CHEM 347 – Organic Chemistry II (for Majors)

Instructor: Paul J. Bracher

Hour Examination #3

Wednesday, April 9th, 2014 6:30–8:30 p.m.

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- If you wish, you may use two sheets (front-andback) of handwritten notes and a plastic model kit.
- You may not use electronic devices or communicate with others for the duration of this exam.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		32
II		23
III		21
IV		24
TOTAL		100

Problem I. Multiple choice (32 points total; +4 points for a correct answer, +1 point 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) Which of the following compounds is the most acidic?

Which of the following conditions would be appropriate for the preparation of compound **B** from compound **A**? Assume all reagents are used in 1:1 equivalence with the starting material.

- (a) 1. LDA, -78 °C; 2. CH₃CH₂I
- (b) 1. LDA, 0 °C; 2. CH₃CH₂I
- (c) 1. NaOH; 2. CH₃CH₂Br
- (d) NaOEt, CH₃CH₂Br
- (e) all of the above conditions would work

(3) D

Which of the following reactions would <u>not</u> produce compound **C** from ethanol? Assume a 1:1 stoichiometric equivalence to ethanol unless noted otherwise.

$$\searrow_0$$

C

- (a) ethanol + acetic anhydride (CH₃COOCOCH₃) + pyridine
- (b) ethanol + acetic acid (CH₃COOH) + catalytic H₂SO₄
- (c) ethanol + acetyl chloride (CH₃COCl) + pyridine
- (d) ethanol + acetamide (CH₃CONH₂) + pyridine
- (e) all of these reactions would produce C in good yield

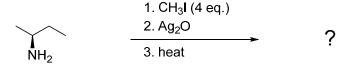
(4) D

Which of the arrows points to the most acidic hydrogen atom(s) in compound **D**?

D

- (a) i
- (b) ii
- (c) iii
- (d) iv
- (e) v

(5) A Which of the following compounds is the <u>major</u> product of the reaction shown below?



- (a) 1-butene
- (b) cis-2-butene
- (c) trans-2-butene
- (d) 1-butanone
- (e) 2-butanone
- (6) B Which of the following compounds will <u>not</u> generate carbon dioxide (CO₂) when heated in aqueous acid?

HO
$$CH_3$$
 $COOH_3$ $COOH_3$ $COOH_4$ $COOH_4$

(7) D

What is the minimum number of molecules of amine **E** that should be added to a solution of **1** mmol of **F** to effect complete conversion of **F** to **G**? Assume there is nothing else in the flask besides an unreactive solvent.

- (a) 1 mmol
- (b) 2 mmol
- (c) 3 mmol
- (d) 4 mmol
- (e) 5 mmol

(8) A

Which of the following reaction mixtures will give the <u>fewest</u> different products of aldol reactions?

$$\begin{array}{c} \text{O} \\ \hline \\ \text{CH}_3\text{OH} \end{array}$$

Problem II. Mechanism (23 points).

(a) (17 points) Draw a sensible mechanism for the conversion of **H** and **J** to **K** in the presence of sodium ethoxide. Remember to use proper "curved arrow notation" to account for the movement of electrons in the making and breaking of bonds. Show all intermediates and all significant resonance forms that account for the stability of these intermediates in the reaction.

(b) (6 points) Draw a sensible mechanism for the tautomerization of **L** to **M** in aqueous acid. Remember to use proper "curved arrow notation" to account for the movement of electrons in the making and breaking of bonds. Show all intermediates and all significant resonance forms that account for the stability of these intermediates in the reaction.

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.

(a) (7 points)

$$H_3CO$$
OCH₃

$$\frac{1. \text{ NaOCH}_3}{2. \text{ excess HCI, H}_2O, \text{ heat}}$$

$$(C_5H_8O)$$

(b) (7 points)

(c) (7 points)

Problem IV. Synthesis (24 points). Design efficient synthetic routes for compounds **Q** and **S** using the indicated starting materials. You may use any other reagents or molecules you wish.

(a) (12 points)

$$P \qquad Q$$

$$CH_3 \qquad H_3C \qquad H_2 \qquad NH_2 \qquad NaNO_2 \qquad H_2 \qquad H_3C \qquad HCI \qquad HCI \qquad HCI \qquad H_3C \qquad COOH$$

(b) (12 points)

reductive amination