


Chemistry 3A - Spring 2001 Midterm 2

Professor Jean Fréchet

March 19, 2001

Your full signature	
Print your full name	J. M. J. Fréchet
(Last name, first name, middle)	
Your SID	7 4 2 9 7
Name of your GS/TA	J. M. J. Fréchet

Please check the section number and

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|---|---|
| <p>___ 161 Padilla-De Jesus, Omayra</p> <p>___ 171 Fox, Daniel</p> <p>___ 181 Furuta, Paul</p> <p>___ 191 Ling, Frank</p> <p>___ 111 Cordaro, Joseph</p> <p>___ 121 Le, Scheherazade</p> <p>___ 131 Thalji, Reema</p> <p>___ 141 Catherine Seeley</p> <p>___ 261 Peterka, Darcy</p> <p>___ 271 Miljanic, Ognjen</p> <p>___ 211 Dertz, Emily</p> <p>___ 221 Simon, Matthew</p> <p>___ 361 Barry, David</p> | <p>___ 371 Miljanic, Ognjen</p> <p>___ 311 Sivamani, Raja</p> <p>___ 321 Li, Ben</p> <p>___ 461 Huang, Alan</p> <p><input checked="" type="checkbox"/> 471 Liang, Catherine</p> <p>___ 411 Phillips, Scott</p> <p>___ 421 Saxon, Eliana</p> <p>___ 431 Osterhout, Robin</p> <p>___ 561 Merolle, Mauro</p> <p>___ 511 Klopp, John</p> <p>___ 521 Wu, Sarah</p> <p>___ 531 Rao, Vikas</p> |
|---|---|


If you are making up an I-grade, indicate the semester you took 3A _____ and the Professor _____.

This exam has 10 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 90 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



9

1. _____ (12)

2. _____ (10)

3. _____ (10)

4. _____ (10)

5. _____ (10)

6. _____ (14)

7. _____ (12)

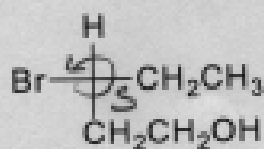
8. _____ (10)

Total **81** (100)

1. (12 points)

Name or draw, as appropriate, the following molecules. Do not forget stereochemistry where appropriate.

(a)



(IUPAC name)

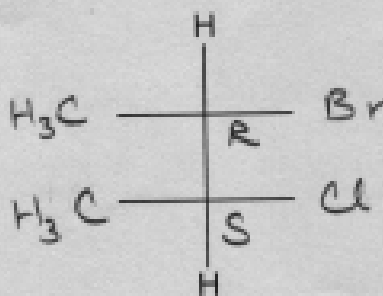
~~(3S)-3-bromo-1-pentanol~~

3

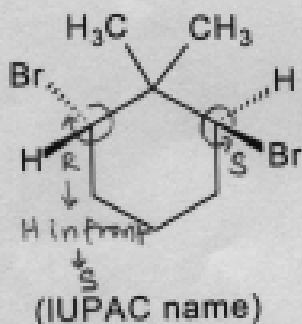
(b) (2R,3S)-2-bromo-3-chlorobutane

(Fischer Projection)

3



(c)

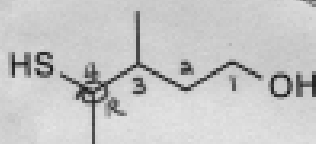


(IUPAC name)

~~trans-(1S,3S)-1,3-dibromo-2,2-dimethylcyclohexane~~

3

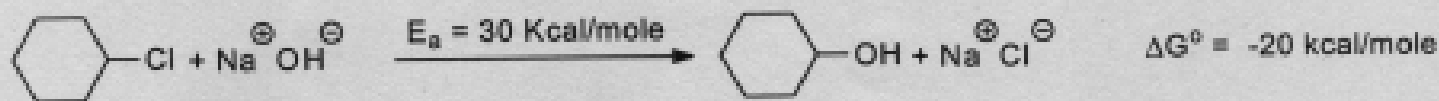
(d)

