Chemistry 3A - Spring 1998
Final Exam

Professor Jean Fréchet

May 18, 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 DeForest,Sarah**
_____**121 Berseth,Polly**
_____**131 Richards,Steven**
_____**141 Yamamoto,Kana**
_____**151 Brennan,Paul**
_____**211 Esker,Todd**
_____**221 Kriesel,Josh**
_____**231 Zylstra,Eric**
_____**361 Liang,Scott**
_____**371 Paisner,Sara**
_____**381 Kim,Esther**
_____**391 Bise,Ryan**

_____**311 DeForest,Sarah**
_____**321 Keet,Corinne**
_____**331 Ponte,Maya**
_____**341 Seymour,Sean**
_____**351 Werkema,Evan**
_____**411 Esker,Todd**
_____**421 Peters,Eric**
_____**431 Freeman,Adam**
_____**511 Liang,Scott**
_____**521 Magliery,Thomas**
_____**531 Kwon,David**
_____**541 Winans,Katherine**
_____**551 Janes,Jeff**

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

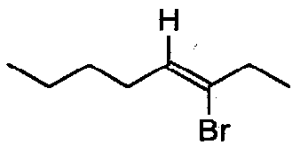
This exam has **14** pages; **make sure that you have them all.** We will only grade answers that are in the designated spaces. Please do your scratch work on the backs of the exam pages. Write only **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

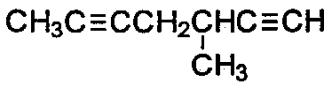
Note: This examination runs for a total of 180 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **no credit**.

Grades will be posted on the bulletin board next to 305 Latimer after 12 noon on Thursday, May 21.

Do Not Write in this Box.	
1.	(15)
2.	(20)
3.	(20)
4.	(20)
5.	(15)
6.	(18)
7.	(15)
8.	(22)
9.	(14)
10.	(14)
11.	(14)
12.	(13)
Total	(200)

1. [15 points] (a) Give the IUPAC name for each of the following compounds:





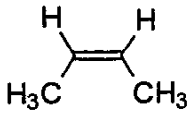
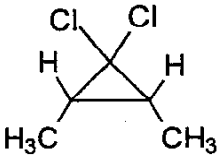
1. (b) Write a clear structure with any applicable stereochemistry for each of the following:

2-chloro-bicyclo[2.2.1]heptane

(S)-2-chlorobutane

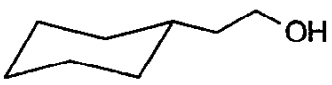
2. [20 points]. Complete the following reactions showing the missing reagent(s) (and solvent if important). If reactions involve more than one step label each step 1) then 2)...

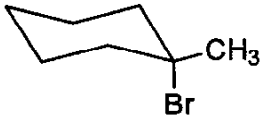
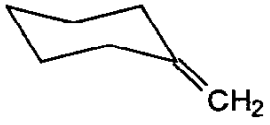
(a) $CH_3CH_2CH{=}CH_2$ → $CH_3CH_2CH_2CH_2Br$

(b)  → 

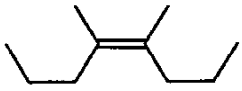
(c) $H_3C{-}C{\equiv}C{-}H$ → $CH_3CH_2{-}C(=O){-}H$

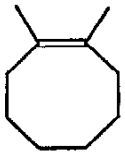
(d) $H_3C{-}C{\equiv}C{-}H$ → $H_3C{-}C{\equiv}C{-}CH_3$

(e)  → 

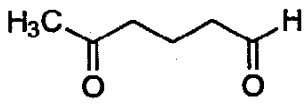
(f)  → 

3. [20 points]. Show the **major** product(s) obtained in each of the following reactions:

(a)  $\xrightarrow[2)\ H_2O\ \ NaHSO_3]{1)\ OsO_4}$

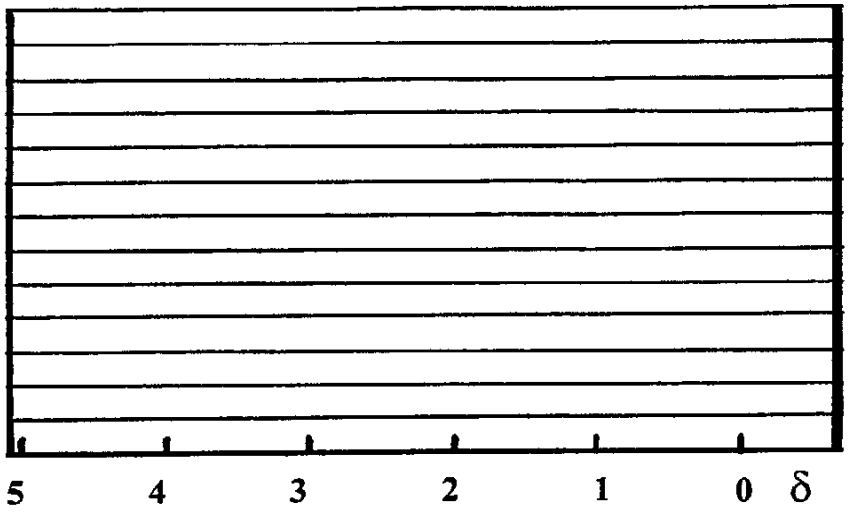
(b)  $\xrightarrow[H^{\oplus}\ \ H_2O]{KMnO_4}$

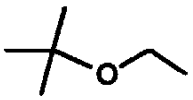
(c) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow[\Delta]{H_2SO_4}$

(d)  $\xrightarrow[Pt]{H_2}$

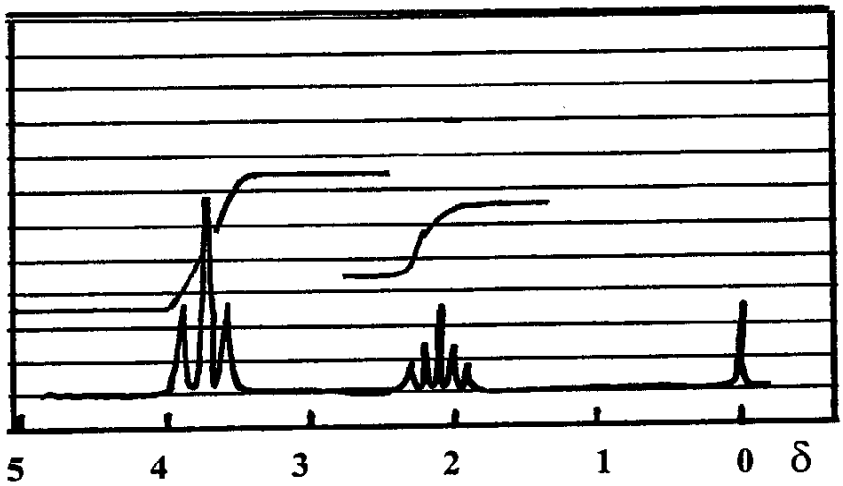
(e) $CH_3CH_2CH_2CH_2Br \xrightarrow[DMSO]{(C_6H_5)_3P}$

4. [20 points]. (4a) Sketch the ^{1}H NMR spectrum of *t*-butyl ethyl ether showing clearly the multiplicity of each set of signals and the integration of the spectrum



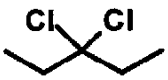


(4b) Which of the compounds below has the ^{1}H NMR spectrum shown below. Circle your answer and indicate using arrows which part of the molecule is responsible for each peak.



A 

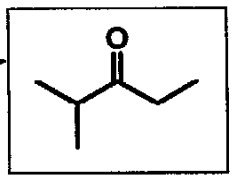
B 

C 

D 

E 

F 

(4c) Consider the ^{13}C NMR spectrum of the following molecule: 

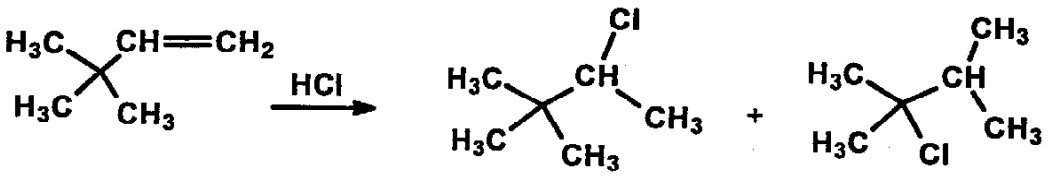
(i) How many peaks are seen in its "normal" ^{13}C NMR spectrum?

ANSWER:

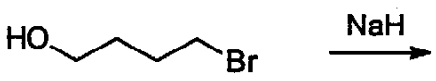
(ii) How many peaks are seen in its DEPT-90 spectrum?

ANSWER:

5. [15 points]. (a) Explain with one sentence and a detailed step by step mechanism (with arrows) why two products are formed in the following reaction.



(b) In the presence of a base such as sodium hydride, 4-bromobutanol reacts to form a product with the molecular formula C_4H_8O. Write a clear structure for the product and show a step by step mechanism for its formation.



Mechanism:

6. [18 points] (a) The length of the C≡C triple bond is: (circle one answer)

1.72Å 1.62Å 1.54Å 1.44Å 1.32Å 1.20Å 1.11Å 1.08Å

(b) Which anion is the strongest base? (Circle one answer)

$CH_3COO^{\ominus}$ $CH_3CH_2O^{\ominus}$ $CH_3CH_2S^{\ominus}$ $CH_3CH_2^{\ominus}$ $I^{\ominus}$ $OH^{\ominus}$

(c) Which one of the following statements is true (circle the number of one answer)

1. All mirror images are enantiomers
2. All molecules with chiral centers are enantiomers
3. All isomers that are not superimposable on their mirror images are enantiomers
4. All non-superimposable mirror images are enantiomers
5. All enantiomers have the same rotation

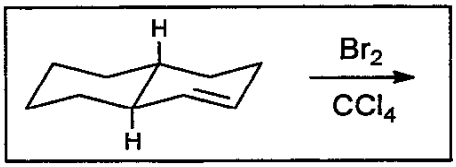
(d) Pentane and 2-methylbutane are examples of: (circle the number of one answer)

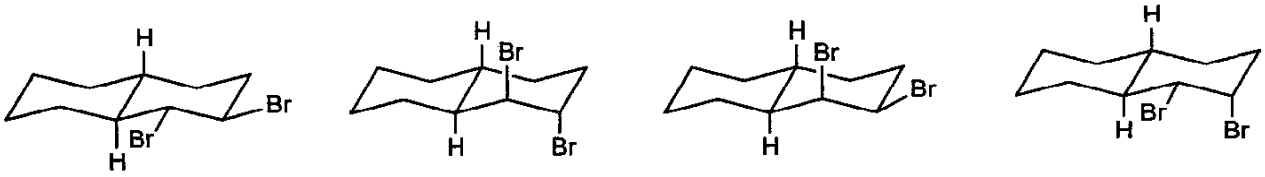
1. Stereoisomers
2. Diastereomers
3. Enantiomers
4. Constitutional isomers
5. Conformational isomers
6. None of these

(e) Which alkene reaction proceeds with anti addition? (Circle the number of one answer)

1. Acid catalyzed hydration
2. Hydroboration-oxidation
3. Catalytic hydrogenation
4. Oxymercuration-demercuration
5. Cleavage by permanganate
6. None of the above

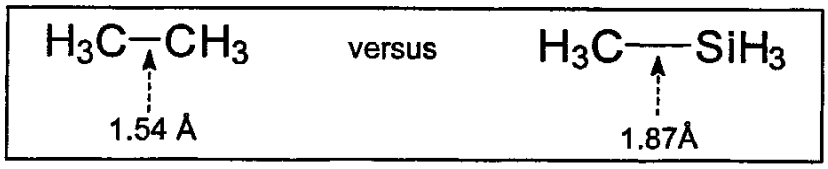
(f) Circle the major organic product obtained in the reaction below.





7. [15 points]

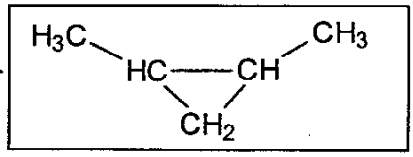
7a. In ethane the barrier to rotation is due to eclipsing strain. What effect on the barrier to rotation would you expect if the carbon-carbon bond of ethane (length C-C = 1.54 Å) was replaced by a carbon-silicon bond (length C-Si = 1.87Å). **Explain your reasoning.**



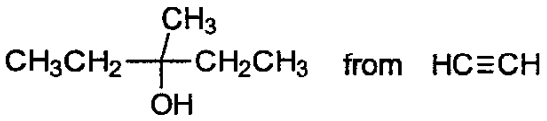
7b. An old bottle of 2-iodobutane has a label marked "2-Iodobutane mixture of enantiomers". The optical rotation α of a solution of 0.4g of this mixture in 2 mL of solvent measured in a 5 cm tube is found to be +0.64°. Given that the specific rotation of pure (S)-2-iodobutane is $[\alpha]_D$ = +16°, What is the optical purity of the sample? Calculate the percentages of (S) and (R) enantiomers in the old bottle. Show the equatio used for the calculation of $[\alpha]_D$ as well as the details of your calculation.

Answers:	Optical Purity =	% (S) =	% (R) =

8. [22 points]. Your answers should show all steps and reagents used, no mechanisms are needed. (a) propose a synthesis of from any organic compound with 2 C atoms or less.

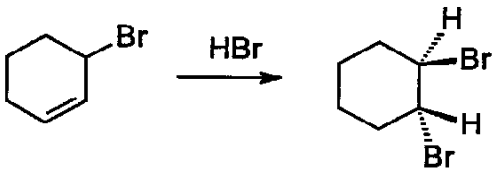


(b) Propose a synthesis of the compound below from ethyne as the sole source of C atoms



from HC≡CH

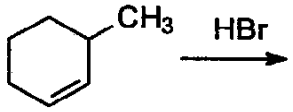
9. [14 points]. The reaction of 3-bromocyclohexene with HBr leads to racemic *trans*-1,2-dibromocyclohexane as the **sole product.** In contrast, the reaction of 3-methylcyclohexene with HBr leads to at least four products: *cis*- and *trans*-1-bromo-3-methylcyclohexane and *cis*- and *trans*-1-bromo-2-methylcyclohexane (if you think there might be more products, simply ignore them!).
Write a **step by step** mechanism for the reaction of 3-bromocyclohexene with HBr showing clearly the structure of the **key intermediate** involved. Also show the structure of the **intermediate(s)** involved in the addition of HBr to 3-methylcyclohexene and **explain** why one reaction produces only one product while the other produces many.



key intermediate is

Step-by-step mechanism:

Show the intermediate(s) involved in the reaction below.



Intermediate(s)

Explain...

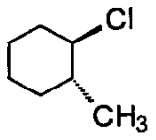
10. [14 points]. (a) The energy difference between gauche and anti butane is about 0.9 Kcal/mole which corresponds to an equilibrium constant K_{eq} = [anti] / [gauche] =1.9
Calculate the percentage of each conformer at equilibrium. Show your calculation.

Answers: | % anti = | | % gauche = |

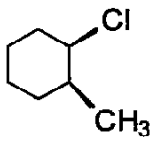
(b) Label each pair of compounds below as:

A: conformational isomers B: stereoisomers

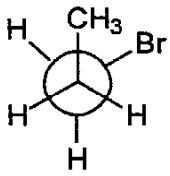
C: constitutional isomers D: identical



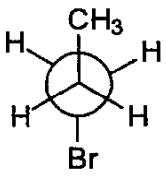
and



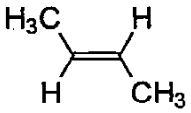
Answer:



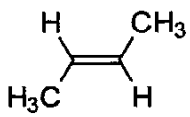
and



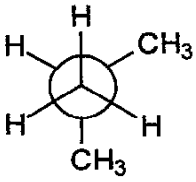
Answer:



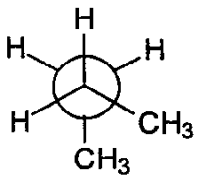
and



Answer:



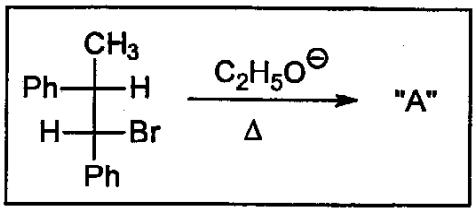
and

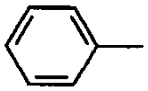


Answer:

11. [14 points].

Consider the reaction:

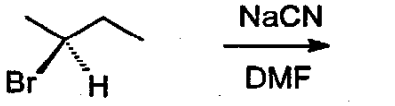


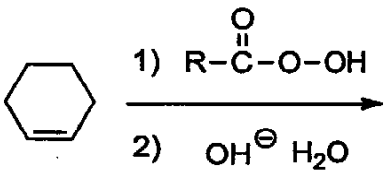
in which Ph = 

(a) Draw a Newman projection of the **reactive conformation** of the starting material

(b) Show the **structure** of the product of the reaction with clear **stereochemistry**

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



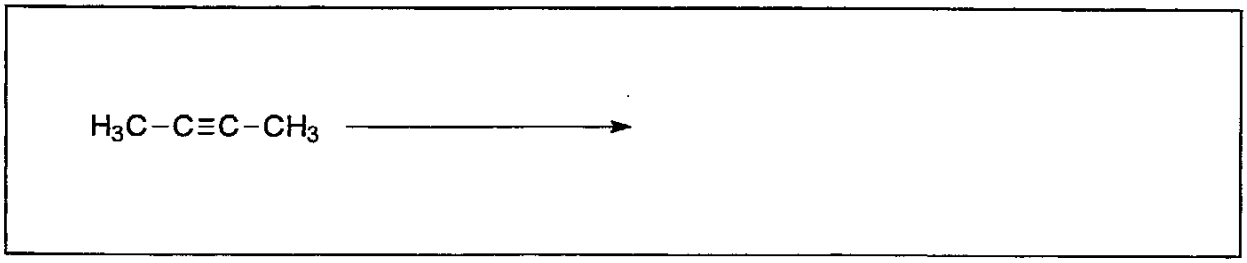


P. 14 not included (periodic table)

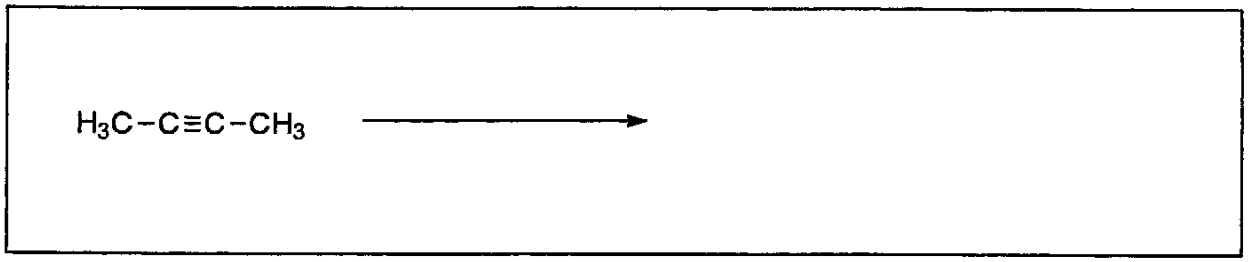
12. [13 points]

(a) Show with clear equations (indicating stereochemistry and showing all reagents) how 2-butyne can be transformed into:

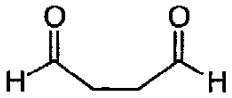
(i) E-2-butene



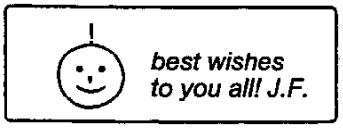
(ii) Z-2-butene



(b) Draw the structure of a hydrocarbon that absorbs two molar equivalents of hydrogen upon catalytic hydrogenation with platinum catalyst and gives only the molecule below on ozonolysis.



(c) Name the chemist who discovered the reaction of alkyl magnesium halides and aldehydes or ketones.



Answer: