

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

Instructor: Paul J. Bracher

**Quiz #2**Friday, July 11<sup>th</sup>, 2014

6:00 p.m. (in Monsanto Hall 103)

Student Name (Printed)	Solutions
Student Signature	N/A

**Instructions & Scoring**

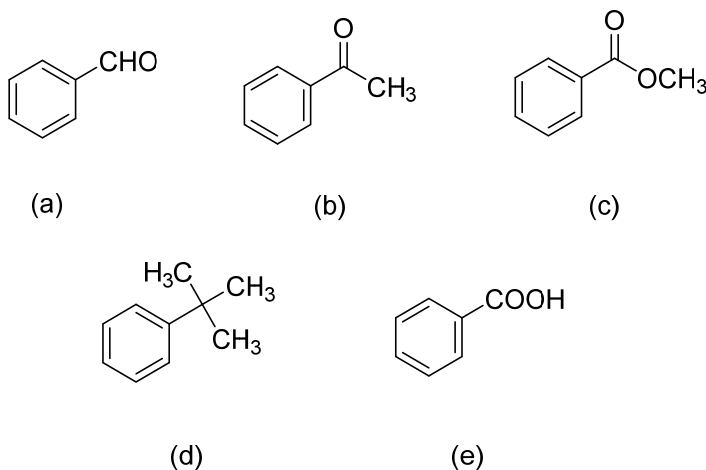
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use any resources you wish and collaborate with others.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		28
II		21
III		21
IV		30
TOTAL		100

**Questions, Required Information, Supplementary Information**

**Problem I.** Multiple choice (28 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)      <sup>B</sup> Which of the following compounds is expected to give rise to an NMR spectrum that includes a singlet peak near 2.5 ppm?



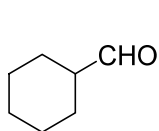
- (2)      <sup>D</sup> Which of the following mixtures would be the easiest to separate by extraction?

- (a) 2-pentanone and 3-pentanone
- (b) 3-chloropentanal and pentanal
- (c) pentanal and 2-pentanone
- (d) pentanoic acid and 2-pentanone
- (e) pentanoic acid and benzoic acid

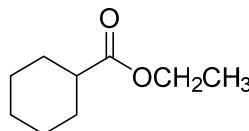
- (3)      <sup>C</sup> Which of the following compounds has the highest  $pK_a$ ?

- (a) 2,3-difluorobutanoic acid
- (b) 3,3-dichlorobutanoic acid
- (c) 3-chlorobutanoic acid
- (d) 3-fluorobutanoic acid
- (e) 2-fluorobutanoic acid

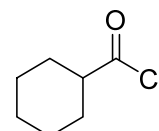
- (4)     D     Which of the following starting materials will generate a product that is different from the others' after treatment with  $\text{LiAlH}_4$  followed by work up with mild acid (1.  $\text{LiAlH}_4$ , 2. mild  $\text{H}_3\text{O}^+$ )?



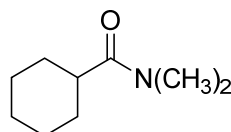
(a)



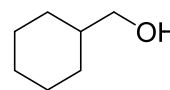
(b)



(c)

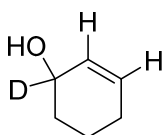
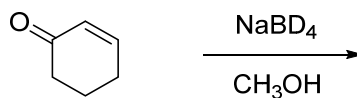


(d)

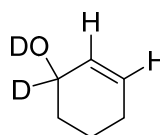


(e)

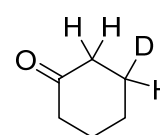
- (5)     A     What is the product of the following reaction?



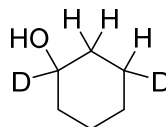
(a)



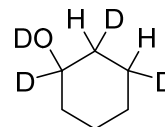
(b)



(c)

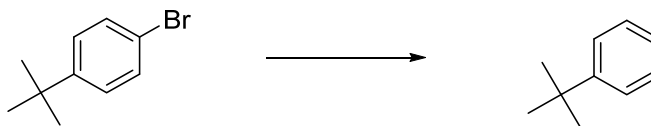


(d)



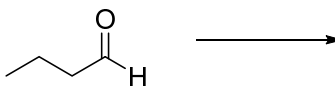
(e)

(6)       <sup>D</sup> What conditions will accomplish the following transformation?