~~(1R)-4-mercapto-3,4-dimethyl-1-pentanol~~

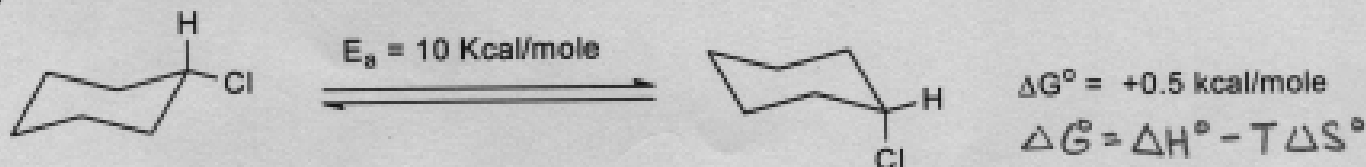
4-mercapto-3-methyl-1-pentanol

6

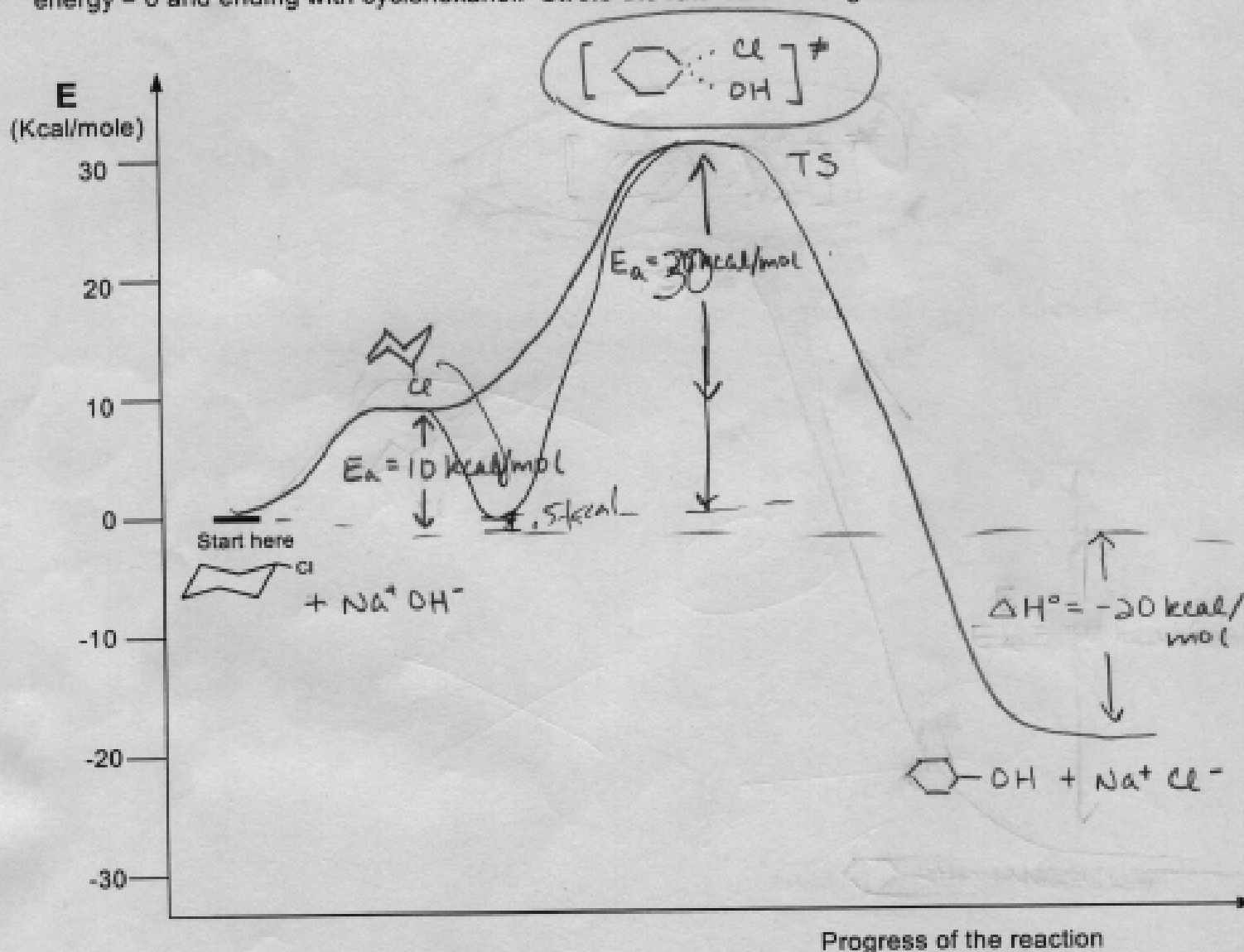
2. (10 Points). Consider the reaction of chlorocyclohexane with sodium hydroxide leading to cyclohexanol and sodium chloride as shown below.

 S_{02}

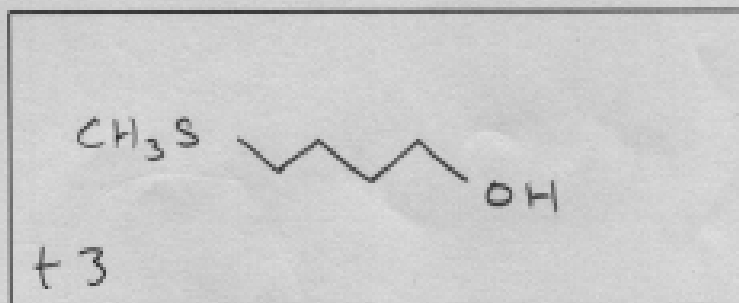
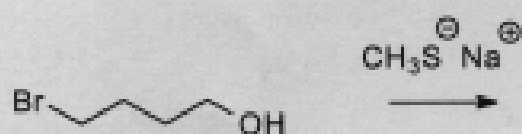
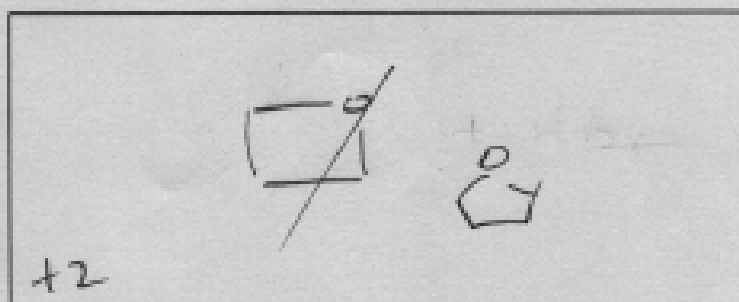
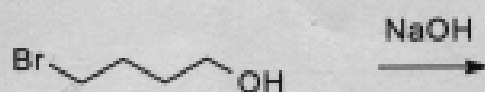
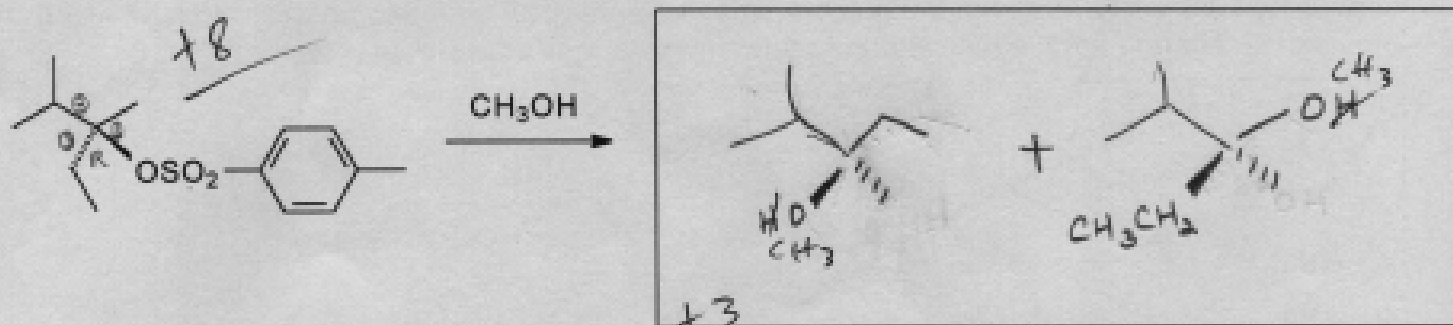
For the purpose of this exam, let us assume that the reaction not only follows second order kinetics but also that it proceeds through the axial form of chlorocyclohexane. Therefore, the equilibrium below precedes the attack by the hydroxide anion above.



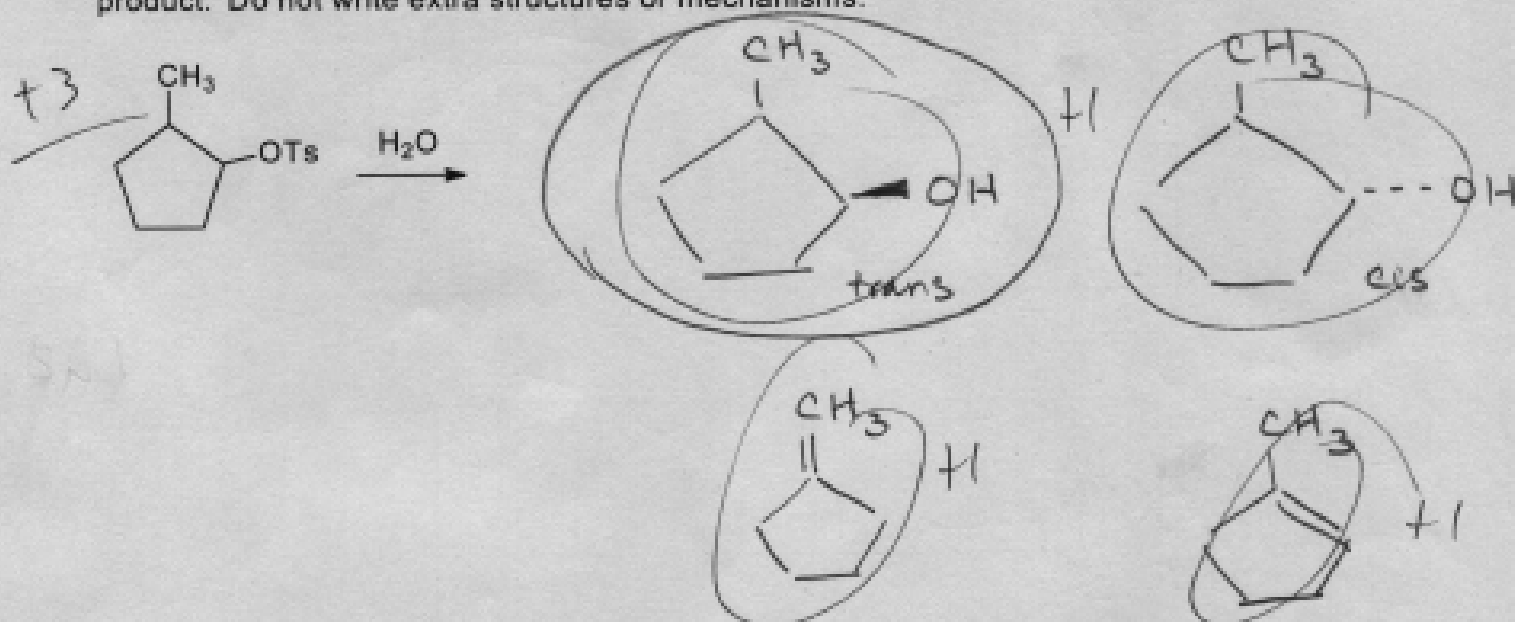
Using the thermodynamic data provided, draw a scaled and **fully labeled** potential energy diagram for the overall process, starting from equatorial chlorocyclohexane arbitrarily assigned the relative energy = 0 and ending with cyclohexanol. **Circle the rate-determining transition state.**



3. (16 Points) (a) Show the major product (or major products) obtained in the reactions below.

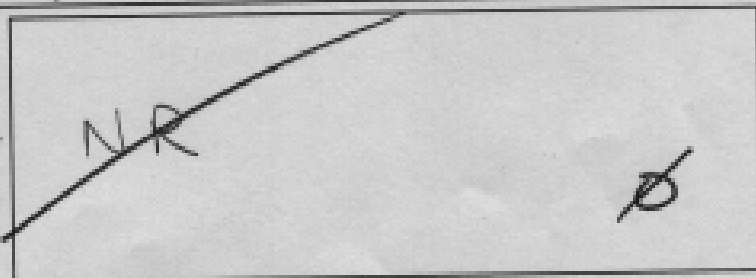
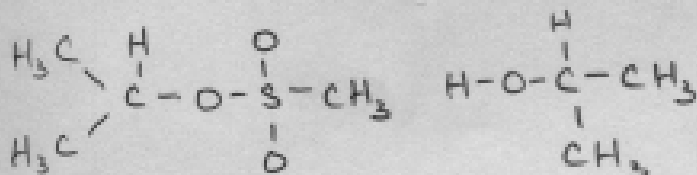
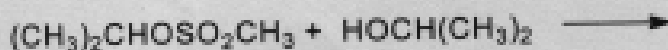
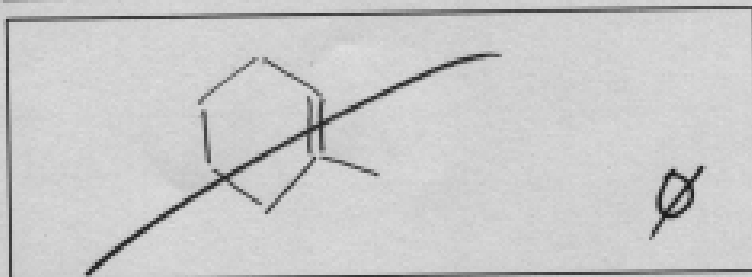
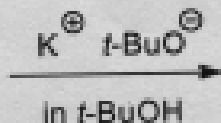
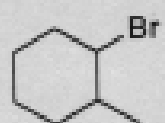
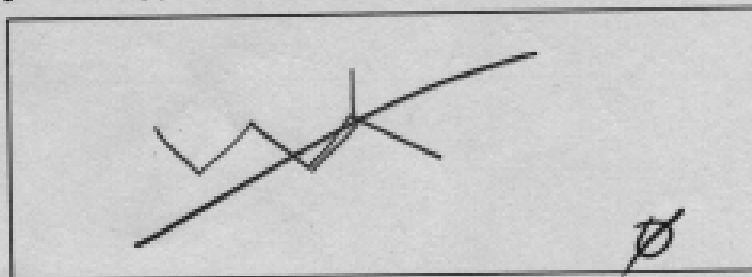
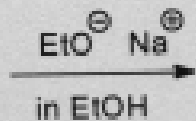
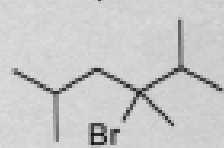


