CHEM 346 - Organic Chemistry I - Fall 2014

Instructor: Paul Bracher

Hour Examination #3

Wednesday, November 12th, 2014 6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	
Student Signature	

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front and back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		25
II		24
III		21
IV		10
V		20
TOTAL		100

This exam focuses on Chapters 9 through 12 in Janice Smith's Organic Chemistry, 4th ed.

Problem I. Multiple choice (25 points total; +5 points for a correct answer, +2 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) _____ What is the best name for the <u>major product</u> of the reaction shown below?

$$\begin{array}{c} H \\ \hline \\ CI \\ \end{array} \begin{array}{c} \text{1 eq. H}_2 \\ \hline \\ \text{Lindlar's} \\ \text{catalyst} \end{array} ?$$

Α

- (a) (3Z,7Z)-4-chloro-3-methyl-3,7-octadiene
- (b) (1Z,5Z)-5-chloro-6-ethyl-1,5-heptadiene
- (c) (1E,5Z)-5-chloro-6-methyl-1,5-octadiene
- (d) (1*Z*,5*E*)-5-chloro-6-methyl-1,5-octadiene
- (e) (Z)-5-chloro-6-methyl-1,5-octadiene

(2) _____ Which of the following compounds would you expect to observe as the major product of the following reaction?

$$\begin{array}{ccc} O & & & 1. \text{ LiAlH}_4 \\ H & \text{CH}_3 & & & \hline \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

В

- (a) 2-methyl-2-propanol
- (b) 2-methyl-1-propanol
- (c) 2-methoxypropane
- (d) 1-methoxypropane
- (e) 2-methyl-propane

(3)

What statement best describes the role of the first set of reagents in the following preparation of compound **D**?

OH
$$\frac{1. \text{ TsCl, pyridine}}{2. \text{ K}^+ / \text{CN}}$$

- (a) it prevents the formation of a primary carbocation
- (b) it converts the hydroxyl group into a good leaving group
- (c) it deprotonates the hydroxyl group to make the alkoxide
- (d) it gives an alkene intermediate by E2 elimination
- (e) it protonates the hydroxyl group which then leaves as water

(4)

What statement does <u>not</u> accurately describe at least one step or aspect of the mechanism for the reaction drawn below?

$$\begin{array}{c} & & & Br \\ \hline \end{array}$$

- (a) a bromide anion serves as a nucleophile
- (b) the π bond on the alkene serves as a nucleophile
- (c) the addition of the Br groups takes place with syn geometry
- (d) an intermediate with a three-membered ring forms
- (e) the final product is saturated (degree of unsaturation = zero)

(5) _____ Which of the following routes is the most appropriate to prepare pentanal (**F**) from 1-pentene (**E**)?

(a)
$$\begin{array}{c|c} H_2SO_4 & TsCl & tBuOK \\ \hline H_2O & pyridine & tBuOH \\ \end{array}$$

(b)
$$\frac{1. \text{ BH}_{3} \cdot \text{THF}}{2. \text{ H}_{2}\text{O}_{2}, \text{ NaOH}} \xrightarrow{\text{K}_{2}\text{Cr}_{2}\text{O}_{7}} \frac{\text{K}_{2}\text{Cr}_{2}\text{O}_{7}}{\text{H}_{2}\text{SO}_{4}, \text{H}_{2}\text{O}}$$

(c)
$$H_2SO_4 \longrightarrow K_2Cr_2O_7 \longrightarrow H_2SO_4, H_2O$$

(e)
$$\frac{SOCl_2}{pyridine} \frac{1. O_3}{2. S(CH_3)_2}$$

Problem II. Mechanisms (24 points).

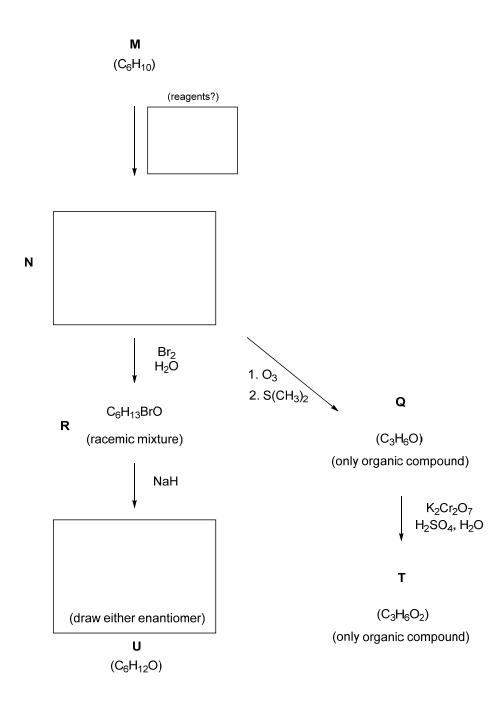
(1) (16 points) Draw a sensible mechanism for the following reaction. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reaction.

$$H_2SO_4$$
 H_2SO_4
 H

(2) (8 points) Draw a sensible mechanism for the following reaction. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reaction.

Problem III. (21 points) Roadmap Problem. Provide structures for compounds **N** and **U**, as well as the reagents for the conversion of $\mathbf{M} \to \mathbf{N}$. Do not write the structures of the other compounds on your answer sheet.

Compound \mathbf{M} has the molecular formula C_6H_{10} . When \mathbf{M} is treated with a set of reagents (that you must identify), it is converted to compound \mathbf{N} . When \mathbf{N} is subjected to ozonolysis with a reductive workup, compound \mathbf{Q} is the only organic product. It has the molecular formula C_3H_6O and yields compound \mathbf{T} ($C_3H_6O_2$) when treated with aqueous acidic dichromate. When \mathbf{N} is treated with bromine in water, a racemic mixture of products with the molecular formula C_6H_{13} BrO is produced. When a dilute solution of this racemic mixture is treated with sodium hydride, a racemic mixture of compound \mathbf{U} of molecular formula $C_6H_{12}O$ is produced. On your answer sheet, provide structures for compounds \mathbf{N} and \mathbf{U} (only one enantiomer necessary) and the reagents for the conversion of \mathbf{M} to \mathbf{N} that are consistent with these data.



Problem IV. Explanations (10 points). Your orgo lab TA hands you a bottle of cyclopentanol and asks you to synthesize cyclopentene. You pour some of the cyclopentanol into a round-bottomed flask, attach a condenser, and heat the compound using the maximum setting on your heating mantle. Name two things you can add or do to maximize your percent yield of **X** by the end of your two-hour lab period. (Note: there are more than two correct answers)

Problem V. Synthesis (20 points). Provide a synthetic route—i.e, a sequence of reactions—to produce hexanal (**Z**) from acetylene (**Y**) and any reagents you need so long as no synthon/reagent supplies more than two carbon atoms (of the six) in the final product.