

Chem 0320
Dennis P. Curran
April 28, 2010
Final Exam

Name: _____

Signature: _____

Suggested Answers

Answer all questions on this exam. If you need more space than that provided, use the back of any page.

1. _____ (20 points) Names and Structures
 2. _____ (80 points) Short Answers (three parts)
 3. _____ (40 points) Reactions
 4. _____ (40 points) Mechanisms
 5. _____ (20 points) Short Syntheses
- (200 points)

TOTAL _____

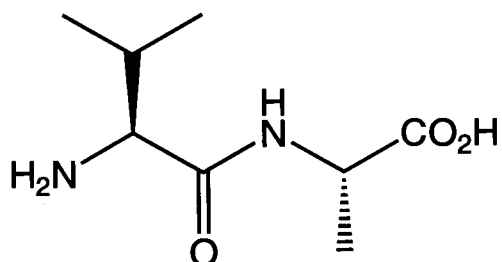
The test has **11** pages (including this cover page and the sugars on the last page) and **5** questions. The exam ends at 9:50 am sharp.

Good Luck !!!

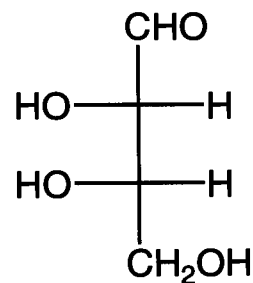
Note: The structures of the D-Aldohexoses are on the last page.

1) Names and Structures (20 points)

a) Provide acceptable names (IUPAC or trivial) for the following compounds. Be sure to include stereochemical descriptors if needed. (2 x 4 points):



Valyl ALANINE
-OH-
VAL-ALA

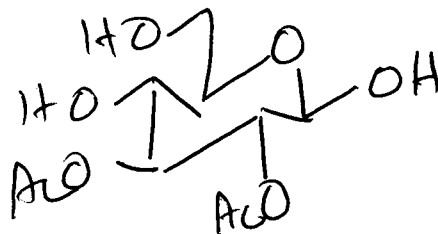


(Fischer projection)

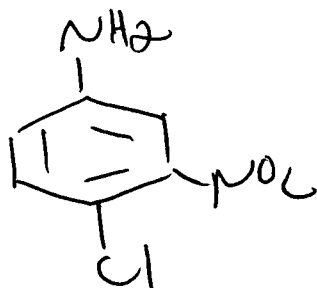
L-erythrose -OH-
(2R,3S)-2,3,4-trihydroxy-
butanal

b) Provide clear structures for the following compounds. (3 x 4 points):

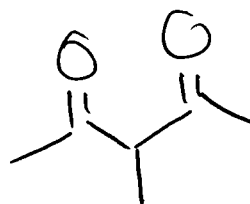
methyl 2,3-di-O-acetyl-β-D-glucopyranoside



4-chloro-3-nitroaniline

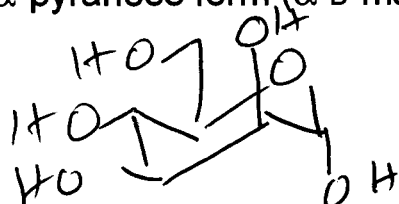


3-methylpentan-2,4-dione

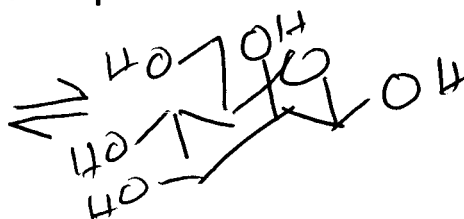


2a) Short Answers: carbohydrates (30 points) Answer the following questions regarding **D-mannose** (see Fischer projections on the last page).

a) Draw the α -pyranose form (α -D-mannopyranose) in the most stable chair.

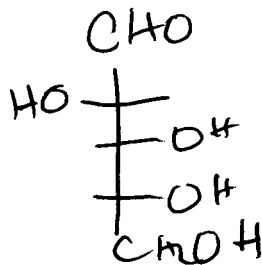


b) Mutarotation occurs when α -D-mannopyranose is dissolved in water. What is the product of mutarotation and how does it form?

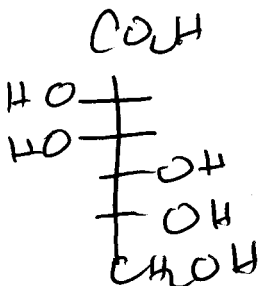


opens from hemiacetal to aldehyde reversibly

c) Draw a Fischer projection of the sugar that you would use as a starting material to make D-mannose in a Kiliani-Fischer synthesis.

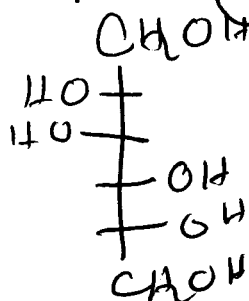


d) Draw a Fischer projection of a sugar that forms the same phenyl osazone as D-mannose.