(b) Write clear structures for all of the plausible products of the reaction below and circle the major product. Do not write extra structures or mechanisms.

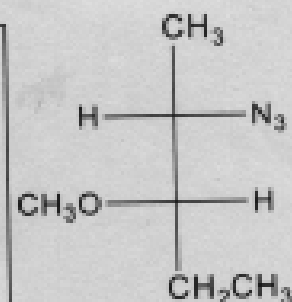
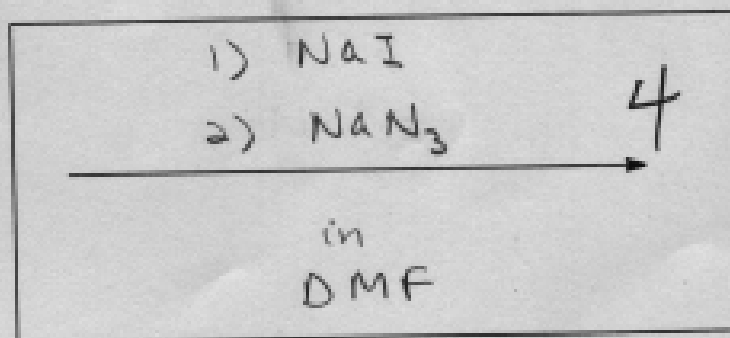
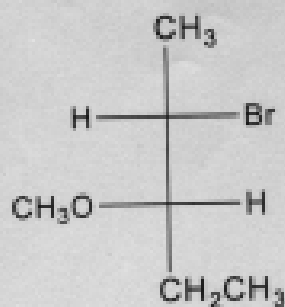
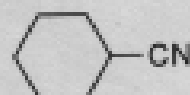
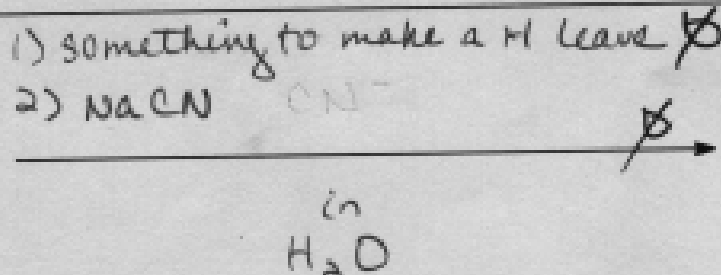
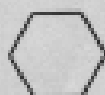


4. (14 points). (a) Complete the following reactions showing the structure of the **MAJOR** product. Show clear stereochemistry where appropriate. Write **NR** if there is no reaction.

