FINAL EXAMINATION
Chemistry 3A

Name:__________________________ **SID #:**______________________
Print first name before second! ***Make sure the number is correct!***
Use capital letters!

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

Peter Vollhardt
May 15, 2019

Please write the last four digits of your Cal ID# on the back of each page of this exam.

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

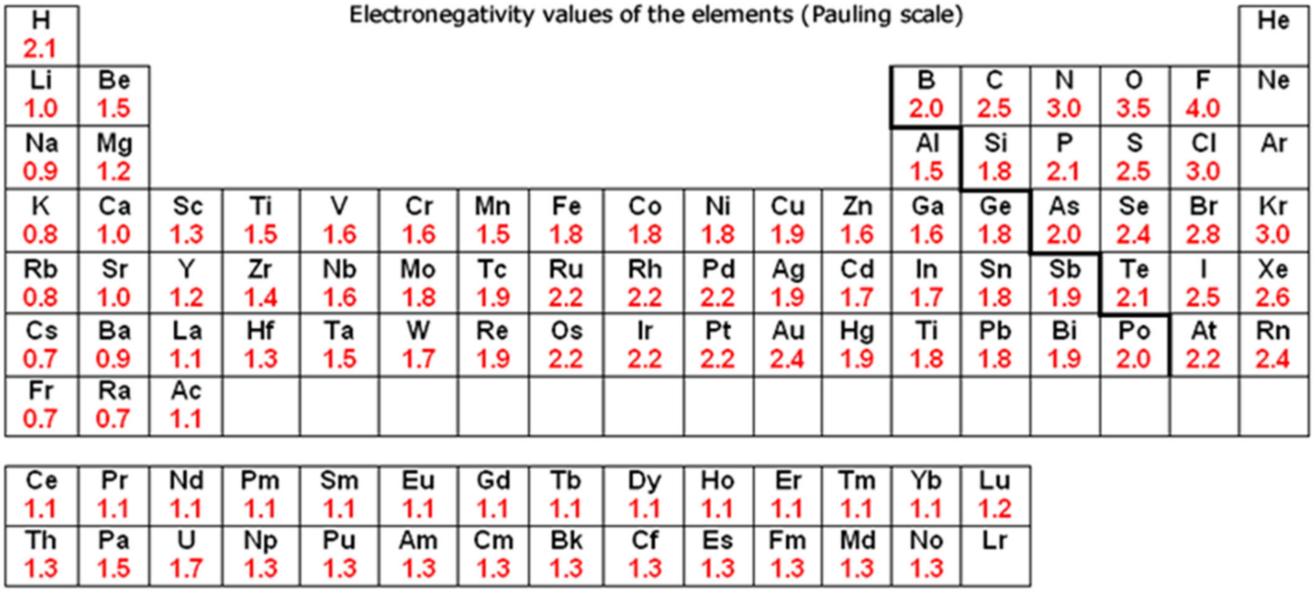
Auditor _____

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

Do not remove this (or any other) page from the exam. It will compromise the consonance of scanned copies in Gradescope.

Do scratch work on the back of the pages. This test should have **25** 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 probably will not need it for the exam, but here it is for added comfort:



Electronegativity values of the elements (Pauling scale)

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Ti 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn 2.4
Fr 0.7	Ra 0.7	Ac 1.1															

Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.1	Lu 1.2
Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr

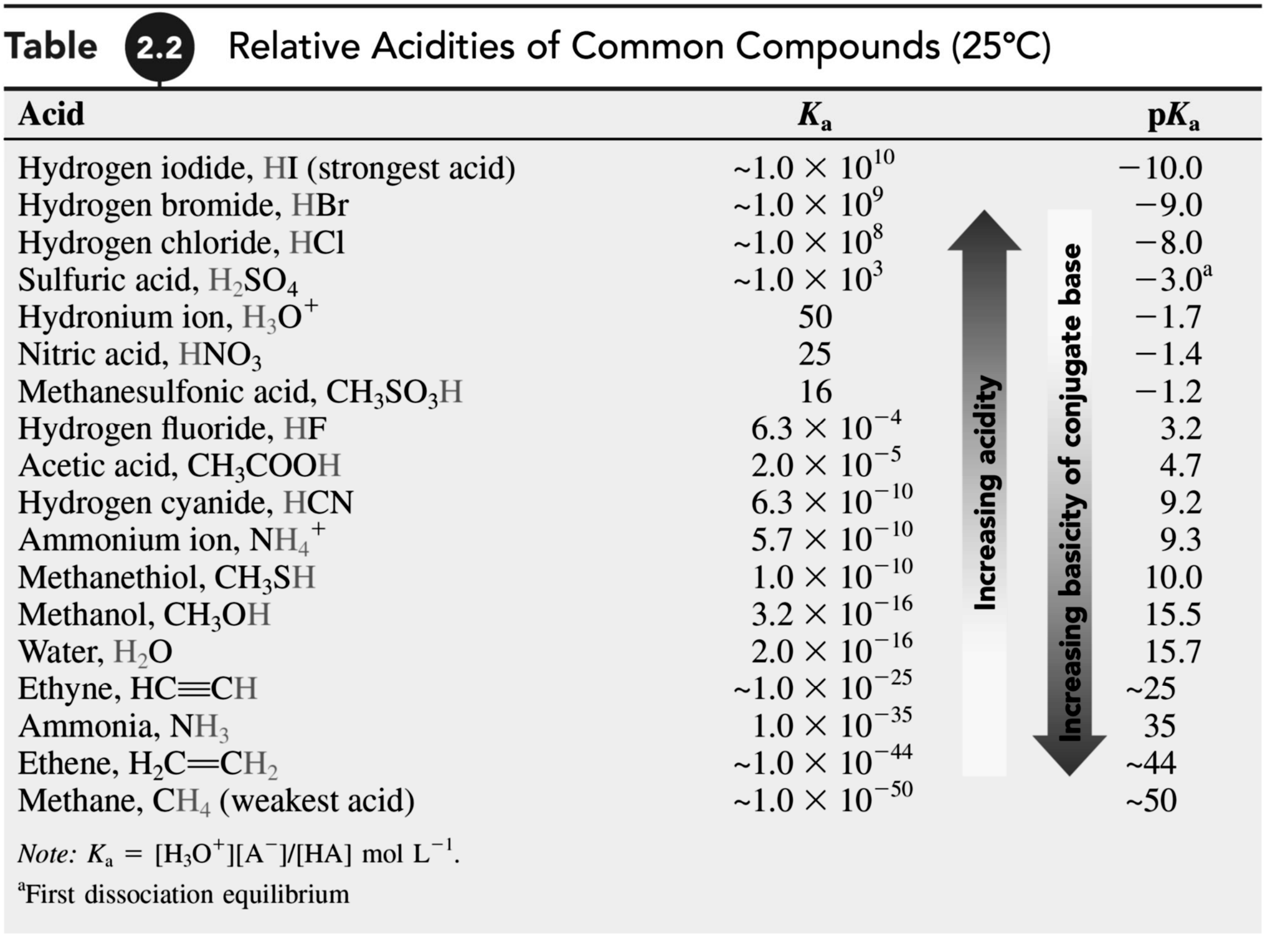


Table 2.2 Relative Acidities of Common Compounds (25°C)

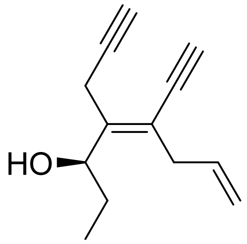
Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	$\sim 1.0 \times 10^{10}$	-10.0
Hydrogen bromide, HBr	$\sim 1.0 \times 10^{9}$	-9.0
Hydrogen chloride, HCl	$\sim 1.0 \times 10^{8}$	-8.0
Sulfuric acid, H_2SO_4	$\sim 1.0 \times 10^{3}$	-3.0^{a}
Hydronium ion, H_3O^+	50	-1.7
Nitric acid, HNO_3	25	-1.4
Methanesulfonic acid, CH_3SO_3H	16	-1.2
Hydrogen fluoride, HF	6.3×10^{-4}	3.2
Acetic acid, CH_3COOH	2.0×10^{-5}	4.7
Hydrogen cyanide, HCN	6.3×10^{-10}	9.2
Ammonium ion, NH_4^+	5.7×10^{-10}	9.3
Methanethiol, CH_3SH	1.0×10^{-10}	10.0
Methanol, CH_3OH	3.2×10^{-16}	15.5
Water, H_2O	2.0×10^{-16}	15.7
Ethyne, $HC{\equiv}CH$	$\sim 1.0 \times 10^{-25}$	~25
Ammonia, NH_3	1.0×10^{-35}	35
Ethene, $H_2C{=}CH_2$	$\sim 1.0 \times 10^{-44}$	~44
Methane, CH_4 (weakest acid)	$\sim 1.0 \times 10^{-50}$	~50

Note: $K_a = [H_3O^+][A^-]/[HA]$ mol L^{-1}.

[a] First dissociation equilibrium

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!

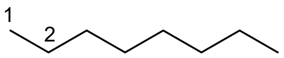
a.



This enantiomer

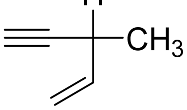
b.

(*R*,*Z*)-2-(2-Chloro-2-butenyl)octane-1-thiol



Complete the stencil

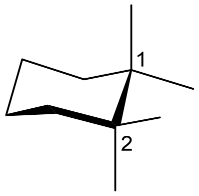
c.



(This is a Fischer projection;
name this enantiomer)

d.

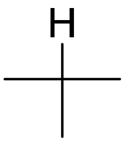
Meso-1,2-dimethoxy-1,2-bis(methylthio)cyclohexane



Complete the stencil

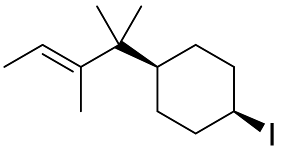
e.

(*R*)-3-Methylpent-1-en-4-yne



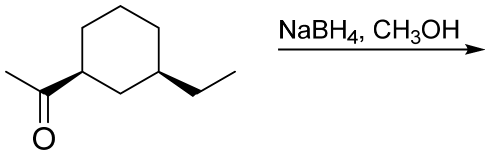
Complete the Fischer stencil.

f.



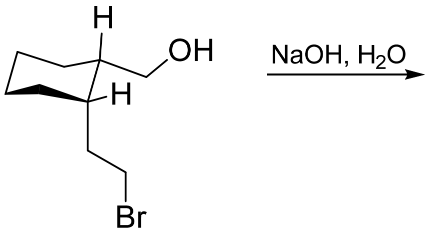
II. [100 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). Don't forget ***stereochemistry***! Complete the stencils, when provided. **Note**: In the reagent boxes above the arrows, enter one step only. Multistep sequences are clearly indicated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

a.



Two diastereomers

b.



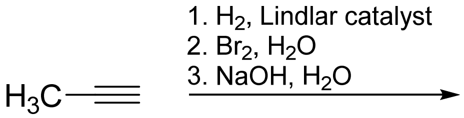
This enantiomer

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

Is the product chiral? Yes No

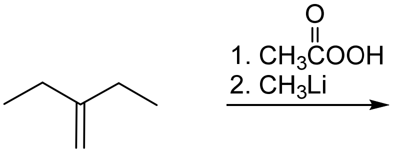
Is the product optically active? Yes No

c.

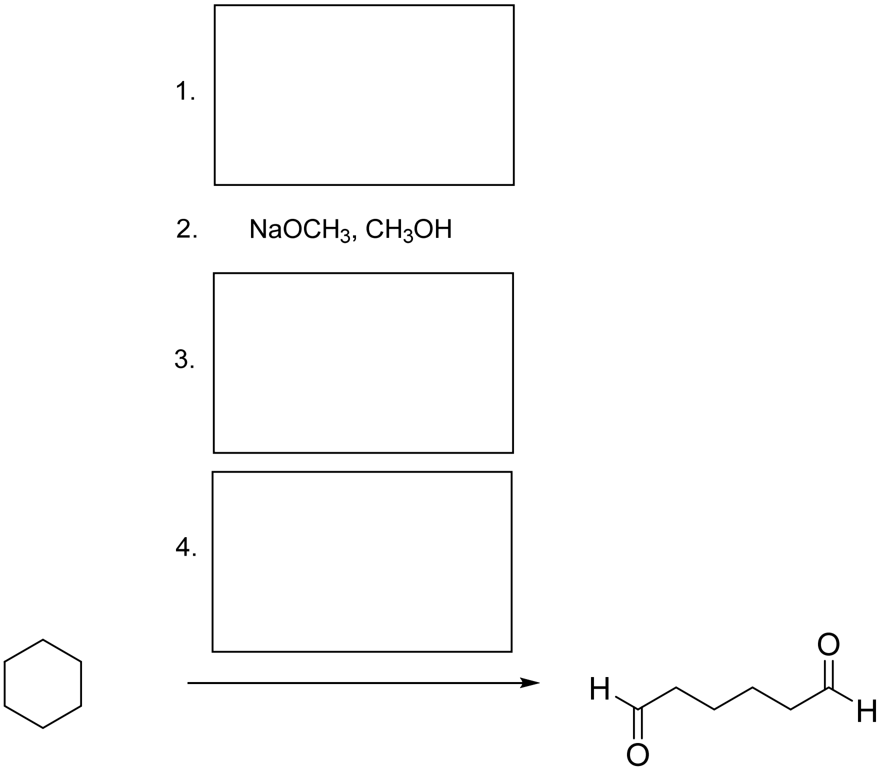

1. H_2, Lindlar catalyst
2. Br_2, H_2O
3. NaOH, H_2O
H_3C

C_3H_6O

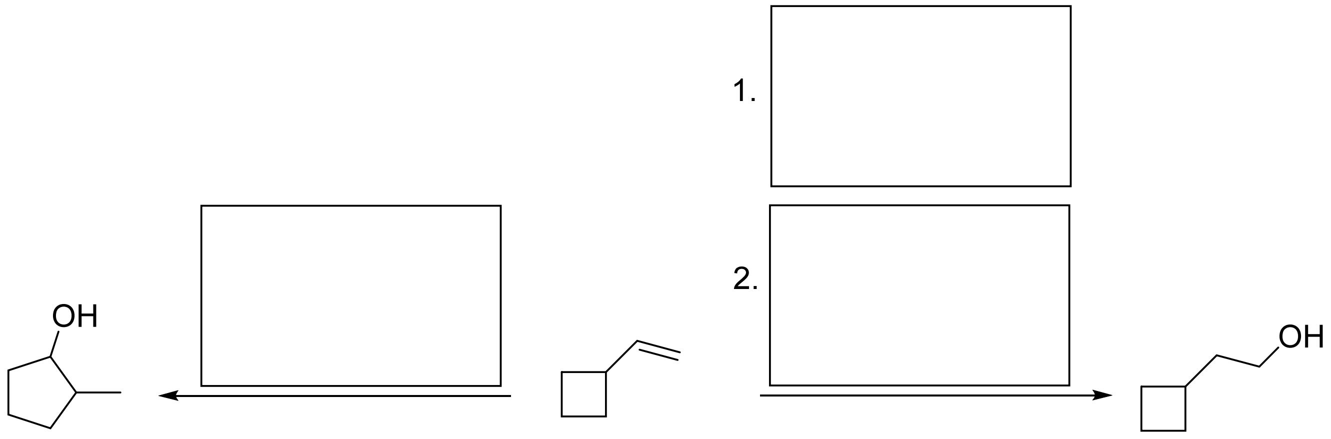
d.


