EXAMINATION 2
Chemistry 3A

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

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

Peter Vollhardt
April 9, 2019

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

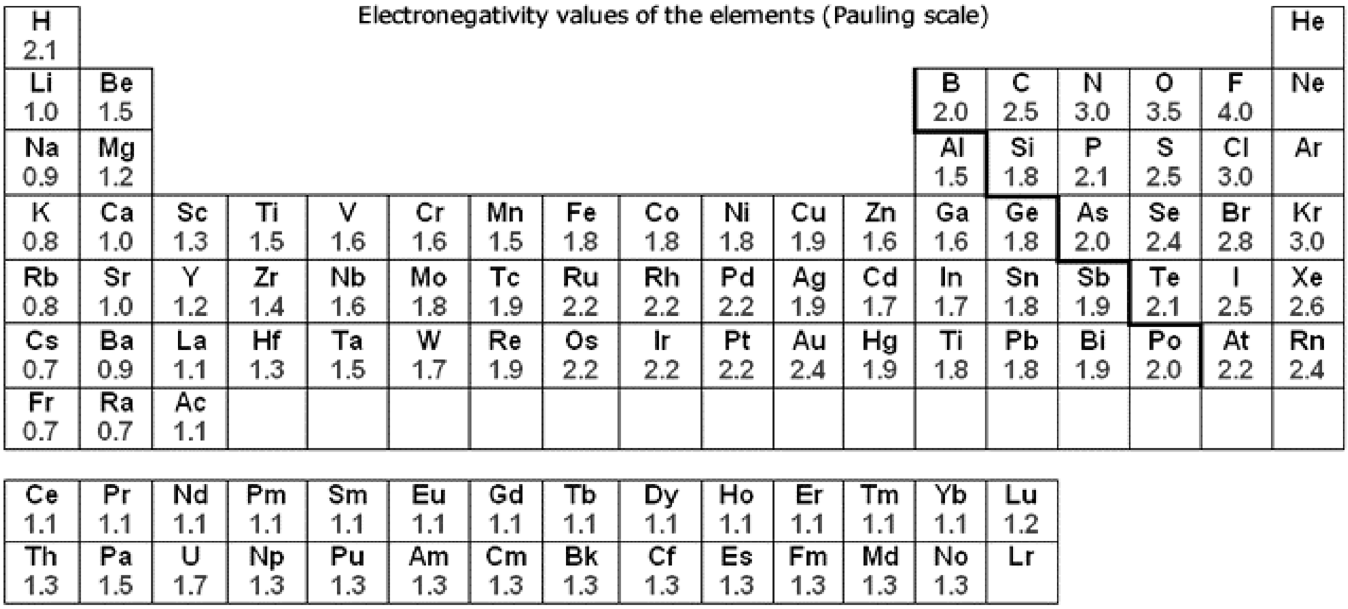
Auditor _____

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 **14** 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*!**

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

You probably will not need them for the exam, but here they are 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

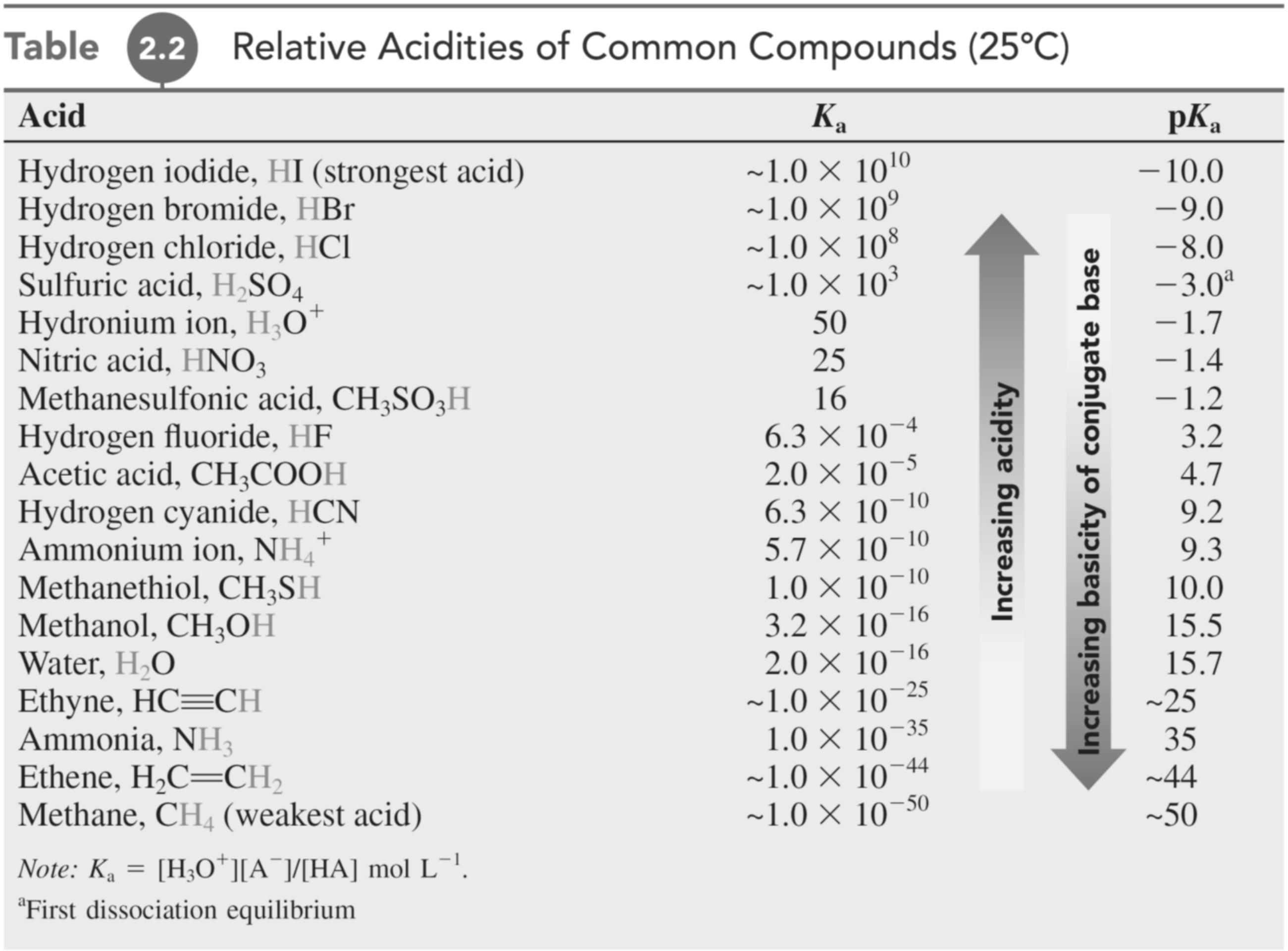


Table 2.2 Relative Acidities of Common Compounds (25°C)

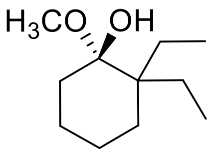
Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	$\sim 1.0 \times 10^{10}$	-10.0
Hydrogen bromide, HBr	$\sim 1.0 \times 10^{9}$	-9.0
Hydrogen chloride, HCl	$\sim 1.0 \times 10^{8}$	-8.0
Sulfuric acid, H_2SO_4	$\sim 1.0 \times 10^{3}$	-3.0^{a}
Hydronium ion, H_3O^+	50	-1.7
Nitric acid, HNO_3	25	-1.4
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. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary.

a.

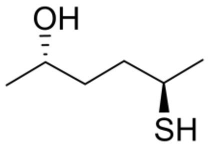


This enantiomer

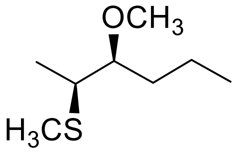
(*S*)-2,2-Diethyl-1-methoxycyclohexanol

b.

(2*S*,5*R*)-5-Mercapto-2-hexanol



c.

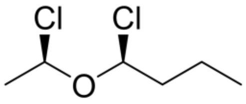


This enantiomer

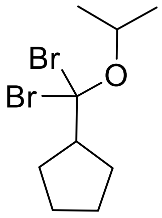
(2*S*,3*S*)-3-Methoxy-2-methylthiohexane

d.

(*S*)-1-Chloro-1-[(*R*)-1-chloroethoxy]butane



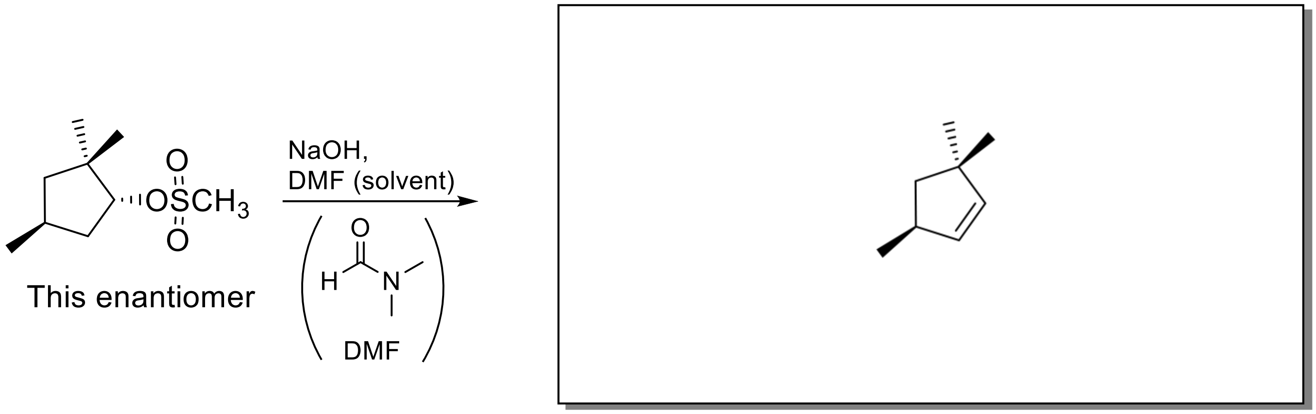
e.



[Dibromo(1-methylethoxy)methyl]cyclopentane

II. [80 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). **Caution:** Do not forget to consider ***stereochemistry***!

a.

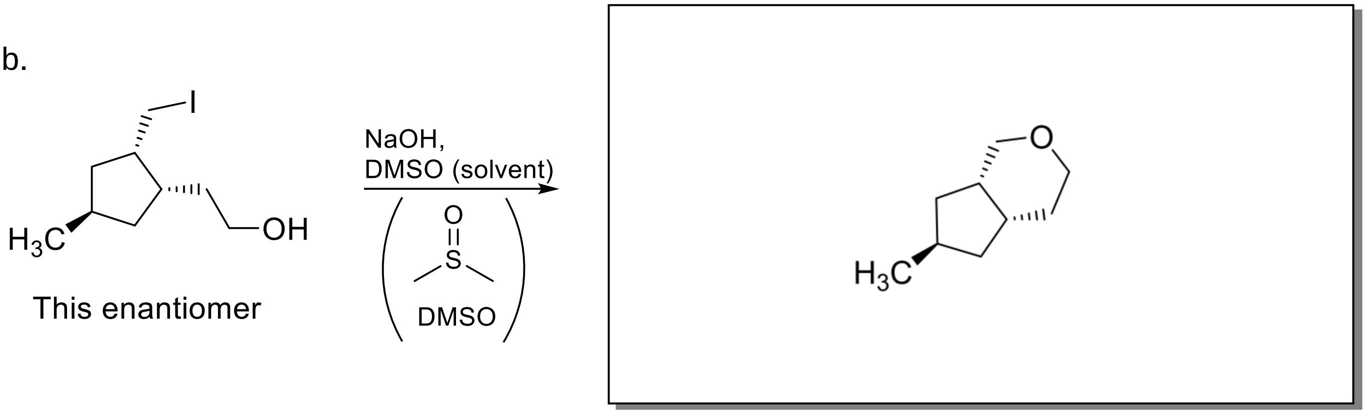


For the following questions, circle your choice of an answer:

Is the product chiral? [✓ Yes] No

Is the product optically active? [✓ Yes] No

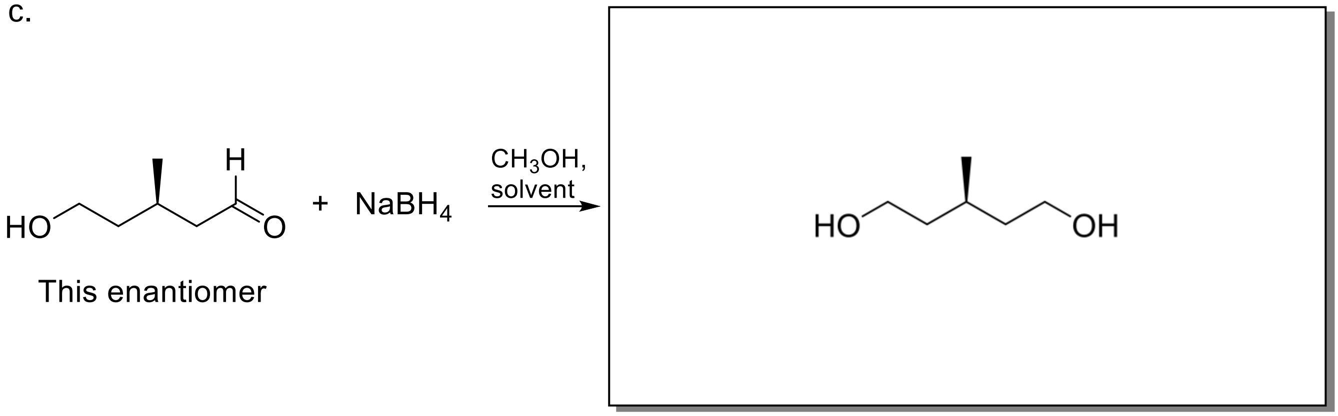
b.



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

Is the product chiral? [✓ Yes] No

Is the product optically active? [✓ Yes] No c.



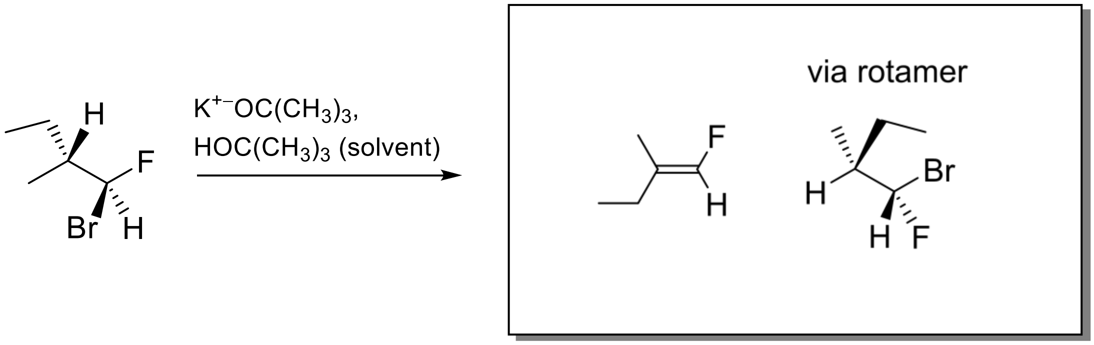
This enantiomer

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

Is the product chiral? Yes [✓ No]

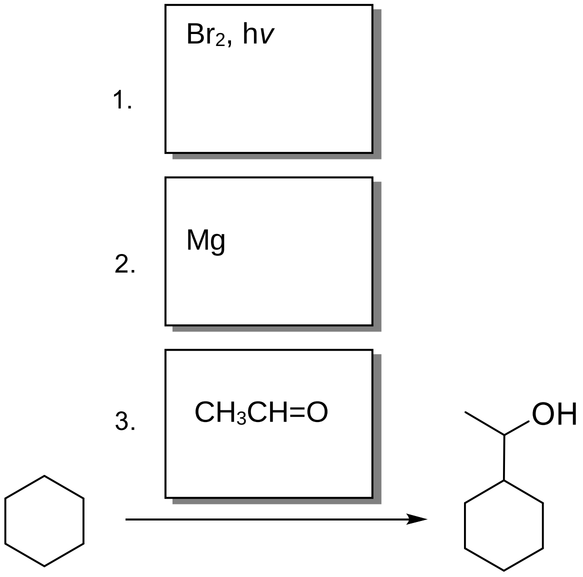
Is the product optically active? Yes [✓ No]

d.



via rotamer

e.