4

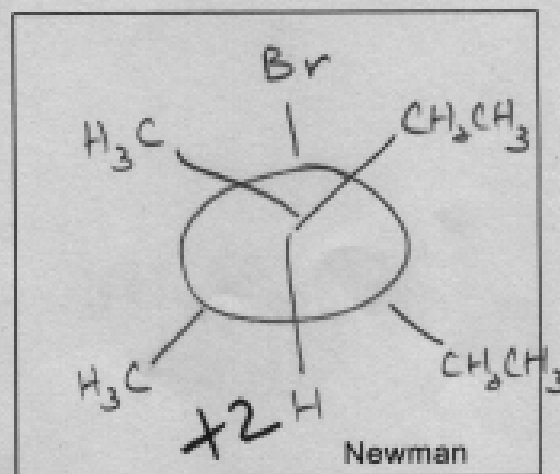
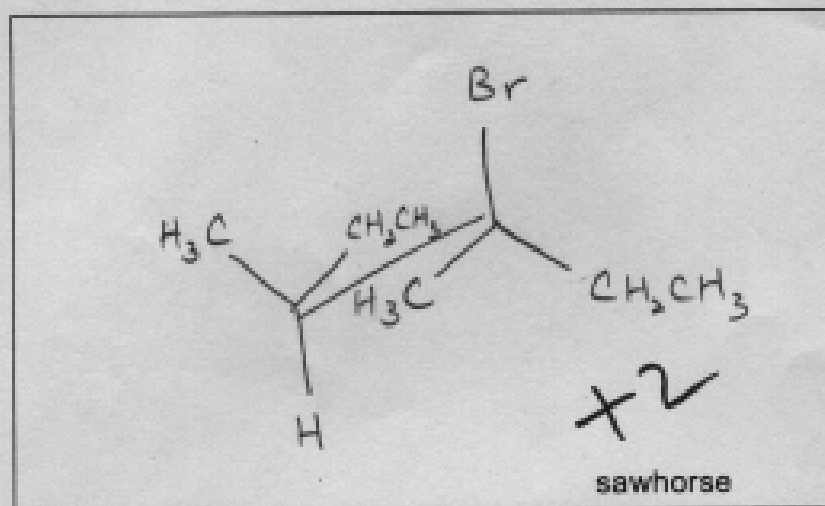
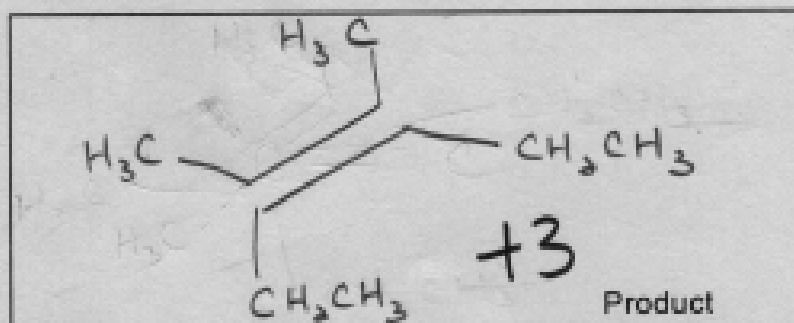
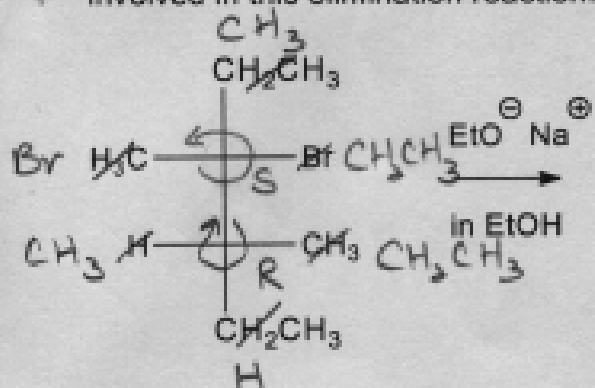


- (b) Complete the following reactions showing **all the reagents** and special conditions needed to obtain the product. If more than one step is required label the steps 1) then 2), etc.

