Chemistry 3A - Fall 1998
Final Exam

Professor Jean Fréchet

December 9, 1998

Your full signature_____

Print your full name_____
(Last name, First name, Middle)

Your SID_____

Please check the section number and name of your GSI/TA.

___**111 Turculet,Laura**
___**121 Klei,Steven**
___**131 Krumper,Jennifer**
___**141 Downey,Karen**
___**211 Eng,Christina**
___**221 Shiau,Timothy**
___**311 Kita,Ryoko**
___**321 Davis,Anna**
___**331 Yeh,Robert**
___**341 Mork,Benjamin**
___**361 Fischer,Fabian**
___**371 Bennett,Miriam**
___**381 Fujdala,Kyle**
___**411 Hodges,Alan**
___**421 Ahrendt,Kateri**
___**431 Borths,Christopher**
___**511 Saxon,Eliana**
___**521 Wiener,John**
___**531 de Graffenried,Christopher**
___**541 Dosa,Peter**

If you are making up an I-grade, indicate the semester you took 3A_____ and the Professor_____.

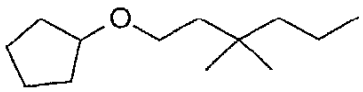
This exam has **14** pages; **make sure that you have them all.** We will only grade answers that are in the designated spaces. Please do your scratch work on the backs of the exam pages. Write only **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

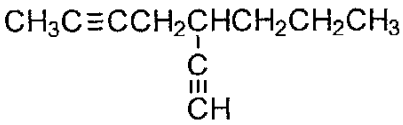
Note: This examination runs for a total of 180 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **no credit**.

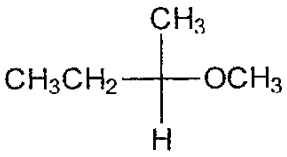
A partial periodic table and data needed for calculations can be found on page **14** of the exam.

Do Not Write in this Box.
1._____(12)
2._____(18)
3._____(15)
4._____(12)
5._____(11)
6._____(12)
7._____(12)
8._____(11)
9._____(14)
10._____(11)
11._____(10)
12._____(12)
Total_____(150)

1. [12 points] (a) Give the IUPAC name for each of the following compounds:







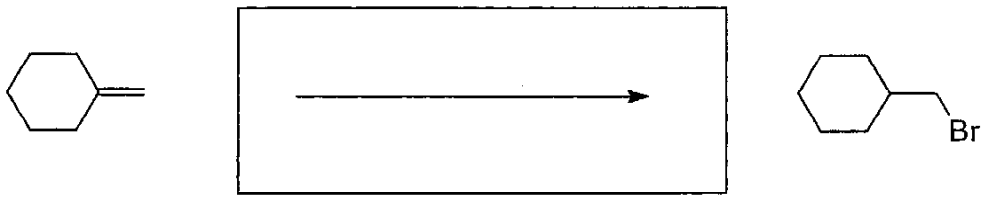
(Fischer projection!)

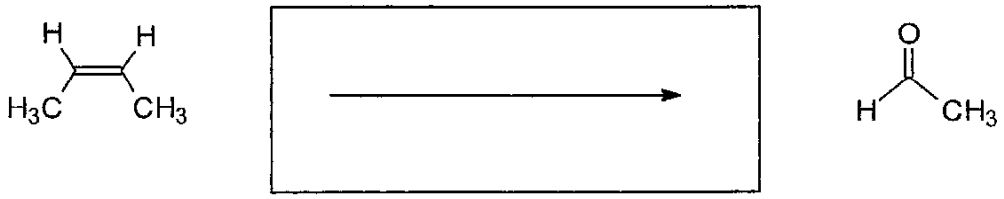
1. (b) Write a clear structure with any applicable stereochemistry for each of the following:

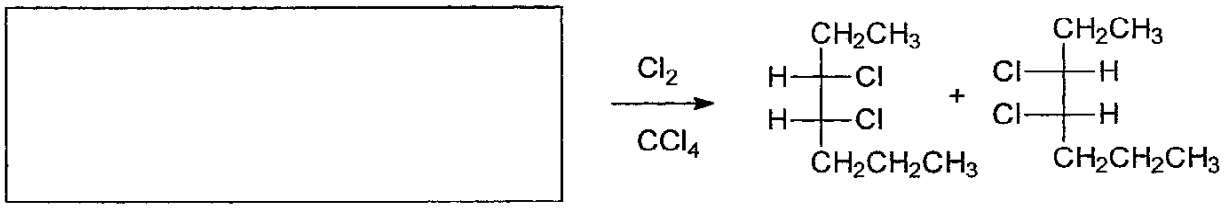
(E)-4-Bromo-2,3-dimethyl-3-octene

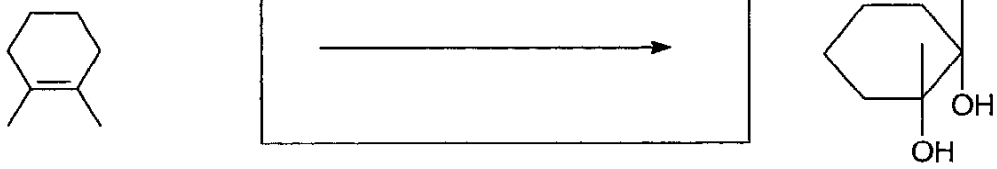
2-Ethoxy-2-methylpropane

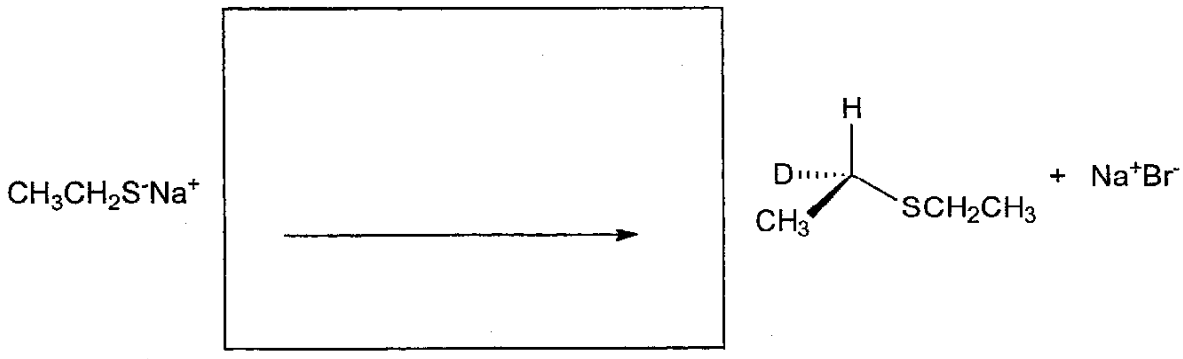
2. [18 points]. Complete the following reactions showing the missing starting material or reagent(s) (and solvent if important). If reactions involve more than one step label each step 1) then 2)...

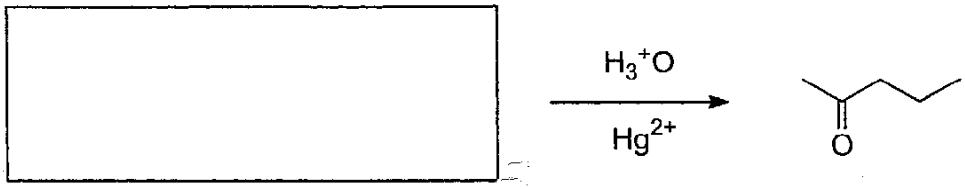
(a) 

(b) 

(c) 

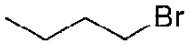
(d) 

(e) 

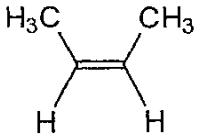
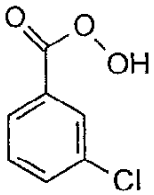
(f) 

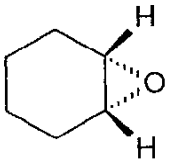
3. [15 points]. Show the **major** product(s) obtained in each of the following reactions, if no reaction occurs, write "NR"

(a) $H_3C-C\equiv C-CH_3$ $\xrightarrow{K^+NH_2^-}$

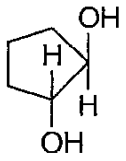
(b)  $\xrightarrow{(CH_3)_3N}$

(c)  $\xrightarrow[\Delta]{O^-K^+}$

(d)  $\xrightarrow{}$ 

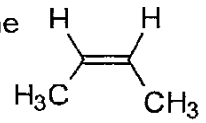
(e)  $\xrightarrow[CH_3OH]{CH_3O^-Na^+}$

4. [12 Points]

(a) Show a step-by-step synthesis of 

from cyclopentene  (no mechanism)

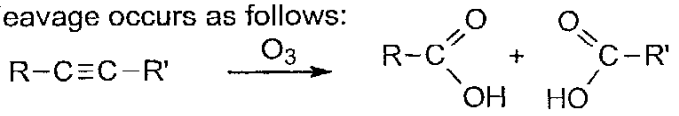
(b) Show a clear structure for all the products obtained by reaction of cis-2-butene with 1 mole of N-bromosuccinimide in the presence of light. Use an equation to explain why more than one is formed.



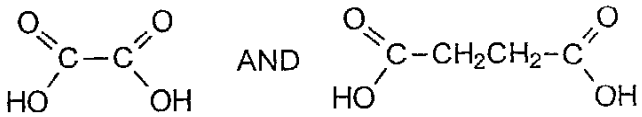
Explanation:

Structures of the products

5. [11 Points] (a) We have studied the cleavage of carbon-carbon multiple bonds by ozone. In the case of internal alkynes cleavage occurs as follows:



A hydrocarbon "A" with the formula $C_{12}H_8$ absorbs 8 moles of hydrogen (8 H_2) upon catalytic hydrogenation in the presence of Pd catalyst to afford hydrocarbon "B". Reaction of starting hydrocarbon "A" with excess ozone affords only two products:



Show clear structures for hydrocarbons "A" ($C_{12}H_8$) and well as hydrogenated hydrocarbon B

Structure of A	*Structure of B*

(b) Consider the reaction: $CH_3S^- + CH_3CH_2I \longrightarrow CH_3SCH_2CH_3$ in DMF

(1) Which of the following best describes this reaction (write the letter corresponding to your answer in the box below.)

(A) S_N1 (B) E_1 (C) S_N2 (D) E_2 (E) Carbocation (F) Radical

ANSWER: [ ]

(2) Write an expression for the rate law for this reaction

ANSWER: [ ]

(3) By what factor would the rate of the reaction change if the concentration of all reactants was doubled?

ANSWER: [ ]

6. [12 points] Multiple choice questions: write the ***number*** corresponding to the **best answer** in the box

(a) The length of the carbon-carbon double bond of ethene is

(1) 1.72Å (3) 1.54Å (5) 1.34Å (7) 1.11Å

(2) 1.62Å (4) 1.44Å (6) 1.20Å (8) 1.06Å

ANSWER: ☐

(b) Which is the strongest acid?

(1) H_2O (3) CH_4 (5) $H_2C{=}CH{-}CH_3$ (7) $I^{\ominus}$

(2) NH_3 (4) $H{-}C{\equiv}C{-}H$ (6) $CH_3COO^{\ominus}$

ANSWER: ☐

(c) The addition of bromine to a CCl_4 solution of an alkene proceeds with:

(1) isomerization of the double bond
(2) inversion of configuration
(3) syn stereochemistry
(4) cis streochemistry
(5) anti stereochemistry
(6) retention of hybridization

ANSWER: ☐

(d) The rate of free-radical halogenation of alkanes can be increased by:

(1) Choosing a more selective reagent
(2) increasing the amount of inert solvent
(3) increasing the temperature
(4) increasing the reaction time
(5) cooling to retard termination

ANSWER: ☐

(e) Gilman reagents are easily prepared by reaction of:

(1) an alkyl halide with magnesium in methanol
(2) an alkyl halide with magnesium in ether
(3) an alkyl halide with lithium metal in ether
(4) an alkyl lithium with cuprous iodide in ether
(5) an alkyl lithium with an alkyl halide in THF
(6) two alkyl halides with cuprous iodide in ether

ANSWER: ☐

(f) The strongest base among the compounds below is:

(1) $Na^+NH_2^-$ (3) NaOH

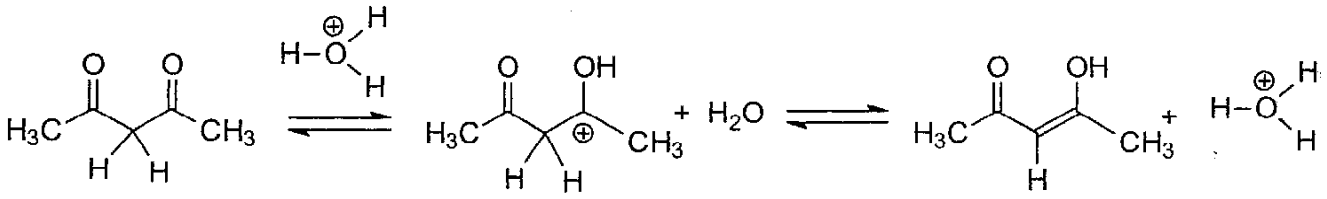
(2) $HC{\equiv}C^-Na^+$ (4) CH_3CH_2Li

ANSWER: ☐

Chem. 3A

7. [12 Points]
Propose a synthesis of 2-ethylbutane $H_3C-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2CH_3$ from ethanol CH_3CH_2OH as the sole source of C atoms.
Show all steps and reagents used

8. [11 Points]. While most enols are generally unstable, the equilibrium below occurs at room temperature



(24% at equilibrium) (76% at equilibrium)

(a) Show the mechanism of this enolization reaction by drawing curved arrows directly in the above equation.

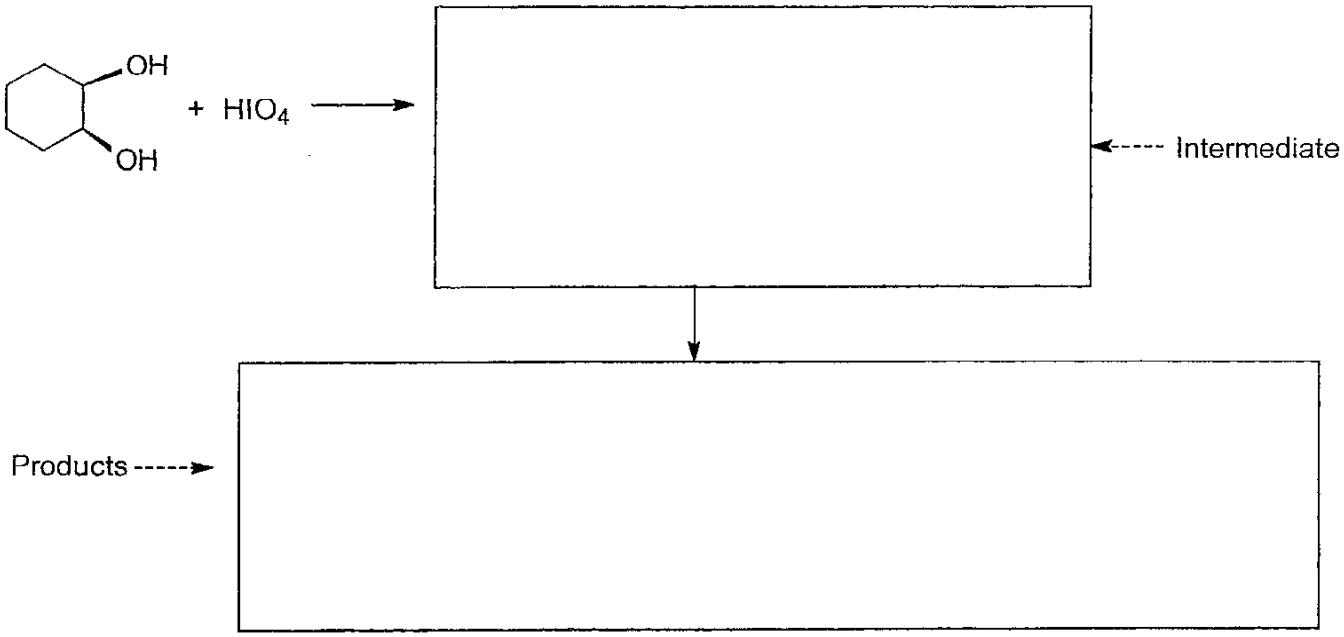
(b) At equilibrium the mixture contains 76% of the enol, calculate K_{eq} for the reaction. Write an equation and show your calculation.

ANSWER: K_{eq} =

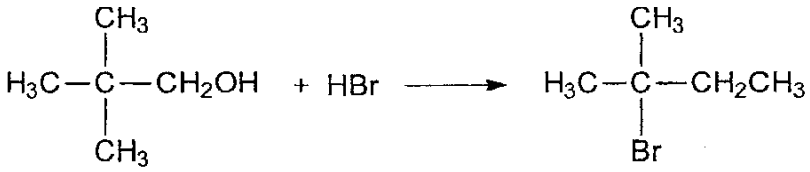
(c) Draw a qualitative energy diagram for the reaction assuming that the first step is rate-determining. Do not forget to **fully label** your energy diagram.

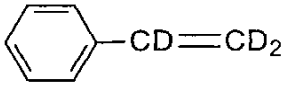
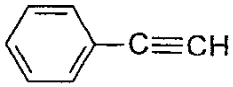
9. [14 Points]

(a) Periodic acid HIO_4 is used to cleave 1,2-diols. Complete the reaction below showing the key intermediate, arrows for its transformation into product, and the structures of the products of the reaction



(b) Propose a step by step mechanism for the reaction below (show curved arrows).



10. [11 Points] (a) Propose a synthesis of  from 

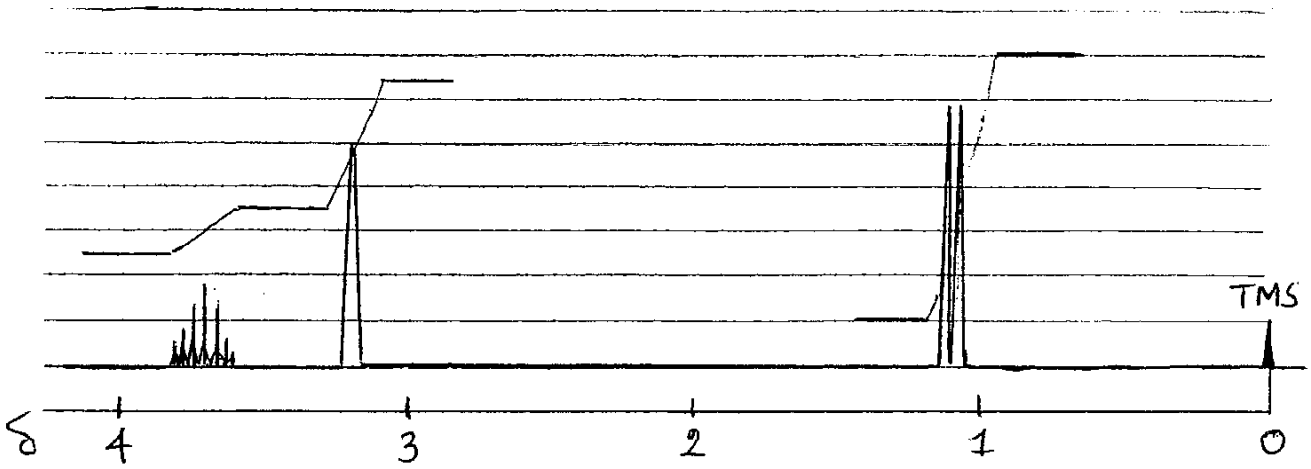
(*Note: D is deuterium ^2H*)

(b) The optical rotation α of a solution of 0.060g of a steroid dissolved in 3.0 mL of dichloromethane and measured in a polarimeter tube 0.05 m long is +2.5 degrees. What is the value of $[\alpha]_D$ for this hormone? Show the formula you use indicating all relevant units and show the details of your calculation.

ANSWER: $[\alpha]_D$ =

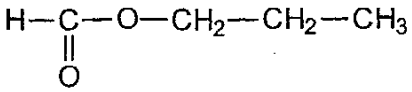
11. [10 points]

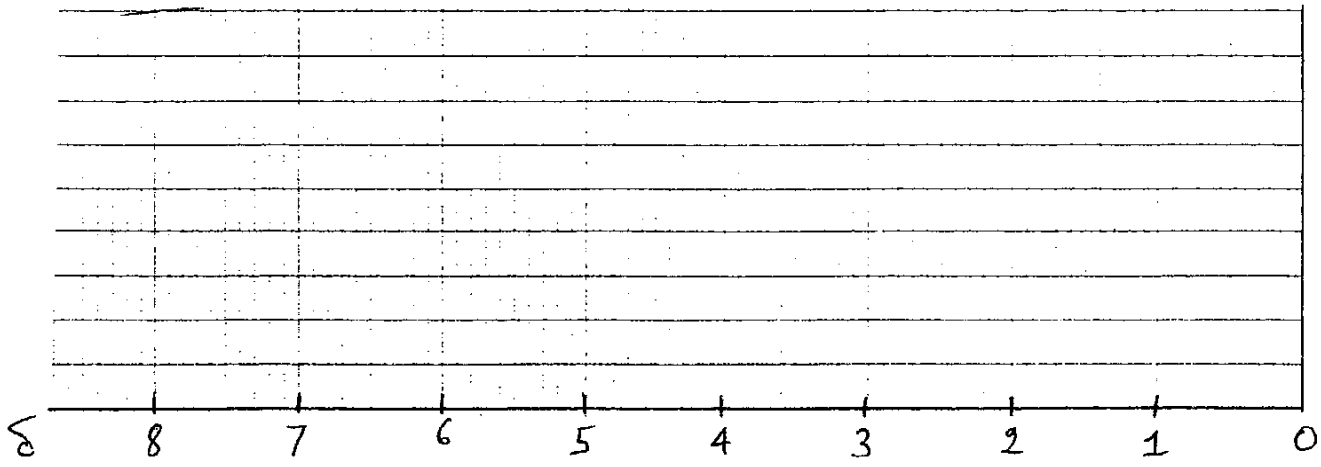
(a) The ^{1}H NMR spectrum of an ether with a formula weight of 74 is shown below. Show a clear structure for this ether?



ANSWER:

(b) **Sketch** the ^{1}H NMR spectrum of the compound below. Also **draw an integration of the signals** and assign each signal by **drawing a line** from each hydrogen or group of hydrogens to the corresponding peak or set of peaks in the structure you draw.

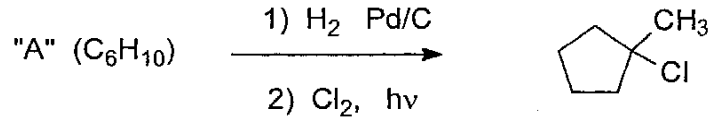




p.14 not included (periodic table)

12. [12 points]

(a) An unknown cyclic compound "A" with the formula C_6H_{10} has a ^{13}C NMR spectrum showing only four peaks at δ 22, 29, 123, and 132 PPM. Compound "A" reacts as shown below:



Draw a clear structure for compound "A" and assign the NMR peaks (show the δ value next to each C atom in the structure of "A")

(b) Complete the reactions below showing the **major** product only.