O
1. CH_3COOH
2. CH_3Li

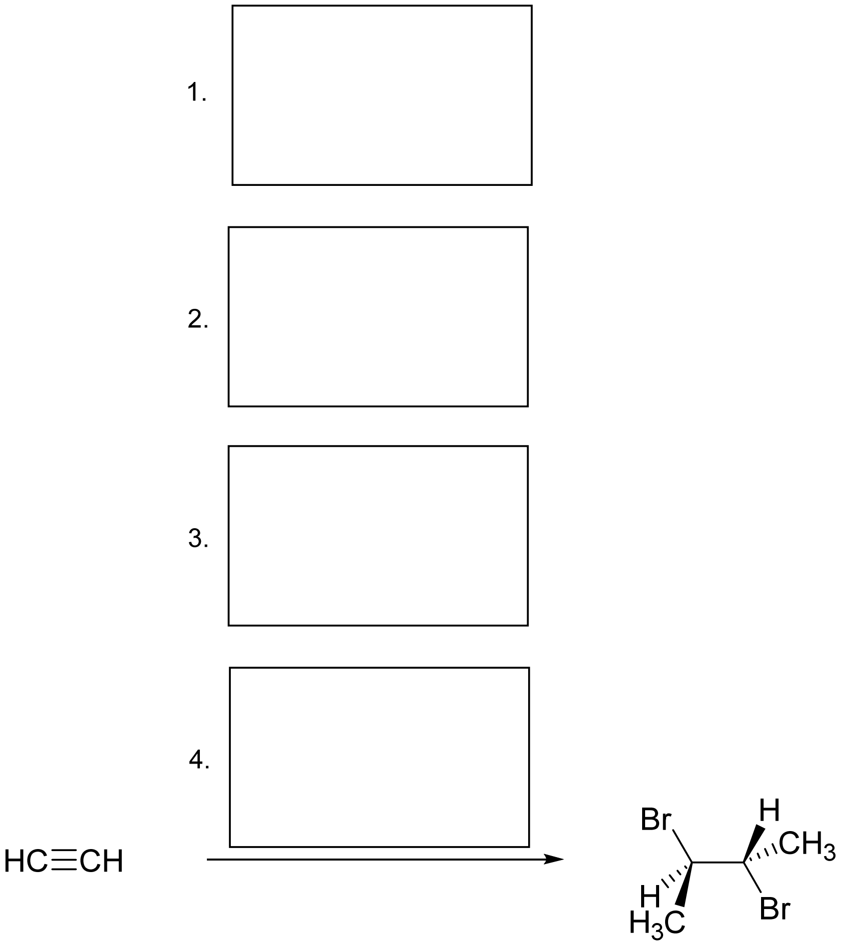
e.


1.
2. $NaOCH_3$, CH_3OH
3.
4.
H
O
O
H

f.

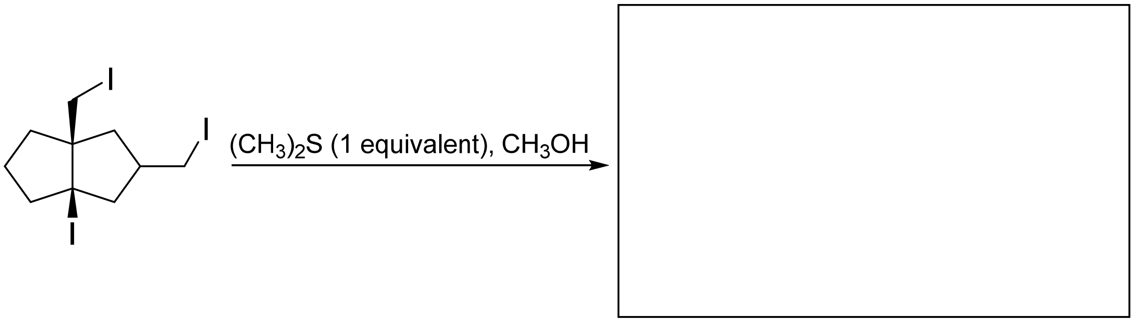


g.

