CHEM 347 – Organic Chemistry II (for Majors)

Instructor: Paul J. Bracher

Hour Examination #2

Wednesday, March 5th, 2014

5:30–8:30 p.m.

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

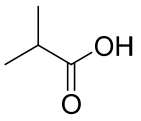
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- If you wish, you may use two sheets (front-and-back) of handwritten notes and a plastic model kit.
- You may not use electronic devices or communicate with others for the duration of this exam.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

Problem	Points Earned	Points Available
I		32
II		21
III		21
IV		26
TOTAL		100

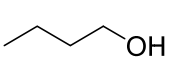
Questions, Required Information, Supplementary Information

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.

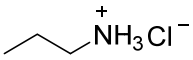
(1) A Which of the following five compounds is the strongest Brønsted–Lowry acid?



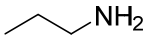
(a)



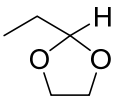
(b)



(c)

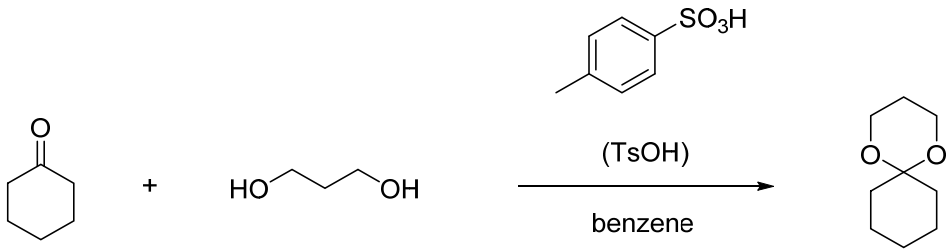


(d)



(e)

(2) C In the reaction drawn below, which of the following modifications would be the most effective means of increasing the percent yield of **C** from **A**?

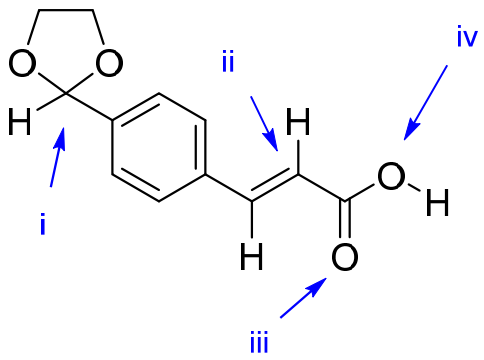


A **B** **C**

(a) increasing the concentration of TsOH
(b) increasing the concentration of cyclohexanone
(c) using a Dean–Stark apparatus to distill away water as an azeotrope
(d) using a separatory funnel to perform a Fischer ketal extraction
(e) all of the above would decrease the percent yield of **C**

- Running this reaction with a Dean–Stark apparatus allows you to distill away the water produced by the reaction. Removing water drives the equilibrium further to the right, increasing the percent yield.

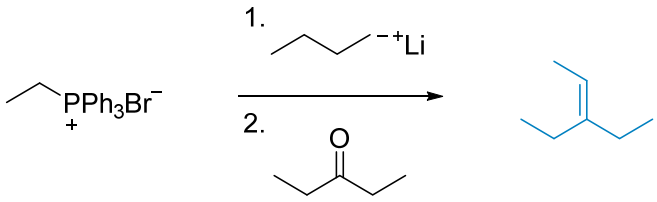
(3) A Which of the labeled atoms in compound **D** is <u>not</u> sp^2 hybridized?



D

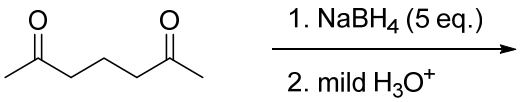
(a) i
(b) ii
(c) iii
(d) iv
(e) all four atoms are sp^2 hybridized

(4) E Which of the following compounds is <u>not</u> a product of the reaction shown below?



(a) lithium bromide
(b) triphenylphosphine oxide
(c) 3-ethyl-2-pentene
(d) butane
(e) all of the above are products of the reaction

(5) D How many different organic products (in >10% yield) are produced from **E** in the following reaction? (Hint: Be careful with your stereochemistry!)

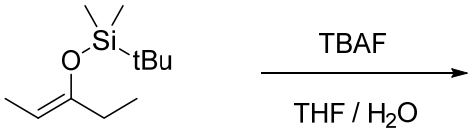


E

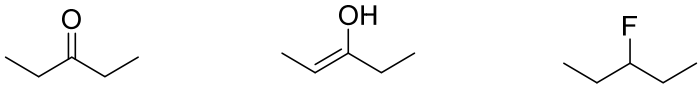
(a) zero (no reaction)
(b) one
(c) two
(d) three
(e) four

- Both carbonyl groups will be reduced to alcohols to make 2,6-heptanediol. The carbonyl carbons will become either *R* or *S* stereocenters. There are three possible combinations: *R*/*R*, *S*/*S*, and *R*/*S* (which is a meso compound equivalent to *S*/*R*).

(6) A Which of the following compounds will be the <u>major</u> product (present in highest concentration) when compound **F** is treated with a solution of tetrabutylammonium fluoride (TBAF) dissolved in a mixture of THF and water?



F



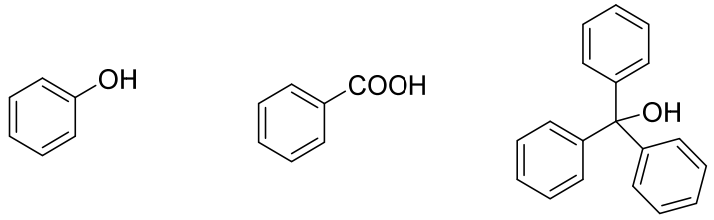
(a) (b) (c)

(d) (e)

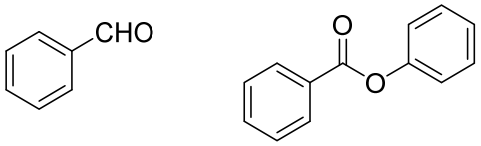
- Remember that keto (a) and enol (b) tautomers can introconvert, and the equilibrium generally favors the keto form.

(7) D

Compound **G** has an odor of marzipan. **G** produces a silver mirror on the side of the reaction vessel when treated with silver oxide in aqueous ammonium hydroxide (Tollens' reagent). The compound gives the ^{1}H NMR and IR spectra shown below. Which of the following structures is consistent with the data provided for compound **G**?

