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

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.

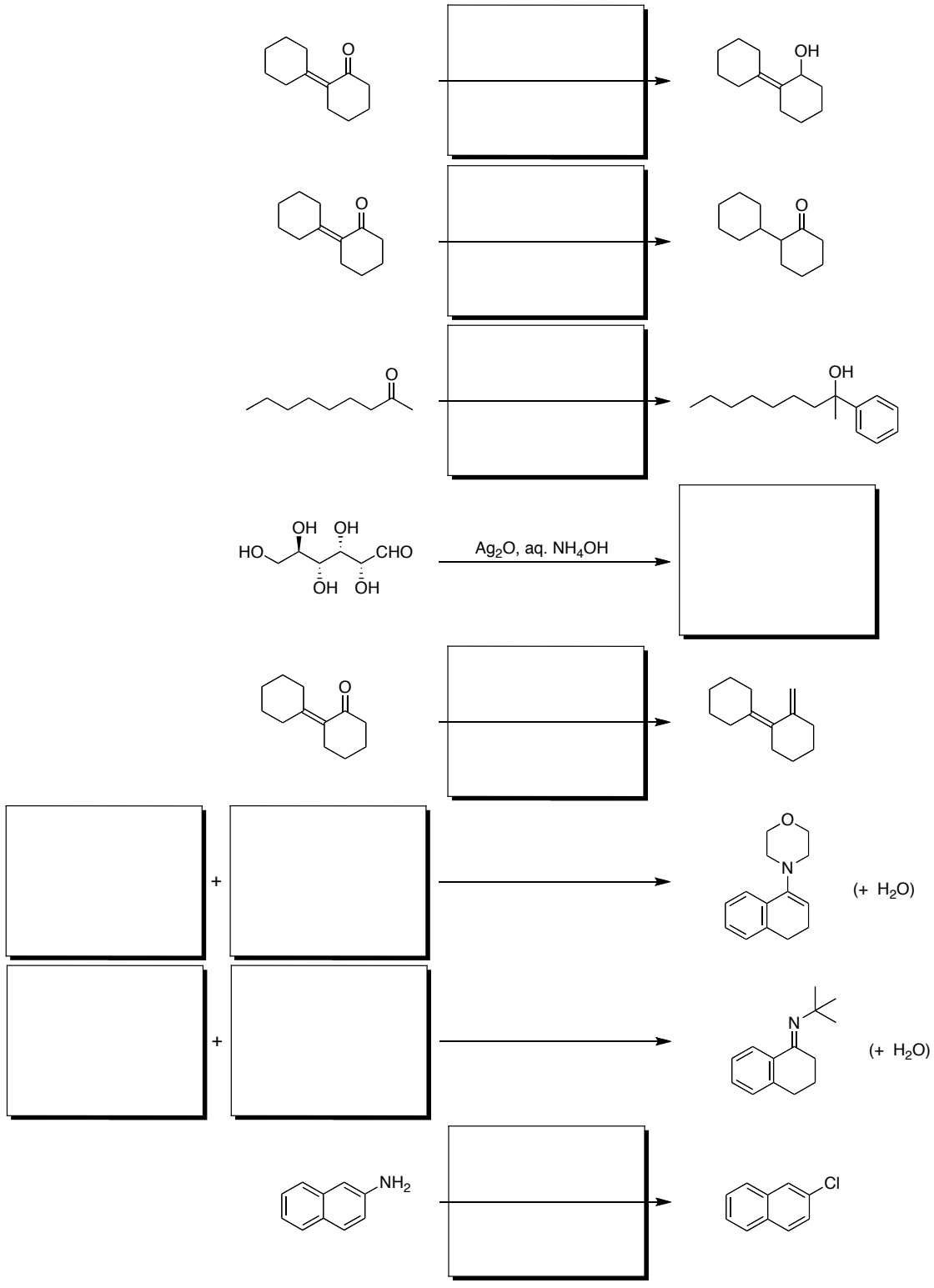
Collusion

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

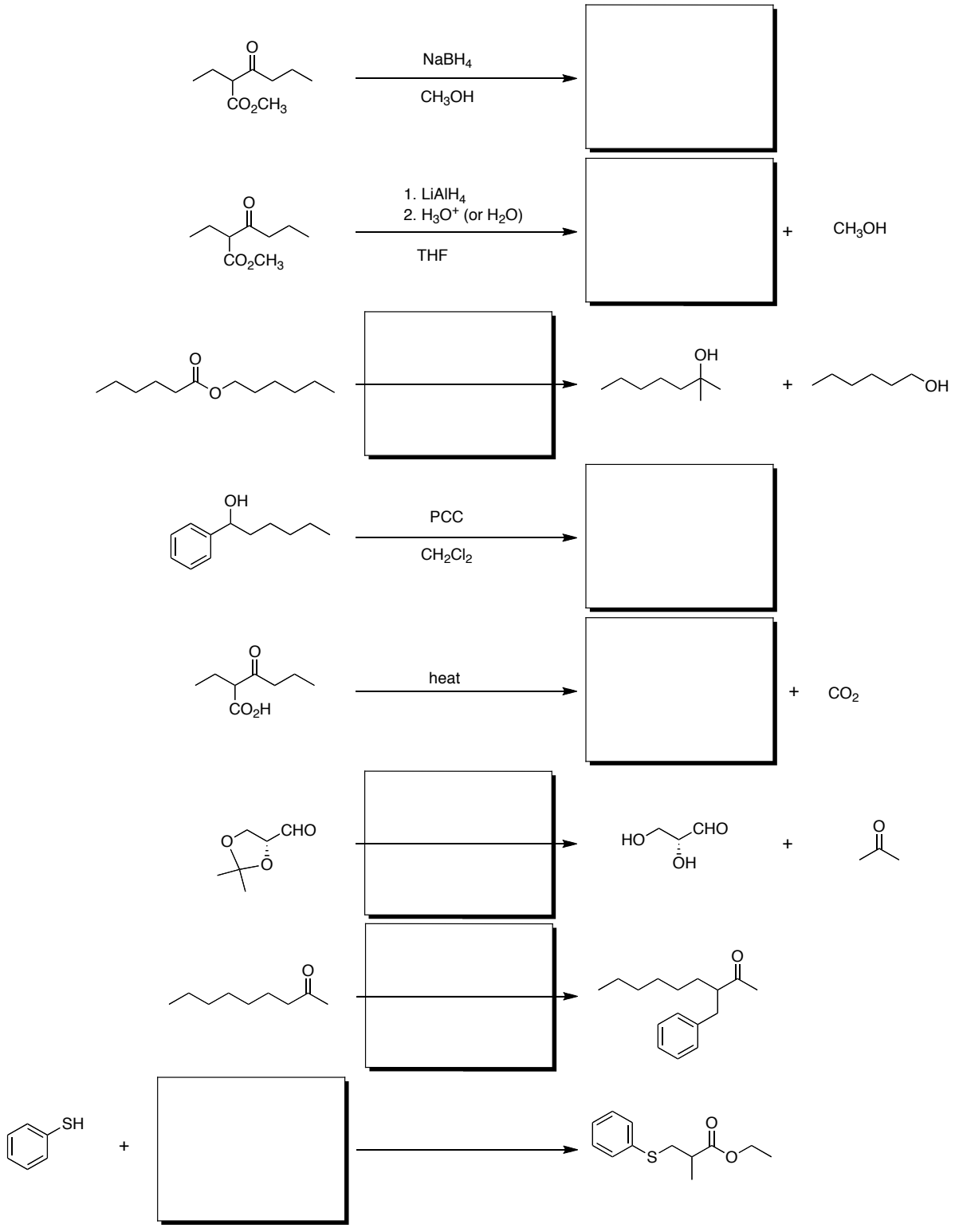
I understand and will abide by this academic honesty policy: _____ (signature)

Seat: _____

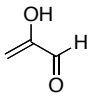
1. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)



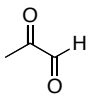
2. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)



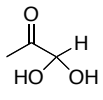
3. The molecule enol pyruvaldehyde was first reported in 2002 [J. Am. Chem Soc. **2002**, *124*, 13047]. This molecule is unstable in water and readily forms methylglyoxal hydrate. The reaction proceeds by way of methylglyoxal. (16 points)



enol pyruvaldehyde



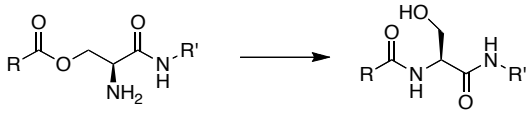
methylglyoxal



methylglyoxal hydrate

Write a curved-arrow mechanism for the formation of methylglyoxal hydrate from enol pyruvaldeyde. 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.

