

FINAL EXAMINATION
Chemistry 3A

Name: _____

SID #: _____

Print first name before second!

Use capital letters!

GSI (if you are taking Chem 3AL): _____

Peter Vollhardt

May 10, 2017

Please provide the following information if applicable.

Making up an I Grade _____

If you are, please indicate the semester during which you took previous Chem 3A and the instructor:

Semester_____
Instructor*Auditor* _____

Please write the answer you wish to be graded in the boxed spaces provided.

Do scratch work on the back of the pages. This test should have **23** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later! Good Luck!**

You will not really need it, but here is a partial periodic table.

TABLE 1-1		Partial Periodic Table						
Period							Halogens	Noble gases
First	H ¹							He ²
Second	Li ^{2,1}	Be ^{2,2}	B ^{2,3}	C ^{2,4}	N ^{2,5}	O ^{2,6}	F ^{2,7}	Ne ^{2,8}
Third	Na ^{2,8,1}	Mg ^{2,8,2}	Al ^{2,8,3}	Si ^{2,8,4}	P ^{2,8,5}	S ^{2,8,6}	Cl ^{2,8,7}	Ar ^{2,8,8}
Fourth	K ^{2,8,8,1}						Br ^{2,8,18,7}	Kr ^{2,8,18,8}
Fifth							I ^{2,8,18,18,7}	Xe ^{2,8,18,18,8}

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

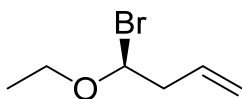
- I. [60 Points] Provide the IUPAC name or draw the structure, as appropriate, of the following molecules. Remember the priority of functional groups in choosing names, indicate the correct stereochemistry (e.g. *R*, *S*, *cis*, *trans*, and *E*, *Z*), and do not forget about the alphabetical ordering of substituents!

a.

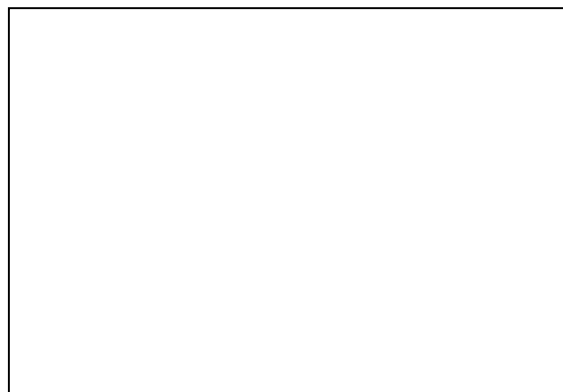
(*R*)-1-Hexen-5-yne-3-thiol



b.



This enantiomer

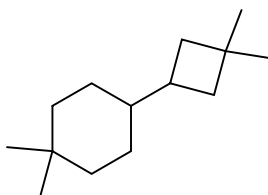


c.

(*R*)-1-Mercapto-4-pentyn-2-ol

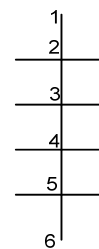


d.

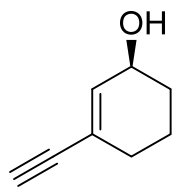


e.

meso-3,4-Dimercapto-1,6-hexanediol



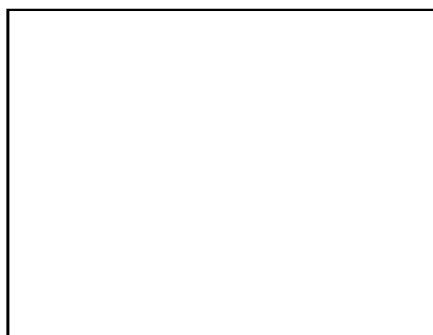
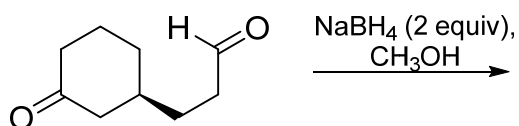
f.



This enantiomer

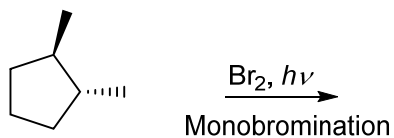
II. [100 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). Don't forget **stereochemistry**! Complete the stencils, when provided. **Note:** In the reagent boxes above the arrows, enter one step only. Multistep sequences are clearly indicated by several boxes labelled "1., 2., 3.," etc.

a.

