Chemistry 3A - Spring 1998
Midterm Exam # 2

Professor Jean Fréchet

April 7, 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 **9** 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 80 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **no credit**.

Do Not Write in this Box.

1._____(12)
2._____(10)
3._____(14)
4._____(10)
5._____(12)
6._____(15)
7._____(12)
8._____(15)

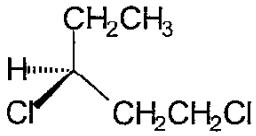
Total_____(100)

1. (12 points)

(a) Draw a Fisher projection of

(2S,3R)-2-chloro-3methylhexane

(b) Name the following compound:
(Use IUPAC nomenclature and do not forget stereochemistry)



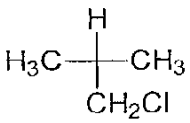
Answer:

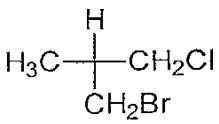
(c) An old bottle of 2-iodobutane has a label marked "2-Iodobutane mixture of enantiomers". The optical rotation α of a solution of 0.08g of this mixture in 2 mL of solvent measured in a 5 cm tube is found to be +0.192°. Given that the specific rotation of pure (R)-2-iodobutane is $[\alpha]_D$ = -16°, What is the optical purity of the sample? Calculate the percentages of (S) and (R) enantiomers in the old bottle. Show the equation used for the calculation of $[\alpha]_D$ as well as the details of your calculation.

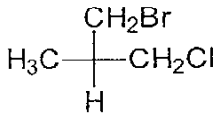
Answers: Optical Purity = | % (S) = | % (R) =

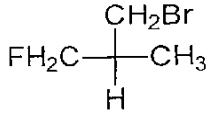
2. (10 points)

(a) Circle any molecule below that has an (R) configuration according to the Cahn-Ingold-Prelog convention





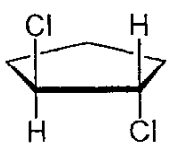


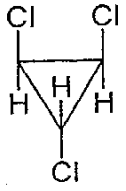


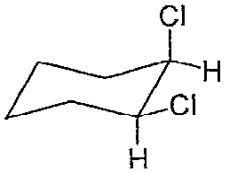
(b) What is the observed reaction rate for the S_N2 reaction below given the following concentrations: $[CH_3Cl] = 0.5$ mol L^{-1}; $[OH^-] = 0.03$ mol L^{-1} and the rate constant $k = 0.003$ mol^{-1} L s^{-1}. Your answer should show an equation for the rate law as well as all calculations.

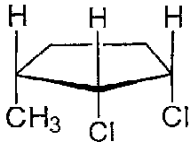
ANSWER Rate =

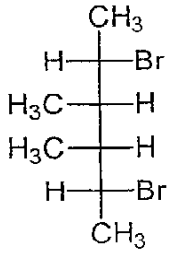
(c) Circle any compound below that is optically active









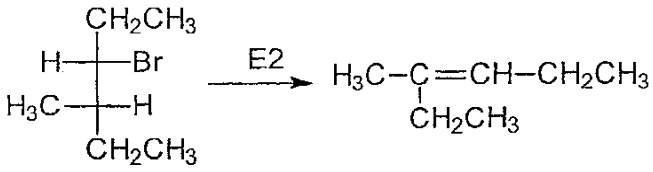


3. (14 points) (a) **Explain** why treatment of (S)-2-iodooctane with NaI causes the optical activity of the starting material to disappear. Your answer must **name** and describe in one sentence the type of reaction mechanism involved and its **stereochemical consequences** and show a complete equation with **all materials** (starting and final) and their **stereochemistry**.*(2-iodooctane is $CH_3CHI(CH_2)_5CH_3$)*

(b) Propose a **step-by step** synthesis of $CH_3CH{=}CHCH_3$ from **ethanol** as the only source of C atoms. Show **all reagents** required for each step but no mechanisms or curved arrows are needed.

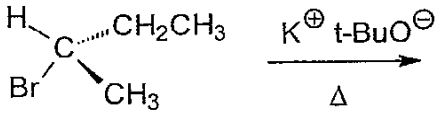
4. (10 points)

(a) Show the most favorable conformation (as a SAWHORSE projection) of the starting material for the E2 elimination below



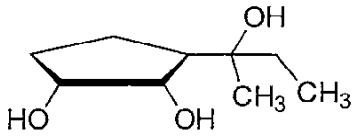
(b) Show a clear stereochemical representation of the alkene produced in this reaction.

(c) Write clear structures for the products containing no oxygen atom that are formed when 2-bromo-~~2-methyl~~butane is allowed to react with excess warm potassium t-butoxide.



5. (12 points)

(a) How many stereoisomers are possible in principle for the compound shown below (circle one number)



2	4	6	8
3	9	16	27
18	20	24	32
36	48	64	81

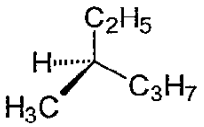
(b) Rank the following nucleophiles in order of reactivity for an S_N2 reaction

H_2O $HS^{\ominus}$ $C_2H_5O^{\ominus}$ $Cl^{\ominus}$

ANSWER: _____ > _____ > _____ > _____

Most reactive *Least reactive*

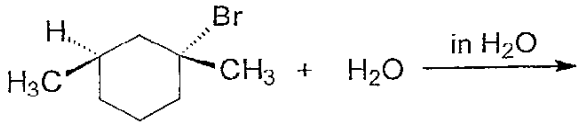
(c) Explain why the free-radical monobromination of affords a racemic mixture. Show the structure of both products and the intermediate leading to them



Structure of intermediate **Structure of products**

Brief Explanation: a racemic mixture is obtained because...

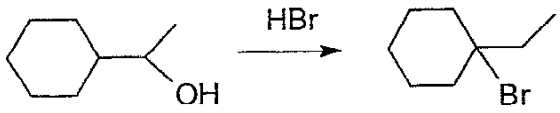
6. (15 points) (a) Show clear structures for **all** of the products normally expected in the reaction below. Assume that no rearrangement occurs and do not show any mechanism.



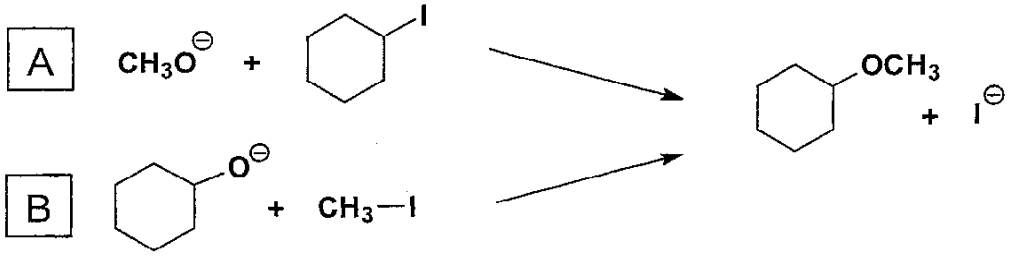
(b) What is the order of the reaction?

ANSWER: Order of reaction =

(c) Show a complete **step-by-step** mechanism (show **all** curved arrows!) for the reaction below



7. (12 points) (a) **Which** of the two synthetic routes, A or B, shown below would be best to obtain a high yield of the desired product? Explain your answer **discussing** briefly the type of mechanism involved and **comparing** the species in each reaction. Also **show a clear structure** for the side-product that might be obtained by the less desirable route.



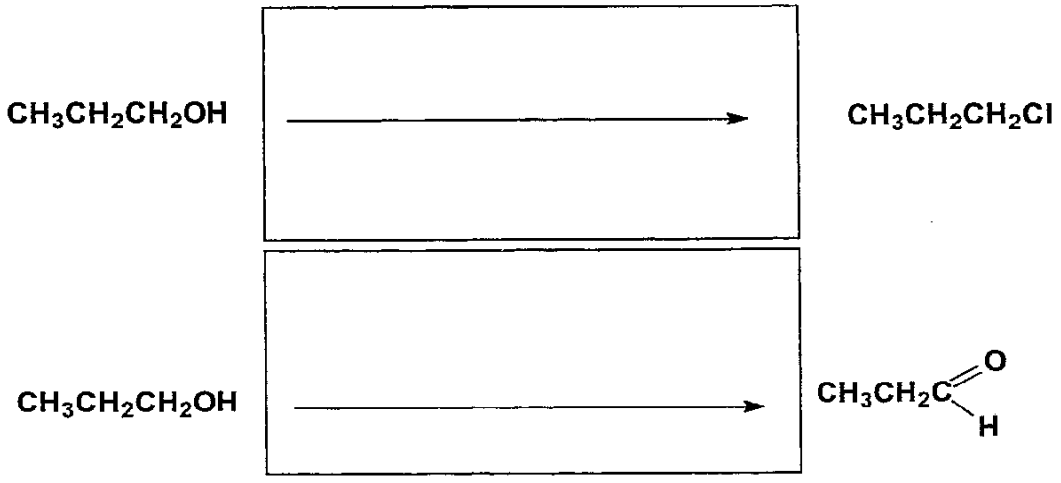
Answer:

Best route to product

Answer:

Structure of side-product for less desirable route

(b) Complete the reactions below showing a clear **structure** for each of the missing reagent(s).



8. (15 points) Show the structure of the **major product(s)** obtained in each of the following reactions. Your answer must show clear **stereochemistry** where applicable, write **NR** if no reaction occurs. Do not show any mechanisms!