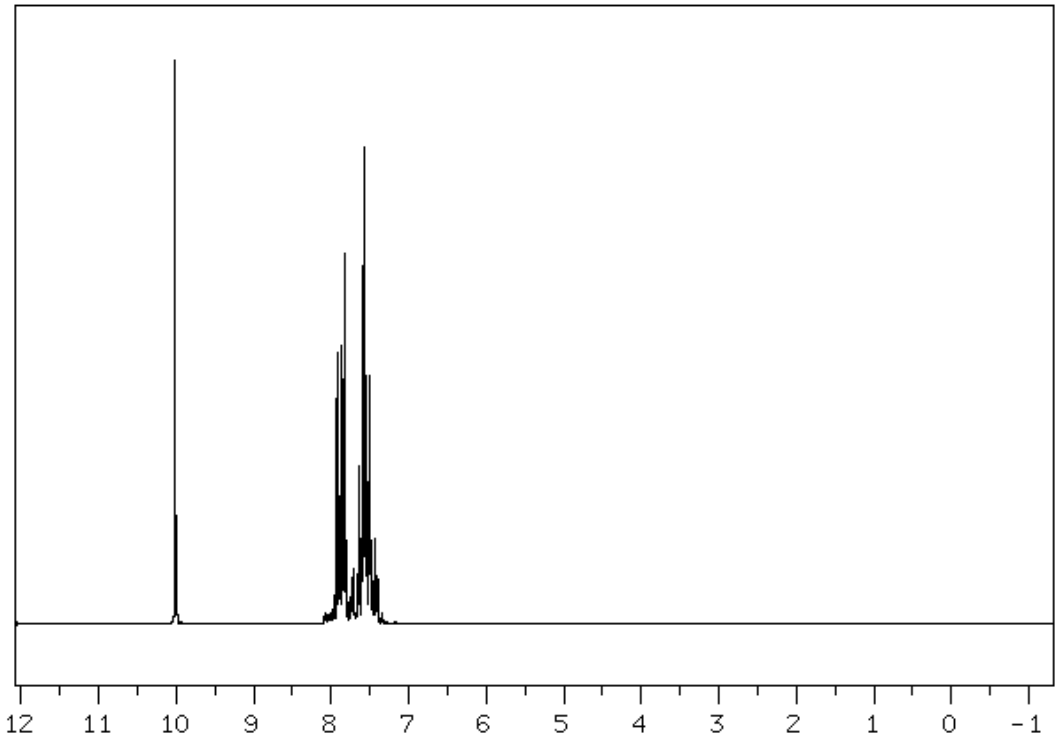


(a) (b) (c)

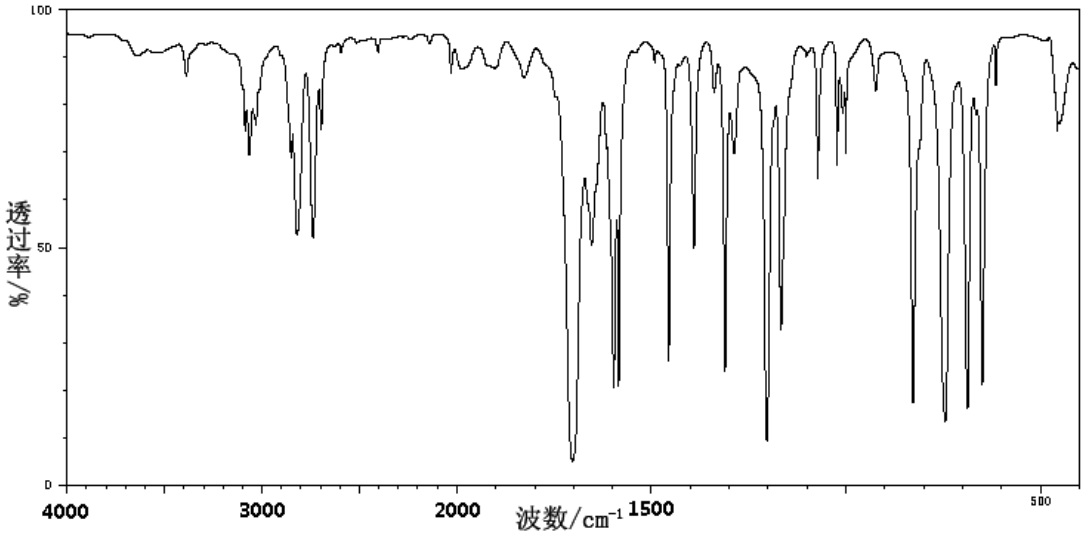


(d) (e)

^{1}H NMR:



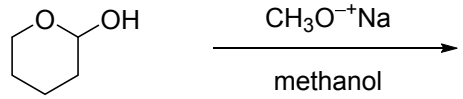
IR:



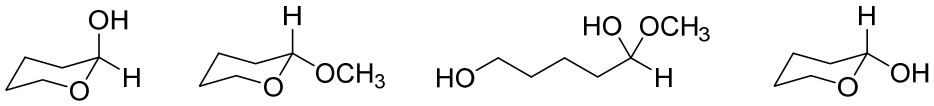
spectral source: chemicalbook.com

(8) B

Which of the following four compounds will have the lowest concentration when 1 mmol of compound **H** is dissolved in methanol, treated with 0.01 mmol of sodium methoxide, and stirred for a few minutes?

