148NE

Fall Semester 2013
Organic Chemistry I
Midterm Examination #1

Name (print): KEY

Name (sign):

Recitation Instructor (name, day):

Instructions

1. Keep the exam closed until you are instructed to begin.

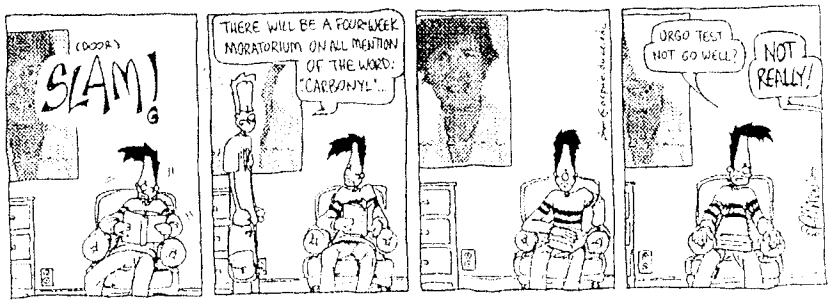
2. The exam consists of 10 questions. The first thing you should do is make sure that no pages are missing. If a page is missing, notify a proctor immediately

3. You will have 1 hour and 15 minutes. Questions are labeled from 'easy' (*) to hard (****). Budget your time wisely.

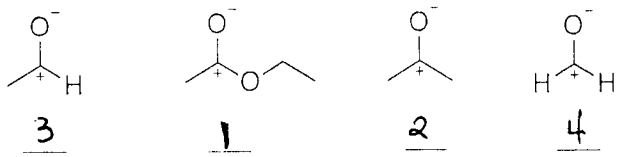
4. Make sure to show all of your work, and this should fit into the space provided. If you need to use the back of the paper, you must make note of it in the space provided for credit.

Good Luck!

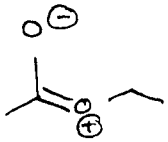
1.___(15 points)
2.___(20 points)
3.___(12.5 points)
4.___(12.5 points)
5.___(10 points)
6.___(20 points)
7.___(10 points)



1a. Rank the following carbocation stability from *most stable(1)* to *least stable(4)* *and briefly explain your answer.* (5 points)*

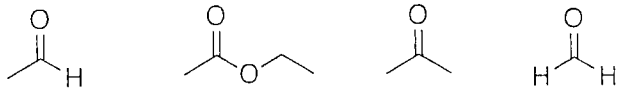


3 1 2 4

Explanation: ① has added resonance stability 

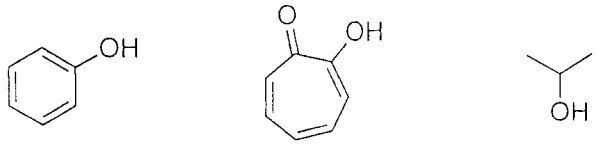
②-④ have decreased stability from ② - "2° carbocation" to ④ "methylene carbocation" based on hyperconjugation argument

1b. Provide a more specific name of the following carbonyls (ester, carboxylic acid, ketone, aldehyde, formaldehyde). Then rank them from *most reactive (1)* to *least reactive (4).* (5 points)*

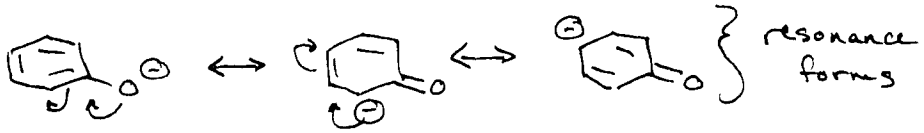


name	aldehyde	ester	ketone	formaldehyde
stability rank	2	4	3	1

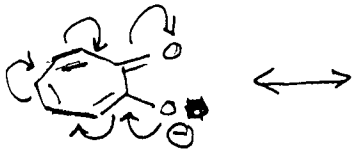
1c. Predict the relative acidity of the following O-H containing molecules and explain your answer, using structures were possible in support. (5 points)* *



___ most acidic least acidic (no resonance)



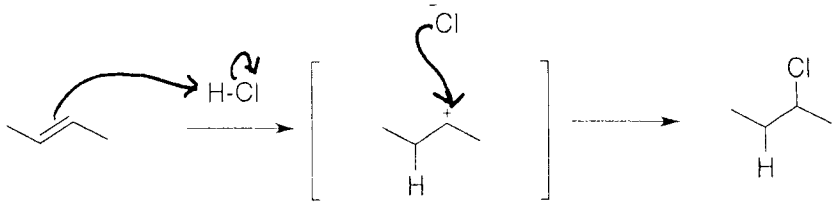
resonance forms



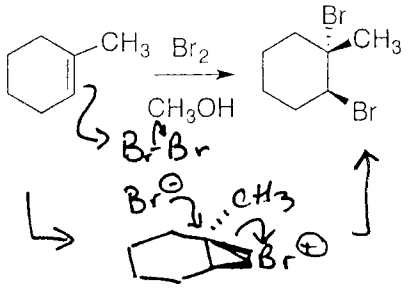
this one has similar resonance forms, but can also delocalize ⊖ charge onto other oxygen

2. Mechanisms (20 points).

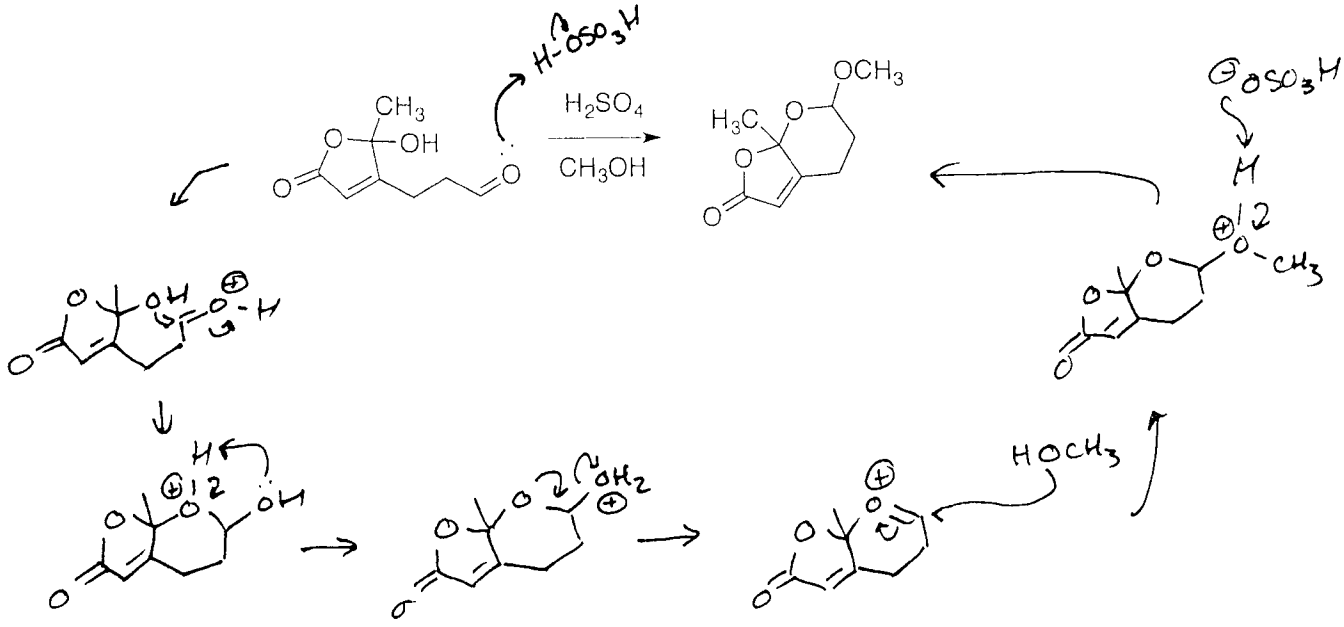
2a. Show the mechanism arrows for the following reaction. (5 points)*



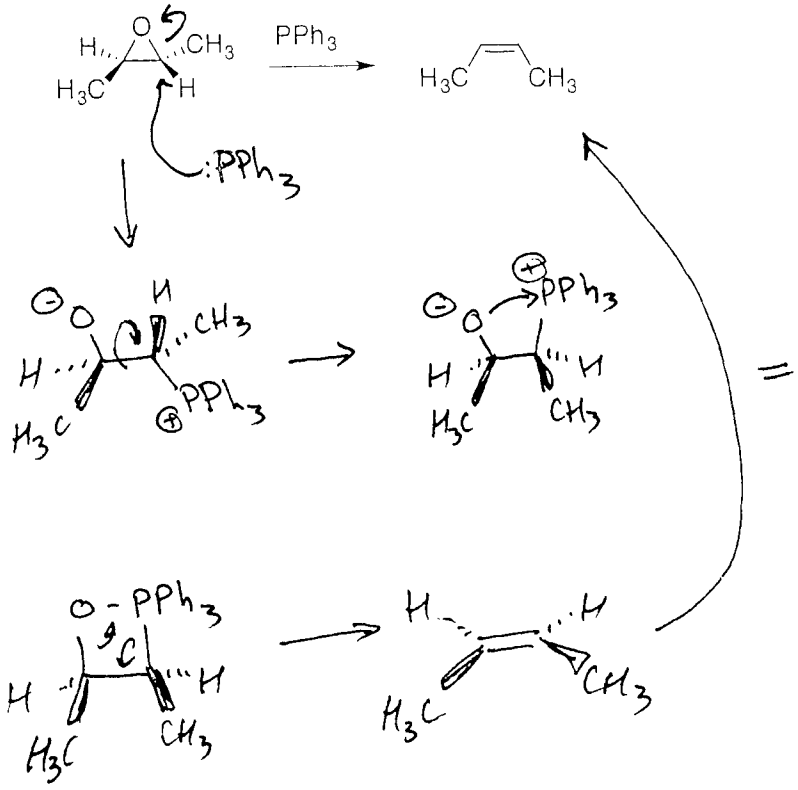
2b. Show a mechanism for the following reaction that explains the diastereoselectivity. (5 points)**



2c. Show a mechanism for the following reaction (5 points)***

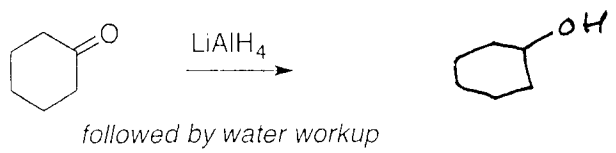


2d. Show a mechanism for the following reaction that explains the diastereoselectivity (5 points)****



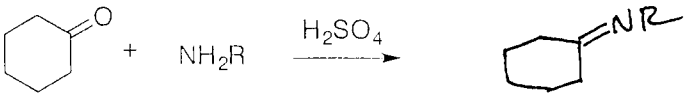
3. Show the product(s) of the following reactions (12.5 points total, 2.5 points each)**

a.

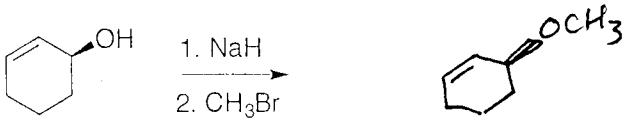


followed by water workup

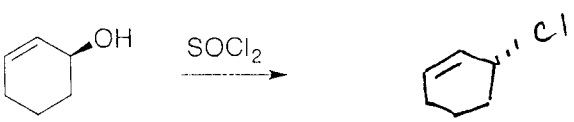
b.



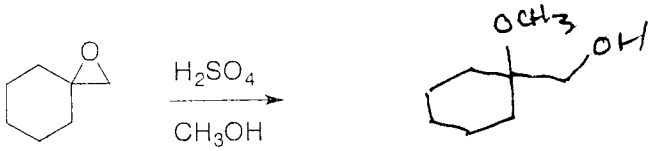
c.



d.

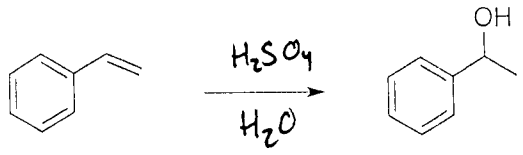


d.

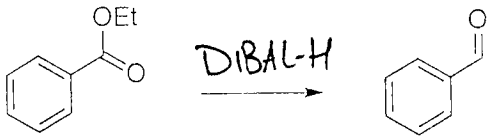


4. Show the reagent(s) necessary for the following reactions (12.5 points total, 2.5 points each)**

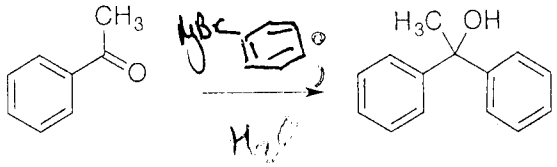
a.



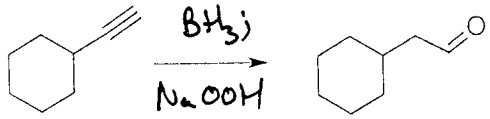
b.



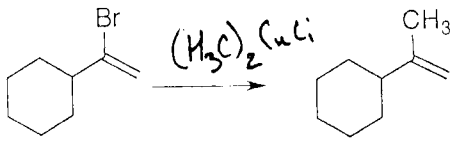
c.



d.

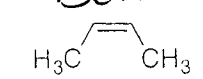


e.



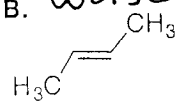
5. The following two alkenes could theoretically be converted into alkynes through a bromination/ double elimination sequence. Which one do you believe would work better/ faster, and explain your answer using structures to explain your answer. (10 points)***

A. Better



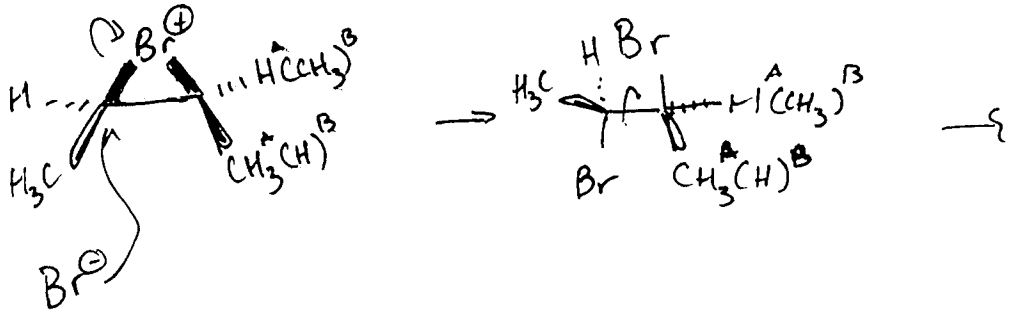
$\xrightarrow[2.\ NaNH_2]{1.\ Br_2}$ $H_3C{-}{\equiv}{-}CH_3$

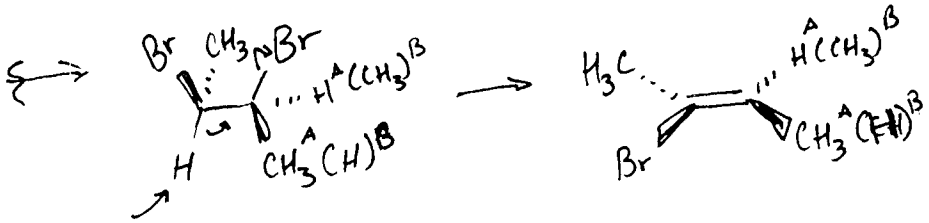
B. Worse



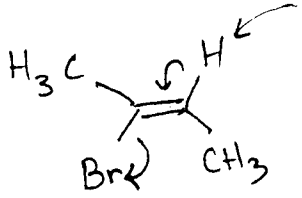
$\xrightarrow[2.\ NaNH_2]{1.\ Br_2}$ $H_3C{-}{\equiv}{-}CH_3$

which one would work better?

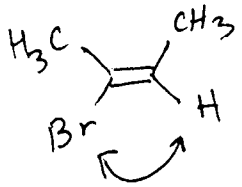




A



B

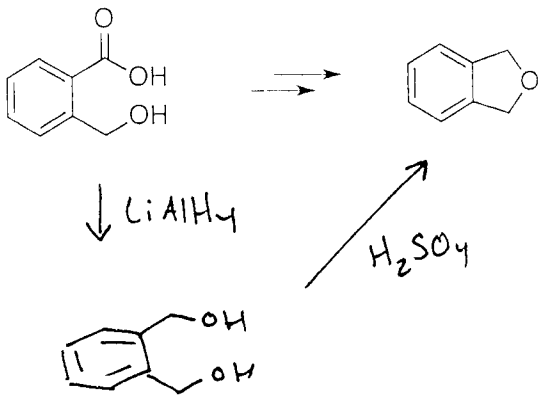


(A) Leads to H ; Br being set up for elimination

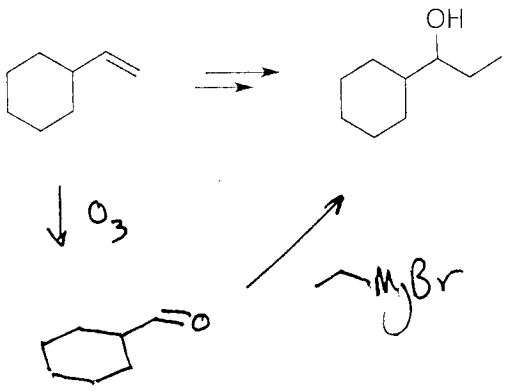
(B) leads to syn H ; Br, which is not good for elimination

6. Synthesis Questions. Make sure to draw out all of your reagents and intermediates clearly and legibly. (20 points)***

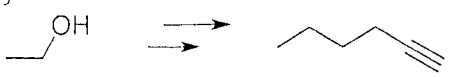
a. (5 points)



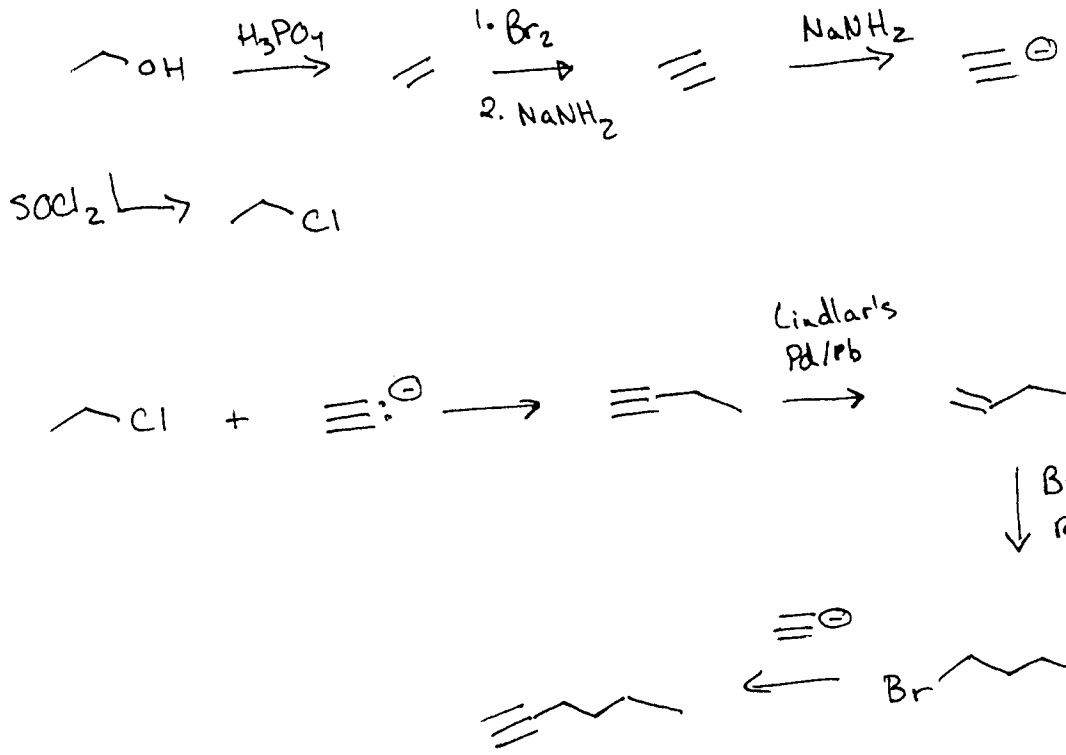
b. (5 points)



c. Propose a synthesis of 1-Hexyne using ethanol as your only carbon-containing starting material. (10 points)



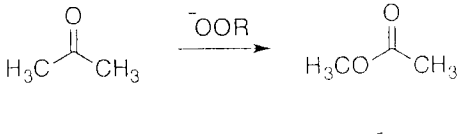
only starting material



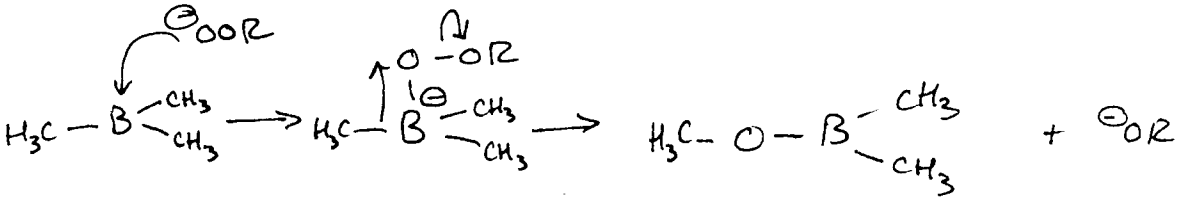
7. One of the ways known to convert ketones into esters is a reaction known as a Baeyer-Villiger oxidation. The mechanism is analogous to the oxidation step of the hydroboration/oxidation reaction. Show a mechanism for both of these reactions, using the specific reactions illustrated below.****

Oxidation step of hydroboration/oxidation

Baeyer-Villiger Oxidation



(A) Mechanism for the oxidation step of a hydroboration/oxidation (5 points).



(B) Mechanism for the Baeyer-Villiger reaction (5 points).