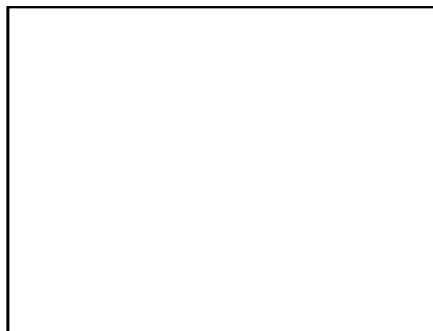


Two diastereomers

b.



This enantiomer



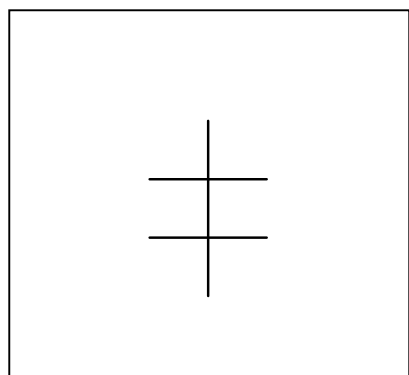
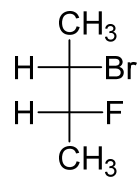
Two diastereomers

For the following questions, circle your choice of an answer:

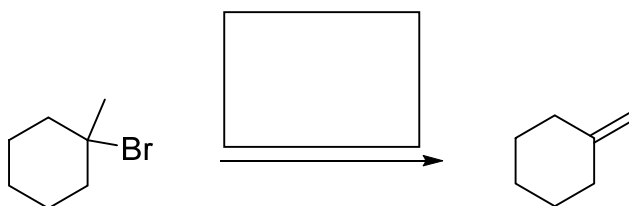
Are both products chiral? Yes No

Are both products optically active? Yes No

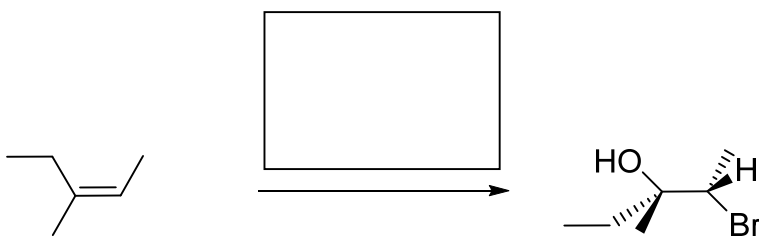
c.


 C_4H_8ClF
 $\xrightarrow{NaBr (1 \text{ equivalent}), CH_3OH}$


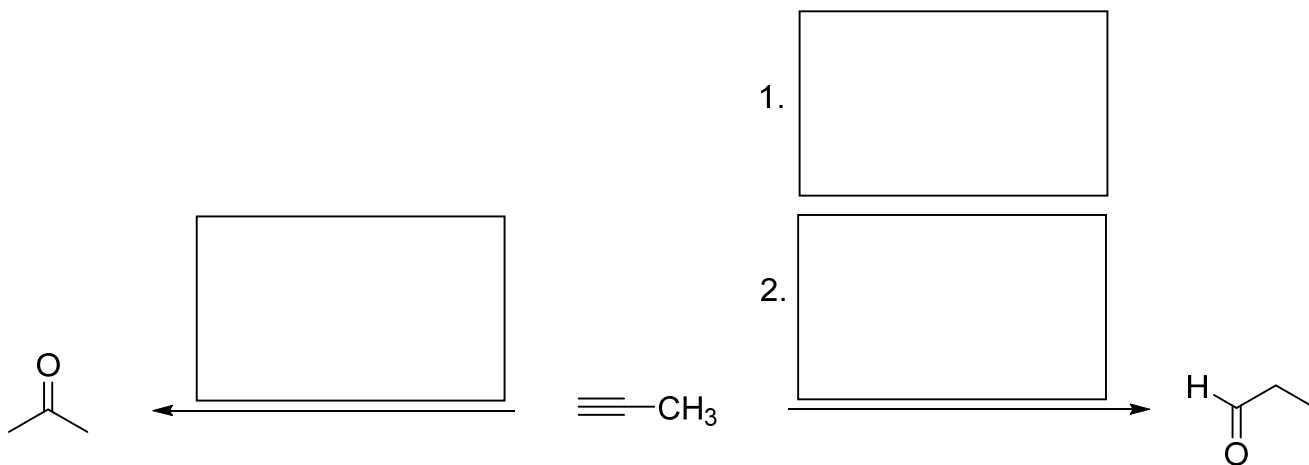
d.



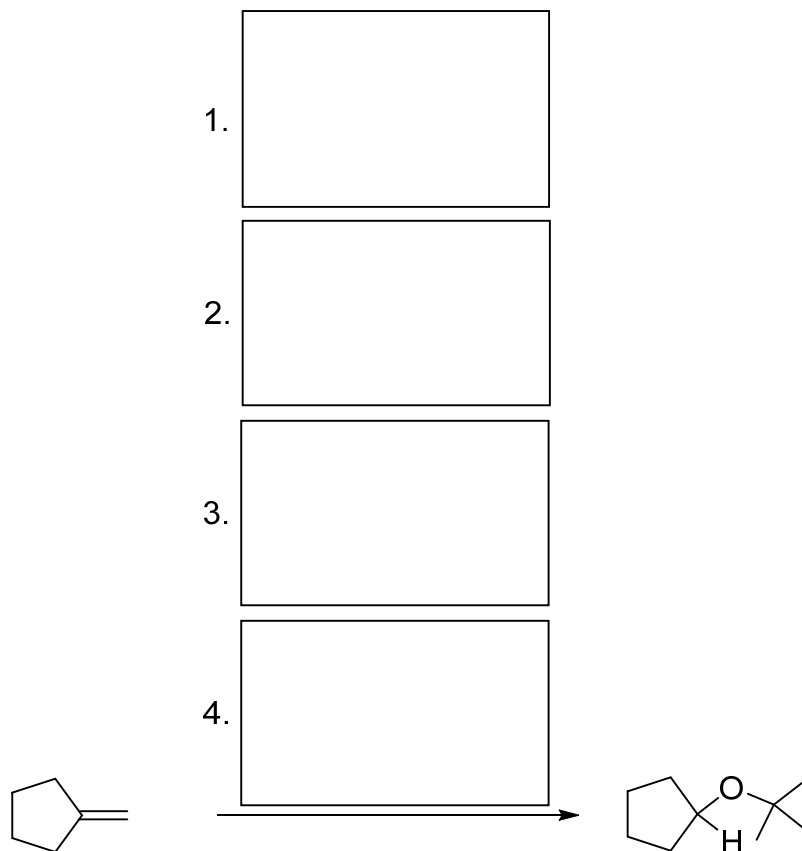
e.



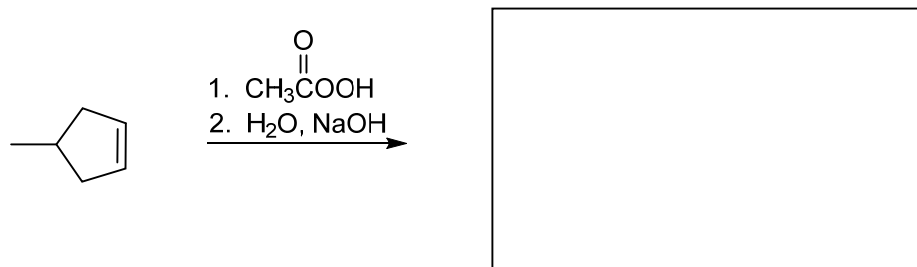
f.



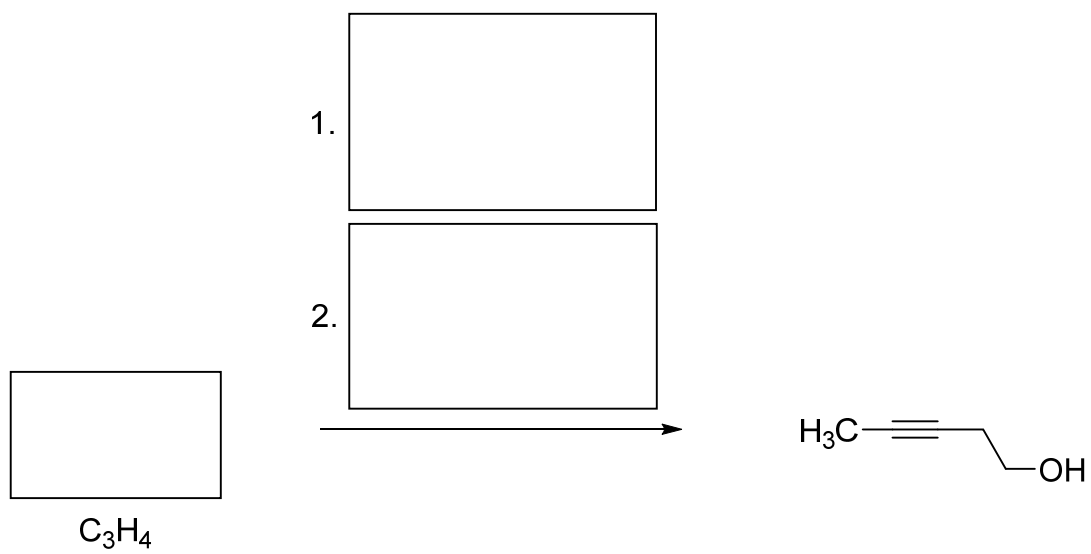
g.



