

Chem 51C Final Exam
197 points; 2 hours
June 11, 2014

Answer Key

Problem	Possible Points	Score
1	24	_____
2	24	_____
3	16	_____
4	12	_____
5	36	_____
6	24	_____
7	12	_____
8	18	_____
9	14	_____
Total	180	_____

Academic Honesty Policy. Academic honesty is strictly enforced on quizzes, exams, and other aspects of this course. Academic dishonesty will result in a failing grade in the class and a letter in the student's file. Activities constituting academic dishonesty include:

Cheating

- Copying from others during an examination.
- Communicating exam answers with other students during an examination.
- Offering another person's work as one's own.
- Taking an examination for another student or having someone take an examination for oneself.
- Tampering with an examination after it has been corrected, then returning it for more credit.
- Using unauthorized materials, prepared answers, written notes, or concealed information during an examination.

Dishonest Conduct

- Stealing or attempting to steal an examination or answer key from the instructor.
- Allowing another student to copy off of one's own work during a test.

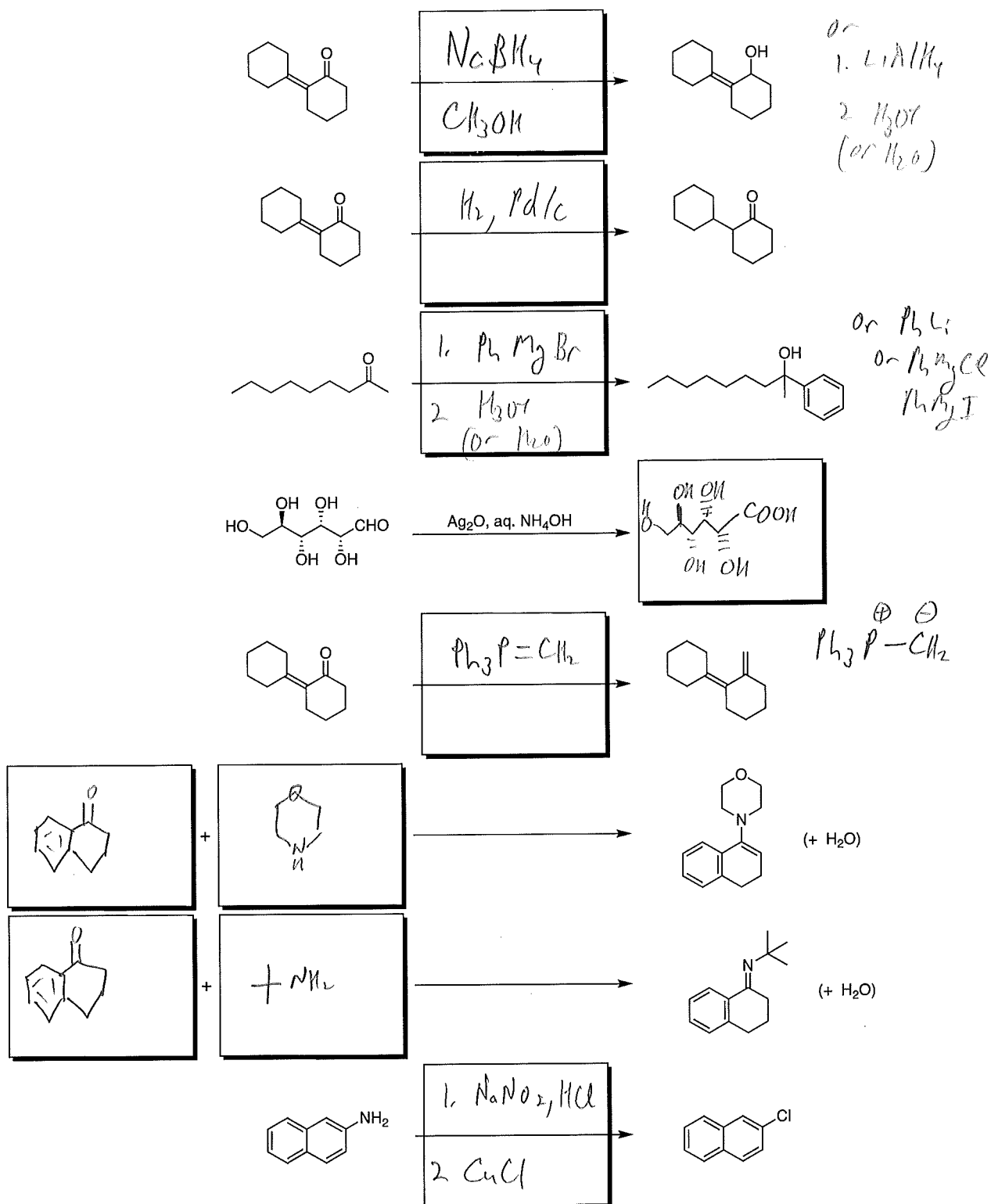
Collusion

- Any student who knowingly or intentionally helps another student perform any of the above acts is subject to discipline for academic dishonesty.

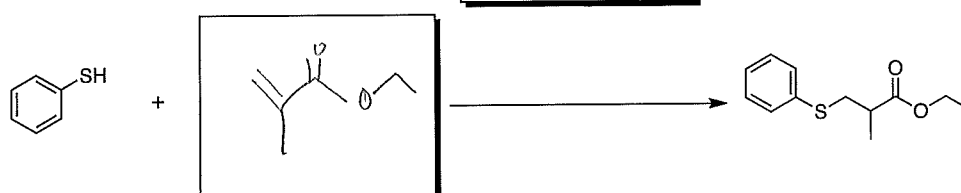
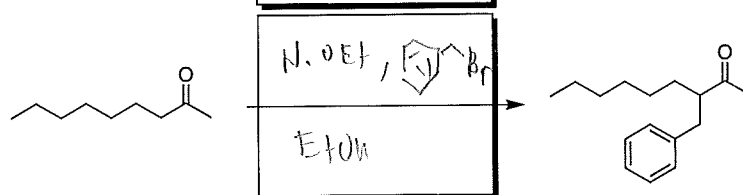
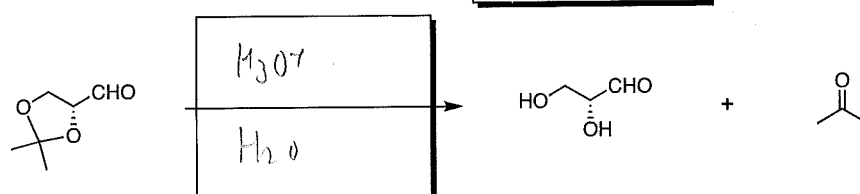
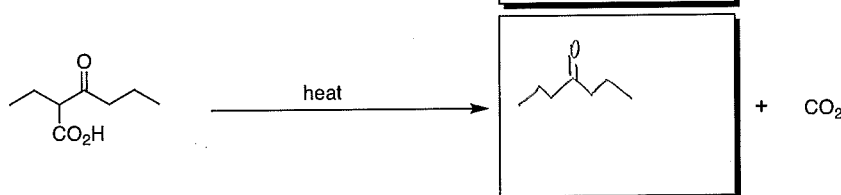
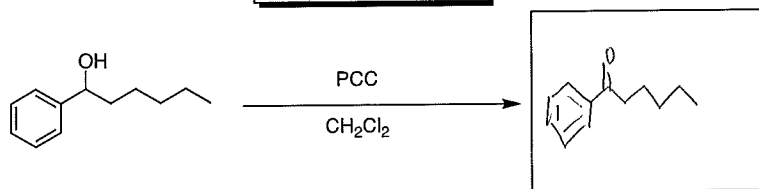
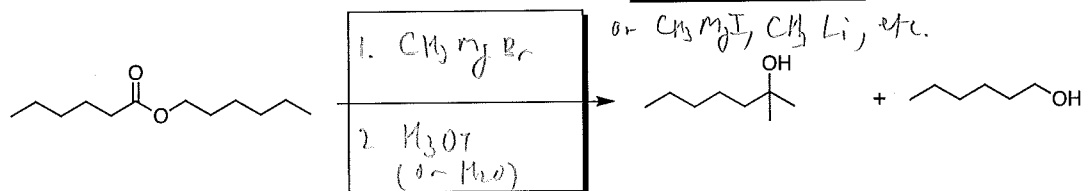
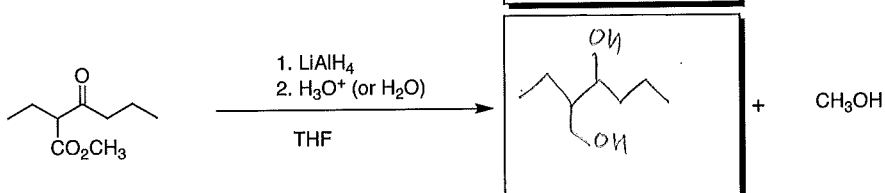
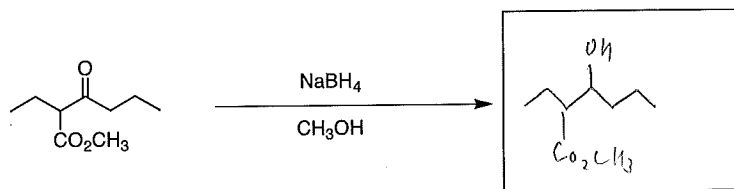
I understand and will abide by this academic honesty policy: _____ (signature)

Seat: _____

1. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)

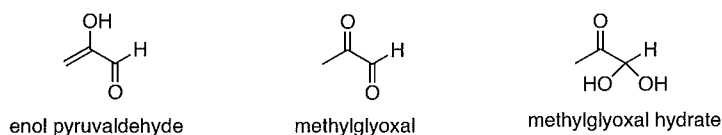


2. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)

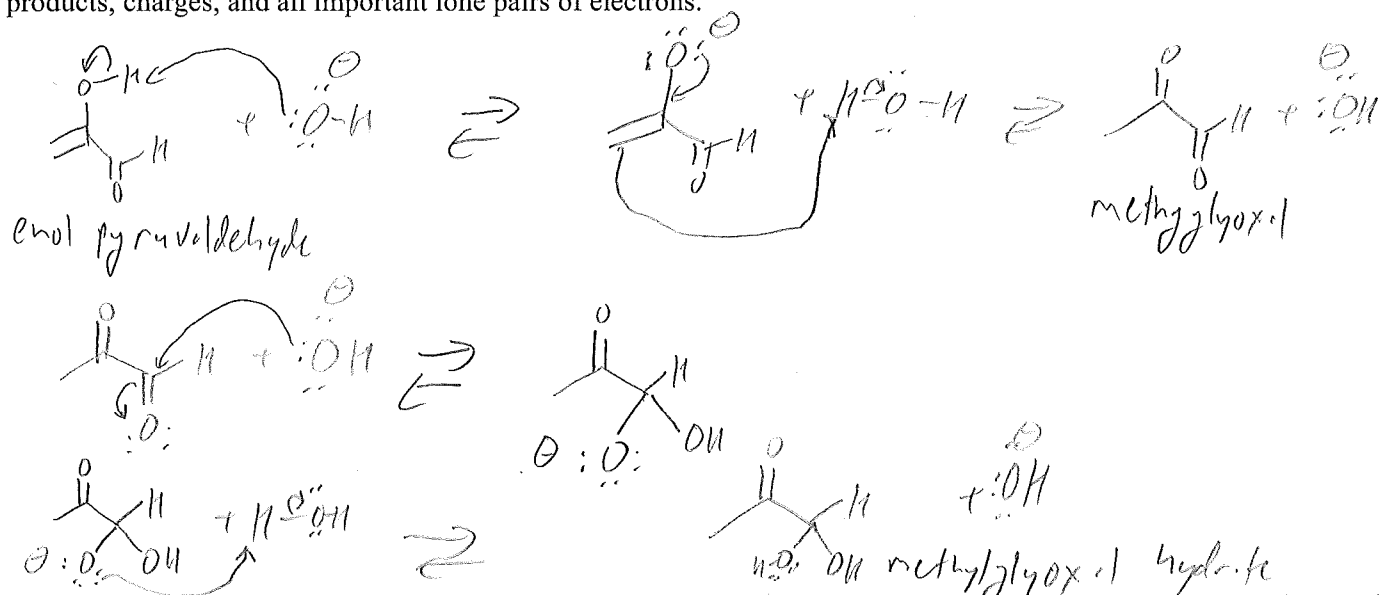


allylation
 using α -alkoxy base
 goes by way of
 the thermodynamic
 enolate

3. The molecule enol pyruvaldehyde was first reported in 2002 [J. Am. Chem. Soc. **2002**, 124, 13047]. This molecule is unstable in water and readily forms methylglyoxal hydrate. The reaction proceeds by way of methylglyoxal. (16 points)



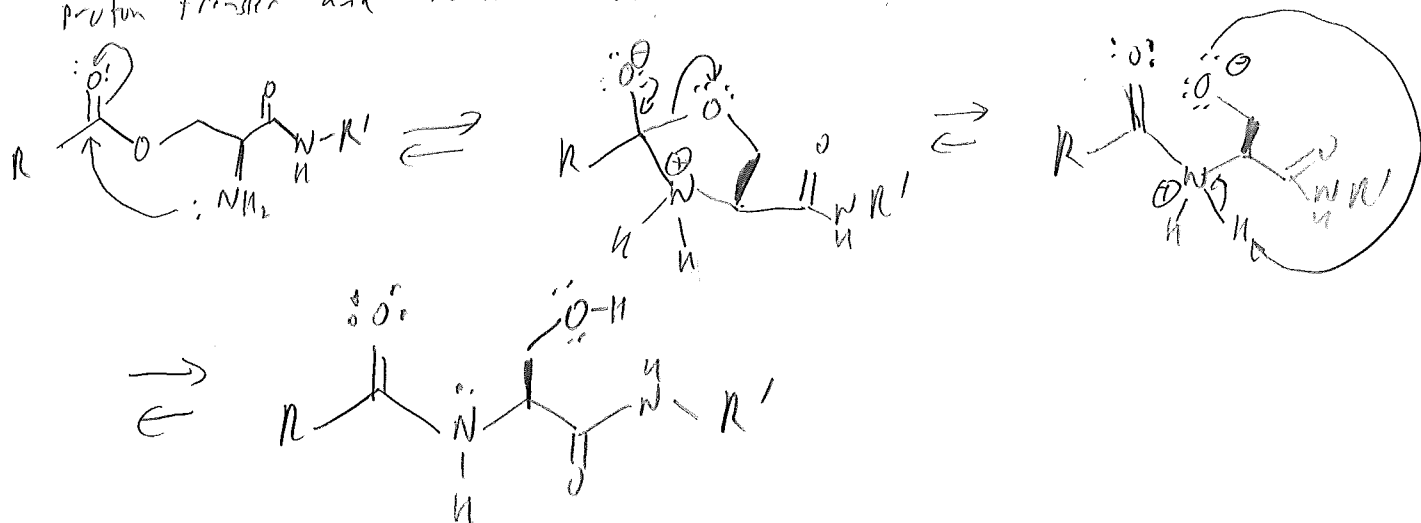
Write a curved-arrow mechanism for the formation of methylglyoxal hydrate from enol pyruvaldehyde. The reaction occurs in H_2O and is catalyzed by OH^- . Make sure to show each step of the reaction and all reactants, intermediates, products, charges, and all important lone pairs of electrons.



4. Esters of serine isomerize to form amides as shown below. Write a curved-arrow mechanism for this reaction. Make sure to show each step of the reaction and all reactants, intermediates, products, charges, and all important lone pairs of electrons. (12 points)



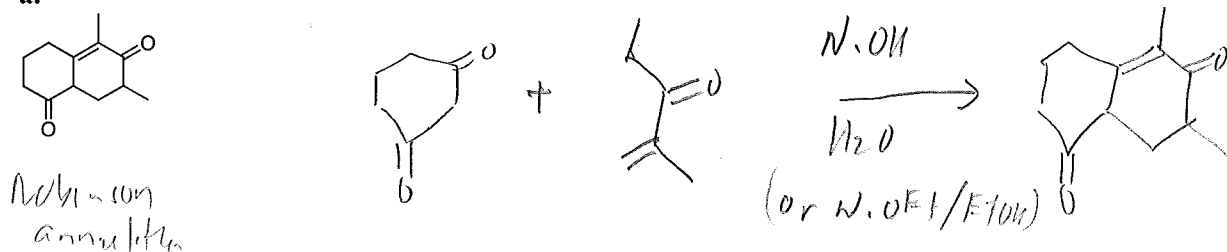
This is intramolecular aminolysis reaction. It involves the attack of amino group on the carbonyl, followed by breakdown of the tetrahedral intermediate. There is a proton transfer in the breakdown of the tetrahedral intermediate, and it is reasonable to envision the proton transfer and breakdown of the tetrahedral intermediate in a number of ways.



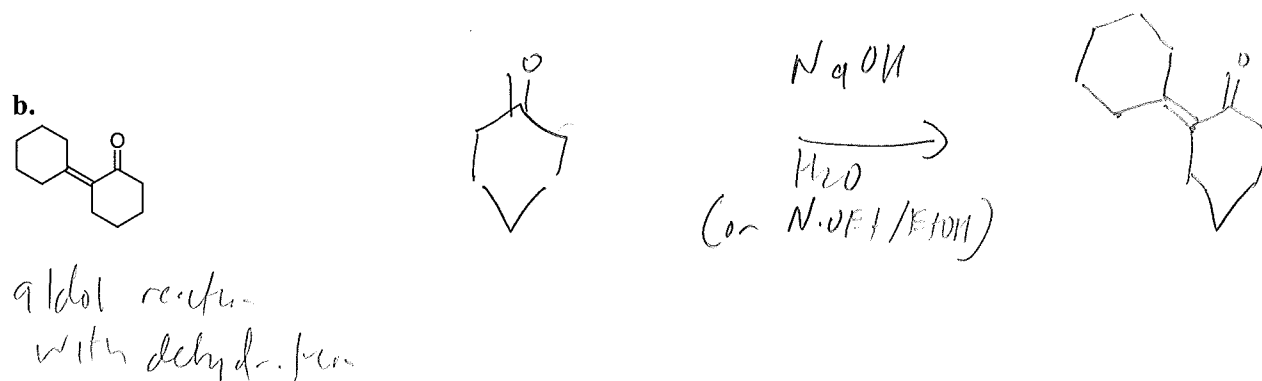
5. Design good syntheses of the following compound starting with compounds containing **six carbon atoms or fewer** as the only organic starting materials. You may use any other inorganic reagents you choose and organic reagents that don't get incorporated into the final product, such as NaOMe, NaOEt, LDA, TsCl, Ph₃P, etc.

Select six of the following eight. (6 points each, 36 points total). Cross out the two that you do not wish to answer or only the first six problems will be graded.

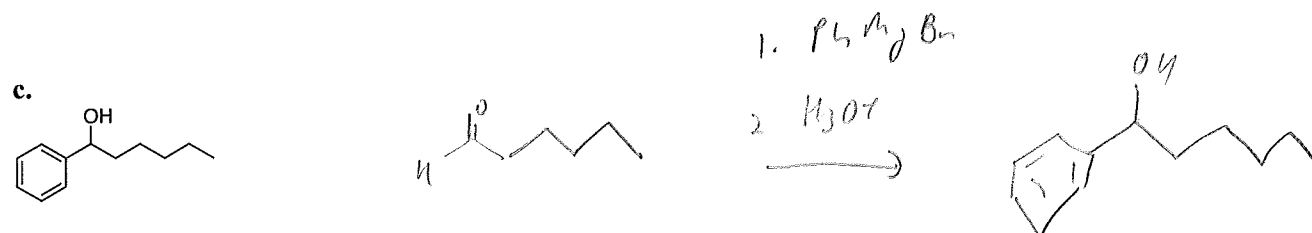
a.



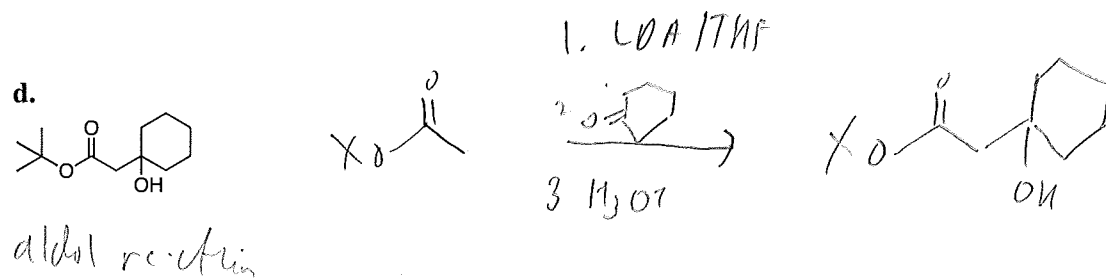
b.



c.



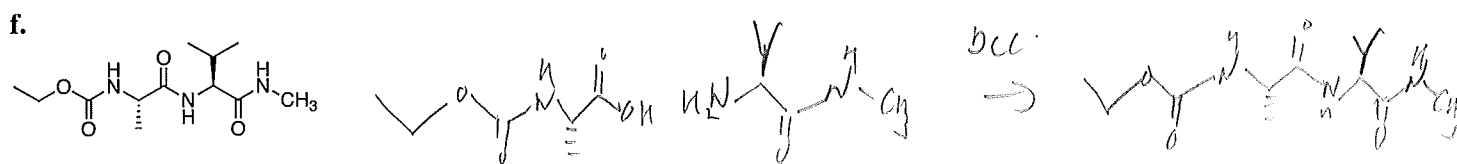
d.



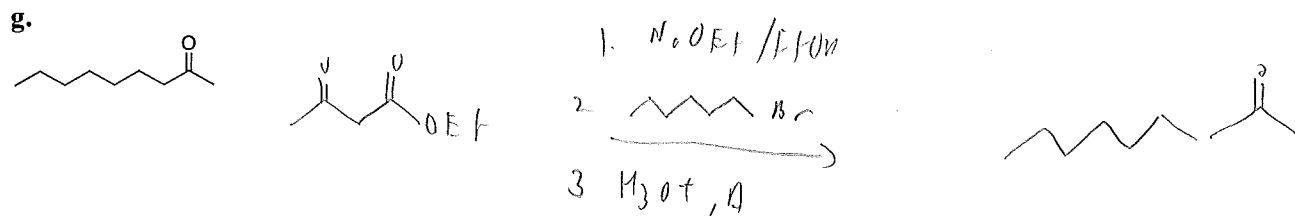


Often pyridine or another base is used although it is not absolutely necessary for ester formation.

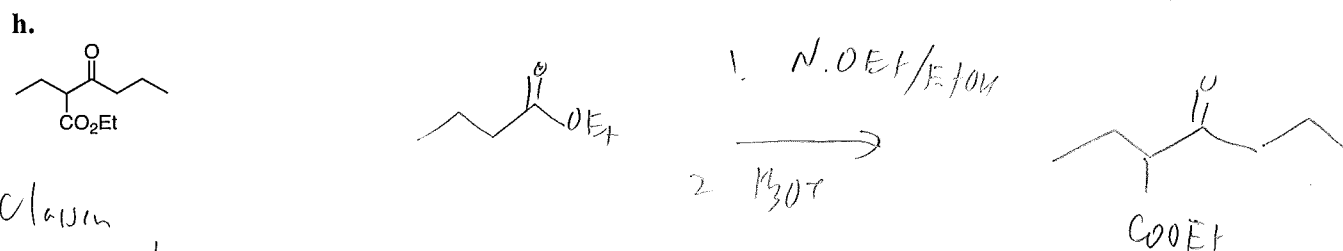
Although Fischer esterification is OK, it would not typically be used for a high molecular weight alcohol like this.



DCC is a great way to make amide bonds. Mixing an amine and a carboxylic acid without DCC is not generally able to form amides, (except under some very unusual and extreme conditions).

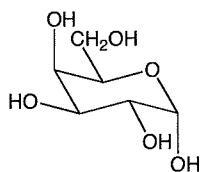
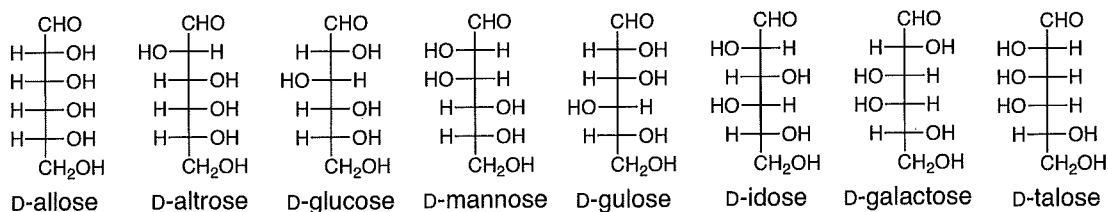


The acetoacetic ester is a great way to make methyl ketones. The alkylation of acetone enolate is also OK.

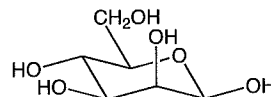


Claisen Condensation

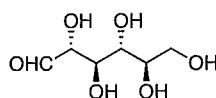
6. Shown below are Fischer projections of the eight D-aldohexoses. Under each drawing write the name of the corresponding structure. If there is stereochemistry at the anomeric position, make sure to specify whether it is α or β . Fischer projections of the D-aldhexoses are provided for reference. (24 points)



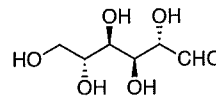
Name: α -D-galactose



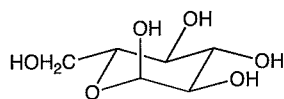
Name: β -D-mannose



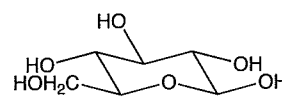
Name: D-allose



Name: D-mannose

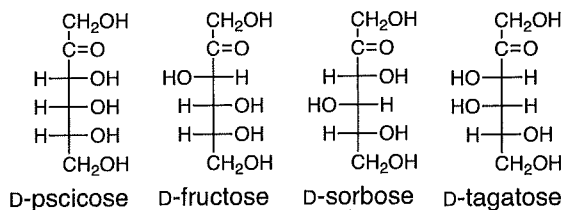
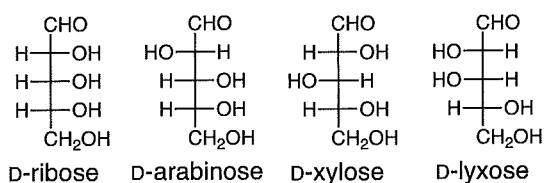


Name: α -D-glucose



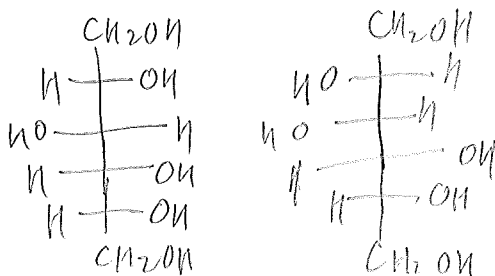
Name: β -L-glucose

7. Shown below are Fischer projections of the four D-aldopentoses and the four D-ketohexoses with the keto group at the 2-position. (12 points)

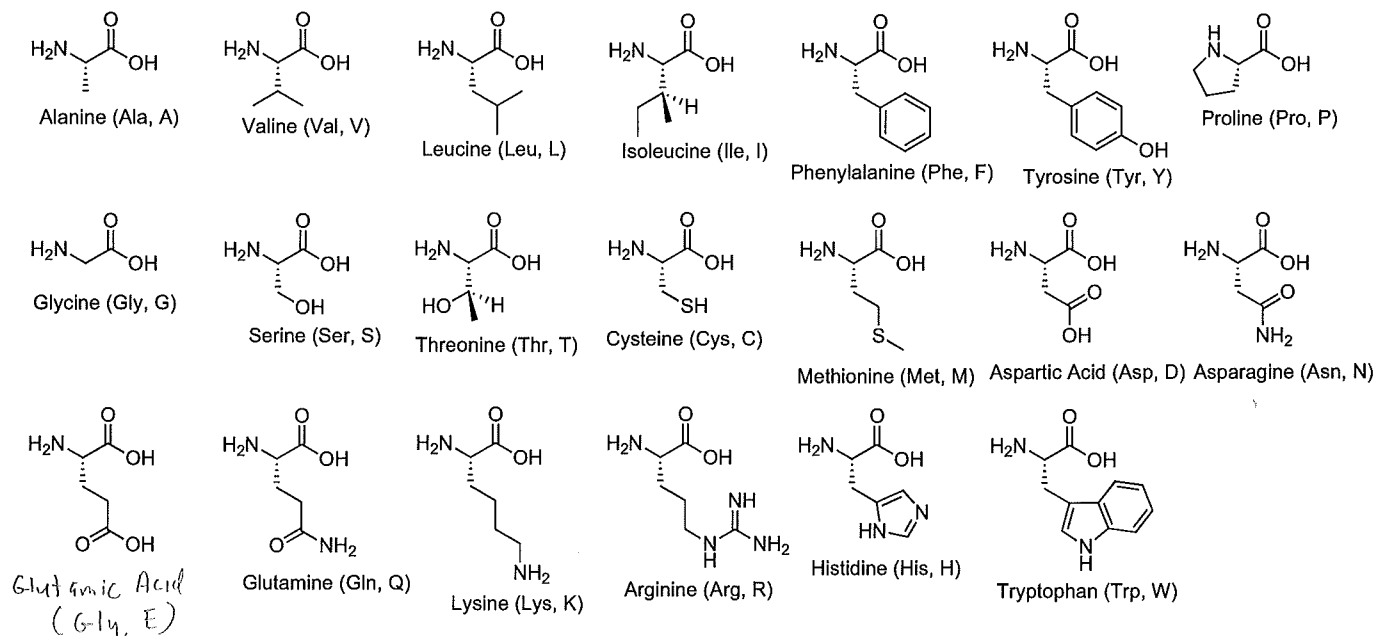


a. Write the names of the two D-aldohexoses that form from the when D-ribose is subjected to Kiliani-Fischer synthesis: D-allose and D-altrose

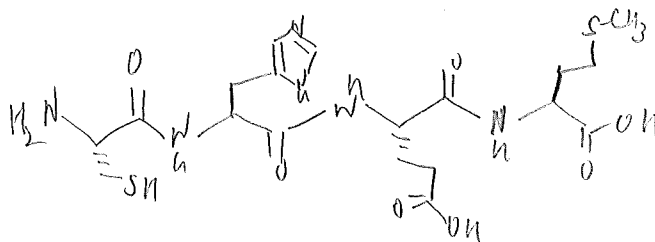
b. Reduction of the ketohexose D-fructose with sodium borohydride gives sorbitol and mannitol, which are commonly used as sweeteners in "sugarless" gum and candies. Write the structures of sorbitol and mannitol:



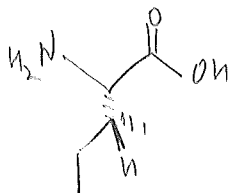
8. Shown below are the 20 amino acids common in proteins. (18 points, 6 points each).



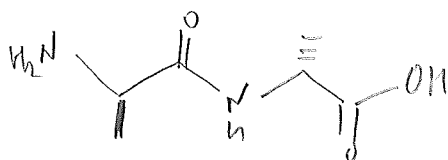
a. Draw the structure of the tetrapeptide CHEM (Cys-His-Glu-Met).



b. The amino acids isoleucine and threonine have stereogenic centers in the side chains, as well as at the α -carbon. Draw the structure of the diastereomer of isoleucine, which is called allo-isoleucine.



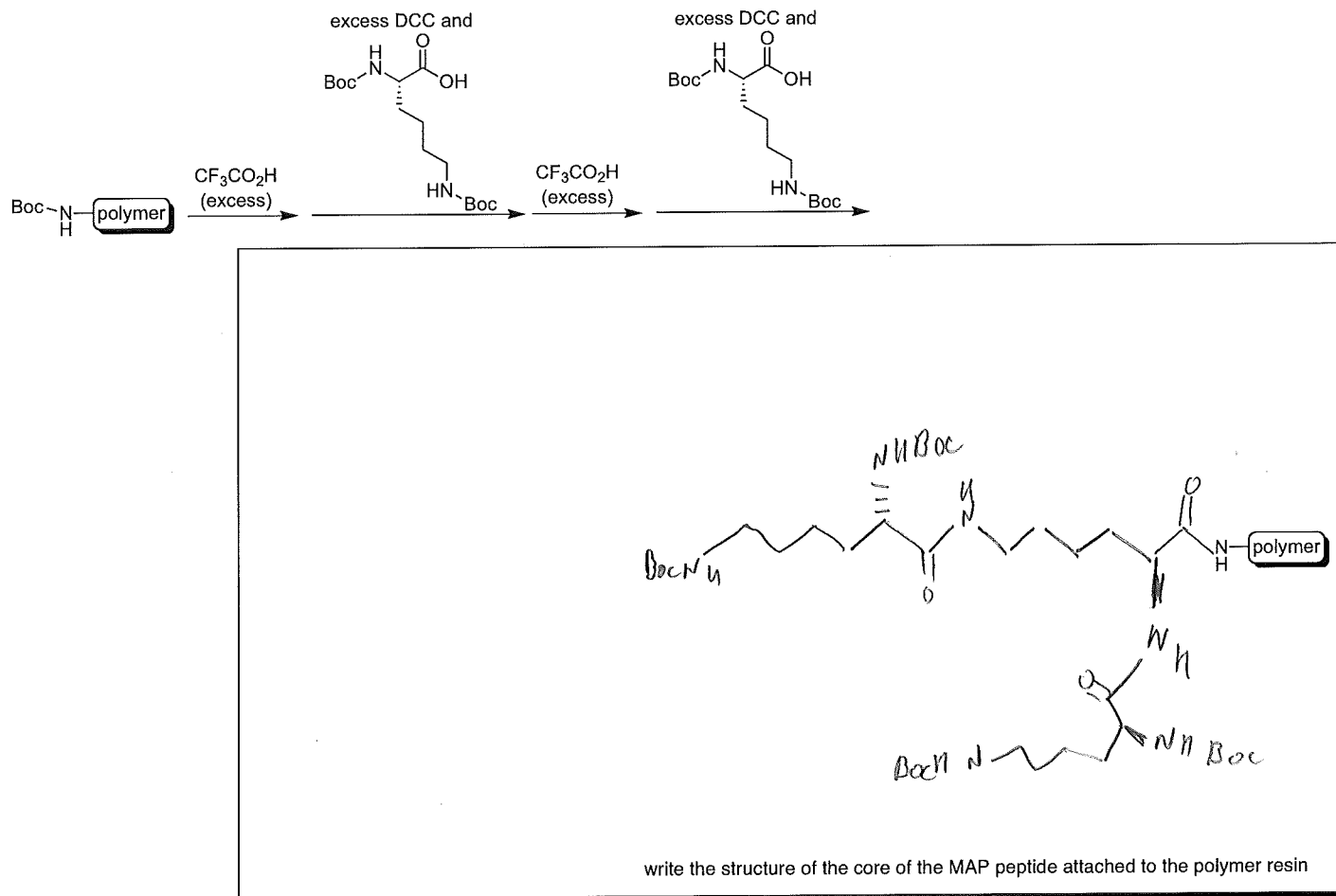
c. In naturally occurring proteins, all 20 of the amino acids occur as the L-enantiomers (shown above). In contrast, a dipeptide that makes up bacterial cell walls consists of two molecules of the D-enantiomer of alanine. Draw the structure of the D-Ala-D-Ala dipeptide.



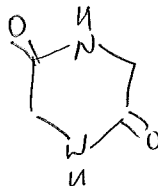
9. 14 points, total: 8 points part a; 6 points part b.

a. Using of lysine in which both the α -amino group and the side-chain amino group are protected with Boc in solid-phase peptide synthesis gives branched peptides called MAPs (multiple antigenic peptides), which are useful in generating antibodies. The first steps in the synthesis of MAPs is to generate the core of the MAP peptide on the polymer with four branching points.

Using the template below, write the structure of the core of a MAP peptide, produced by the following sequence of reactions:



b. Reaction of the carboxy group and amino group of a peptide to form an amide gives a cyclic peptide. Write the structure of the cyclic peptide formed from the dipeptide Gly-Gly. (The compound is called a diketopiperazine and has a molecular formula $\text{C}_4\text{H}_6\text{N}_2\text{O}_2$.)



PLEASE REVIEW THE ACADEMIC HONESTY STATEMENT ON PAGE 1 AND SIGN IT IF YOU ARE ABLE