- (a) 1.  $\text{NaBH}_4$ ,  $\text{CH}_3\text{OH}$ ; 2. mild  $\text{H}_3\text{O}^+$
- (b) 1. 2 Li; 2. mild  $\text{H}_3\text{O}^+$
- (c) 1. Mg,  $\text{O}(\text{CH}_2\text{CH}_3)_2$ ; 2.  $\text{CH}_3\text{COOH}$
- (d) both (b) and (c) will work
- (e) (a), (b), and (c) will all work

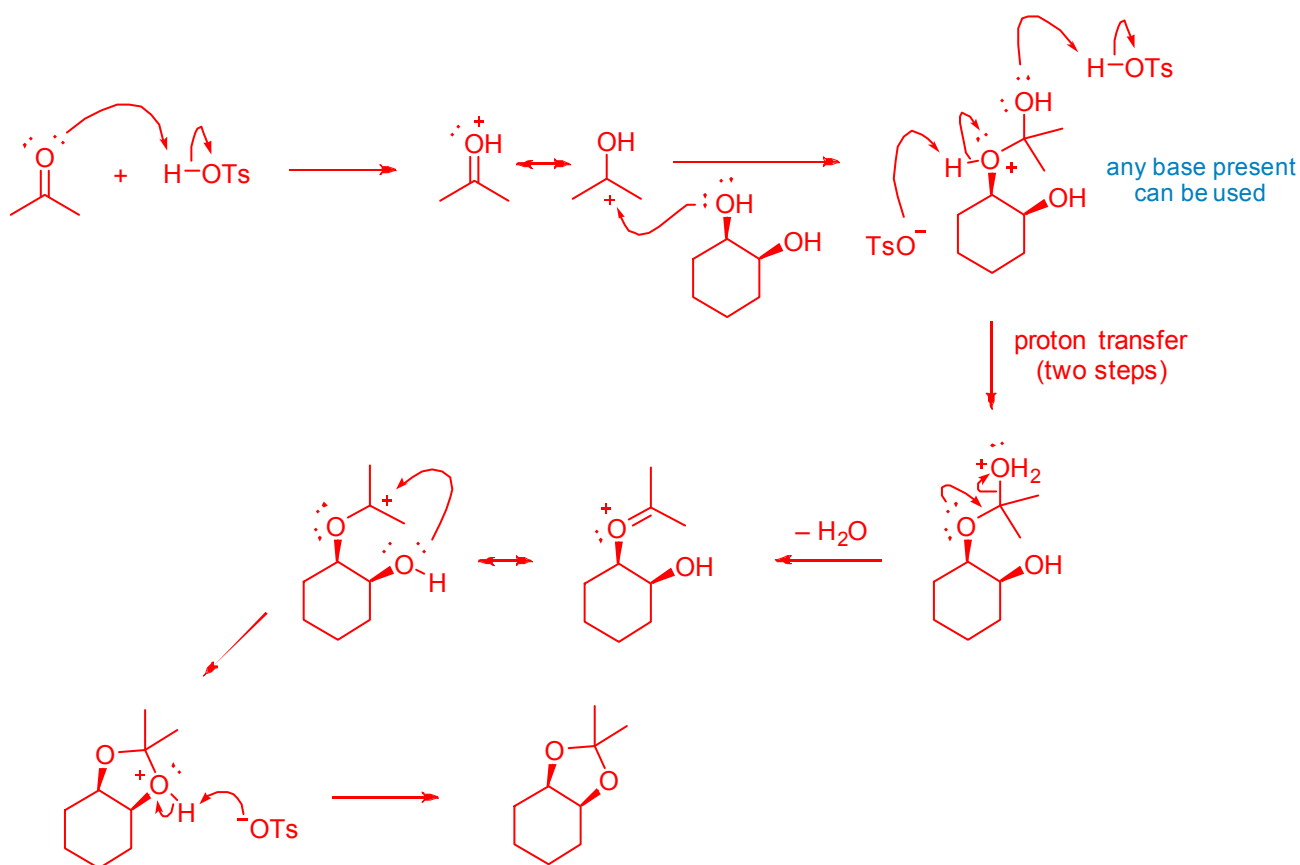
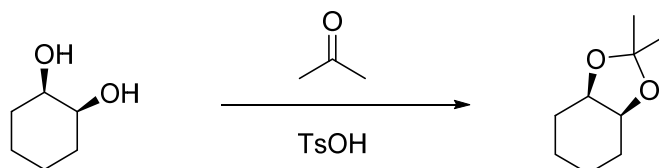
(7)       <sup>E</sup> For the reaction of butanal, which of the following reagents and conditions is not paired correctly with their expected product?



- (a) 1.  $\text{LiAlH}_4$ ; 2. mild  $\text{H}_3\text{O}^+$   $\rightarrow$  1° alcohol
- (b)  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4$   $\rightarrow$  carboxylic acid
- (c)  $\text{CH}_3\text{NH}_2$ , mild acid  $\rightarrow$  imine
- (d)  $(\text{CH}_3)_2\text{NH}$ , mild acid  $\rightarrow$  enamine
- (e) 1.  $\text{CH}_3\text{MgBr}$ ; 2. mild  $\text{H}_3\text{O}^+$   $\rightarrow$  ketone

**Problem II. Mechanism (21 points).**

(1) (15 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.

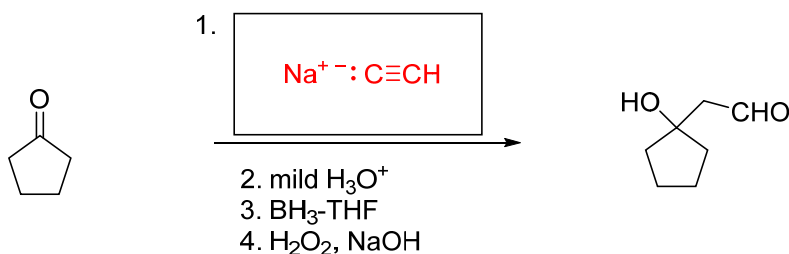


(2) (6 points) If you only had benzene, methanol, and water available in your laboratory's chemical stockroom, which of the three would you choose as a solvent to run the reaction in part (1)? Explain your choice in two or three sentences.

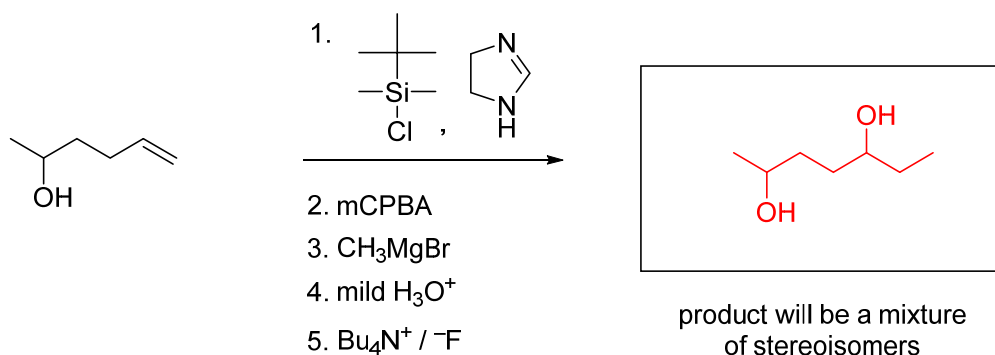
Of the three compounds available, benzene would make the best solvent. Water is a byproduct of acetal formation, so using it as a solvent would drive the equilibrium to the left instead of toward the desired products. Methanol has a hydroxyl group and will compete with the diol to form a different acetal. Benzene is not reactive under these conditions, and thus, will make a suitable solvent for 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.

(1) (7 points)



(2) (7 points)

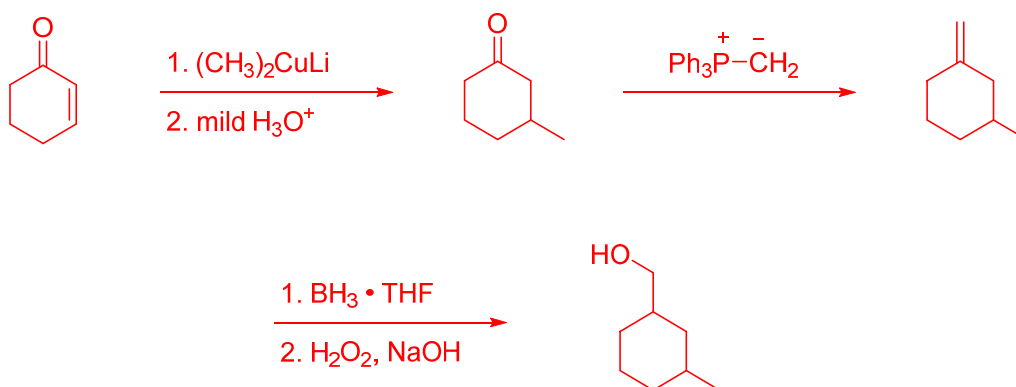
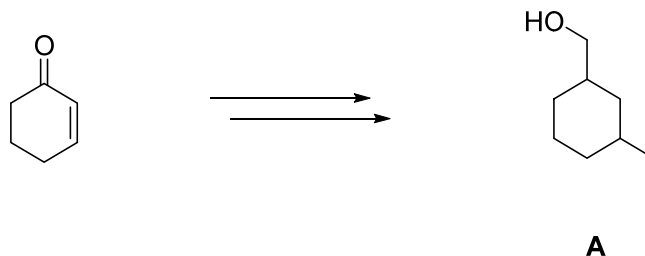


(3) (7 points)

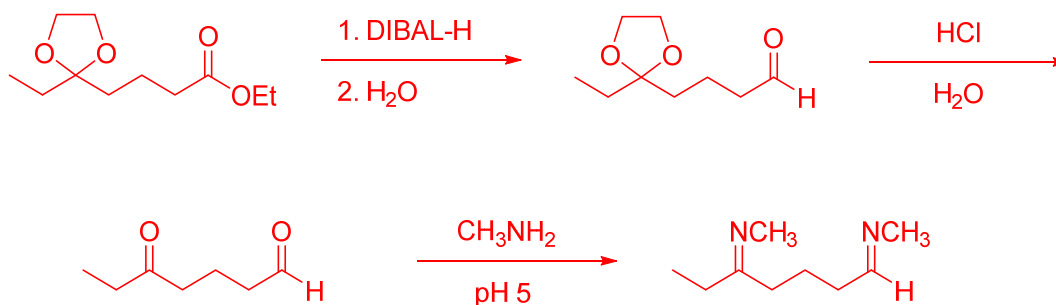
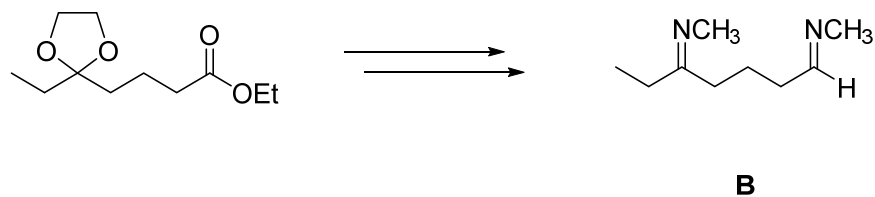


**Problem IV. Synthesis (30 points).** Design efficient synthetic routes for compounds **A** and **B** from the indicated starting materials and any other reagents you wish.

(1) (15 points) Note: Do not fret over the stereochemistry of the product.



(2) (15 points)



- Note: If you want to combine the hydrolysis of the acetal with the workup of the reduction reaction by using acid instead of H<sub>2</sub>O, that is a perfectly acceptable way to “save a step”. The reactions are run as separate steps above as a matter of clarity.