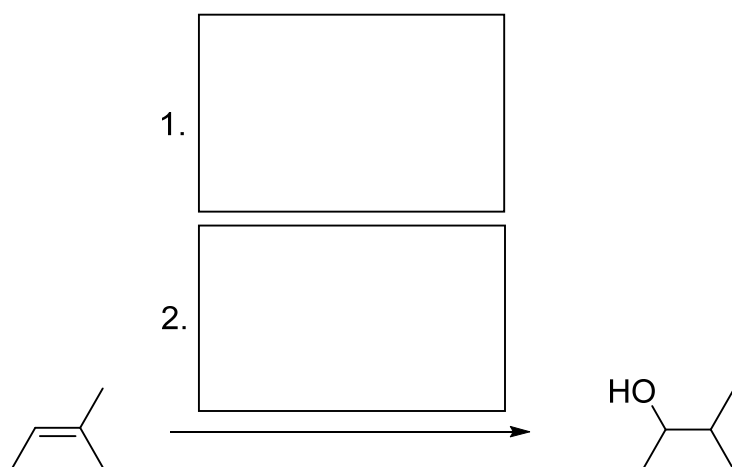
h.



i.



j.



III. [50 Points] The potential radical addition of HI to 1-propene is too slow to compete with the conventional Markovnikov hydroiodination.

a. Write the two propagation steps for the radical chain reaction:

Step 1.

Step 2.

b. Using $DH^\circ_{\text{C-H}} = 65 \text{ kcal mol}^{-1}$ and the appropriate data in the Table below, calculate the ΔH° of both propagation steps. Show your work.

Table 3-1 Bond-Dissociation Energies of Various A–B Bonds in the Gas Phase [DH° in kcal mol^{-1} (kJ mol^{-1})]							
A in A–B	B in A–B						
	–H	–F	–Cl	–Br	–I	–OH	–NH ₂
H–	104 (435)	136 (569)	103 (431)	87 (364)	71 (297)	119 (498)	108 (452)
CH ₃ –	105 (439)	110 (460)	85 (356)	70 (293)	57 (238)	93 (389)	84 (352)
CH ₃ CH ₂ –	101 (423)	111 (464)	84 (352)	70 (293)	56 (234)	94 (393)	85 (356)
CH ₃ CH ₂ CH ₂ –	101 (423)	110 (460)	85 (356)	70 (293)	56 (234)	92 (385)	84 (352)
(CH ₃) ₂ CH–	98.5 (412)	111 (464)	84 (352)	71 (297)	56 (234)	96 (402)	86 (360)
(CH ₃) ₃ C–	96.5 (404)	110 (460)	85 (356)	71 (297)	55 (230)	96 (402)	85 (356)

ΔH° of propagation step 1:

ΔH° of propagation step 2:

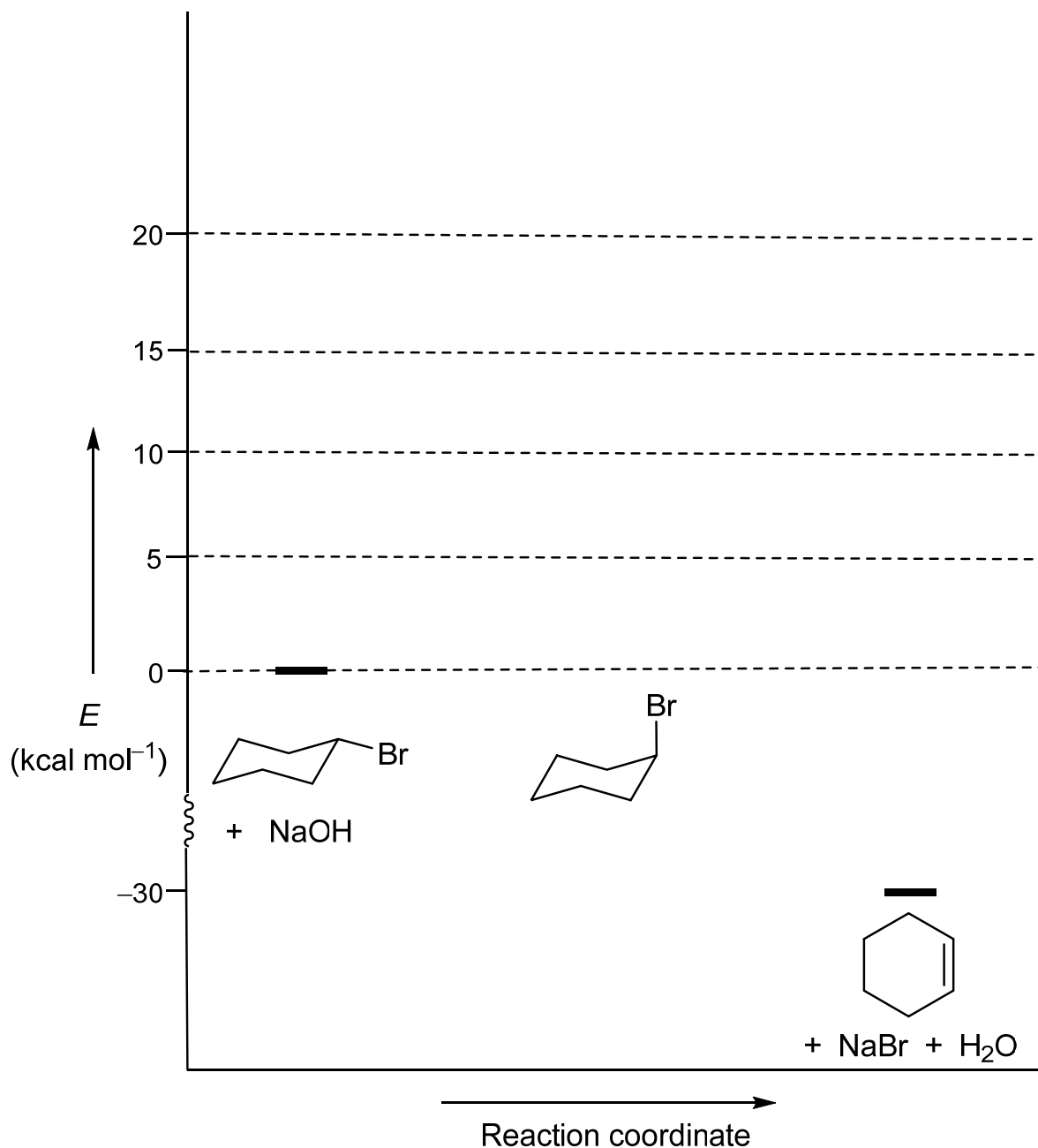
c. Which propagation step makes this reaction kinetically noncompetitive?
(Place an "X" mark next to your answer in the box provided).

Step 1

Step 2

IV. [30 Points] The mechanism for the E2 reaction of bromocyclohexane with NaOH proceeds through the axial conformer [ΔG° (equatorial-axial) = +0.5 kcal mol⁻¹, E_a (equatorial-axial) = 10 kcal mol⁻¹] with an activation barrier of 20 kcal mol⁻¹. Draw the potential energy diagram for this process. The starting material energies are set at 0 kcal mol⁻¹. Show clearly the position of the transition states (use the labels "TS1" and "TS2") and of the axial conformer, using short horizontal "energy level" lines.

Potential-Energy Diagram



V. [20 Points] Using key words or a short sentence, list four techniques or experiments that support the mechanism of the S_N1 reaction.

1.

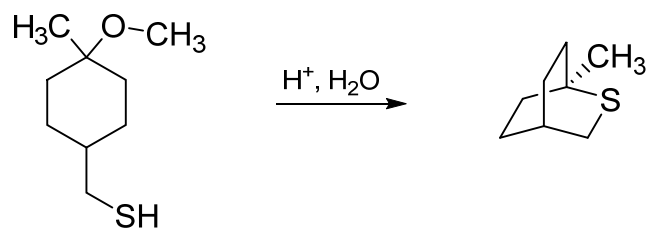
2.

3.

4.

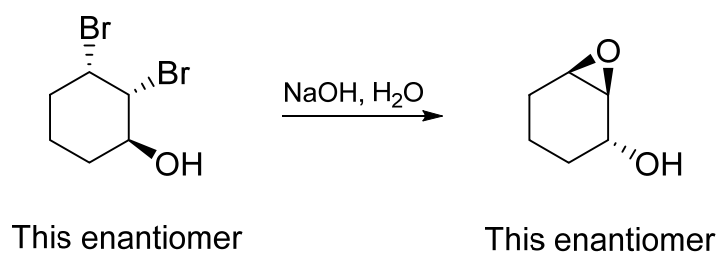
VI. [75 Points] Write detailed step-wise mechanisms for the following transformations. Use only structures and “arrow-pushing of electron dots” techniques. Note: These are not synthetic problems. Do not add any reagents! What you see is what you have!

a.



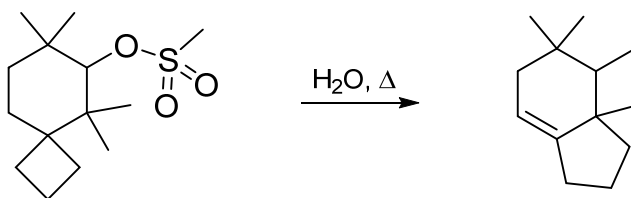
Work from left to right in the following spaces. There is much more space than you will need.

b.



Work from left to right in the following spaces. There is much more space than you will need.

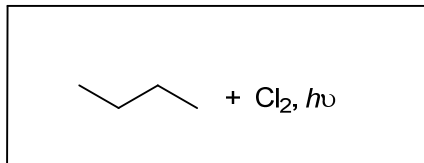
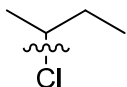
c.



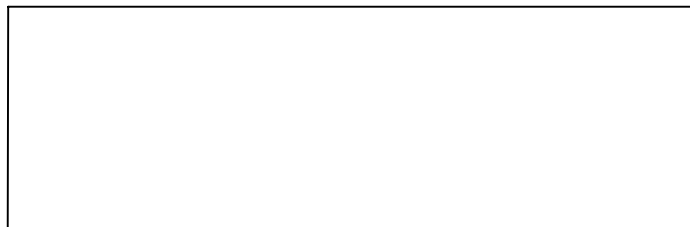
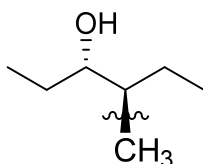
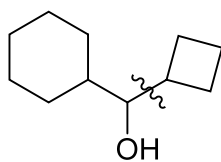
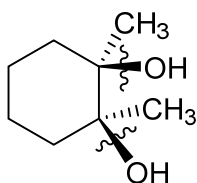
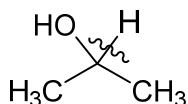
Work from left to right in the following spaces. There is much more space than you will need.

VII. [20 Points] For the following retrosynthetic disconnections (indicated by “~”), enter in the box provided the process that would make the ruptured bond. Follow the format indicated in the sample problem below.

Sample problem:

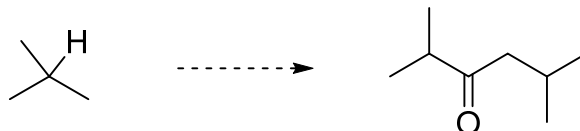


Problems to be answered:



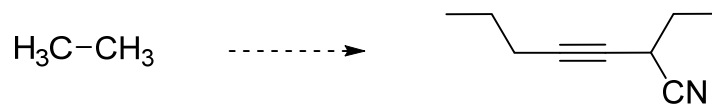
VIII. [75 Points] Show synthetic **forward connections** (reagents, intermediates; no mechanisms!) between the following starting materials and the final products. Note: several steps are required in each case; there may be several solutions to each problem, but you should use only one; it is best to work backwards (retrosynthetically) on the back of the exam pages, to enable you to dissect the products into less complex precursors. However, the answer to be graded should be a *forward* scheme. In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less**.

a.



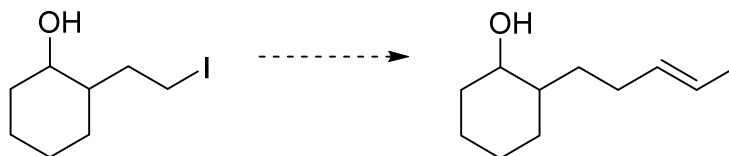
Work from left to right in the following spaces. There is much more space than you will need.

b.



Work from left to right in the following spaces. There is much more space than you will need. Remember: In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less**.

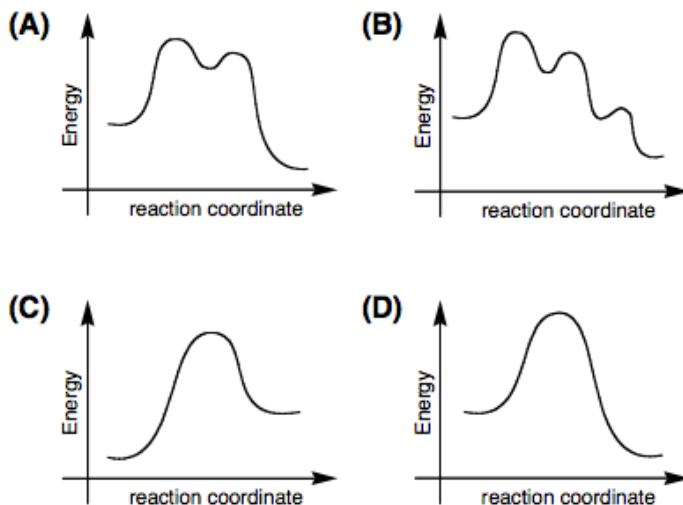
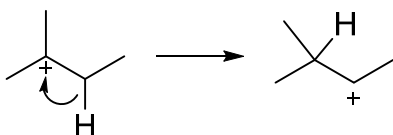
c.



Work from left to right in the following spaces. There is much more space than you will need. Remember: In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less**.

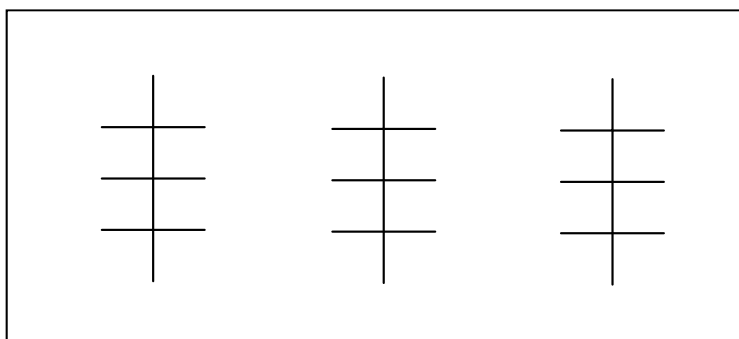
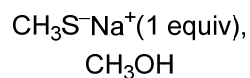
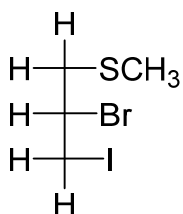
IX. [70 Points]

a. Which of the following potential energy diagrams describes the hydride shift depicted below left? Give your answer (**A**, **B**, **C**, or **D**) in the box provided.



Answer:

b. The following reaction proceeds (predominantly) by the S_N2 , S_N1 , E2, or E1 pathway. Give the major product (or products) and answer the questions by **circling** the most applicable statement. Use the Fischer stencils provided. There are more than you will need.



This enantiomer

Mechanism:

S_N2

S_N1

E2

E1

On changing $\text{CH}_3\text{S}^-\text{Na}^+$ to $\text{CH}_3\text{O}^-\text{Na}^+$, which one of the following ratios will increase:

S_N1 / S_N2

$S_N1 / E1$

$E1 / E2$

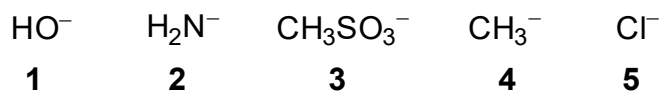
$E2 / S_N2$

Is/are the product(s) optically active?

Yes

No

c. For the following groups, the order of increasing leaving group ability is



Place an "X" mark next to your answer.

- _____ **1, 2, 3, 5, 4**
- _____ **4, 2, 1, 5, 3**
- _____ **3, 1, 2, 4, 5**
- _____ **4, 2, 5, 1, 3**

d. Using the Table below, draw the most stable conformation of (1*S*,2*R*,4*S*)-4-chloro-2-ethyl-1-methylcyclohexane. Use the stencil provided in the box.

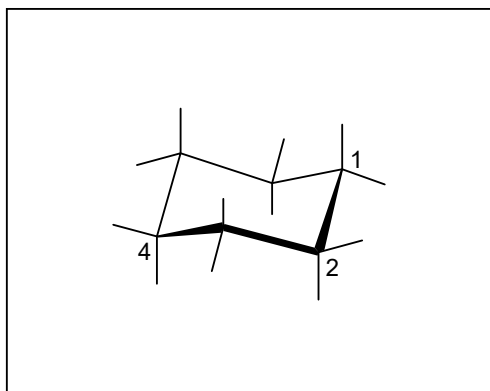
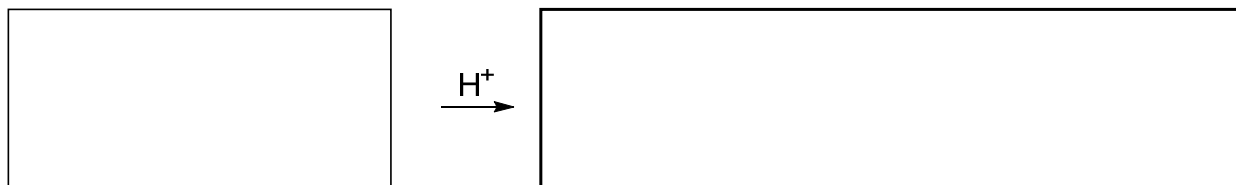


Table 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial			
Substituent	ΔG° [kcal mol ⁻¹ (kJ mol ⁻¹)]		
H	0	(0)	<div style="display: flex; align-items: center; justify-content: center;"> <div style="writing-mode: vertical-rl; transform: rotate(180deg); font-weight: bold; margin-right: 5px;">Increasing size</div> <div style="font-size: 2em; margin-right: 10px;">↓</div> <div style="writing-mode: vertical-rl; transform: rotate(180deg); font-weight: bold; margin-left: 5px;">Increasing ΔG°</div> </div>
CH ₃	1.70	(7.11)	
CH ₃ CH ₂	1.75	(7.32)	
(CH ₃) ₂ CH	2.20	(9.20)	
(CH ₃) ₃ C	≈ 5	(21)	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO} \end{array}$	1.41	(5.90)	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{OC} \end{array}$	1.29	(5.40)	
Substituent	ΔG° [kcal mol ⁻¹ (kJ mol ⁻¹)]		
F	0.25	(1.05)	
Cl	0.52	(2.18)	
Br	0.55	(2.30)	
I	0.46	(1.92)	
HO	0.94	(3.93)	
CH ₃ O	0.75	(3.14)	
H ₂ N	1.4	(5.9)	

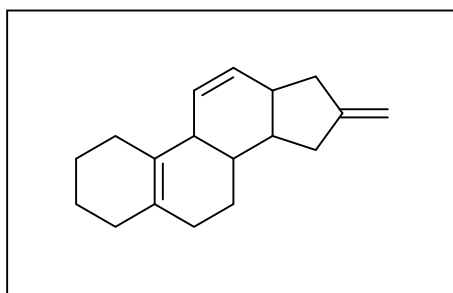
Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

e. 1-Methoxy-2-methyl-1-propene undergoes “anti-Markovnikov” protonation at the more substituted double-bond carbon. Draw the structure of 1-methoxy-2-methyl-1-propene and the cation resulting from this protonation. What feature is responsible for the stability of the cation?

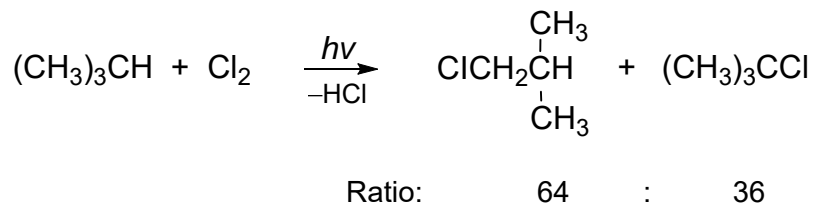


1-Methoxy-2-methyl-1-propene

f. Consider the oxacyclopropanation of the steroid shown below. Which double bond will be attacked first? (Circle it).



g. Consider the following radical chlorination.



The result suggests that the relative reactivity of H_{tert} : H_{prim} is about (place an “X” in the appropriate box):

- 1:1
- 9:1
- 5:1
- 36:64



"I have the results of your cholesterol test. One of your arteries is blocked by a slice of pizza."

* The End *

Have a great summer!