CHEM 347 – Organic Chemistry II (for Majors)

Instructor: Paul J. Bracher

Quiz #5

Due in Monsanto Hall 103 by:

Monday, April 28th, 2014, 5:00 p.m.

Student Name (Printed)	
Student Signature	

Instructions & Scoring

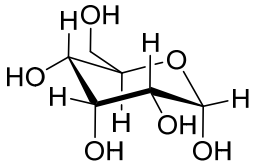
- This quiz must be turned in by the due date listed above.
- You are allowed access to any materials you wish and may discuss the questions with other students.
- Place your answers on the official answer sheet. If you print your own, please print it back-to-back on a single sheet of paper.
- Your quiz may be photocopied.

Problem	Points Earned	Points Available
I		28
II		17
III		21
IV		16
V		18
TOTAL		100

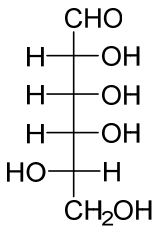
Please write your answers on an answer sheet and not in this booklet

Problem I. Multiple choice (28 points total; +4 points for a correct answer, +1 points for an answer intentionally left blank, and 0 points for an incorrect answer.) For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

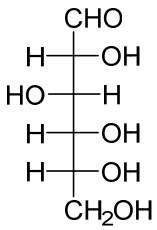
(1) _____ The pyranose **A** is equivalent to the aldohexose represented by which of the Fischer projections below?



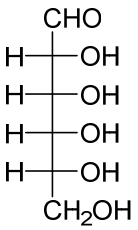
A



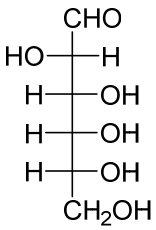
(a)



(b)



(c)

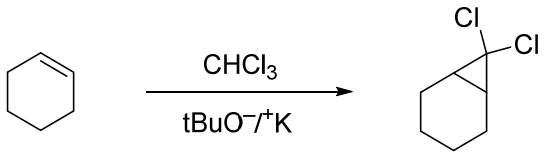


(d)

none of the above

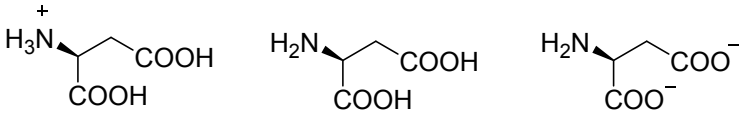
(e)

(2) _____ Which of the following statements best describes the following reaction?



(a) the *tert*-butoxide serves as a catalyst
(b) the mechanism involves a carbanion intermediate
(c) an intermediate possesses a neutral carbon atom that lacks a full octet
(d) statements (b) and (c) are both correct
(e) statements (a), (b), and (c) are all correct

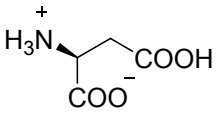
(3) _____ What structure represents the predominant form of the amino acid Asp when it is dissolved in an aqueous medium buffered at pH 7? You'll want to know Asp's pK_{a1} = 2.10, pK_{a2} = 3.86, and pK_{a3} = 9.82.



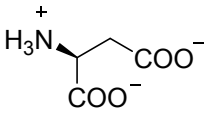
(a)

(b)

(c)

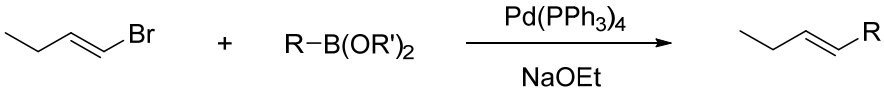


(d)



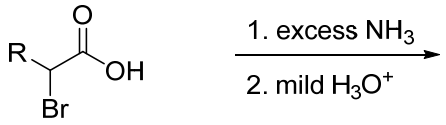
(e)

(4) _____ Which of the following is <u>not</u> a correct statement about the reaction shown below?



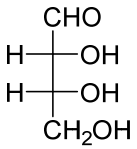
(a) the mechanism involves an oxidative addition to the palladium atom
(b) the mechanism involves a reductive elimination to form the product
(c) the presence of base accelerates the reaction
(d) the Pd complex is present in higher concentration than the vinyl halide
(e) the reaction works better for aryl boronic esters than alkyl boronic esters

(5) _____ Rank the following amino acids in order of increasing simplicity/ease of preparation by the reaction shown below. The hardest amino acid to prepare by this method should be listed first in your answer. Assume the R group is the natural side chain of the amino acid without any modification.

