Final Exam
Chemistry 345
Professor Gellman
13 May 2010

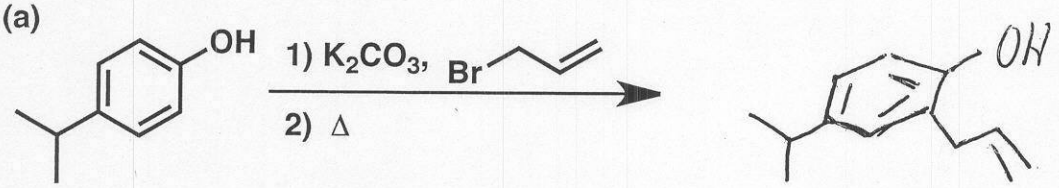
Last Name Answer

First Name Key

General Instructions:
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit.
(ii) Print your name on each page.

1. (39 points) Show the major product or products expected from each reaction:

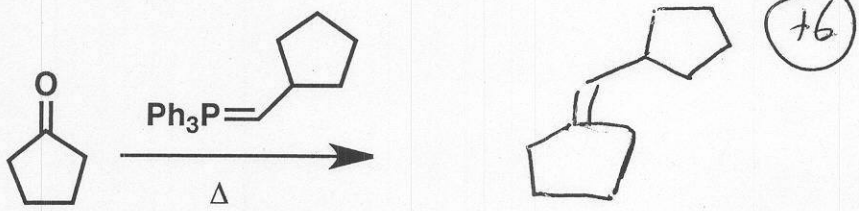
(a)



+6

Allyl ether +2
Vinyl "prod" +3

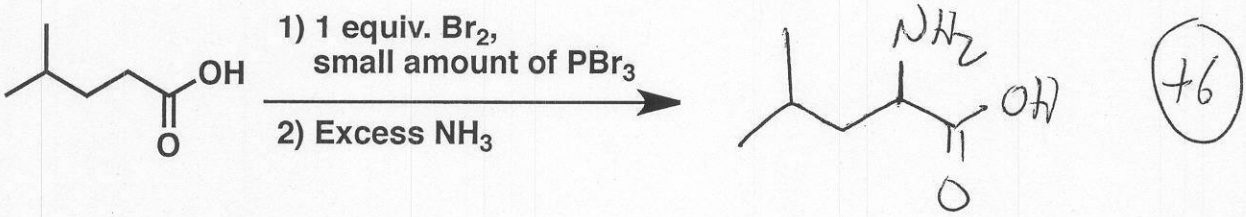
(b)



+6

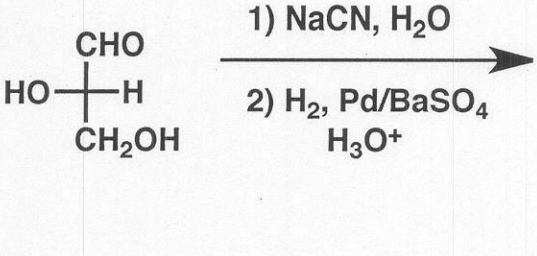
(+ Ph_3P=O)
[Not required]

(c)



+6

(d)



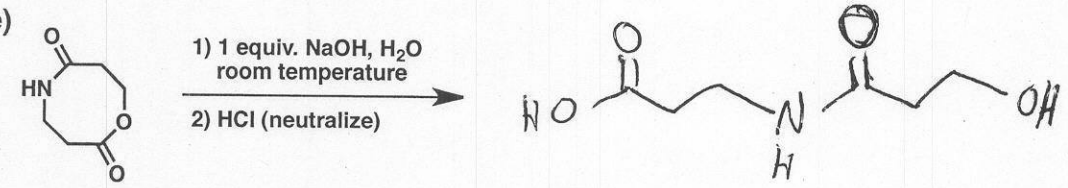
+6 for one
+9 for both

-- cont. on next page --

1. (cont.)

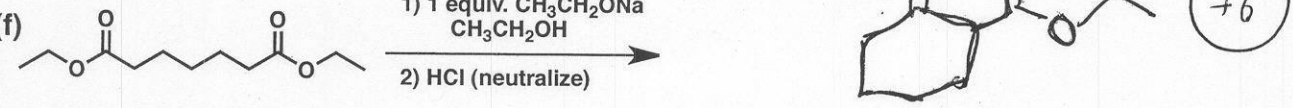
Name _____

(e)



+6

(f)



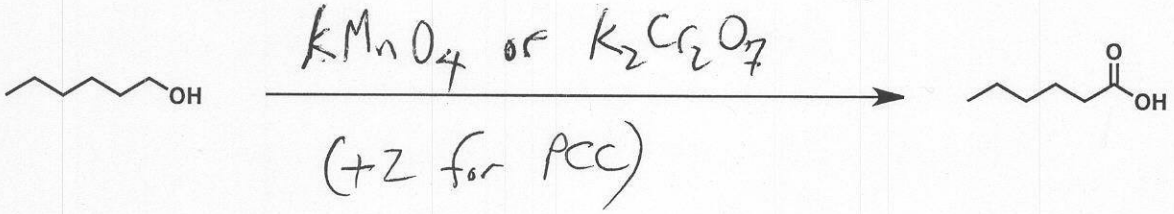
+6

[Note: In the IR region 1700 - 1800 cm^{-1}, the starting material has a single strong signal at 1745 cm^{-1}, but the product has two signals, at 1745 cm^{-1} and 1725 cm^{-1}.]

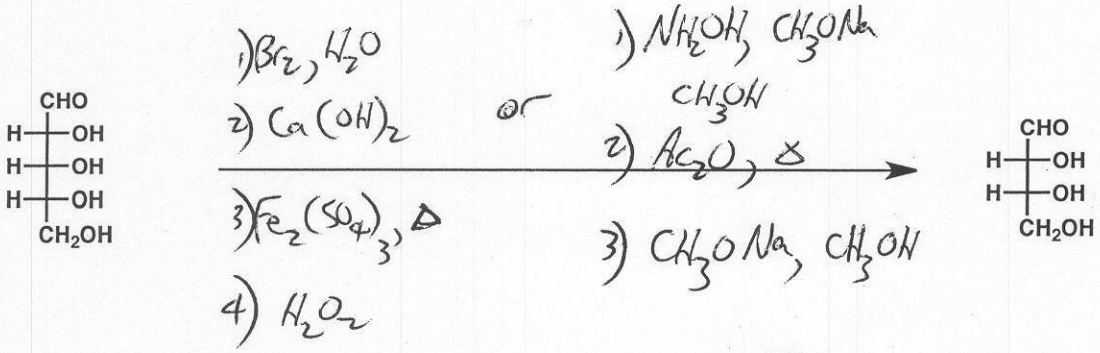
2. (45 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc.

+5

(a)



(b)

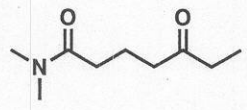


+8

(cont. on next page)

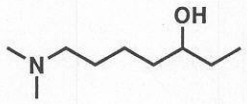
Name _____

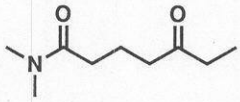
2. (cont.)

(c) 

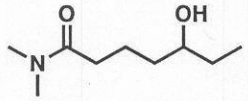
1) $LiAlH_4$ (+4)

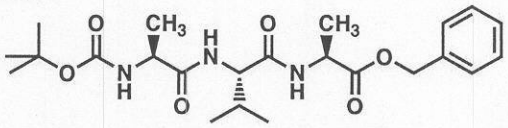
2) H_2O (+1)



(d) 

$NaBH_4$ (+4)

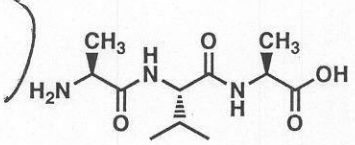


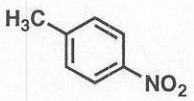
(e) 

1) HCl (+3) [any acid ok]

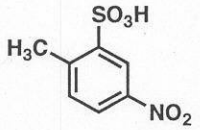
2) H_2, Pd/C (+2) (+2)

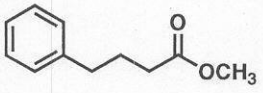
} [reverse order ok]



(f) 

(+3) SO_3, H_2SO_4 (+3)



(g) 

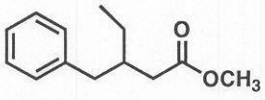
1) LDA (+2)

2) PhSeSePh (+2)

3) H_2O_2 (+2) or KIO_4

4) $(CH_3CH_2)_2CuLi$ (+3)

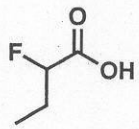
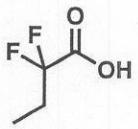
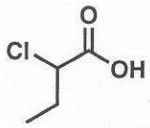
5) H_2O (+1)



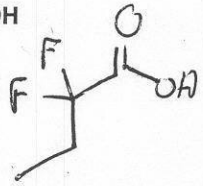
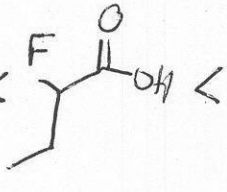
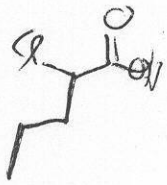
Name _____

3. (8 points) For each set of compounds below, rank the molecules, left to right, from <u>lowest pK_a</u> to <u>highest pK_a</u> (i.e., your answer should have the form X < Y < Z).

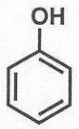
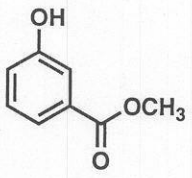
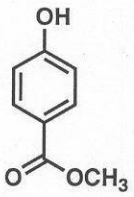
(a)

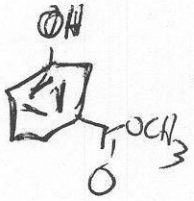
+4

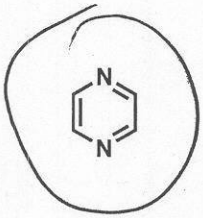
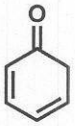
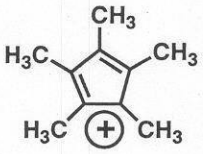
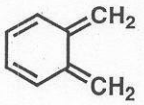
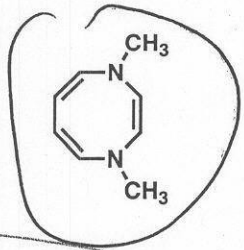
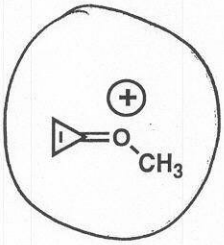
(b)

+4

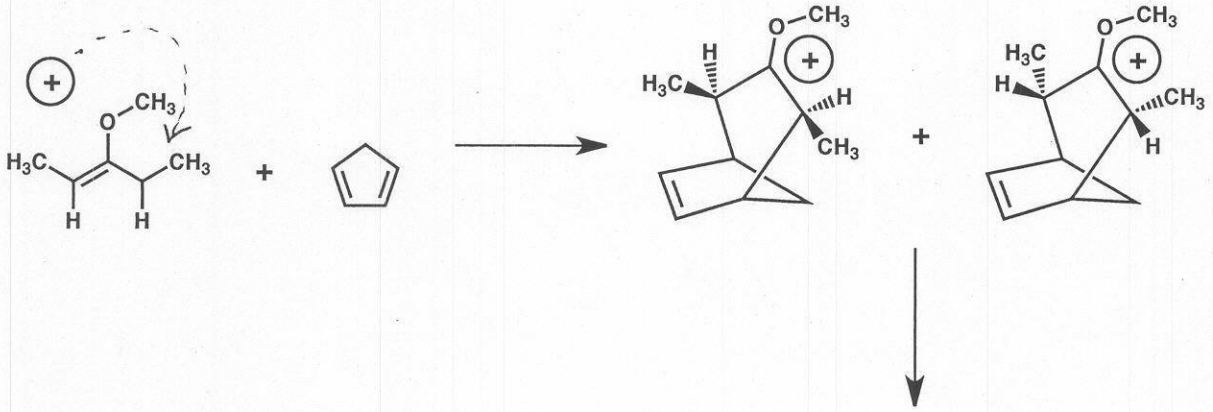

4. (12 points) Among the species shown below, CIRCLE those that you would expect to benefit from aromatic stabilization.

+2 for each correct circle/no circle

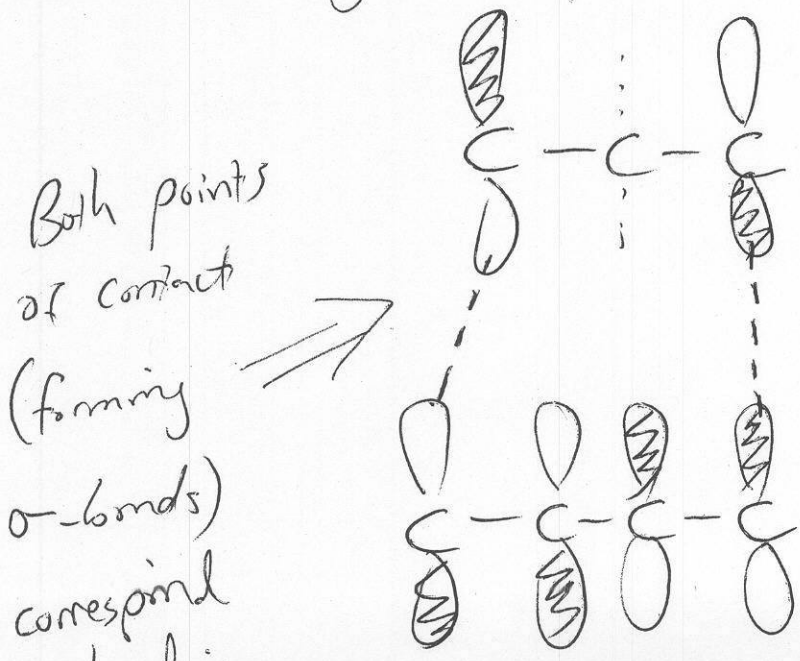
Name _____

5. (10 points) The cation shown on the left below would be expected to react with cyclopentadiene to form the two isomeric bicyclic cations shown on the right (these intermediate would then go on to form more stable species). Provide a molecular orbital rationale for the expectation that these specific bicyclic cations would form (and not isomers with *trans* methyl groups).



Stable products

Reaction expected is a cycloaddition involving the allylic cation LUMO and the diene HOMO; stereochemistry arises because the reaction is concerted.



Both points of contact (forming σ-bonds) correspond to bonding interactions.

Allylic cation LUMO (ψ_2)

Diene HOMO (ψ_2)

Stated at exam: "Be sure to draw major resonance structures."

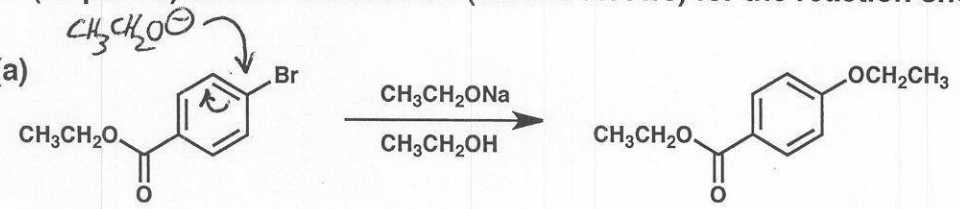
Name _____

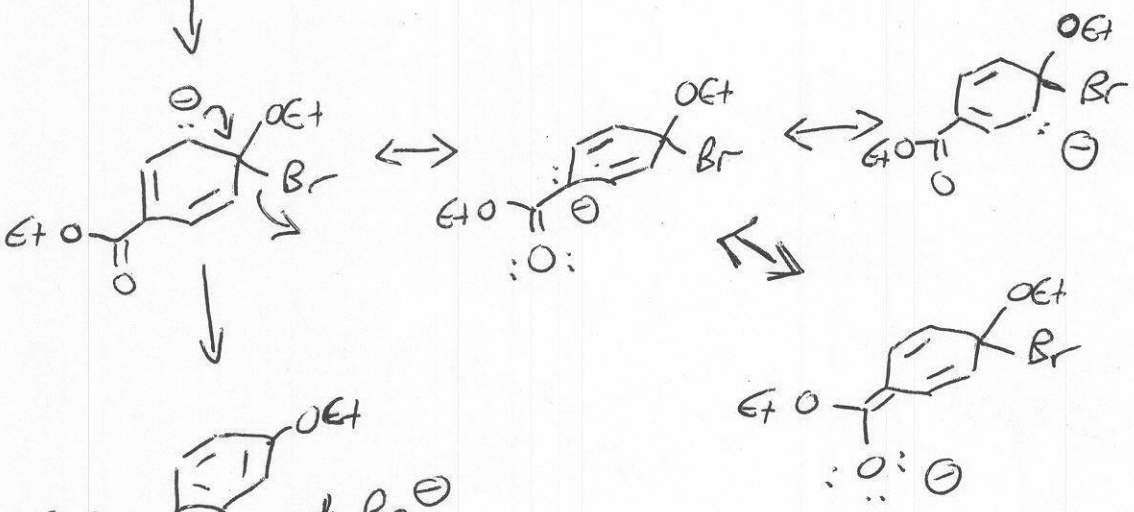
6. (18 points) Draw a mechanism (curved arrows) for the reaction shown below.

+ 2 for each set of mechanistic arrows (4 total)

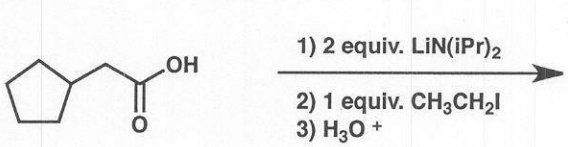
+1 for each res. structure of intermediate (4 total)

(a)

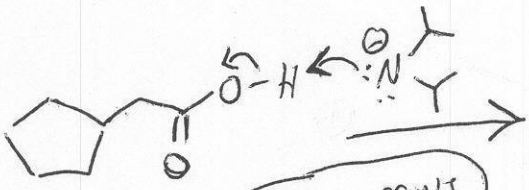




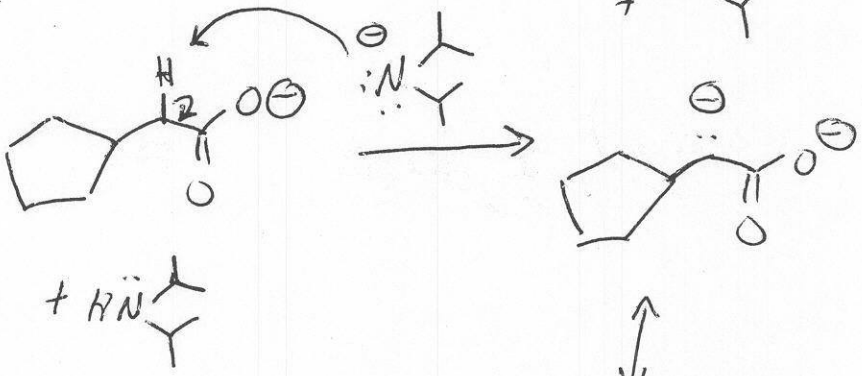
(b)



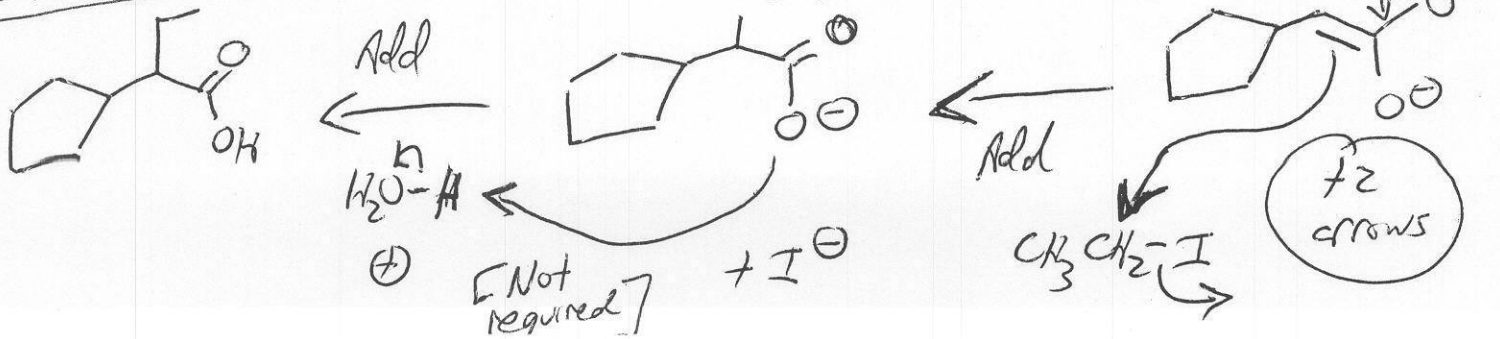
+2 arrows



+2 arrows

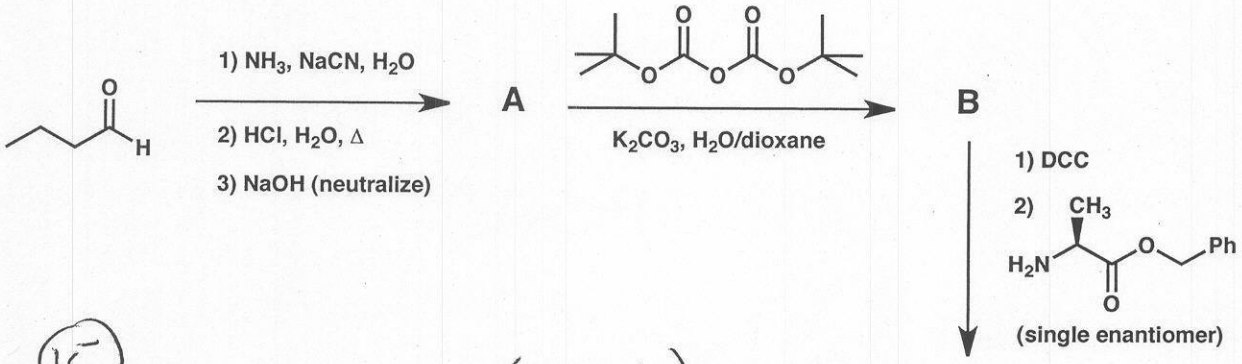


+1 for each intermediate structure (4 total)

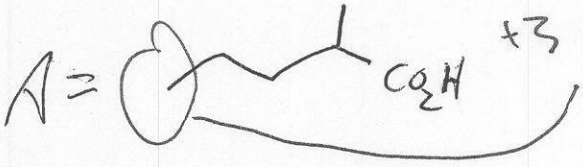


Name _____

7. (20 points) When the aldehyde shown below is subjected to the sequential reaction conditions indicated, A is formed. Further reactions, as shown, generate B and then a final product that turns out to have two chromatographically separable and isomeric components, C and C'. Give the structures of A, B, C and C'.



+5

A = 

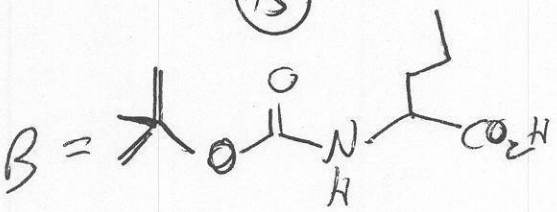
(racemic)

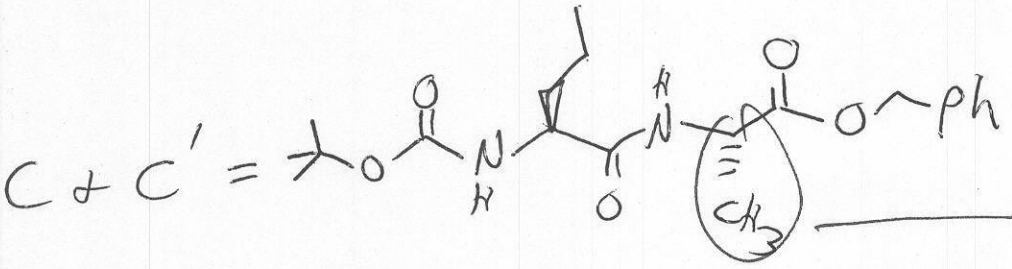
+3 if IC F.

B missing [Not required]

+5

(racemic)

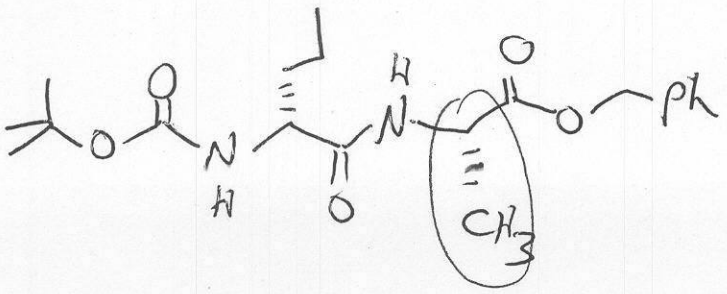
B = 

C + C' = 

+5

-4 if wrong enantiomer used

and

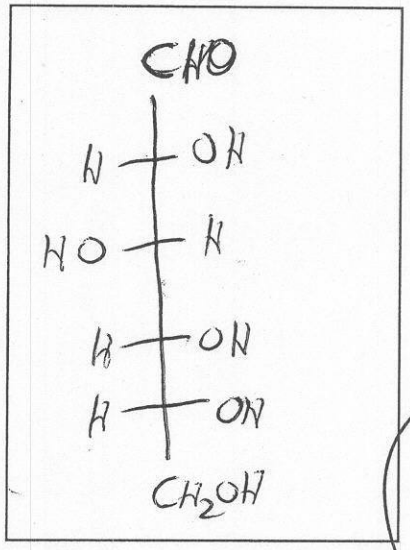


+5

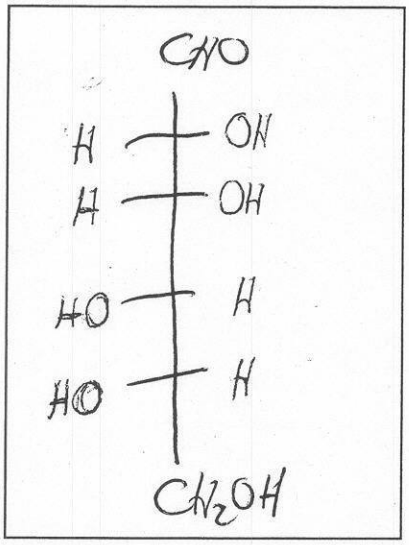
Name _____

8. (20 points)

(a) Draw the Fischer projection of D-glucose (open chain form; not cyclic).



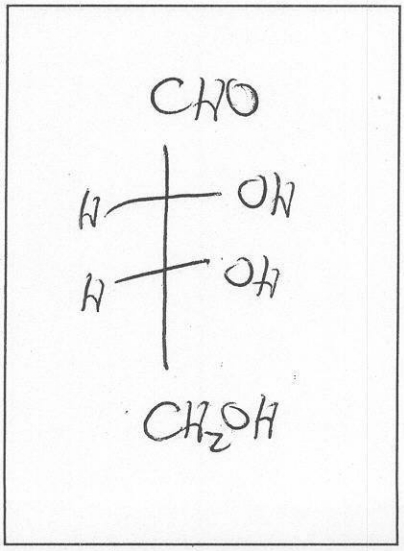
(b) Mannose is the 2-epimer of glucose. Draw the Fischer projection of L-mannose (open chain form; not cyclic).



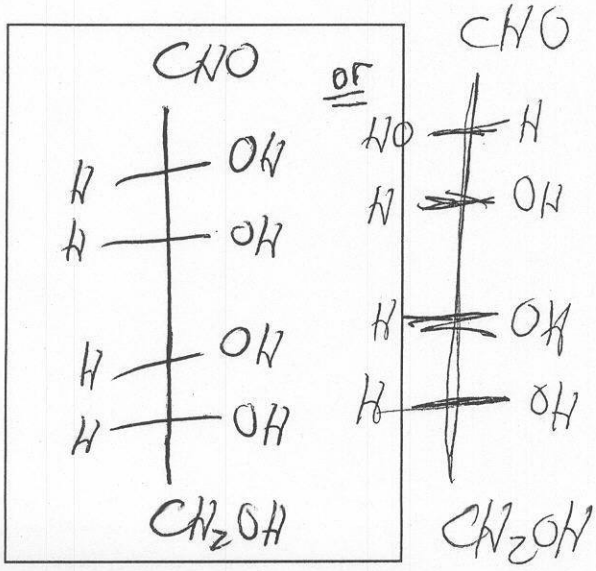
+5 for each structure

(c) Compound X is an aldohexose. When X is treated with 3 equivalents of $PhNHNH_2$ in acetic acid, the osazone formed is different from the osazone obtained from D-glucose or D-mannose (these two give the same osazone). However, when X is subjected to two cycles of the Wohl degradation process, the resulting aldotetrose, D-erythrose, is the same as the aldotetrose generated from two cycles of Wohl degradation of D-glucose or D-mannose.

Draw the Fischer projection of D-erythrose.



Draw the Fischer projection of X.

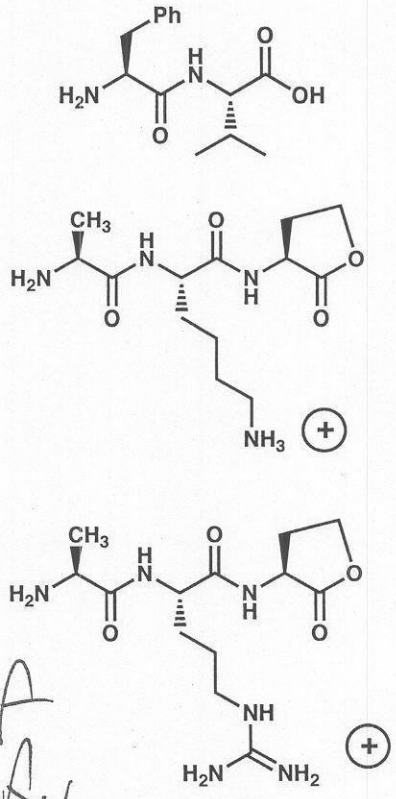


(+2 extra credit for "or")

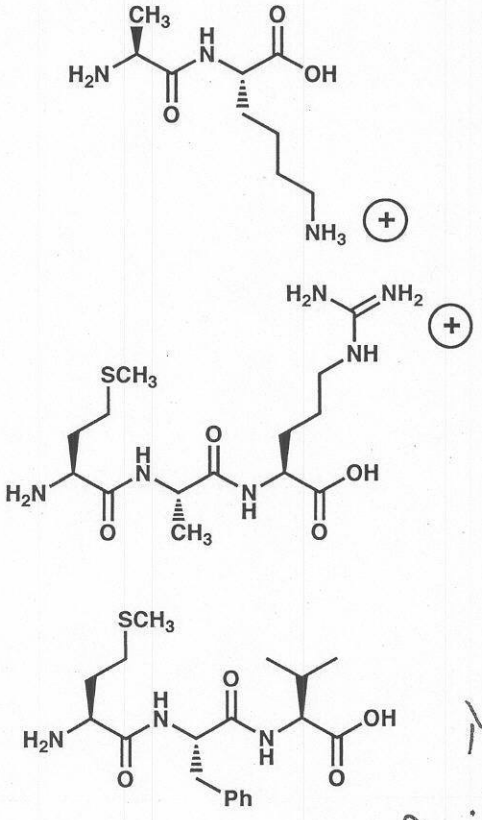
Name _____

9. (12 points) When peptide Z is treated with CNBr, three short fragments are generated, as shown below. When peptide Z is instead treated with the enzyme trypsin, a different set of three short fragments is generated, as shown. Based on this information, what is peptide Z?

Fragments from degradation with CNBr:



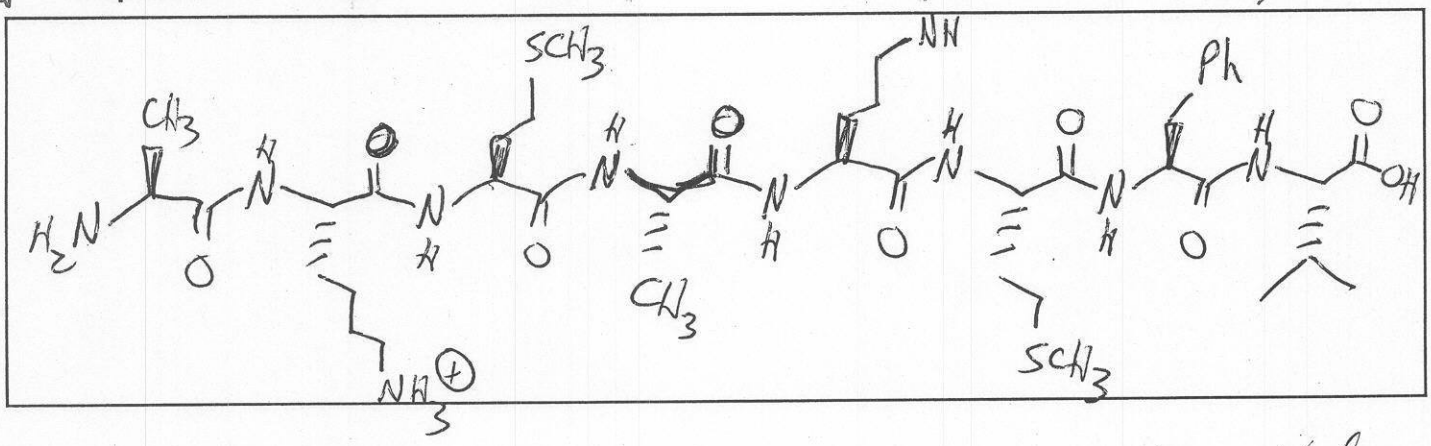
Fragments from degradation with trypsin:



+2 if identity C terminus or N terminus +12

-3 if 2 internal residues switched

Peptide Z =

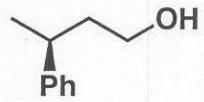


Ala – Lys – Met – Ala – Arg – Met – Phe – Val

+15 if in correct order but missing 1 residue

Name _____

10. (16 points) Propose a synthesis of the target molecule shown below from the indicated starting material. You may use other reagents that contain no more than one carbon atom.

Starting Material = 

(single enantiomer)

Target =