

**CHEM 343 –Principles of Organic Chemistry II – Summer 2014**

Instructor: Paul J. Bracher

**Hour Examination #2**Tuesday, July 15<sup>th</sup>, 2014

8:00–9:15 a.m. (in class)

Student Name (Printed)	Solutions
Student Signature	N/A

**Instructions & Scoring**

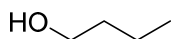
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use one sheet of handwritten notes and a plastic model set. You must turn in your notes with your examination.
- You may not communicate with others during this examination, and you may not access electronic devices.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		35
II		24
III		21
IV		20
TOTAL		100

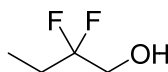
Questions, **Required Information**, **Supplementary Information**

**Problem I.** Multiple choice (35 points total; +5 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.

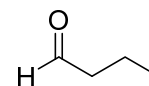
- (1)     C     Which of the following compounds is the weakest Brønsted–Lowry acid (i.e., has the highest  $pK_a$ )?



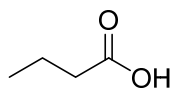
(a)



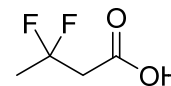
(b)



(c)

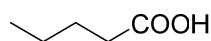


(d)



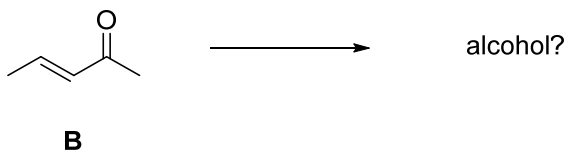
(e)

- (2)     E     Which of the following statements is not true of pentanoic acid (**A**)?

**A**

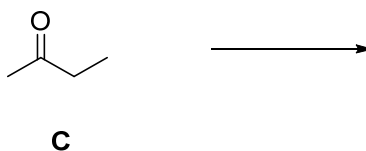
- (a) will produce 1-pentanol following treatment with 1. excess  $\text{LiAlH}_4$ , 2.  $\text{H}_3\text{O}^+$
- (b) will react with  $\text{CH}_3\text{MgBr}$  to produce methane
- (c) can be separated easily from 3-pentanone by extraction
- (d) has a singlet signal in its  $^1\text{H}$  NMR spectrum downfield (left of)  $\delta$  8.0
- (e) all of the above statements are true

- (3)       <sup>D</sup> Which of the following sets of conditions will not produce an alcohol as the major product expected from compound **B**?



- (a) excess H<sub>2</sub>, Pd-C
- (b) 1. NaBH<sub>4</sub>; 2. mild H<sub>3</sub>O<sup>+</sup>
- (c) 1. CH<sub>3</sub>Li; 2. mild H<sub>3</sub>O<sup>+</sup>
- (d) 1. (CH<sub>3</sub>)<sub>2</sub>CuLi; 2. mild H<sub>3</sub>O<sup>+</sup>
- (e) all of the above conditions will produce alcohols from **B**

- (4)       <sup>C</sup> Which of the following sets of reagents and conditions will not produce two stereoisomers—enantiomers or diastereomers—of the major product expected from 2-butanone (**C**)?

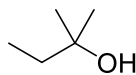
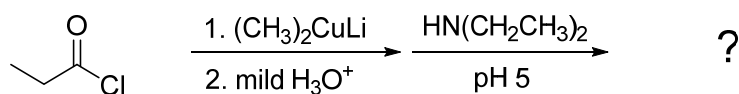


- (a) excess H<sub>2</sub>, Pd-C
- (b) CH<sub>3</sub>NH<sub>2</sub>, pH 5
- (c) 1. CH<sub>3</sub>Li; 2. mild H<sub>3</sub>O<sup>+</sup>
- (d) Ph<sub>3</sub>PCHCH<sub>3</sub> (this is an ylide)
- (e) 1. LiAlH<sub>4</sub>; 2. mild H<sub>3</sub>O<sup>+</sup>

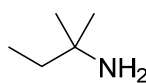
(5)     E     Which of the following reactions will not generate pentanoic acid?

- (a) pentanal with  $K_2Cr_2O_7$ ,  $H_2SO_4$
- (b) 1-pentanol with  $K_2Cr_2O_7$ ,  $H_2SO_4$
- (c) 1-bromobutane with 1. Mg, ether; 2.  $CO_2$ ; 3. mild  $H_3O^+$
- (d) 1-hexyne with 1.  $O_3$ ; 2.  $H_2O$
- (e) all of the above will generate pentanoic acid

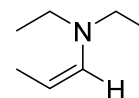
(6)     D     What is the major product expected of the sequence of reactions below?



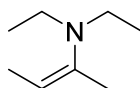
(a)



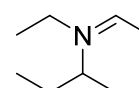
(b)



(c)



(d)



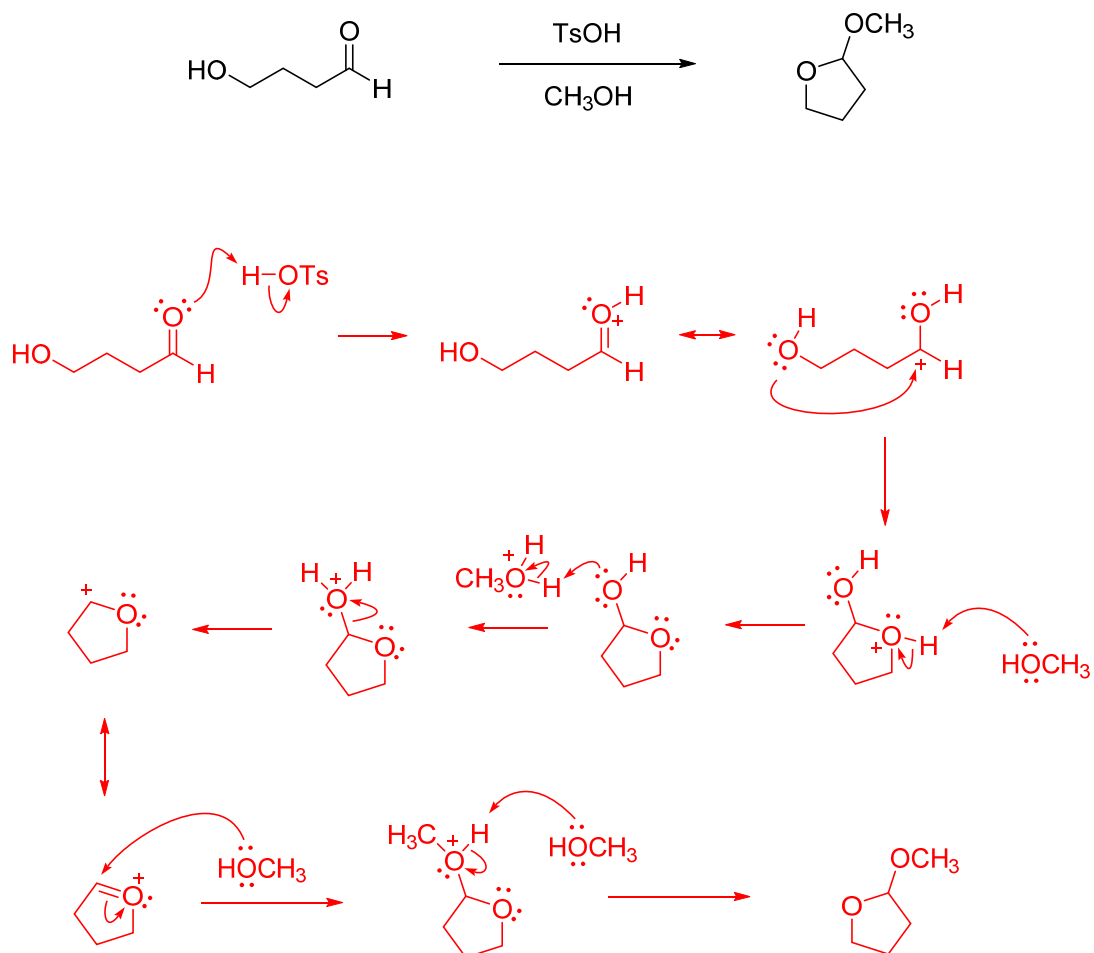
(e)

(7)     A     Compound **D** has a signal in its  $^1H$  NMR spectrum at  $\delta$  9.7 that does not disappear upon addition of  $D_2O$ . The compound produces a silver deposit on the walls of its flask upon treatment with Tollens' reagent (aqueous  $[Ag(NH_3)_2]NO_3$ ,  $NaOH$ ). Which of the following compounds is consistent with the identity of **D**?

- (a) butanal
- (b) 1-butene
- (c) butanoic acid
- (d) 2-butanone
- (e) 1-butyne

**Problem II. Mechanism (24 points).**

(1) (18 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.

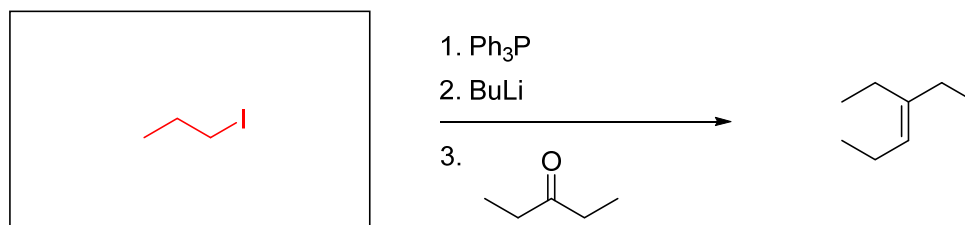


(2) (6 points) Give two reasons why a drop of vinegar (an aqueous solution of acetic acid) would make a worse choice of catalyst for this reaction than adding a crystal of tosic acid ( $\text{TsOH}$ ,  $\text{H}_3\text{CC}_6\text{H}_4\text{SO}_3\text{H}$ ). Note: There are more than two good reasons to choose from.

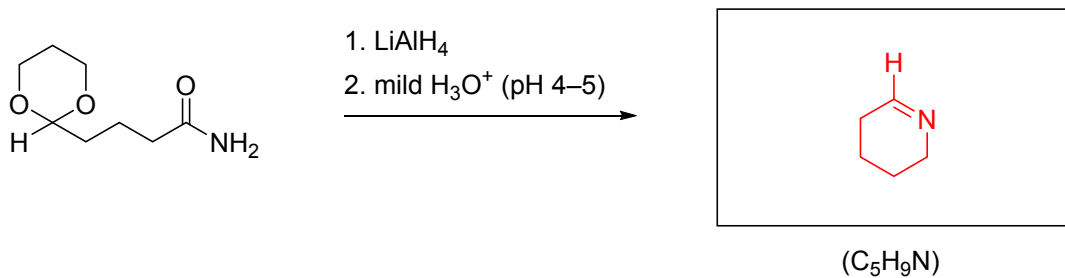
- Vinegar contains water, which is a byproduct of the above reaction. Adding water would help drive the equilibrium to the left, reducing the yield of the product.
- Acetic acid ( $\text{p}K_a = 4.8$ ) is a weaker acid than tosic acid ( $\text{p}K_a = -2.8$ ).
- Acetic acid has a carbonyl group and is capable of reacting under the conditions of the experiment.

**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.

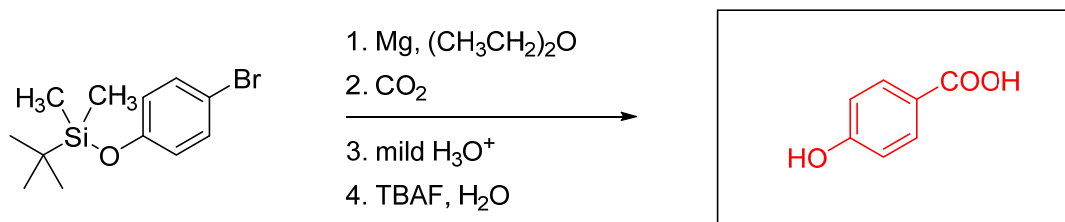
(1) (6 points)



(2) (8 points)



(3) (7 points)



**Problem IV.** Synthesis (20 points). Design an efficient synthesis of compound **E** from the indicated starting materials and any other reagents you wish. Note: You can accomplish this synthesis in five steps.