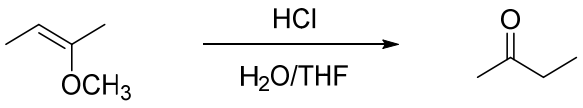


H



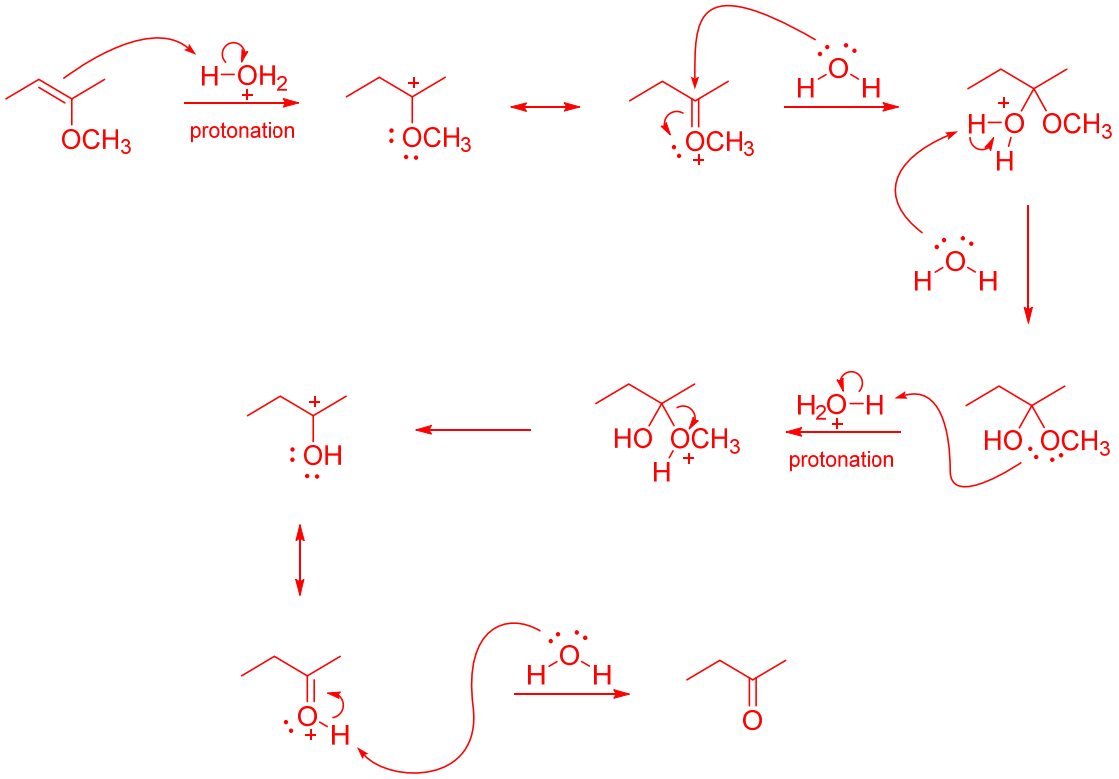
(a) (b) (c) (d)

Problem II. Mechanism (21 points). Enol ethers hydrolyze in the presence of catalytic acid to yield ketones and aldehydes.



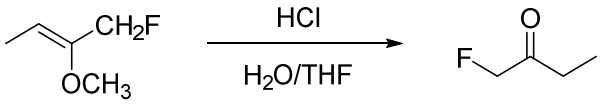
J **K**

(a) (16 points) Draw a sensible mechanism for the conversion of **J** to **K** in aqueous acid. Tetrahydrofuran (THF) is used as a co-solvent because the solubility of the enol ether is relatively low in water. 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 significant resonance forms that account for the stability of these intermediates in the reaction.



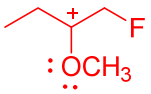
- Note: This reaction occurs under acidic conditions, so you will have (neutral) waters and alcohols serving as a nucleophiles and leaving groups rather than hydroxides and alkoxides. Also, you have protonated water (H_3O^+) serving as an acid and neutral water (not hydroxide!) serving as a base. The concentrations of hydroxide and alkoxides under acidic conditions are very, very small.

(b) (5 points) Would you expect the rate of hydrolysis of **L** (below) to be faster or slower than the rate of hydrolysis of **J**? Very briefly explain why in the space provided.



L **M**

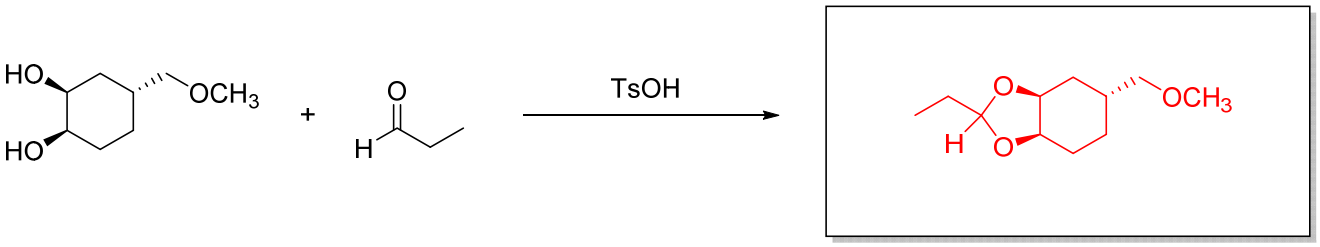
faster or slower
than above?



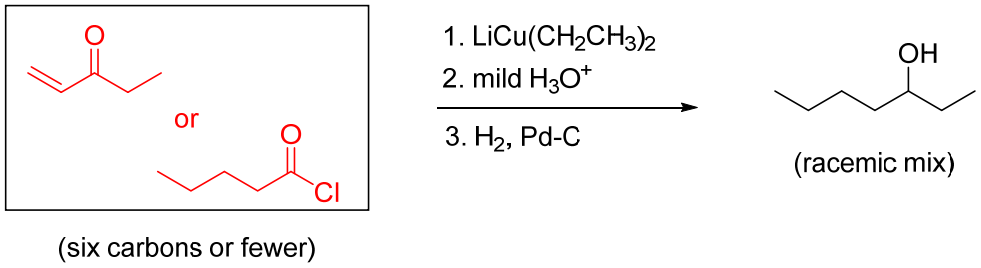
Slower. The electron-withdrawing F atom will destabilize the formation of this carbocation by an inductive effect, making its formation slower, thereby slowing the reaction.

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)



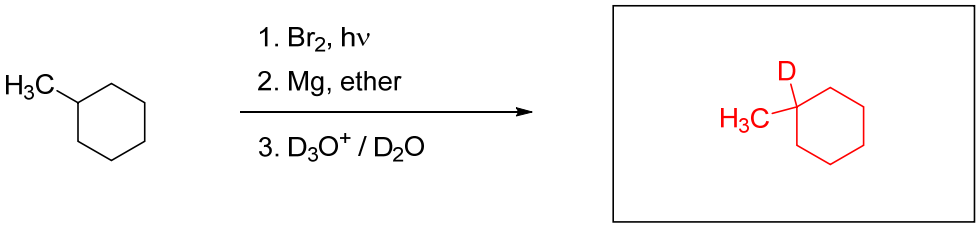
(b) (7 points)



(six carbons or fewer)