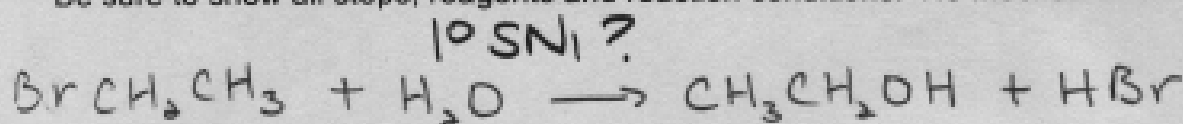


7

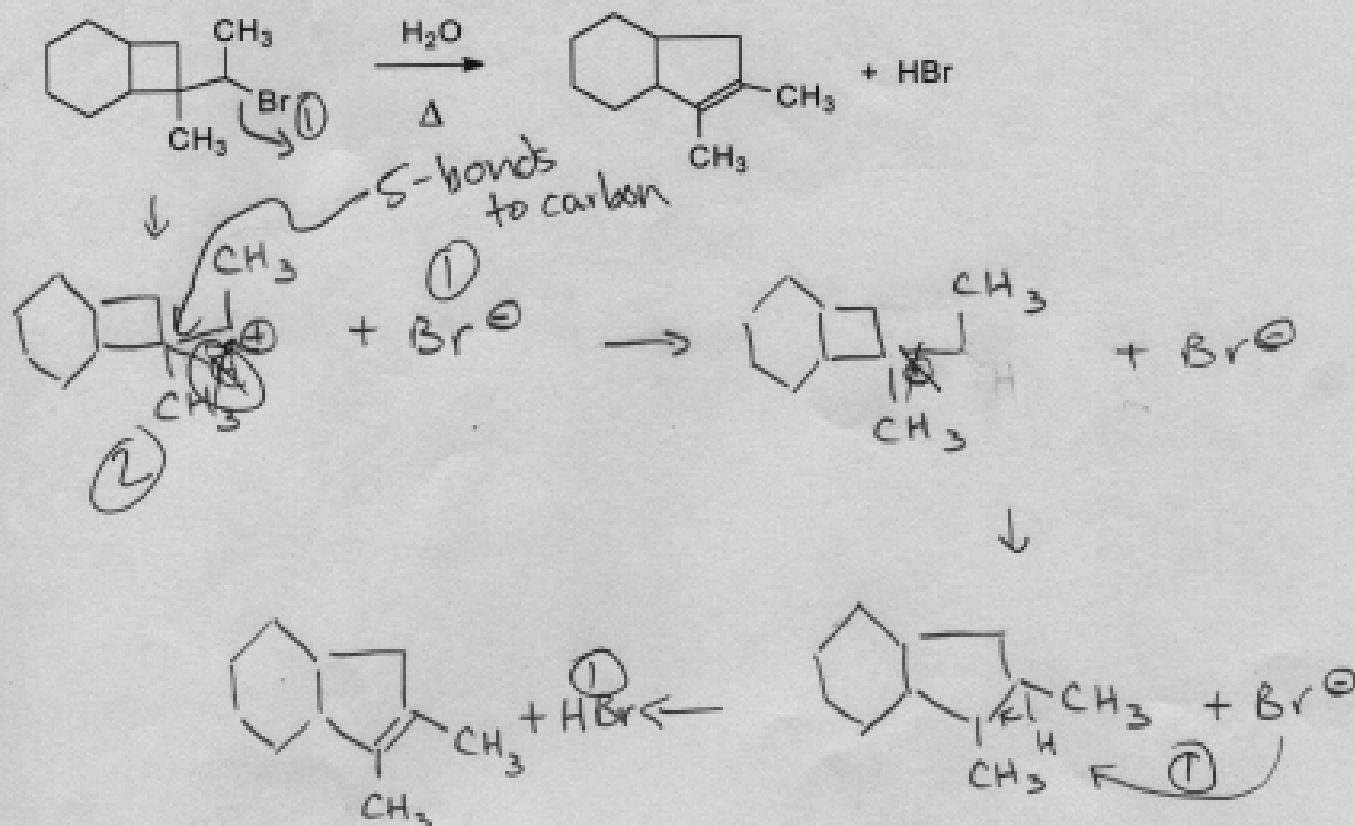
5. (12Points) (a) Show a clear **stereochemical** structure for the major alkene product obtained in the reaction below. Also show both sawhorse and Newman projections of **the reactive conformation** involved in this elimination reaction.



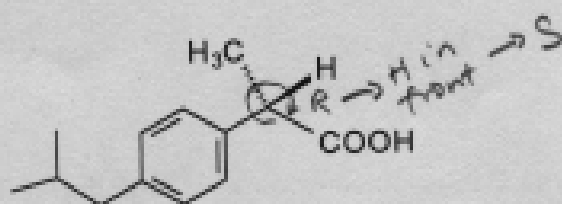
- (b) Show how you would make diethyl ether $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ from bromoethane. You may use any other reagent you need but all the C atoms of the product must originate from bromoethane. Be sure to show all steps, reagents and reaction conditions. No mechanisms needed.



6. (14 points). (a) Write a step-by-step mechanism (include arrows) accounting for the formation of both products in the reaction below:



(b) A commercial synthesis of **Ibuprofen** gives the enantiomer shown in 97% enantiomeric excess. Is this isomer R or S? (Note: do not guess!! wrong answers will incur a point deduction)



Answer:

S

(1)

What is the percentage of the major isomer in the mixture above? Show the details of your work.

$$\text{enantiomer excess} = \% \text{ optical purity} = 97\%$$

97% (S)