THE STRUCTURE AT LEFT IS NOT CORRECT; THE CORRECT ANSWER IS GLUCOSE

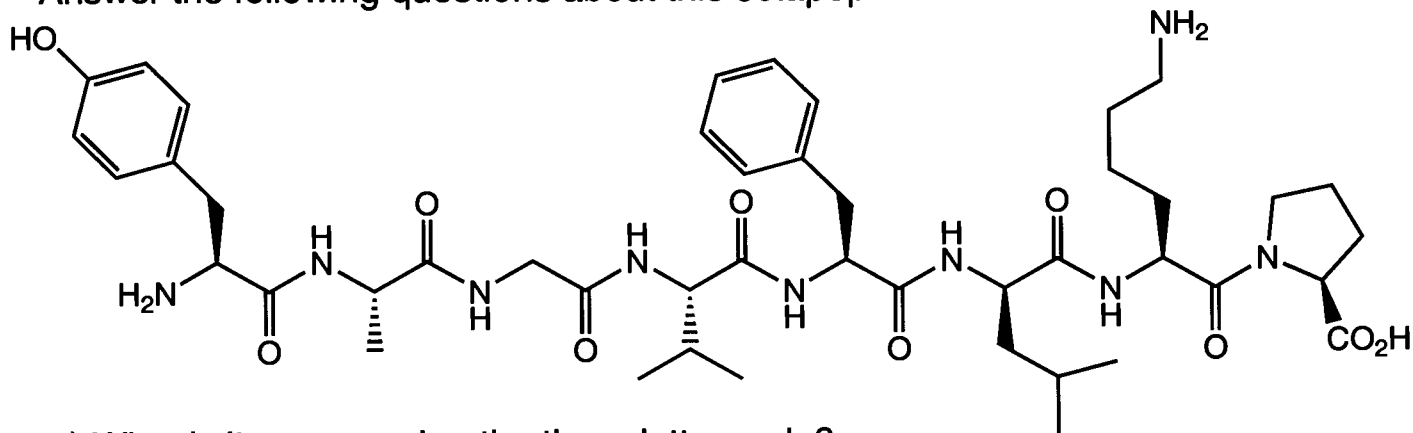
e) Draw a Fischer projection of the product from the reaction of D-mannose with NaBH_4 . Is the product chiral or achiral?



mannitol has C2 symmetry

2b) Short Answers: peptides (30 points)

Answer the following questions about this octapeptide.



a) What is its name using the three-letter code?

tyr-Ala-gly-Val-Phe-D-Leu-Lys-Pro

b) All of the amino acids except one have the natural *S* (or *L*) configuration. What is the common name of the one *R* (or *D*) amino acid?

leu

c) What is the name of the "C-terminal" amino acid?

proline

d) What is the name of the first amino acid to be released by an Edman degradation?

tyrosine

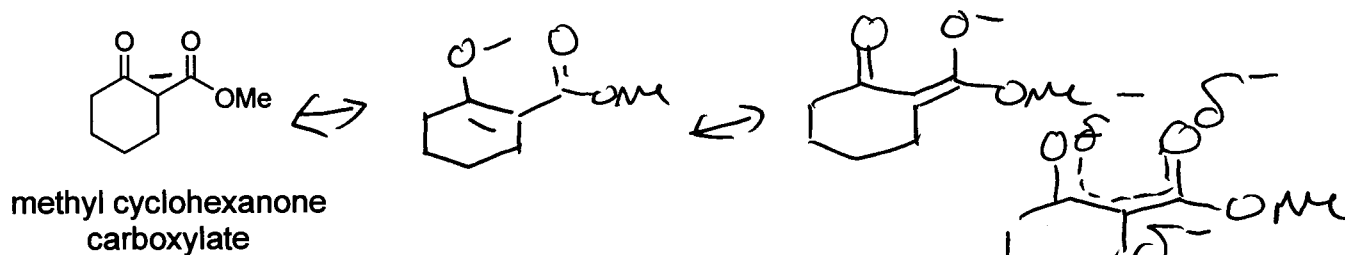
e) At physiological pH (approximately 7.0), is the net charge of this octapeptide about -1, 0, or +1? What groups are ionized at pH 7?

+ charge, tyrosine, lysine
- charge, proline

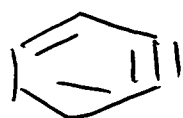
$\approx +1$

2c) Short Answers: others (20 points)
Briefly answer the following questions.

a) Draw all resonance forms of the enolate derived from treatment of methyl cyclohexanone carboxylate with base. Also draw a resonance hybrid.

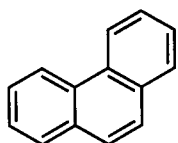


b) What is benzyne and why is it unstable?