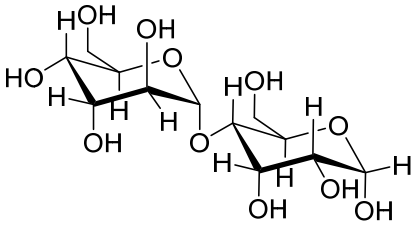


(a) proline < cysteine < phenylalanine
(b) phenylalanine < proline < cysteine
(c) phenylalanine < cysteine < proline
(d) cysteine < proline < phenylalanine
(e) proline < phenylalanine < cysteine

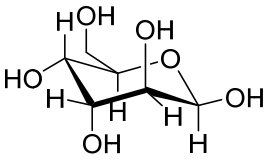
(6) _____ How many of the carbohydrates below will be oxidized by Tollens' reagent to produce a silver mirror on the side of the reaction vessel?



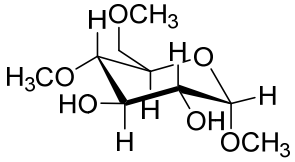
B



C



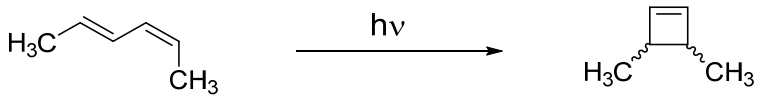
D



E

(a) zero
(b) one
(c) two
(d) three
(e) four

(7) _____ Which of the following statements best describes the photochemical electrocyclic ring closure of (*2E*,*4Z*)-2,4-hexadiene?



(a) the reaction produces two different products
(b) the reaction produces the same product with light as with heat
(c) the reaction proceeds with a disrotatory mechanism
(d) statements (a) and (c) are both correct
(e) statements (a), (b), and (c) are all correct

Problem II. Structural determination of a carbohydrate (17 points). On your way to take an IR spectrum of a pure sample of D-glyceraldehyde, you are abducted by an overweight alien with bad breath and sandals. When you arrive on his home planet, the alien assigns you the task of determining the structure of a compound their species calls Q-billibop. You are given access to a laboratory and you discover the following:

1. Q-billibop is an aldopentose.

2. Treatment of Q-billibop with HNO_3 produces a compound that is optically active.

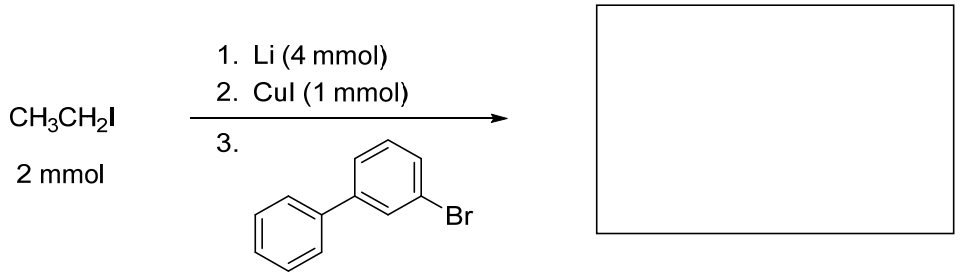
3. Subjecting Q-billibop to the Kiliani-Fischer Synthesis (1. NaCN, 2. H_2, Pd-$BaSO_4$, 3. mild H_3O^+) produces two new compounds that can be separated and purified. Both compounds are optically active, but one of these compounds loses its optical activity when treated with HNO_3.

4. Subjecting Q-billibop to two rounds of Wohl degradation produces an aldotriose that melts at the same temperature as your sample of D-glyceraldehyde, but rotates plane-polarized light in the opposite direction.

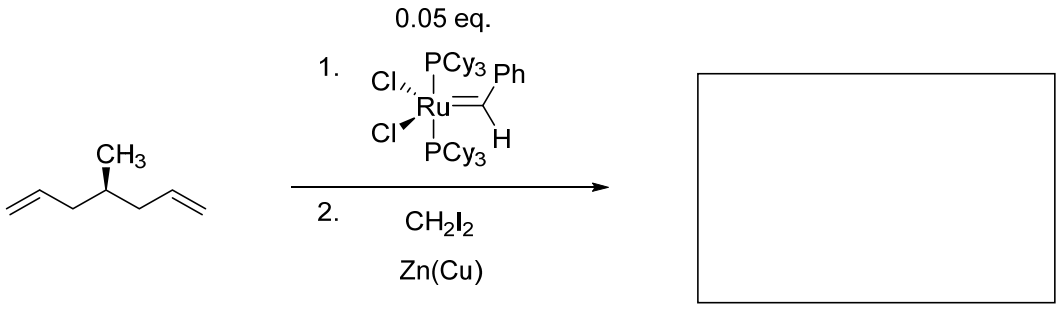
Draw a Fischer projection of Q-billibop and show your work for how you determined the stereochemistry of its chiral carbons.

