CHEM 347 – Organic Chemistry II (for Majors)

Instructor: Paul J. Bracher

Quiz #3

Due in Monsanto Hall 103 by: Friday, February 28th, 2014, 7:00 p.m.

Student Name (Printed)	Solutions
Student Signature	N/A

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		24
II		20
III		21
IV		15
V		20
TOTAL		100

Problem I. Multiple choice (24 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.



How many millimoles (mmol) of methylmagnesium bromide would need to be added to a solution of 1 mmol of compound **A** to carry out the following transformation?

$$H_3CO$$
OH
$$\begin{array}{c}
1. CH_3MgBr \\
\hline
2. H_3O^+
\end{array}$$
HO
OH

- (a) 1 mmol
- (b) 2 mmol
- (c) 3 mmol
- (d) 4 mmol
- (e) 4.01 mmol
- The first equivalent of methylmagnesium bromide will deprotonate the alcohol. The second and third equivalents will add to the carbonyl group.
- (2) A

Which of the following compounds has the highest boiling point?

- (a) pentanoic acid
- (b) pentane
- (c) pentanal
- (d) 2,2-dimethylpropanoic acid
- (e) 2,2-dimethylpropanal
- (3) <u>E</u>

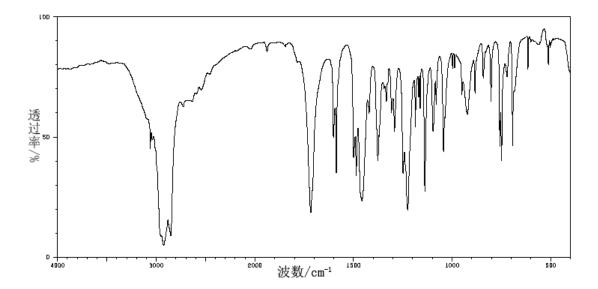
Which of the following reactions would <u>not</u> produce benzoic acid after workup with mildly acidic water?

- (a) propylbenzene + potassium permanganate
- (b) benzonitrile (PhCN) + H₂SO₄/H₂O/heat
- (c) benzyl alcohol + K₂Cr₂O₇/H₂SO₄
- (d) phenylmagnesium bromide + carbon dioxide
- (e) all of these reactions will produce benzoic acid after workup

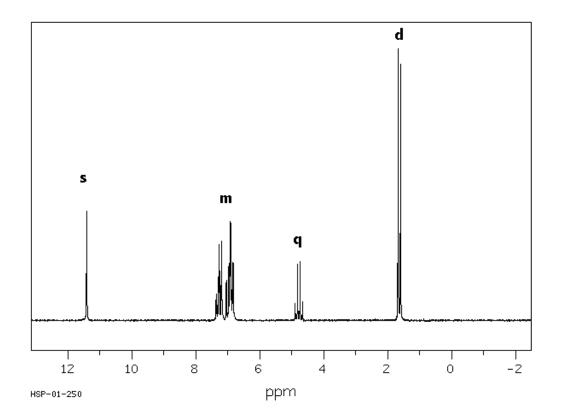
(4) <u>E</u>

Which of the following structures is consistent with the IR and NMR data provided below?

IR Spectrum



¹H NMR Spectrum (in CDCl₃)



$$CHO$$
 CHO
 CHO

(5) Which of the following molecules is the strongest acid?

$$(a) \qquad (b) \qquad H_2N \qquad (c)$$

$$(a) \qquad (b) \qquad (c)$$

$$H_3CO OCH_3 \qquad (d) \qquad (e)$$

(6) When **B** is dissolved in ethanol with a small amount of tosic acid, the major product is **C**?

- (a) true
- (b) false
- The final product will be the acetal with two ethoxy groups, as the concentration of ethanol is large in comparison to the starting material.

Problem II. Mechanism (20 points). Draw a sensible mechanism for the transformation shown below. Remember to use proper "curved arrow notation" to account for the movement of electrons in the making and breaking of bonds. Draw all intermediates, including any additional resonance forms that account for the stability of each intermediate. Show all steps—including proton transfers! (ref: **Dai**. *Tetrahedron* **2011**, *67*, 179–192)

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) (9 points)

(2) (5 points)

$$CH_2Li$$

$$2. H_3O^+$$
OH

(3) (7 points)

• A previous version of this quiz used 2 equivalents of the organocuprate reagent, but the product would have been the same. These reagents undergo very sluggish addition to carbonyl groups.

Problem IV. Synthesis (15 points). Design an efficient synthesis of compound **D** from the indicated starting material and any other reagents you wish.

$$\begin{array}{c} O \\ O \\ O \end{array}$$

$$= \begin{array}{c} O \\ O \\ O \end{array}$$

$$\begin{array}{c} O \\ O \\ O \end{array}$$

ÓН

Problem V. Synthesis (20 points). Design an efficient synthesis of compound **E** using the indicated starting material as the <u>only</u> source of carbon atoms in the product.

$$H_{3}CO$$

$$E$$

$$H_{3}CO$$

$$1. LiAlH_{4}$$

$$2. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$2. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$2. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$2. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$3. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$4. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$5. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$1. DIBAL-H$$

$$1. DIBAL-H$$

$$2. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$3. H_{3}O^{+}$$

$$1. DIBAL-H$$

$$4. H_{3}O^{+}$$

$$4. H$$

mild acid