY ARE BLANK!

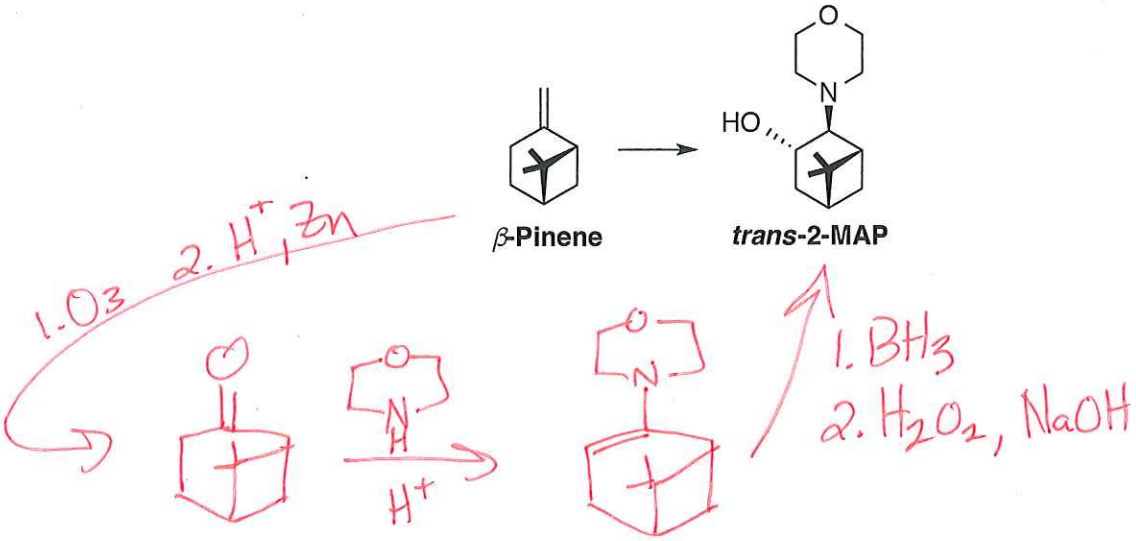
10. (*20 points*) **Multi-Step Synthesis – CHOOSE ONE** 20 pts

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) Show the synthesis of the following cyclopentane derivative. It would be wise to revisit page 8 for assistance!



(b) Dr. B's Ph.D. dissertation focused on the synthesis of amino alcohols for use as chiral catalysts in alkylation reactions. The synthesis of the compound below was accomplished using creative understanding of the reactions from CHEM 108A&B. Impress me with your knowledge and complete the synthesis of *trans*-2-morpholino apopinol (***trans*-2-MAP**) from **β-pinene**!



PUT A LARGE "X" OVER THE ENTIRE REACTION & SPACE YOU ARE SKIPPING AND DO NOT WANT GRADED.
OTHERWISE THE FIRST REACTION WILL BE GRADED, EVEN IF IT IS BLANK!