Problem III. Reactions (21 points). The following chemical reactions are missing their starting materials, products, or reagents. Write the missing compounds into the empty boxes below, as appropriate. For missing products, draw the single organic product that you expect to be produced in the highest yield among all of the possibilities. In some cases, there will be more than one correct answer that will merit full credit.

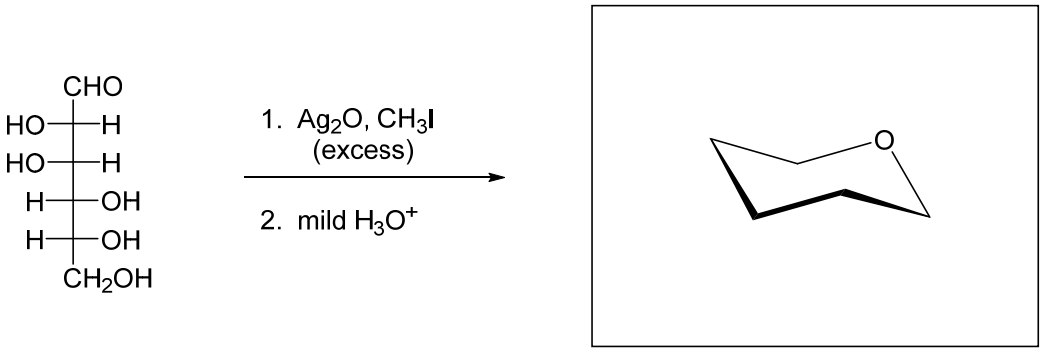
(1) (7 points)



(2) (7 points)

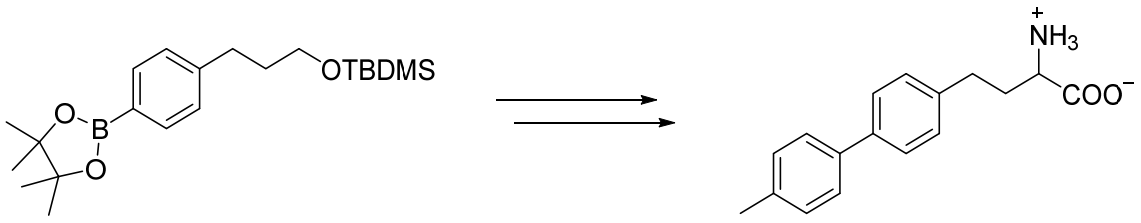


(3) (7 points)



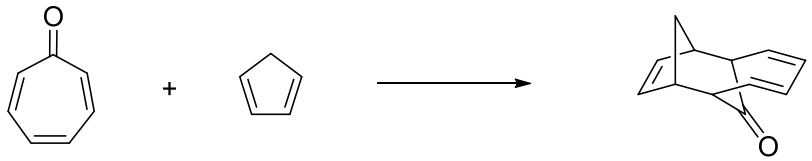
(fill in the rest of this pyranose structure)

Problem IV. Synthesis (16 points). Design an efficient synthesis of amino acid **G** from compound **F** and any other materials you wish. Do not worry about stereoselectivity—you can produce a racemic mixture of the final product.



F **G**

Problem V. Pericyclic Reactions (18 points). Consider the cycloaddition reaction depicted below:



J **K** **L**

(a) Classify the reaction as an [m+n] cycloaddition. Draw all of the molecular orbitals for the two π systems that react to form the new ten-atom ring. Construct these molecular orbitals by showing permutations of atomic p orbitals interacting constructively or destructively. Use different colors or shading to indicate the wavesigns of the orbital lobes. (For an example, see slide 8 of the lecture 34 slides.)

(b) Would you expect this reaction to proceed thermally (with heat), photochemically (with light), or both ways? Explain why in one or two sentences.