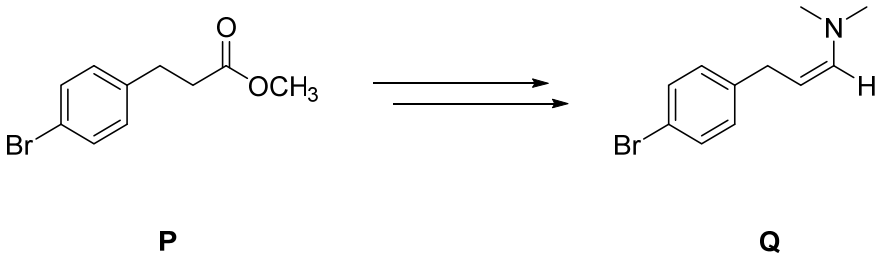
(racemic mix)

(c) (7 points)

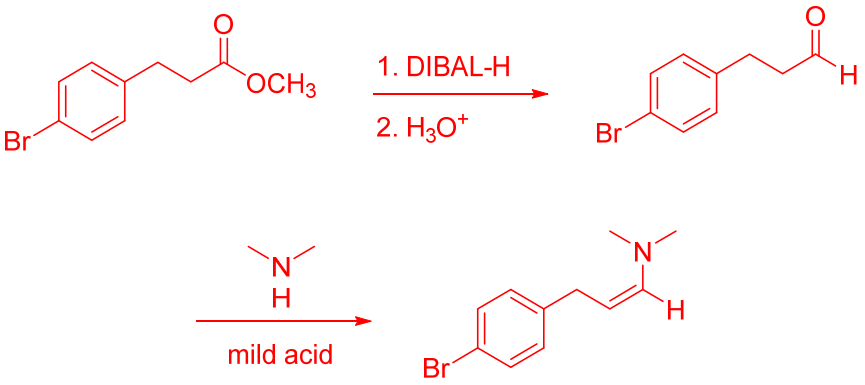


Problem IV. Synthesis (26 points). Design efficient synthetic routes for compounds **Q** and **S** using compounds **P** and **R** as starting materials, respectively. You may use any other reagents or molecules you wish, so long as you do not violate the spirit of the problem by ignoring the starting materials.

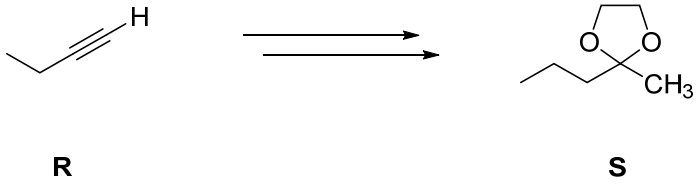
(a) (10 points)



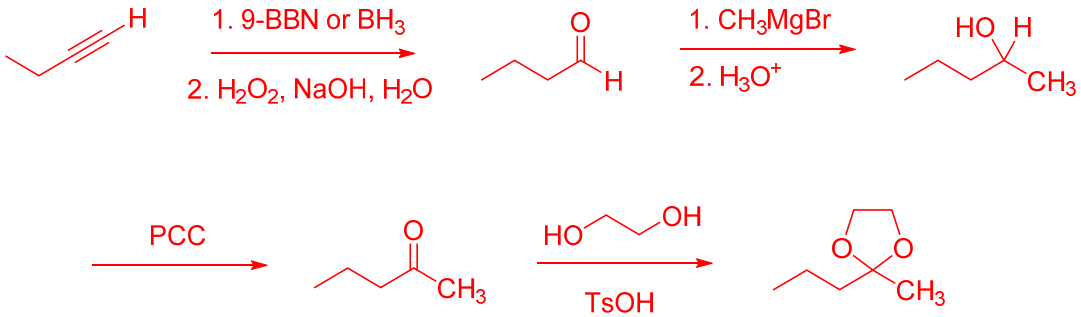
P **Q**



(b) (16 points)



R **S**



- It is important to note that if you take the approach of generating an acetylide anion, methylating it to add the fifth carbon, then hydrating the triple bond, you will unfavorably generate a mixture of 2- and 3-pentanone rather than 2-pentanone specifically: