# Chem. 310N, Spring 2008

## Professor Krische

## Midterm Exam I

## Average = 50

## Grading Scale

**90-100 = A+**

**80-90 = A**

**70-80 = A-**

**65-69 = B+**

**60-64 = B**

**55-59 = B-**

**50-54 = C+**

**45-49 = C**

**40-44 = C-**

**37-40 = D+**

**33-36 = D**

**30-32 = D-**

**0-29 = F**

**Name:**_____

**Problem**

1. (4 points)_____

2. (6 points)_____

3. (24 points)_____

4. (20 points)_____

5. (4 points)_____

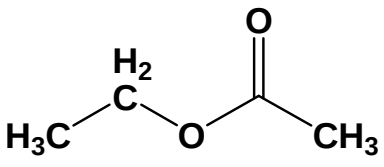
6. (20 points)_____

7. (10 points)_____

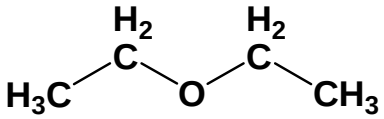
8. (12 points)_____

**Total Points: _____ /100**

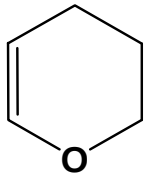
**1.** (4 points) You have enlisted as an undergraduate research assistant in the labs of Dr. Krische. Your graduate student mentor, tormented by over-exposure to Dr. Krische's bad jokes, finally snapped and in the throes of madness removed the labels corresponding to the compounds given below. After tranquilizing your graduate student mentor, you obtain $^{1}$H NMR spectra (labeled **A-D**) corresponding to the four mystery compounds. Your task: match the compound to its spectrum by writing the letter of the spectra in the box beneath the compound to which it corresponds.



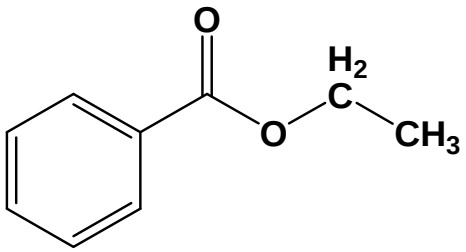

D




A

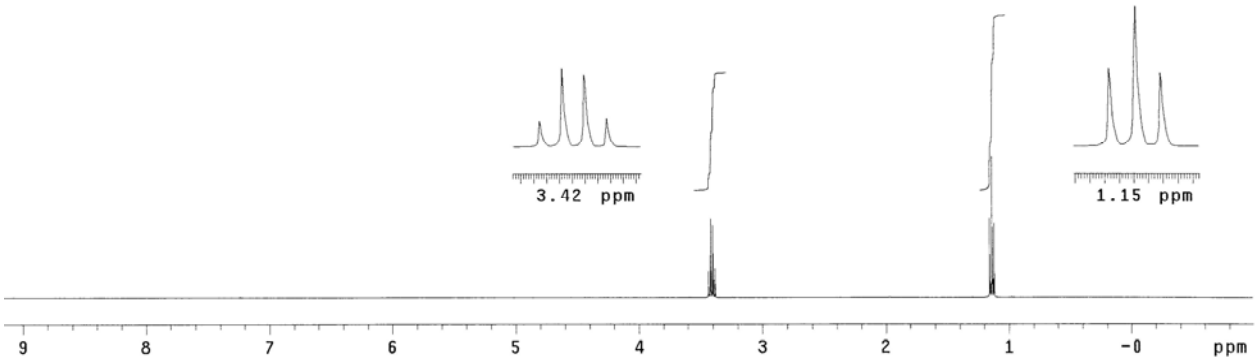



C

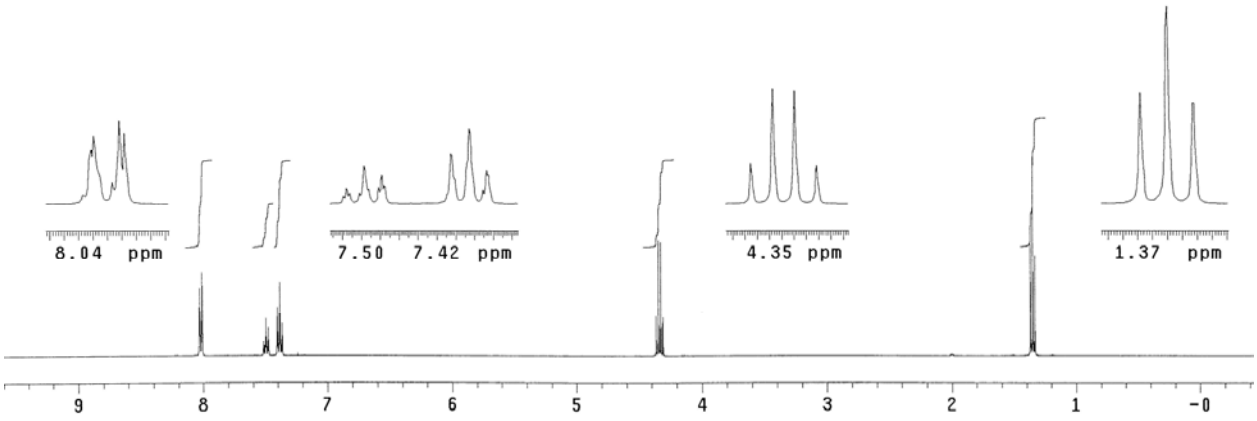



B

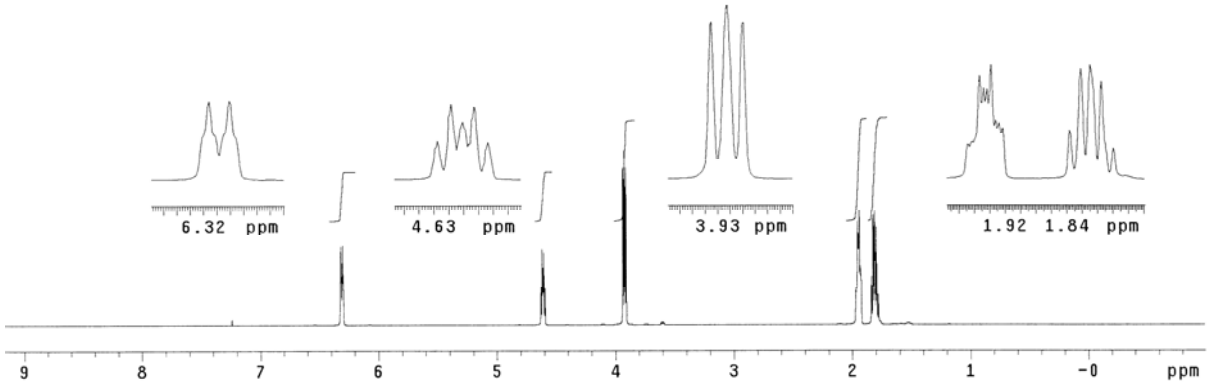
**Compound A**



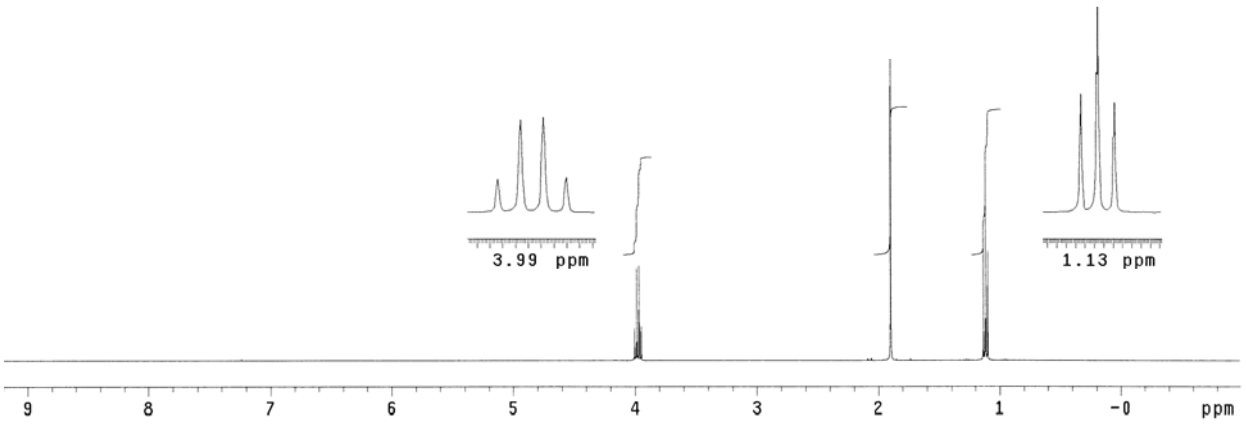
**Compound B**



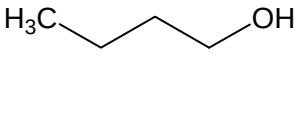

**Compound C**



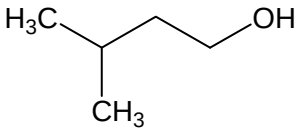

**Compound D**



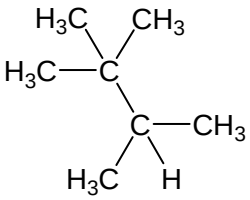
**2.** (6 points) How many signals would you expect to observe in the $^{13}C$ NMR spectra of the following compounds. Write the anticipated number of signals in the box provided (Hint: consider symmetry).



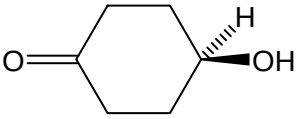

4



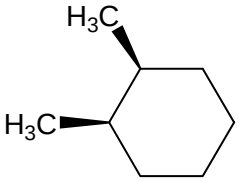

4



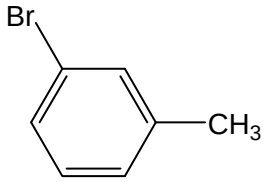

4




4



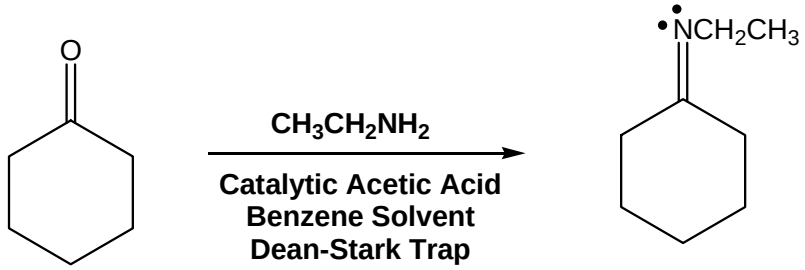

4



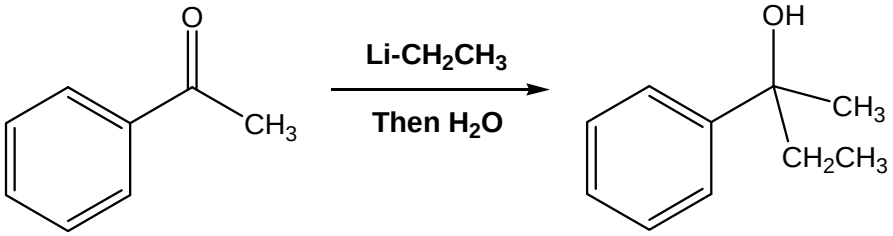

7

**3.** (24 points) Draw the major product expected when the indicated starting materials are subjected to the following reaction conditions.

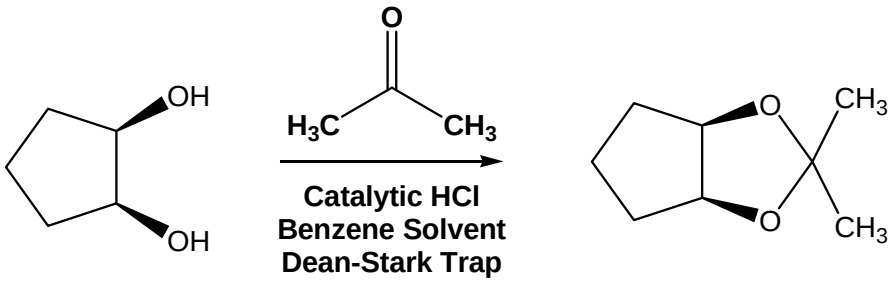
**A.**



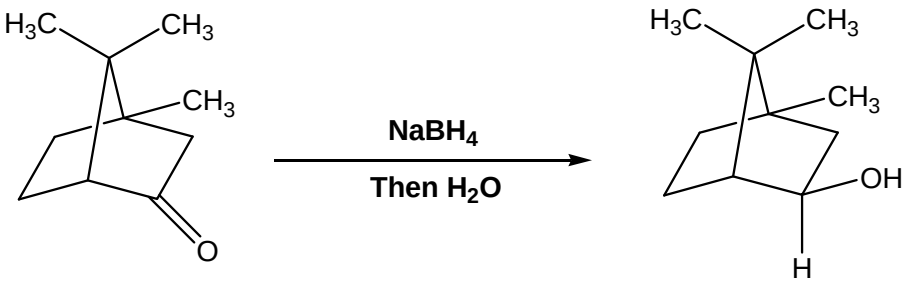

**B.**



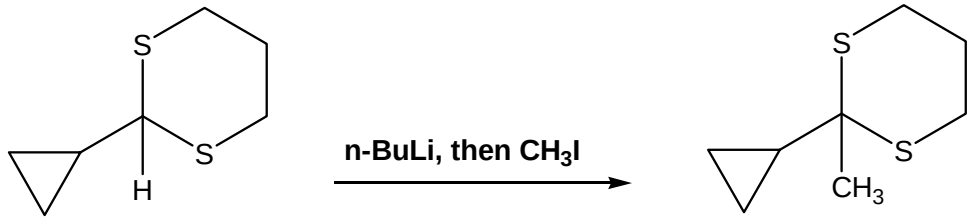

**C.**



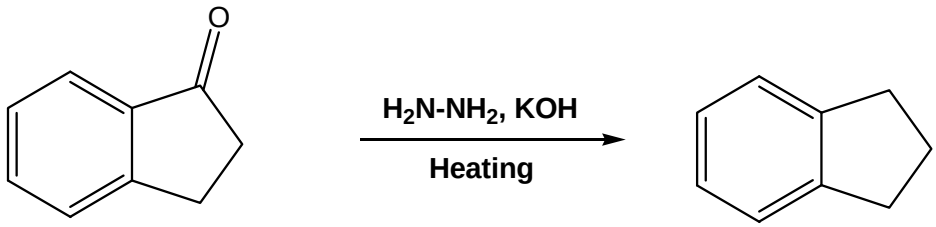

**D. (Indicate Stereochemistry)**



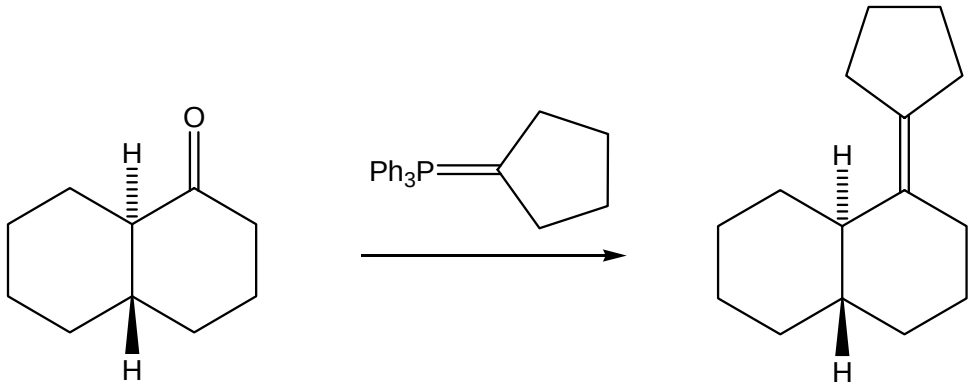
**E.**


S
S
H
n-BuLi, then CH3I
S
S
CH3

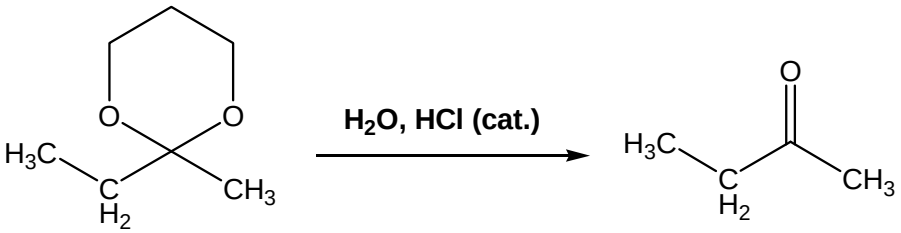
**F.**


O
H2N-NH2, KOH
Heating

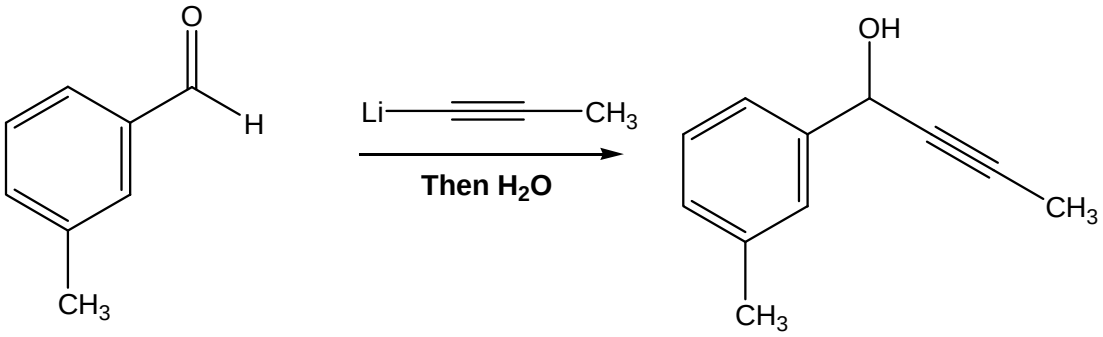
**G.**


O
H
H
Ph3P
H
H

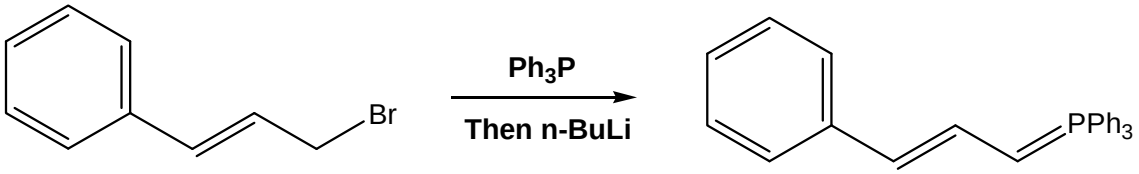
**H.**


O
O
H3C
C
H2
CH3
H2O, HCl (cat.)
O
H3C
C
H2
CH3

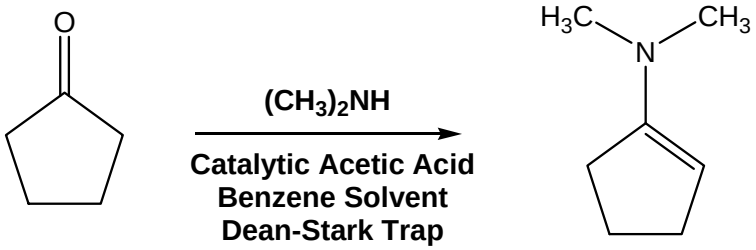
**I.**


O
H
CH3
Li
CH3
Then H2O
OH
CH3
CH3

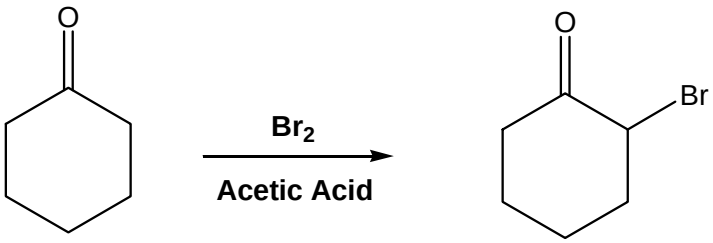
**J.**


Br
Ph3P
Then n-BuLi
PPh3

**K.**

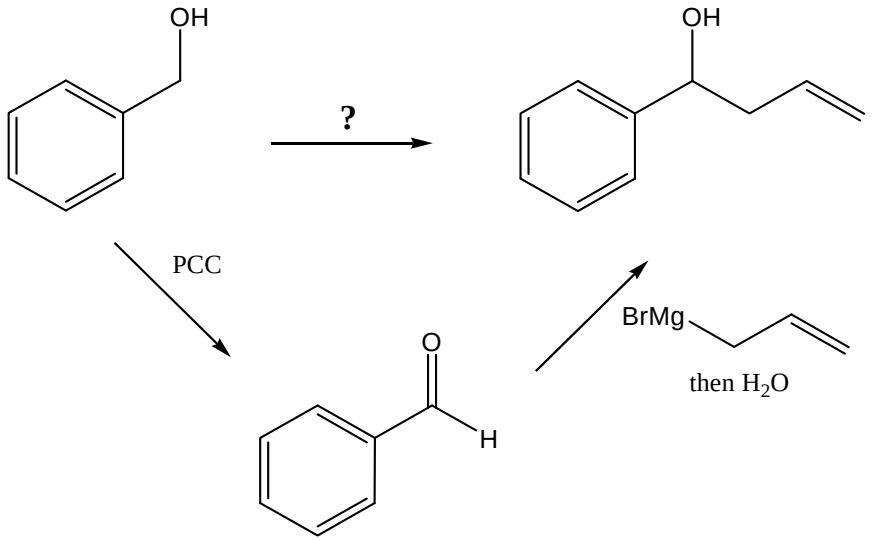

O
(CH3)2NH
Catalytic Acetic Acid
Benzene Solvent
Dean-Stark Trap
H3C
N
CH3

**L.**

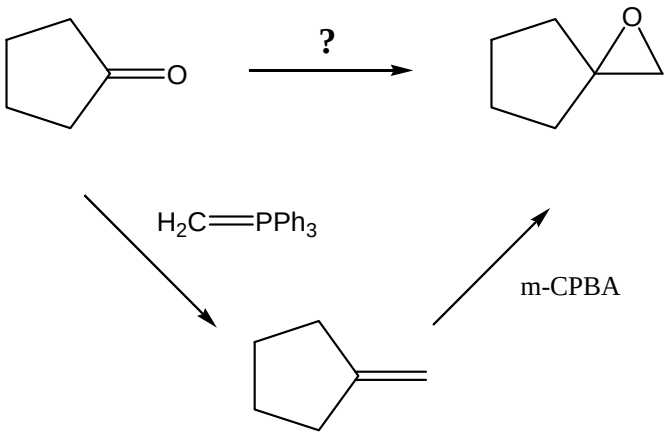

O
Br2
Acetic Acid
O
Br

**4.** (20 points) Devise a synthetic route to accomplish the following transformations. Clearly number each step of your proposed sequence. This is not a mechanism question.

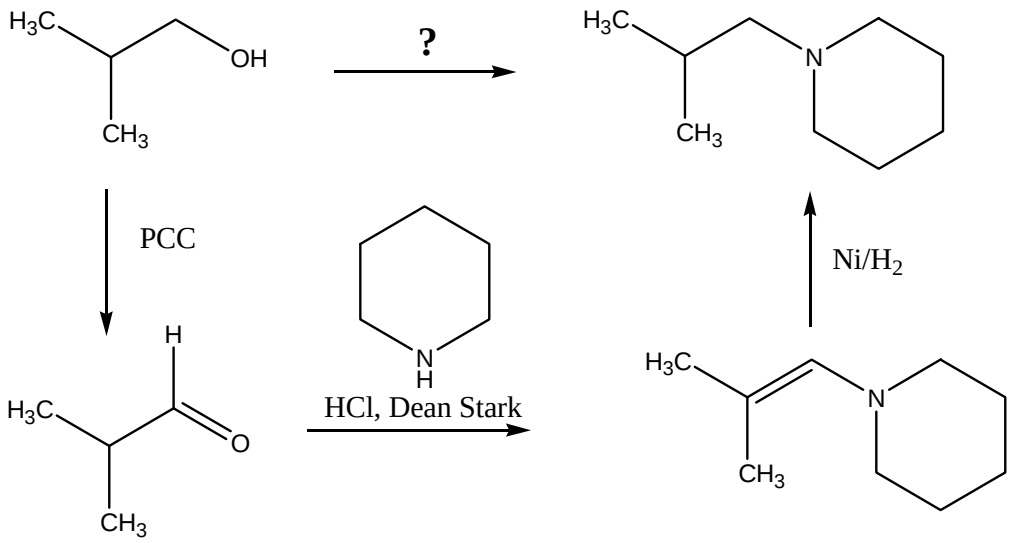
**A. 3pts**



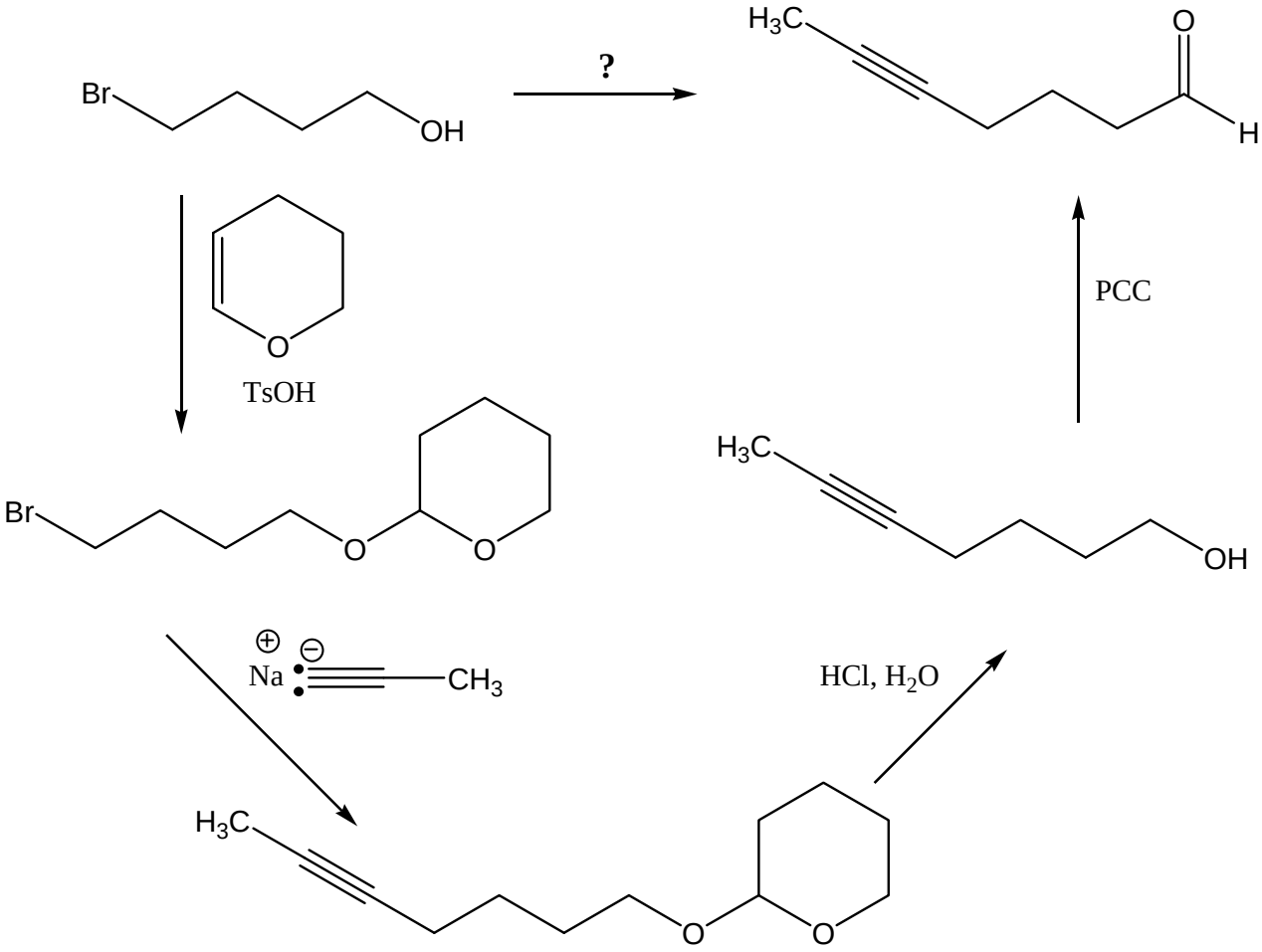

**B. 3pts**



**C. 6pts**

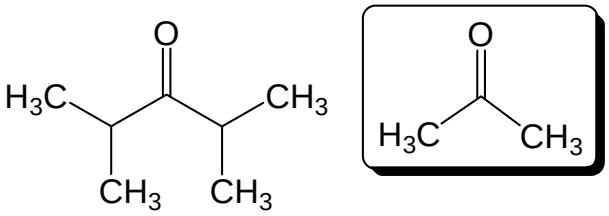



**D.** (Hint: Use protecting group). **8 pts**

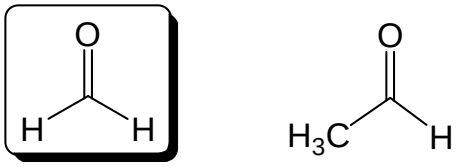


**5.** (4 points) For the following pairs of compounds, circle the compounds that is more susceptible to hydration.

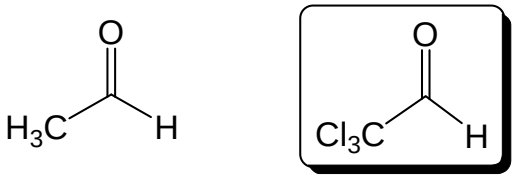
**A**



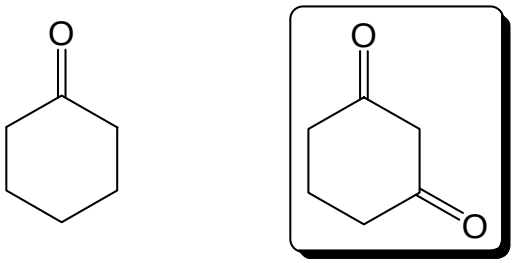

**C**



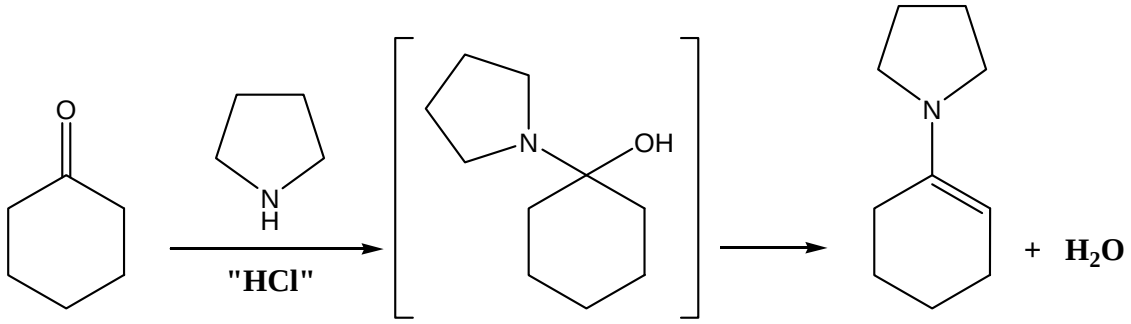

**B**




**D**

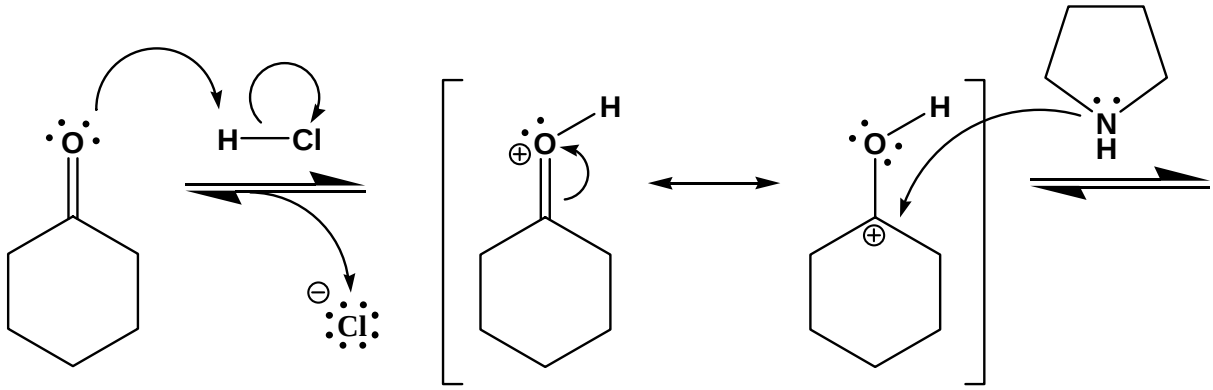


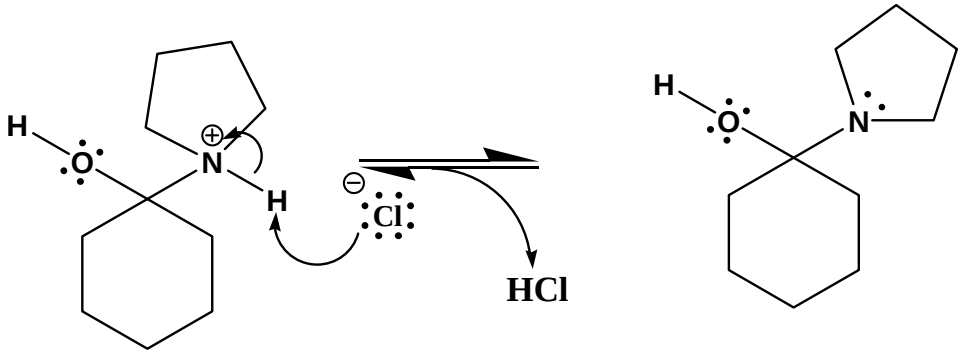
**6.** (20 points) Enamines formation proceeds through the intermediacy of a carbinol amine.



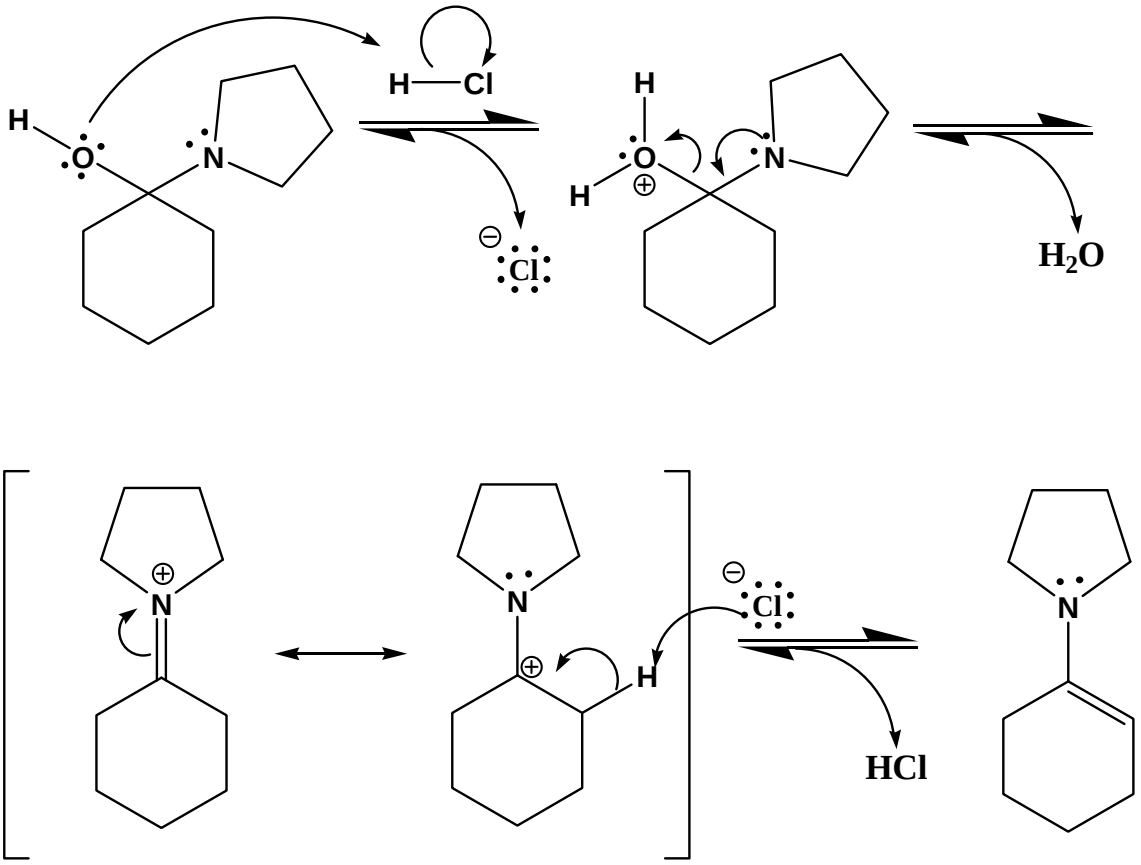

**Carbinol Amine**

(A) Using the arrow pushing formalism, write a mechanism accounting for the conversion of cyclohexanone to the indicated carbinol amine. Draw all important contributing resonance structures for the reactive intermediates. **10 pts**



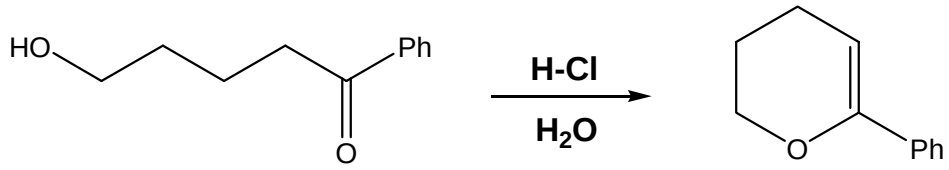



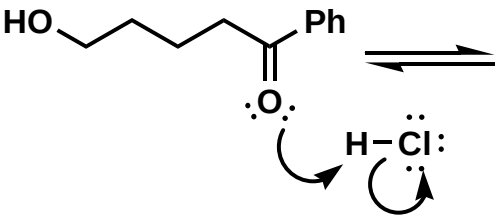
**(B)** Using the arrow pushing formalism, write a mechanism accounting for the conversion of the indicated carbinol amine to the indicated enamine. Draw all important contributing resonance structures for the reactive intermediates. **10 pts**

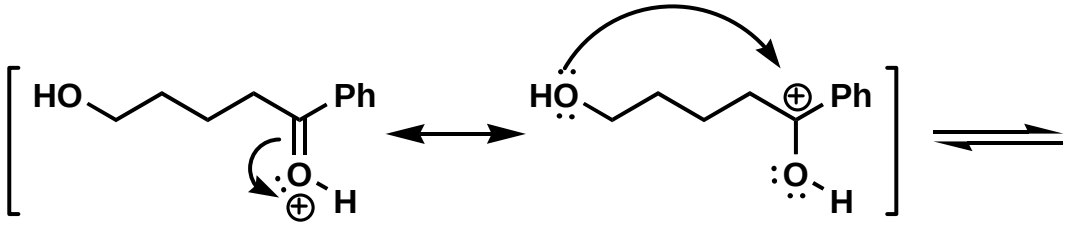


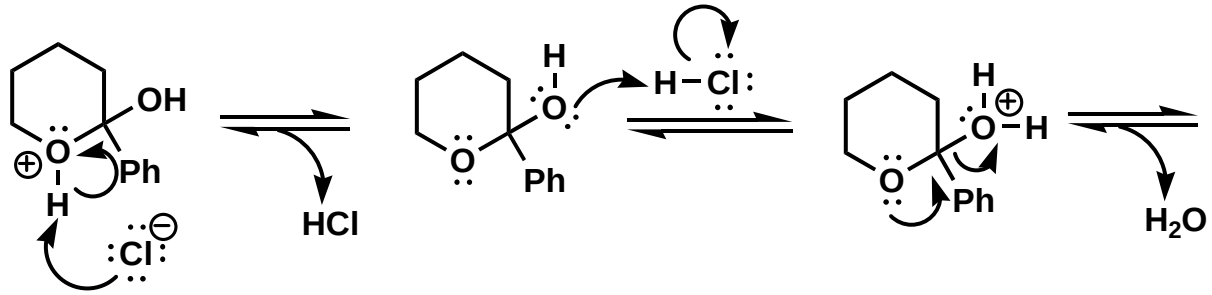
**7**. (10 points) The following "cyclo-dehydration" results in formation of a cyclic enol ether. Using the arrow pushing formalism, draw a mechanism for this transformation indicating all important contributing resonance structures for the reactive intermediates

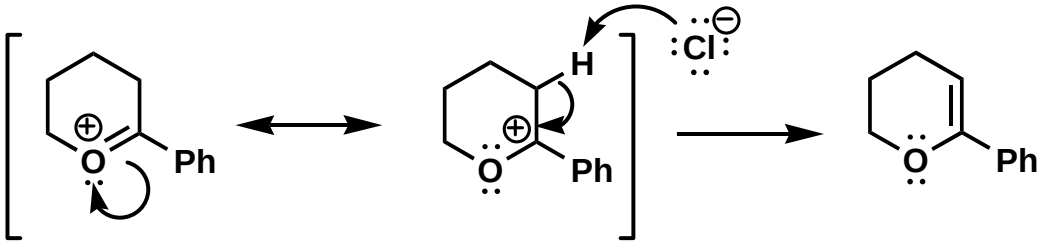
Hint: The first portion of the mechanism involves acid promoted loss of water.



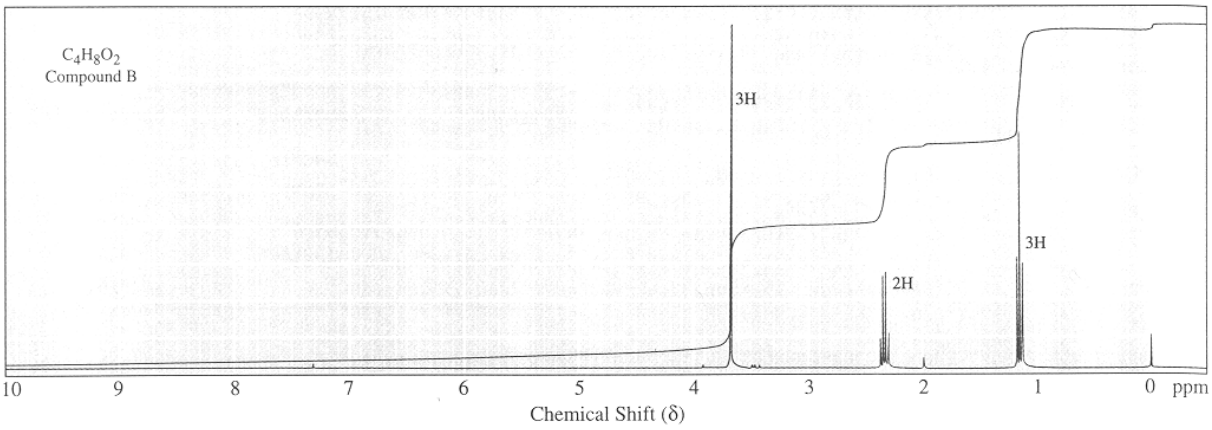



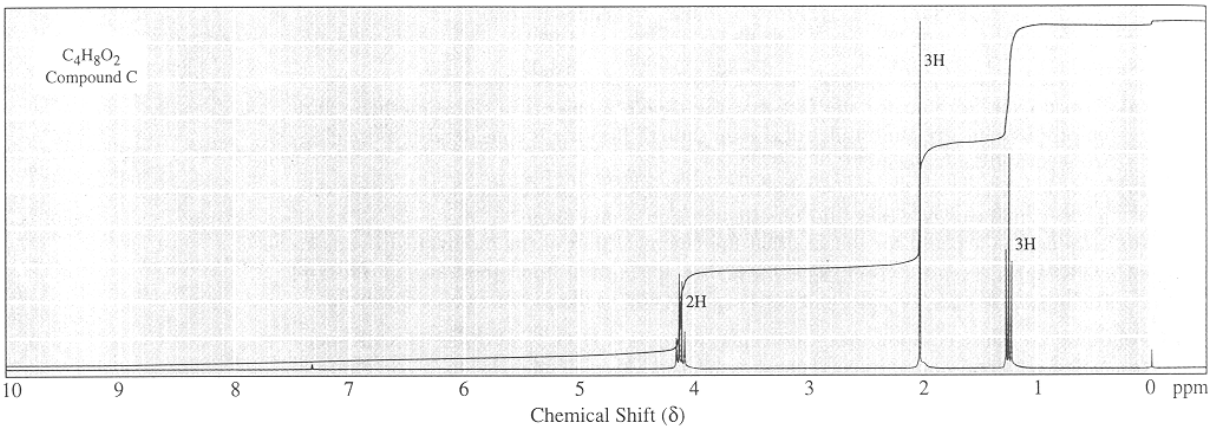
**8.** (12 points) Compounds **B** and **C** both have the molecular formula $C_4H_8O_2$. The $^1H$ NMR spectra for **B** and **C** are given below.

- Calculate the "Index of Hydrogen Deficiency" for **B/C**. **2 pts**

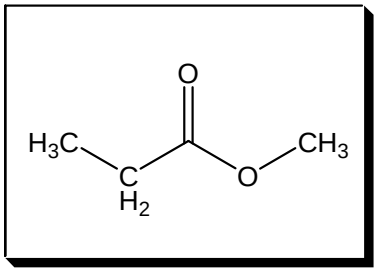
**Degree of Unsaturation = 1 for both compounds**

- Propose structures for **B** and **C** consistent with the $^1H$ NMR data (Hint: **B** and **C** both exhibit a strong absorbance in the infrared at 1735 $cm^{-1}$). **5 pts each**

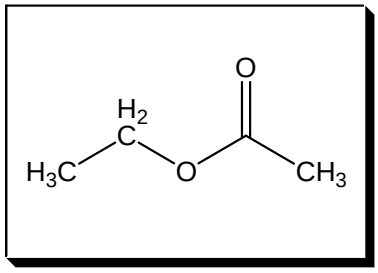



For compound **B**: δ 3.7 (s, 3H), 2.3 (q, 2H), 1.1 (t, 3H).
For compound **C**: δ 4.1 (q, 2H), 2.0 (s, 3H), 1.2 (t, 3H).




**B**




**C**