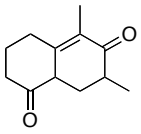
4. Esters of serine isomerize to form amides as shown below. Write a curved-arrow mechanism for this reaction. Make sure to show each step of the reaction and all reactants, intermediates, products, charges, and all important lone pairs of electrons. (12 points)



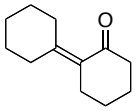
5. Design good syntheses of the following compound starting with compounds containing **six carbon atoms or fewer** as the only organic starting materials. You may use any other inorganic reagents you choose and organic reagents that don't get incorporated into the final product, such as NaOMe, NaOEt, LDA, TsCl, Ph_3P, 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.

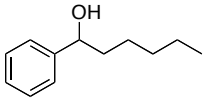
a.



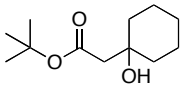
b.



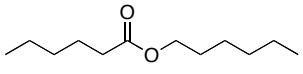
c.



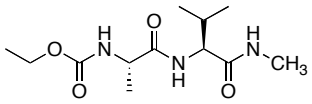
d.



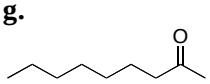
e.



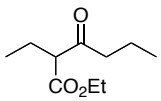
f.



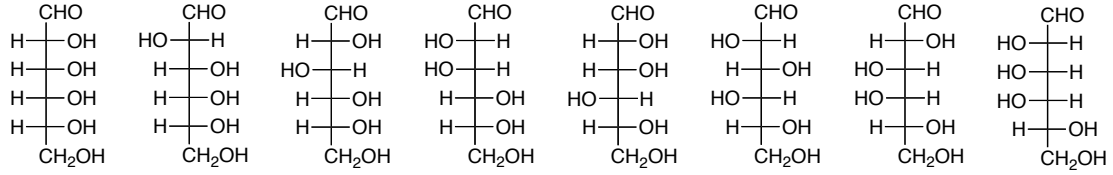
g.

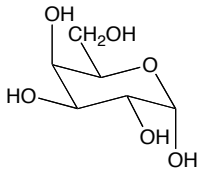


h.

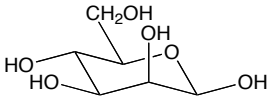


6. Under each drawing write the name of the corresponding structure. If there is stereochemistry at the anomeric position, make sure to specify whether it is α or β. Fisher projections of the eight D-aldhexoses are provided for reference. (24 points)





Name: _____



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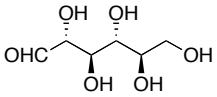

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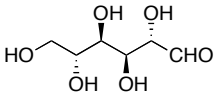

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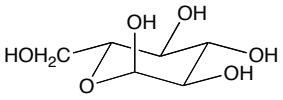

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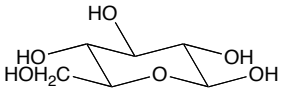
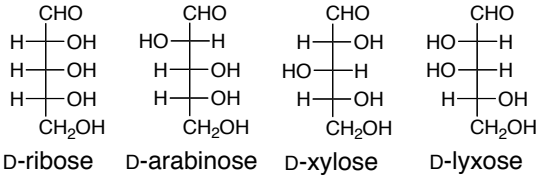
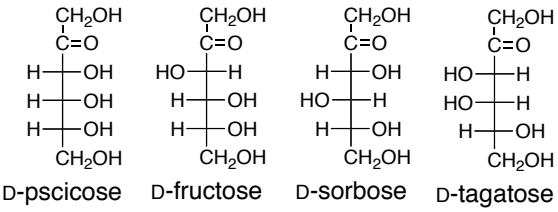


Name: _____

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)

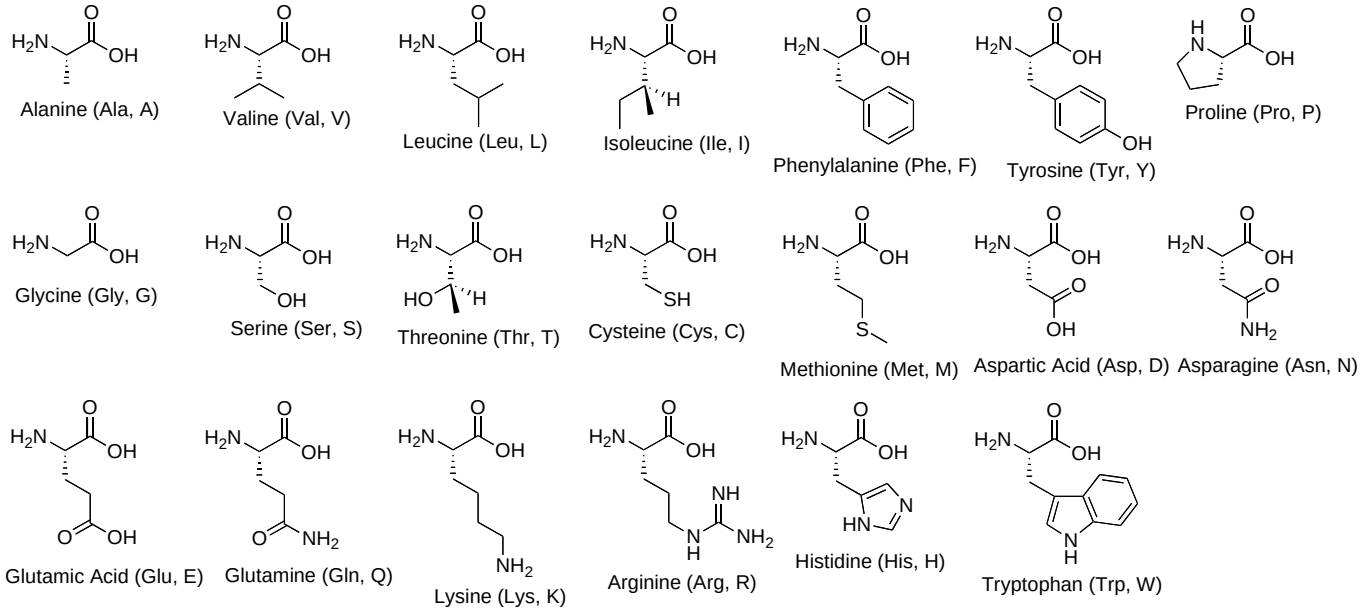




a. Write the names of the two D-aldohexoses that form from the when D-ribose is subjected to Kiliani-Fischer synthesis: _____ and _____

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).

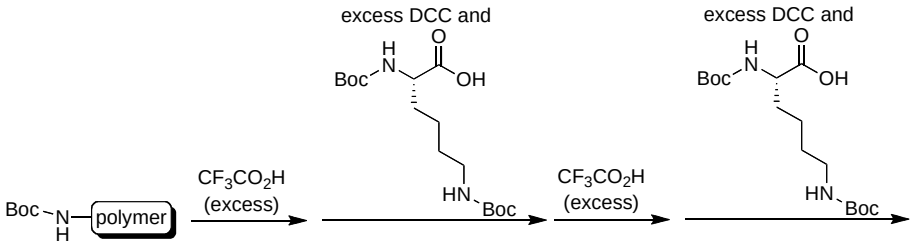
b. The amino acids isoleucine and threonine have stereogenic centers in the side chains, as well as at the α-carbon. Draw the structure of the diastereomer of isoleucine, which is called allo-isoleucine.

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:



write the structure of the core of the MAP peptide attached to the polymer resin

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 diketopiperzine and has a molecular formula $C_4H_6N_2O_2$.)

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