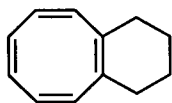


"triple bond" is bent;
poor orbital overlap

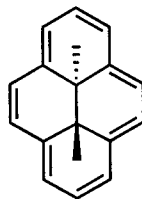
c) Indicate whether the following compounds are aromatic or not.



Y



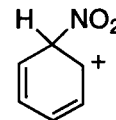
N



Y

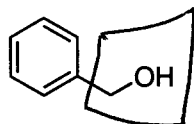


N

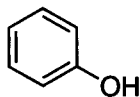


N

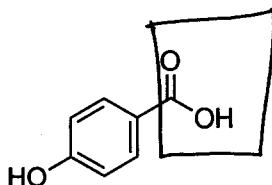
d) Arrange the following compounds in order of increasing acidity (that is, most acidic last).



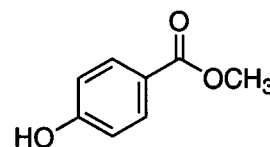
1



2

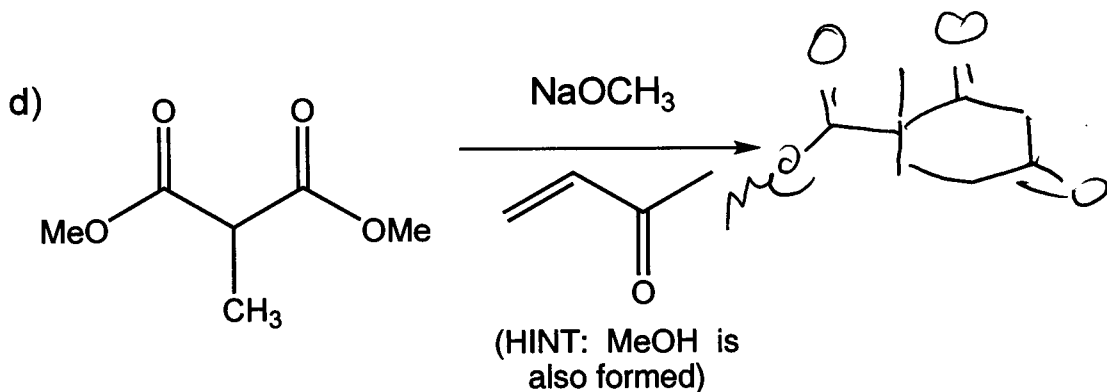
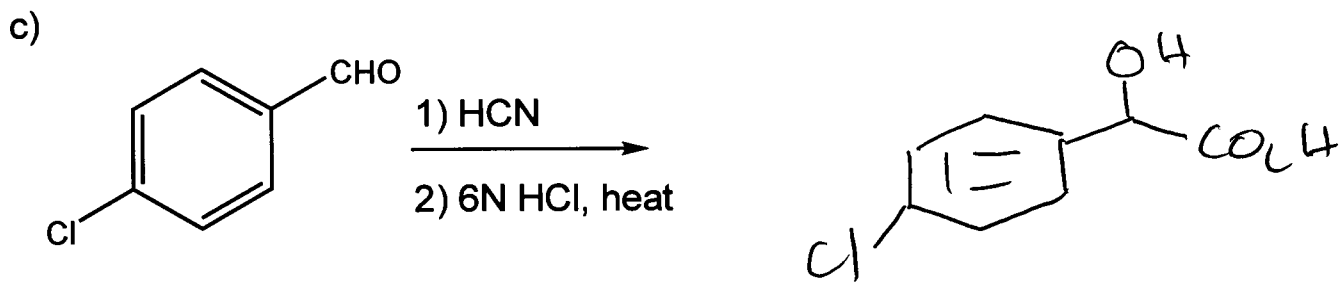
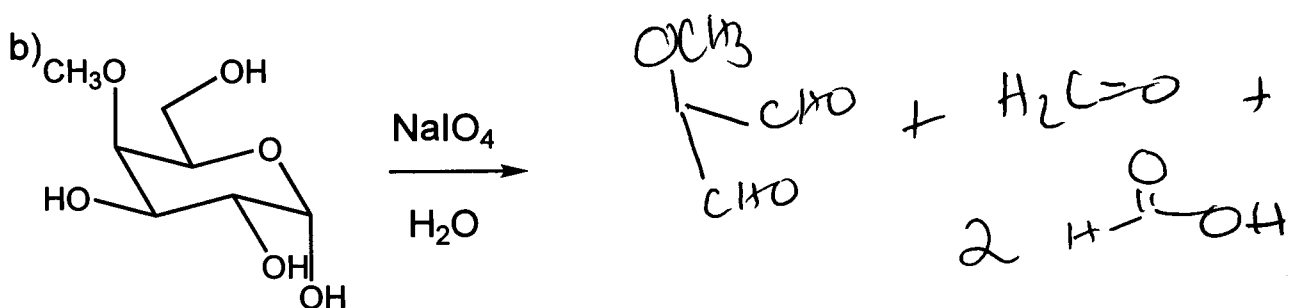
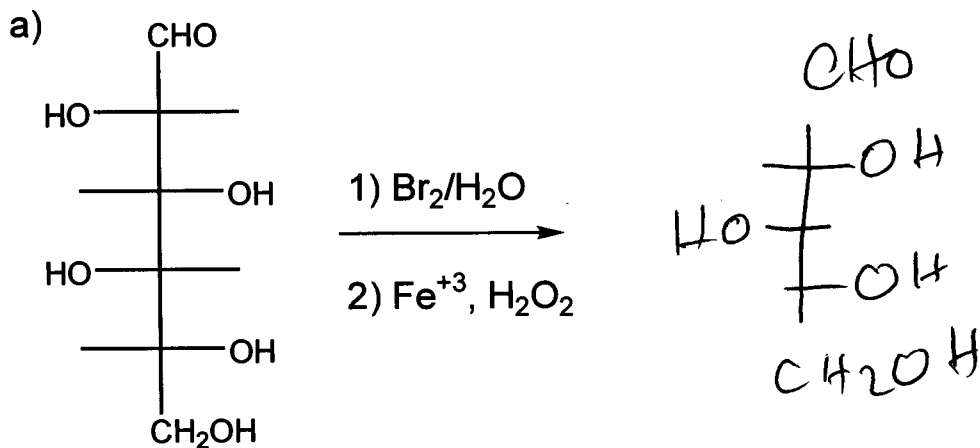