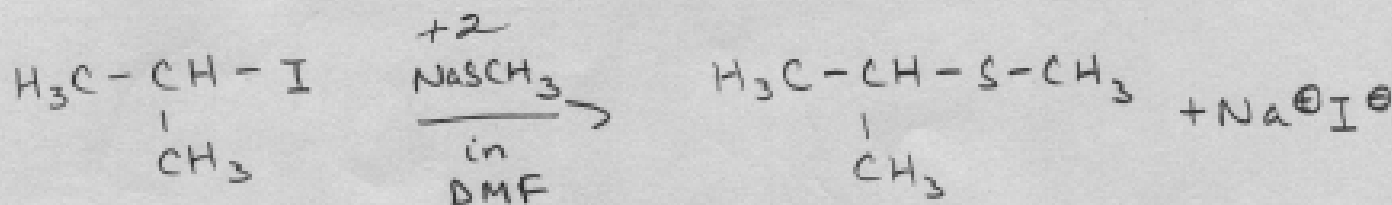
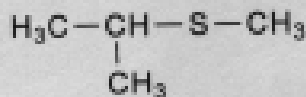
3% racemic \rightarrow 1.5% (R)
 \rightarrow 1.5% (S)

97% + 1.5% = 98.5% (S)

Answer: 98.5 %

(3)

7. (12 points). (a) Using only propane and methane as the sole source of carbon atoms, propose a synthesis of the compound below. You may use any other reagent you require. Show all the steps of the synthesis and all the reagents or special conditions used. No mechanisms are required.



- (b) The optical rotation of a solution of 0.4g of a steroid dissolved in 10.0mL of alcohol measured in a tube 5.0 cm in length at 25°C using the D line of a sodium lamp is +2.18°. Calculate the specific rotation of the steroid. Show the formula you use and the details of your calculations.

$$[\alpha]_{\text{specific}} = \frac{[\alpha]_{\text{observed}}}{\text{length} \times \text{conc.}} + 2$$

$$= \frac{+2.18}{(0.5 \text{ dm}) \left(\frac{0.4 \text{ g}}{10.0 \text{ mL}}\right)}$$

$$= +109$$

$$5.0 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{10 \text{ dm}}{1 \text{ m}} = 0.5 \text{ dm}$$

Answer:

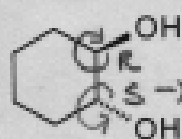
$$+109 + 2$$

6/12

8. (10 Points) For all multiple choice questions circle the number of the correct answer (one only)

- (a) CH_3Cl is:
- (1) a liquid at 0°C (2) a good haloalkane for E2 eliminations
- (3) a chemical found in Kelp (4) a good nucleophile for $\text{S}_\text{N}2$ reactions
- (5) A haloalkane that reacts rapidly with hot water to form methanol CH_3OH

(b) What is the most appropriate name for the molecule shown below



~~(1) meso-1,2-cyclohexanediol~~

(2) (1R,2R)-1,2-cyclohexanediol

~~(3) (1S,2S)-1,2-cyclohexanediol~~

(4) (1R,2S)-1,2-cyclohexanediol

(5) (1S,2R)-1,2-cyclohexanediol

(c) Doubling the concentration of KOH in the reaction

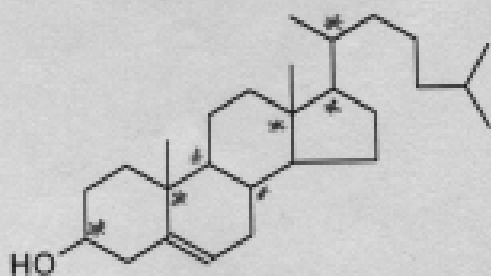


- (1) Changes the mechanism to elimination (2) Has no effect on reaction rate
- (3) Halves the rate of reaction (4) Doubles the rate of reaction
- (5) Changes the order of the reaction (6) Changes the regiochemistry

(d) The discovery of the interaction of optically active substances with plane polarized light is credited to:

- (1) Biot (2) Pauling (3) Saytzev (4) Pasteur (5) Kekule

(e) How many stereocenters are present in the molecule of cholesterol? (circle one number)



- 1 2 3 4
- 5 6 7 8
- 9 10 11 12

Note: There are no questions to be answered on this page, it only contains data that may be of use in solving the questions contained in this exam. Not all of the data given is needed.

Value of gas constant: $R = 2.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$

Value of e (base for natural logarithms) $e = 2.718$

Value of absolute zero (kelvin) = -273°C

Partial periodic table of the elements

GROUP	I A	II A	III B	IV B	V B	VI B	VII B	0
VALENCES	+1	+2	+3	-4 +4	-3 +5	-2 +6	-1 +7	0
PERIOD	1							2
1	H 1.008							He 4.003
2	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3