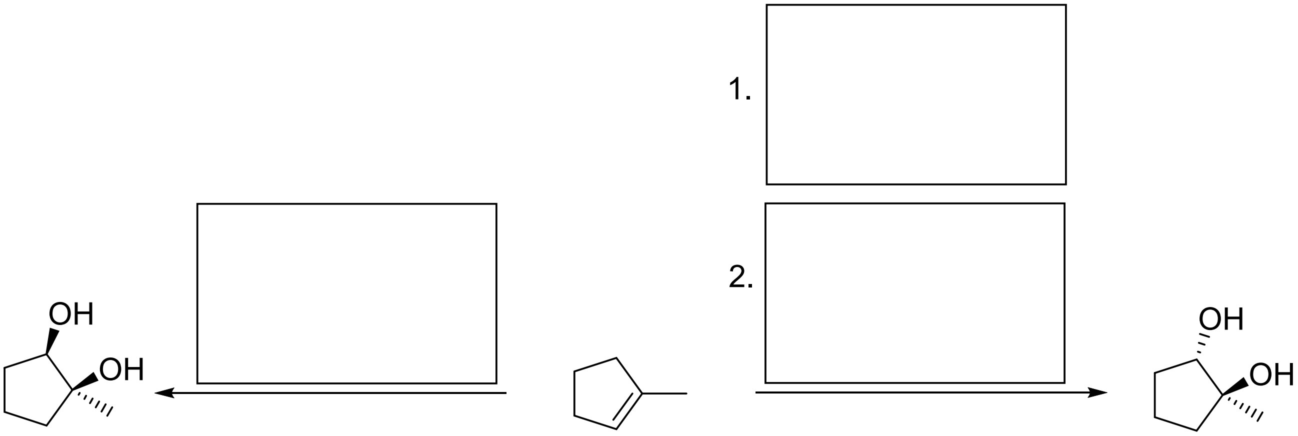


This diastereomer

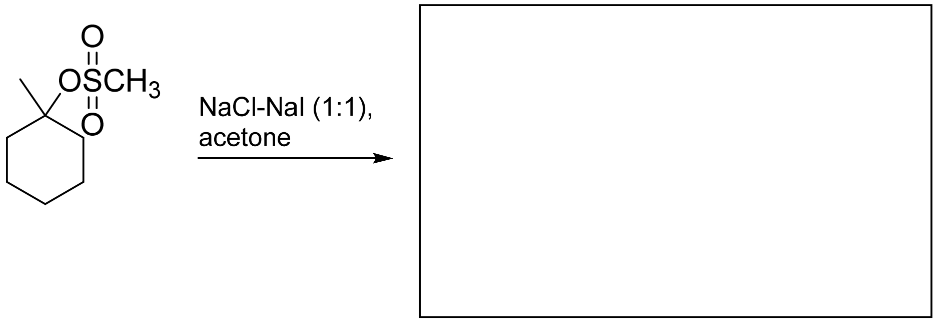
h.


I
I
I
(CH$_3$)$_2$S (1 equivalent), CH$_3$OH

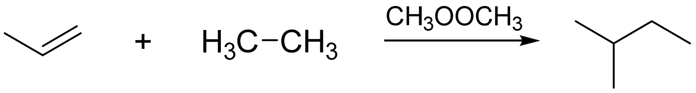
i.


1.
2.
OH
OH
OH
OH

j.


O
OSCH$_3$
O
NaCl-NaI (1:1),
acetone

III. [45 Points] Examine the potential radical addition of ethane to 1-propene to give 2-methylbutane (Eq. 1).



(Eq. 1)

a. Using $DH^\circ_{\pi\ \text{bond}}$ = 65 kcal mol^{-1} and the appropriate bond dissociation data in the Table below, calculate the ΔH° of Eq. 1. Show your work.

Selected C–C Bond-Dissociation Energies (kcal mol^{-1})

$CH_3{\wr}CH_3$	90
$C_2H_5{\wr}CH_3$	89
$CH_3CH_2CH_2{\wr}CH_3$	89
$C_2H_5{\wr}C_2H_5$	88
$(CH_3)_2CH{\wr}CH_3$	88
$(CH_3)(CH_3CH_2)CH{\wr}CH_3$	88
$(CH_3)_3C{\wr}CH_3$	87
$(CH_3)_2CH{\wr}CH(CH_3)_2$	85.5
$(CH_3)_3C{\wr}C(CH_3)_3$	78.5

ΔH° of Eq. 1:

b. Considering that the entropy of the reaction is negative and makes an unfavorable contribution to its ΔG°, amounting to ~ +10 kcal mol^{-1} (at 25°C), is the reaction thermodynamically (**circle** your answer):

Favorable?

Unfavorable?

c. Write the two initiation steps for the radical chain reaction and calculate their respective Δ*H*° values, using an $CH_3O–OCH_3$ bond strength of 39 kcal mol^{-1} and *DH*°(CH_3–O) = 90 kcal mol^{-1}.

Step 1.

Δ*H*° =

Step 2.

Δ*H*° =

e. Write the two propagation steps for the reaction in Eq. 1 and calculate their respective Δ*H*° values using the data given in part (a).

Step 1.

Δ*H*° =

Step 2.

Δ*H*° =

f. Which propagation step would you consider to be relatively slow?
(Place an “X” mark next to your answer in the box provided).

Step 1 ☐

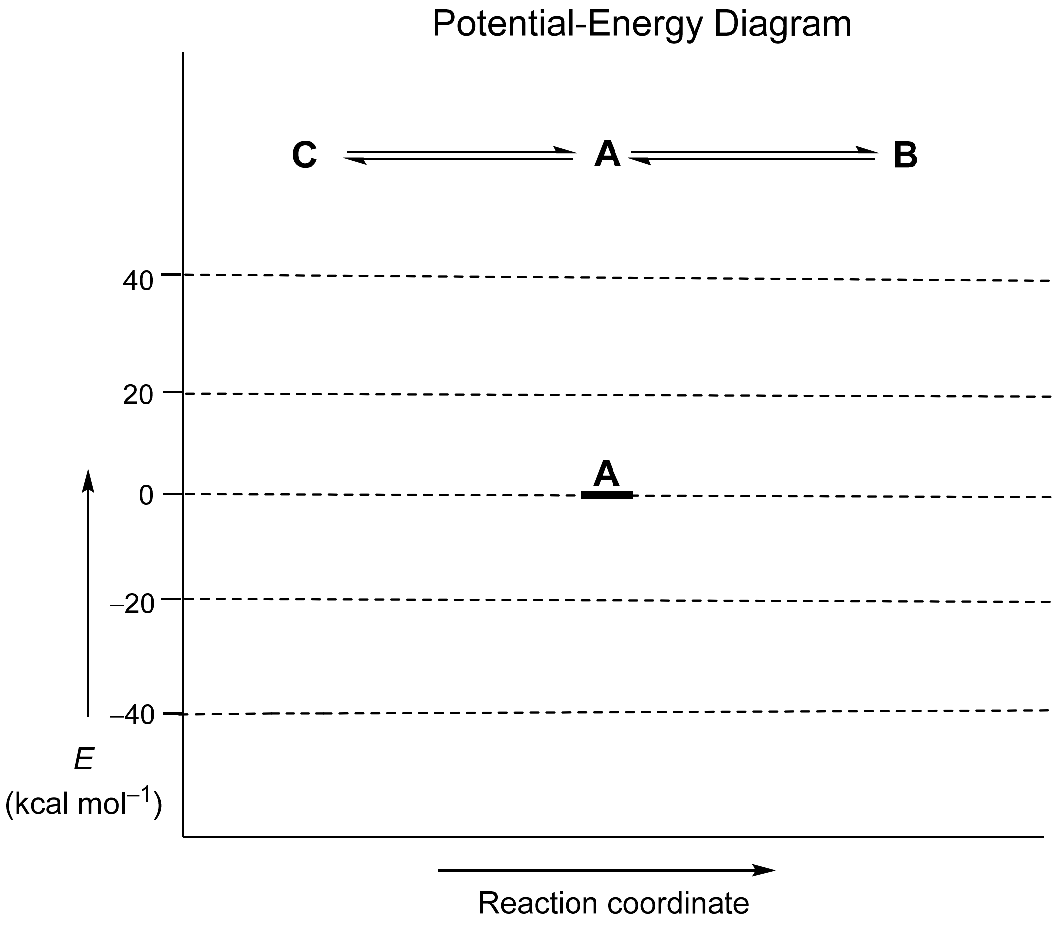
Step 2 ☐

IV. [20 Points] Compound **A** enters into two equilibria. The first is with **B**, proceeds with an activation energy of 40 kcal mol^{-1}, and is favorable with $\Delta G^\circ = -30$ kcal mol^{-1}. The second is with **C**, proceeds with an activation energy of 30 kcal mol^{-1}, and is favorable with $\Delta G^\circ = -10$ kcal mol^{-1}.

$$\Delta G^\circ = -10\ \text{kcal mol}^{-1} \quad \mathbf{C} \overset{E_a = 30\ \text{kcal mol}^{-1}}{\rightleftharpoons} \mathbf{A} \overset{E_a = 40\ \text{kcal mol}^{-1}}{\rightleftharpoons} \mathbf{B} \quad \Delta G^\circ = -30\ \text{kcal mol}^{-1}$$

Complete the energy diagram below as follows:

1. Starting with **A** positioned at level “0” (black bar), indicate the respective positions of **B** (to the right) and **C** (to the left) along the reaction coordinate (use black bars and label them with the respective letters).
2. Show the positions of the two respective transition states (black bars) that reflect the activation energies of the two steps. Label them “**TS$_{AB}$**” and “**TS$_{AC}$**”, respectively.


Potential-Energy Diagram

V. [20 Points] Using key words or a short sentence, list three observations that support the mechanism of the E1 reaction.

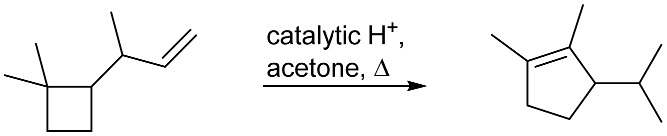
1.

2.

3.

VI. [75 Points] Write detailed step-wise mechanisms for the following two transformations (a. and b.) Use only structures and "arrow-pushing of electron dots" techniques. Note: These are <u>not</u> synthetic problems. Do not <u>add</u> any reagents! What you see is what you have!

a.

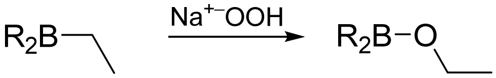


Racemic mixture of diastereomers

Racemate

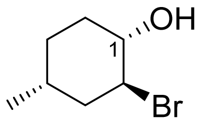
Work from left to right in the following spaces. There is much more space than you will need.

b.

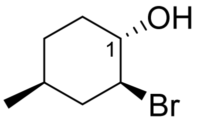


Work from left to right in the following spaces. There is much more space than you will need. Do not forget to include all electron dots.

c. On treatment with base, Compound **A** undergoes intramolecular Williamson ring closure faster than its diastereomer **B**. Why?

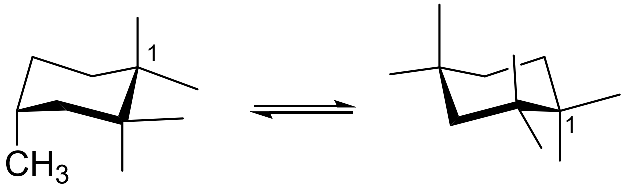


A



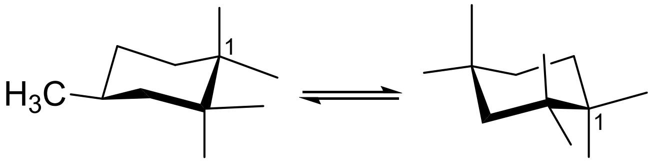
B

1. To find the answer, draw the two chair conformers of **A** and **B** using the stencils in the boxes below. Add H, CH_3, Br, or OH to the ends of the dangling bonds.



A

ΔG° =



B

ΔG° =

2. Using the table below, calculate the ΔG° values for the respective ring flips depicted in the boxes provided above.

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})]	Substituent	ΔG° [kcal mol^{-1} (kJ mol^{-1})]
H	0 (0)	F	0.25 (1.05)
CH_3	1.70 (7.11)	Cl	0.52 (2.18)
CH_3CH_2	1.75 (7.32)	Br	0.55 (2.30)
$(CH_3)_2CH$	2.20 (9.20)	I	0.46 (1.92)
$(CH_3)_3C$	≈ 5 (21)		
$\mathrm{HO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}$	1.41 (5.90)	HO	0.94 (3.93)
		CH_3O	0.75 (3.14)
		H_2N	1.4 (5.9)
$\mathrm{CH_3O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}$	1.29 (5.40)		

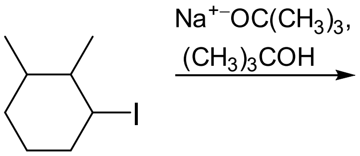
Increasing size ↓

Increasing ΔG° ↓

3. Armed with the results of the above analysis, why does **A** react faster than **B**? Explain in one sentence.

VII. [20 Points] The following reactions proceed (predominantly) by S_N2, S_N1, E2, or E1 pathways, respectively. Give the major products in each case and answer the questions by **circling** the most applicable statement.

a.

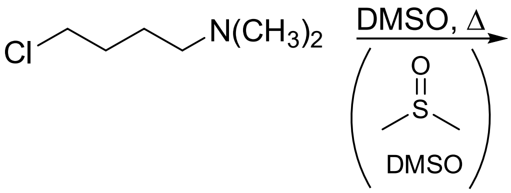


Mechanism: S_N2 S_N1 E2 E1

When using $Na^{+-}SH$ instead of $Na^{+-}OC(CH_3)_3$, which one of the following ratios will increase:

S_N2 / S_N1 S_N1 / E1 E2 / S_N2 S_N2 / E2

b.



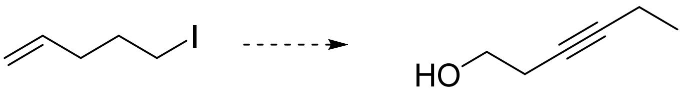
Mechanism: S_N2 S_N1 E2 E1

When changing the $-N(CH_3)_2$ group to $-P(CH_3)_2$, the rate of disappearance of starting material:

Will increase Will decrease Will not change

VIII. [90 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 show 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.

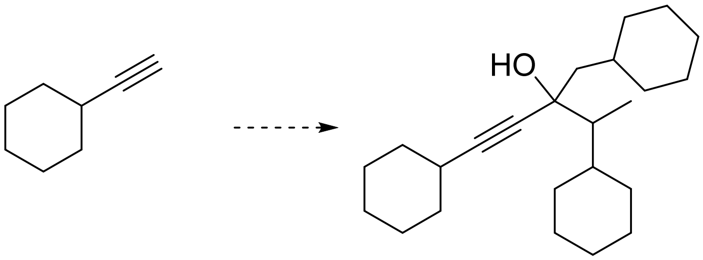
a. Starting from **A** and any organic and organometallic reagents **containing four carbons or less**, propose a synthesis of **B**.



A **B**

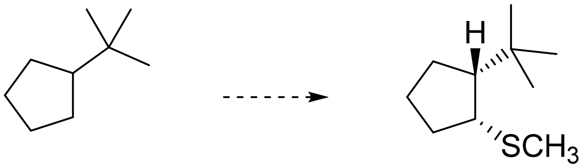
Work from left to right in the following spaces. There is more space than you will need.

b. Provide a scheme using **only the starting material** to supply the necessary building blocks for assembling the product.



Work from left to right in the following spaces.

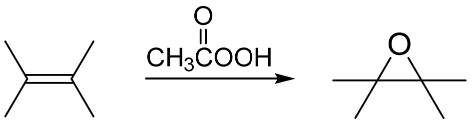
c.



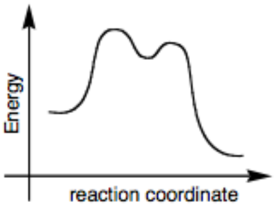
Work from left to right in the following spaces. There is much more space than you will need.

IX. [70 Points]

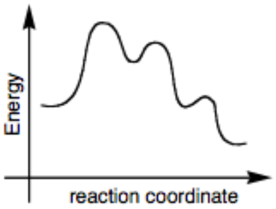
a. Which of the following potential energy diagrams describes the reaction depicted below left? Give your answer (**A**, **B**, **C**, or **D**) in the box provided.



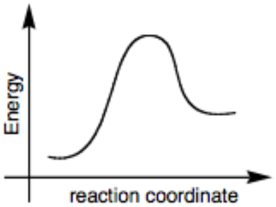
(A)



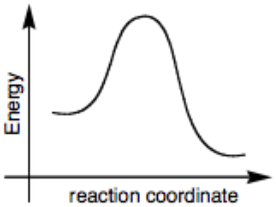
(B)



(C)

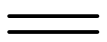


(D)

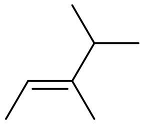


Answer: ☐

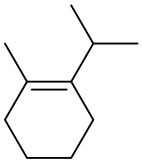
b. Rank the following alkenes in the order of increasing rates of oxacyclopropanation:



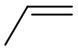
A



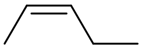
B



C



D



E

Place an “X” mark next to your answer.

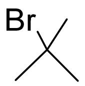
_____ **A, B, C, E, D**

_____ **D, B, A, E, C**

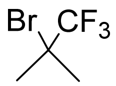
_____ **B, C, D, E, A**

_____ **A, D, E, B, C**

c. Solvolysis of **B** is one million times slower than that of **A**. Why?



A



B

Place an “X” mark next to your answer.

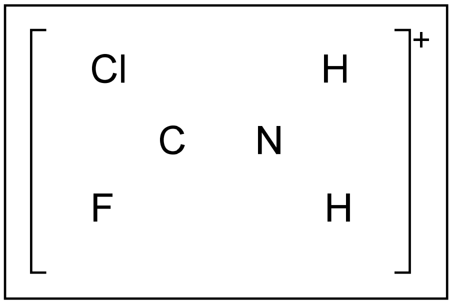
____ **B** is more sterically hindered.

____ The electron pairs on fluorine are electron donating.

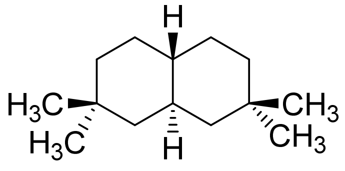
____ **B** is better solvated.

____ CF_3 is electron withdrawing, destabilizing the tertiary cation.

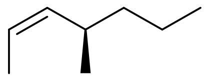
d. Draw the most important contributing resonance form of the species shown below:



e. The molecule shown below has primary, secondary, and tertiary hydrogens. Considering the relative reactivity in radical brominations of C–H: primary : secondary : tertiary = 1 : 80 : 1700, what would you expect the ratio of **all** primary to **all** secondary to **all** tertiary substitution products to be?
Show your work and just give the raw ratio.



f. Consider the bromohydroxylation (Br_2, H_2O) of the alkene enantiomer shown below. How many bromoalcohol isomers do you expect?



(*R*,*Z*)-4-Methyl-2-heptene

Place an “X” mark next to your answer.

_____ two enantiomers

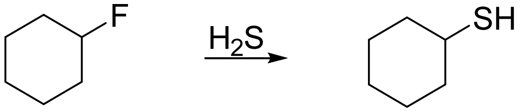
_____ four diastereomers

_____ two chiral and two meso compounds

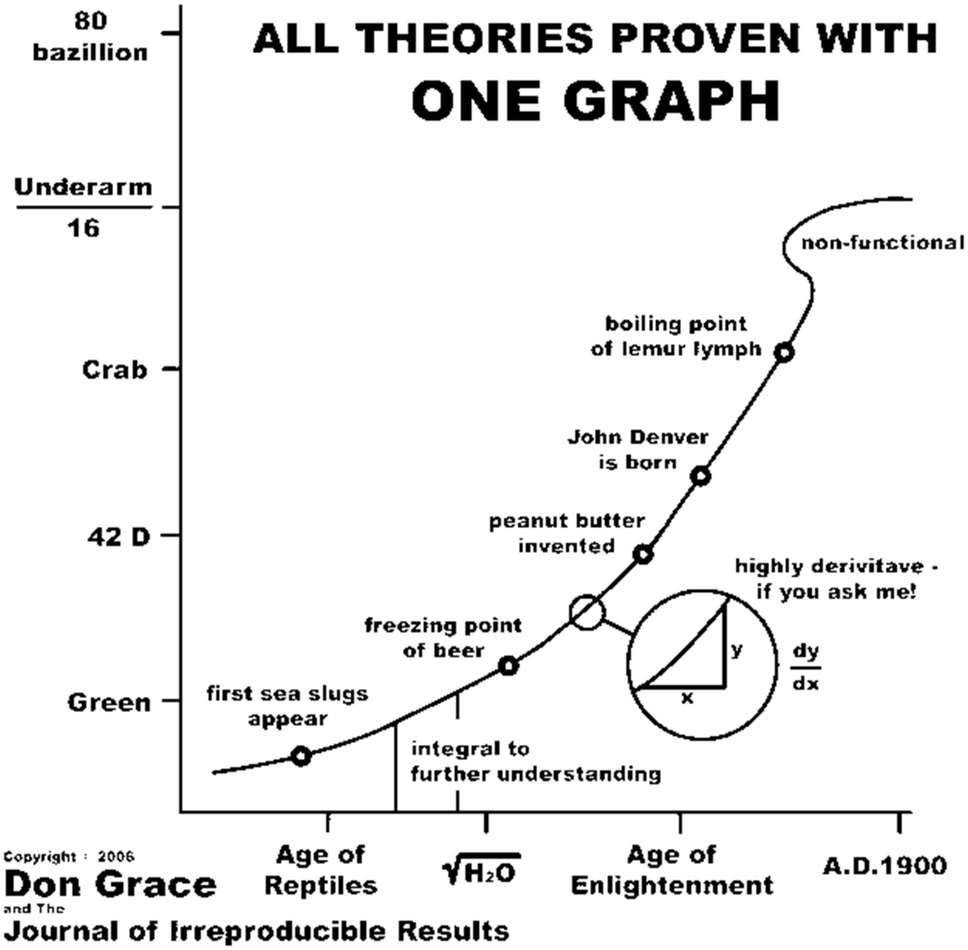
_____ four isomers

_____ eight stereoisomers

g. Consider the following substitution reaction:



Suggest one experiment that would help you decide whether **this particular reaction** occurs by S_N2 or S_N1.



* The End *

Have a great summer!