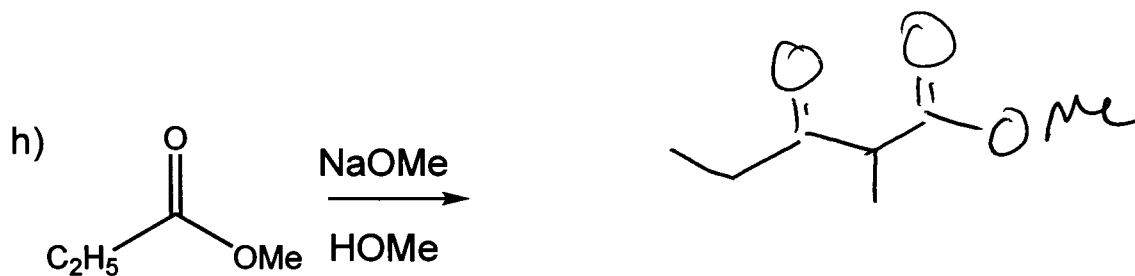
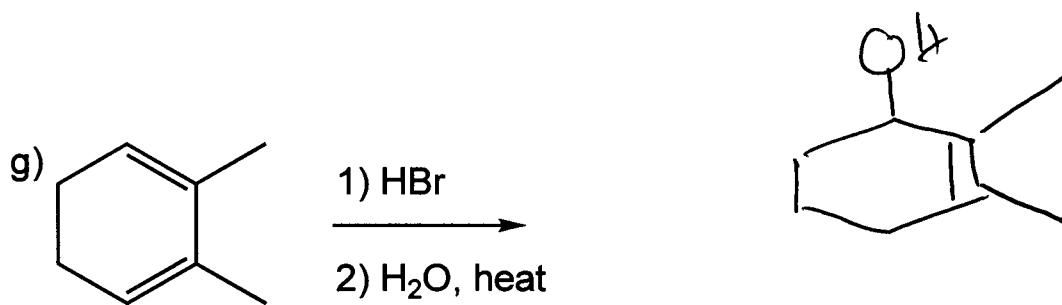
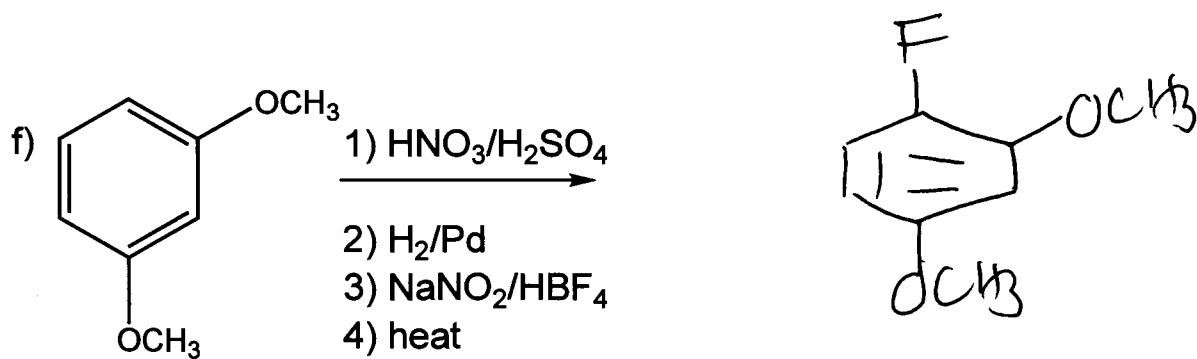
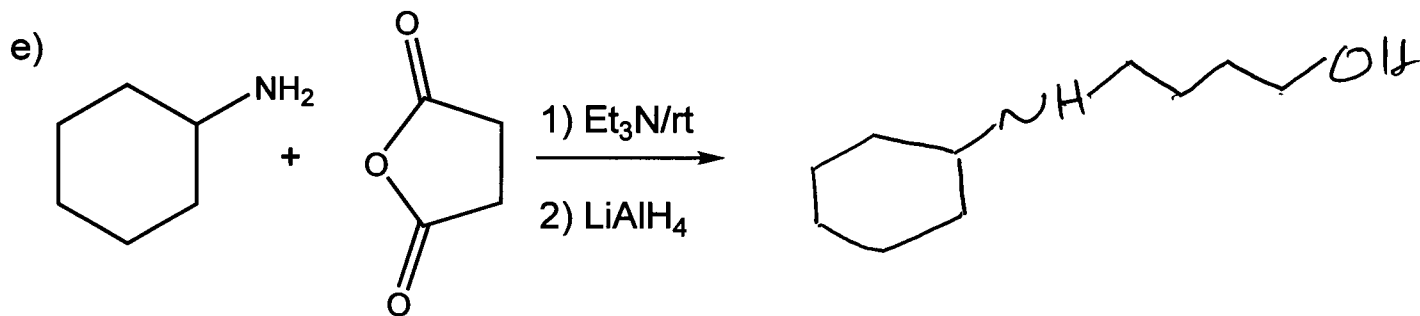
4



3

3) Reactions (40 points) Provide clear products for the following reactions or sequences of reactions. Indicate stereochemistry if relevant. Note, 1), 2), etc. are separate reaction steps with workup in between.

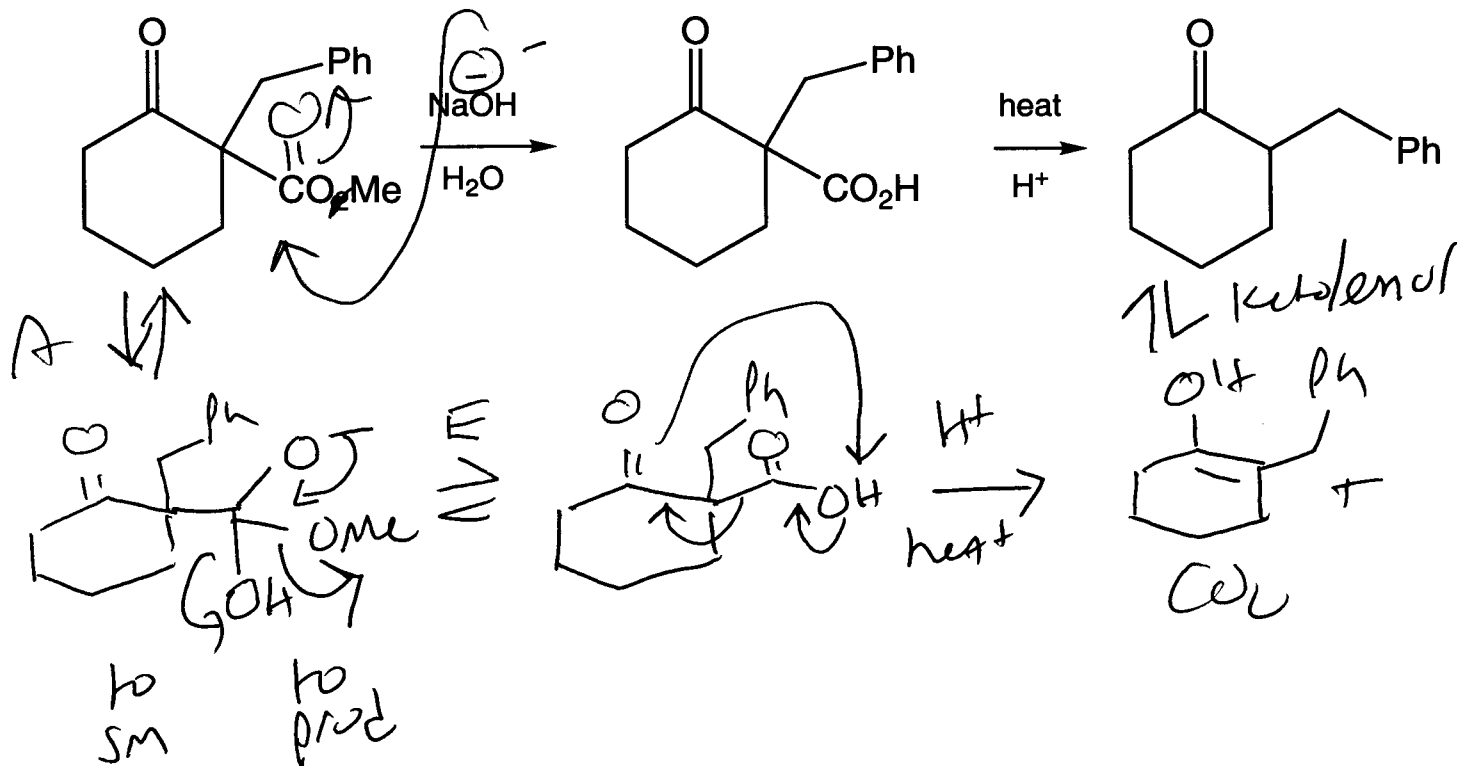




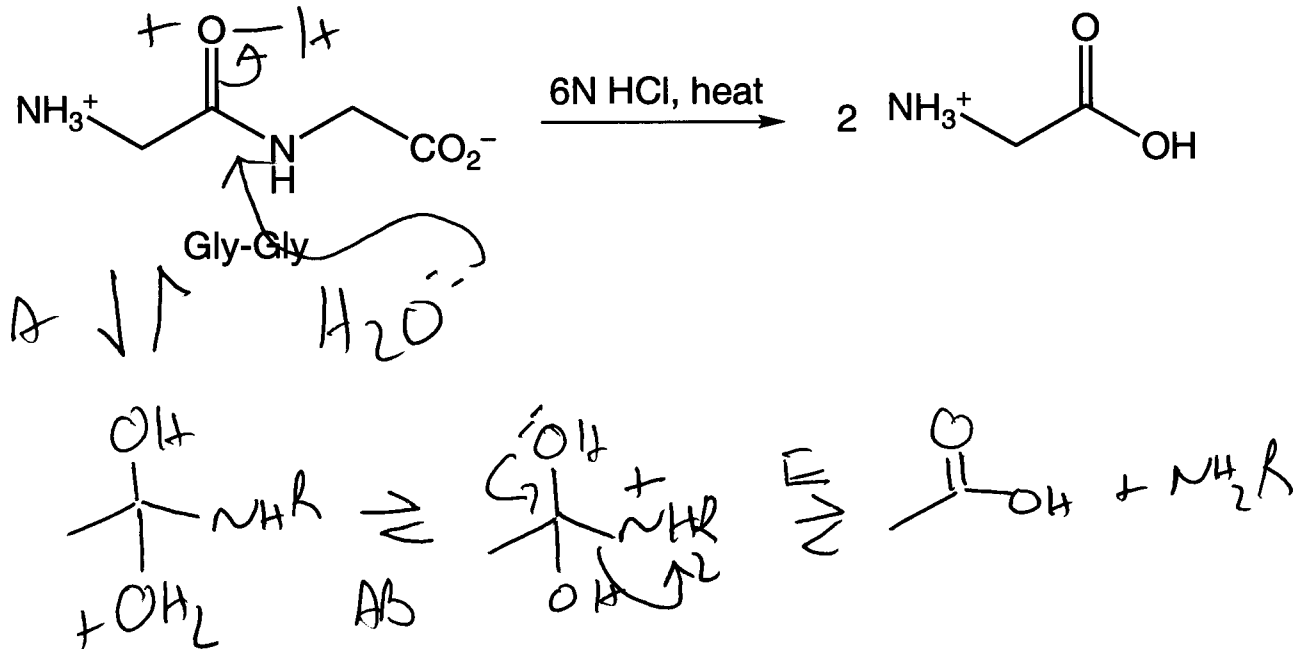
4) Mechanisms

Show clear, step-by-step mechanisms for the following reactions. Use arrows to track electron flow. (4 x 10 points)

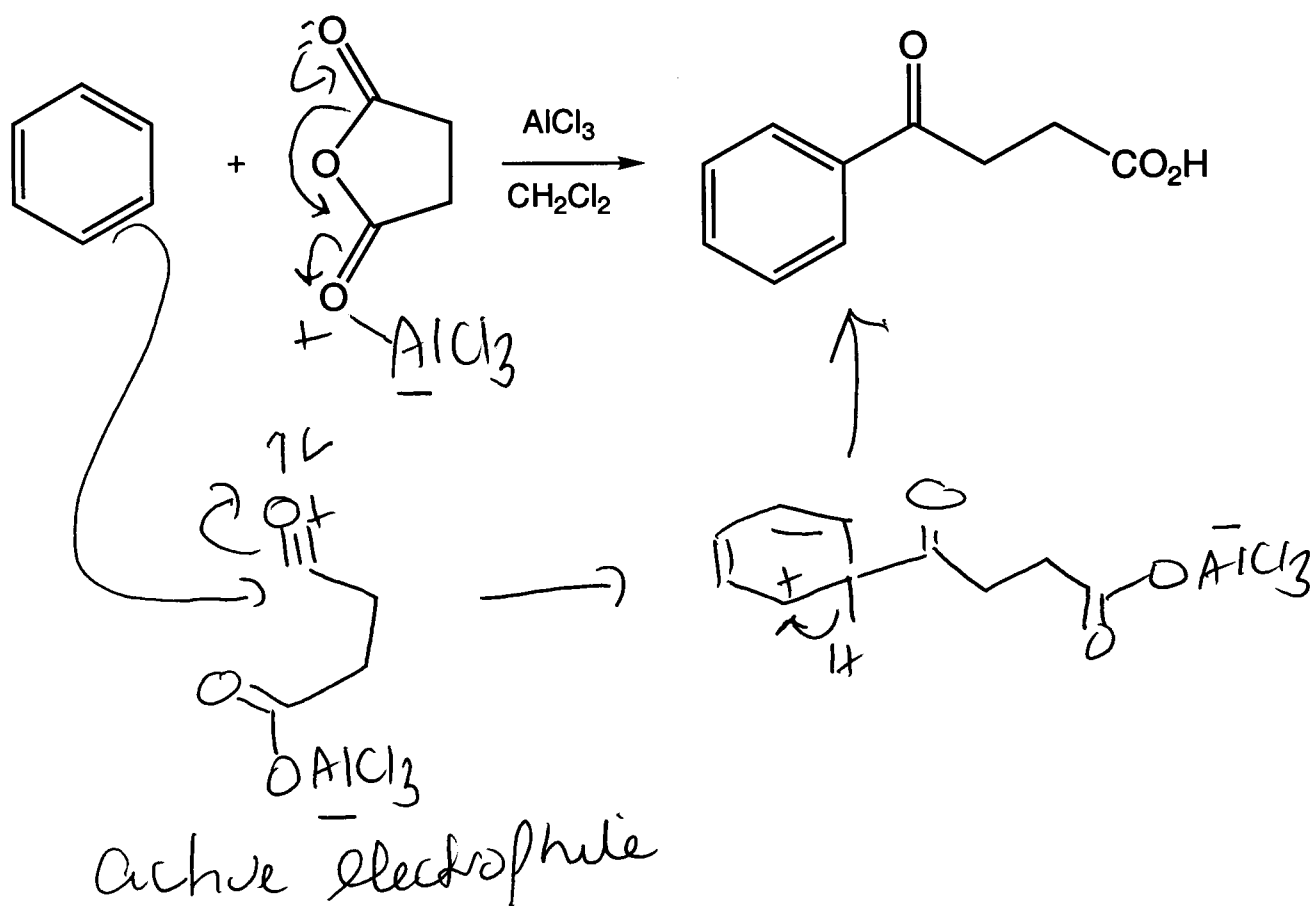
a) Show mechanisms for hydrolysis and decarboxylation of this β -ketoester



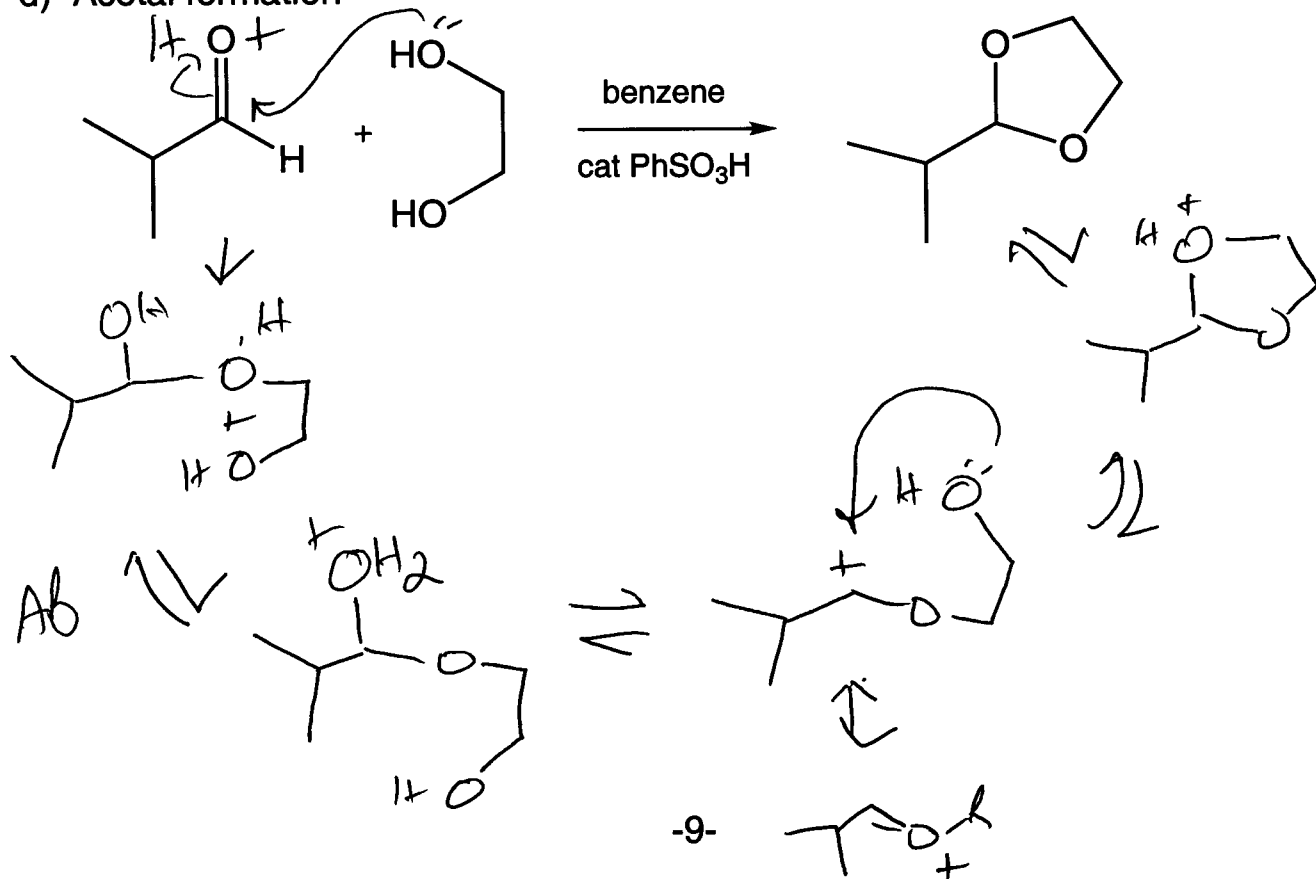
b) Show the mechanism for acidic hydrolysis of Gly-Gly.



c) Friedel-Crafts Reaction

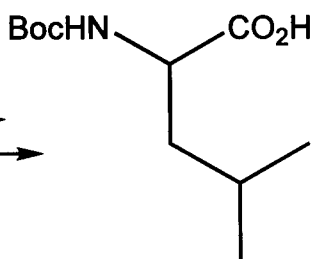
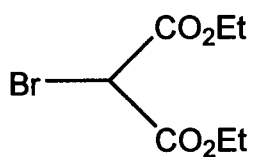


d) Acetal formation



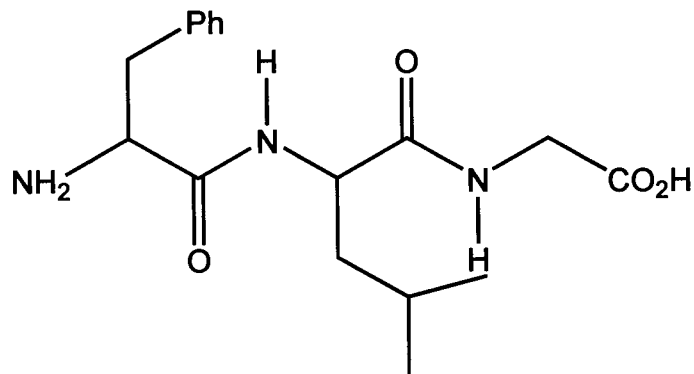
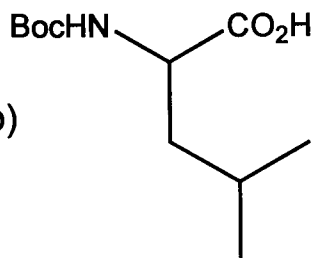
5) Short Syntheses (20 points). For **two of the following three** problems, show reactions to convert the indicated starting materials to the target products. Use any other needed reagents.

a)



- 1) CC(C)CBr
- 2) base,
- 3) NaOH
- 4) BocCl

b)



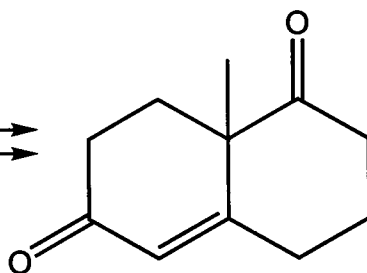
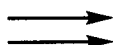
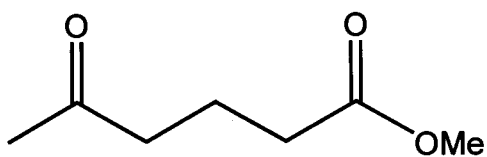
1) DCC, gly

2) TFA

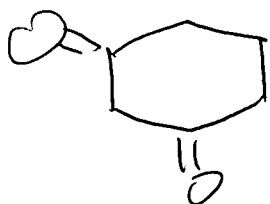
3) Boc-Phe, DCC

4) TFA

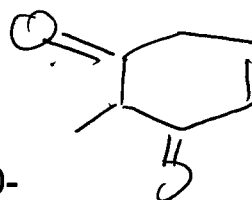
c)



↓ NaOMe



$\xrightarrow{\text{NaH}}$
 CH_2I



$\xrightarrow{\text{base}}$