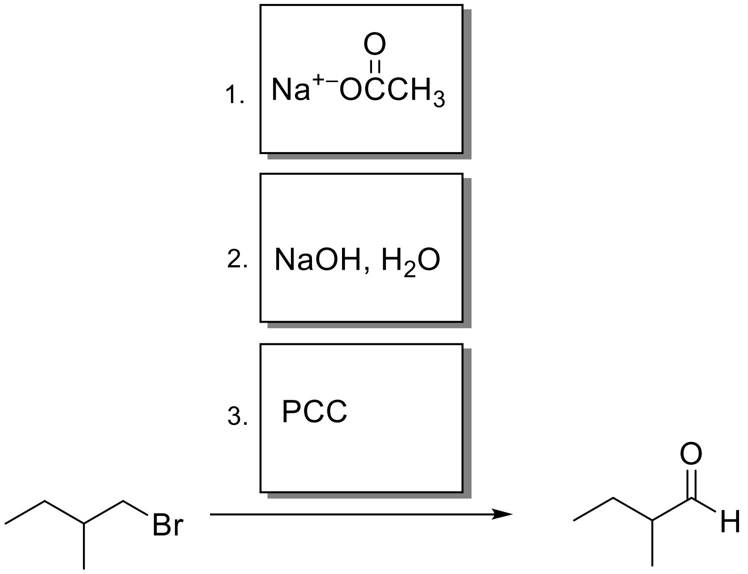


1. Br$_2$, hν

2. Mg

3. CH$_3$CH=O

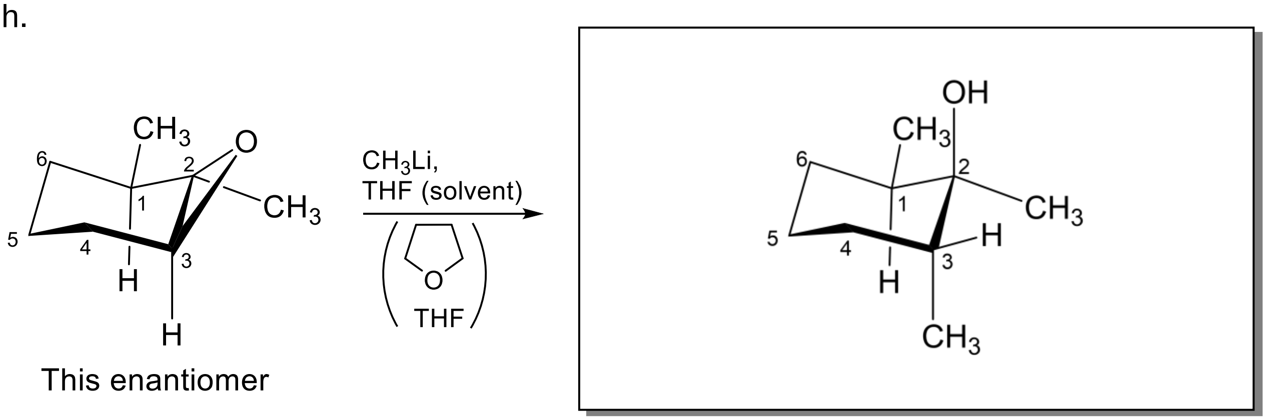
f.



g.

An alcohol

h.



Complete the stencil in the box by adding the missing substituents at C1, C2, and C3

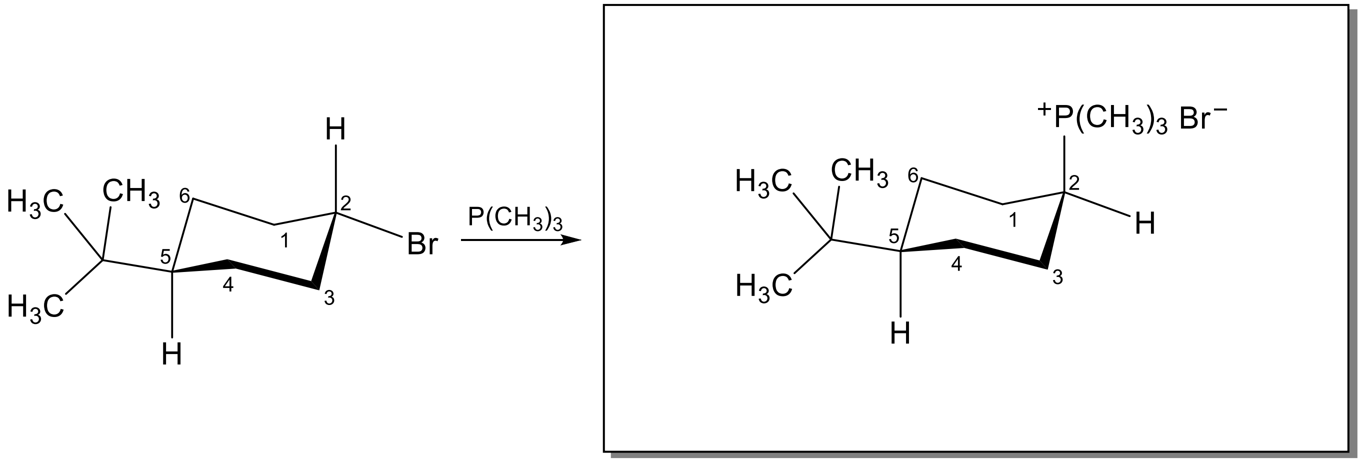
For the following question, circle your choice of an answer:

Is the product chiral? [✓ Yes] No

Is the product optically active? [✓ Yes] No

III. [40 Points] The following reactions proceed (predominantly) by S_N2, S_N1, E2, or E1 pathways, respectively. Give the major organic product in each case and answer the questions by ***circling*** the most applicable statement.

a.



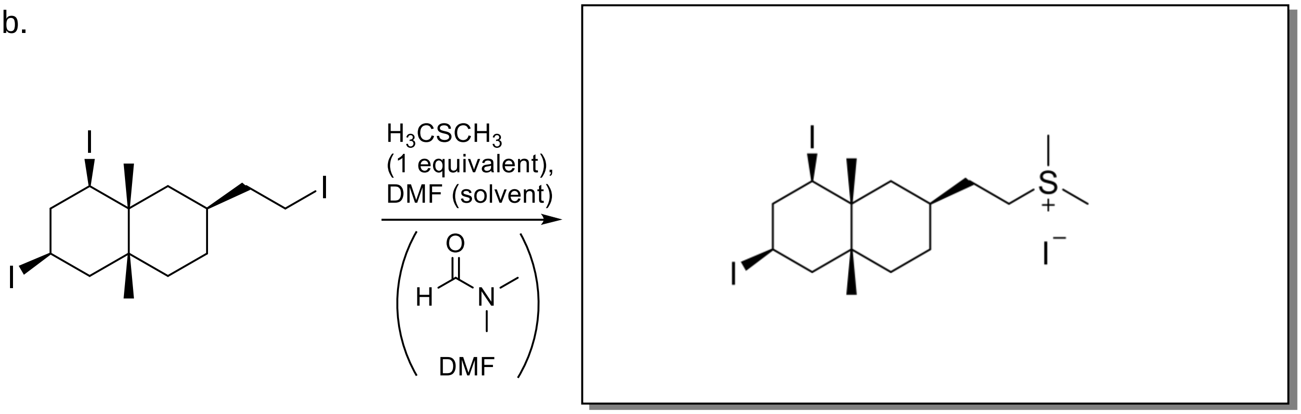
Complete the stencil in the box by adding the missing substituents at C2

Mechanism: [✓ S_N2] S_N1 E2 E1

When using $N(CH_3)_3$ instead of $P(CH_3)_3$, which one of the following ratios will increase:

S_N2 / S_N1 S_N1 / E1 [✓ E2 / S_N2] S_N2 / E2

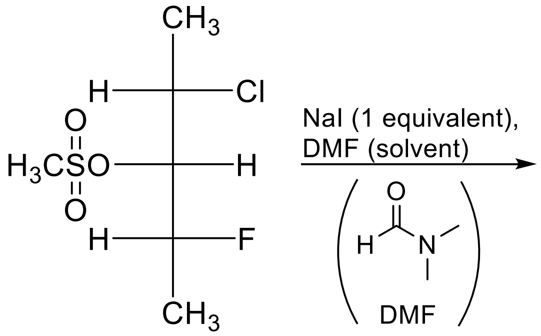
b.

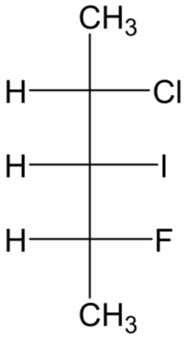


Mechanism: [✓ S_N2] S_N1 E2 E1

Changing the reagent to $Na^{+-}SCH_3$ has one of the following effects:

E2 / S_N1 increases E1 / S_N1 increases [✓ Rate increases] Rate decreases c.





Complete the stencil in the box by adding all missing substituents

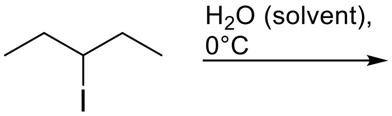
Mechanism: [✓ S_N2] S_N1 E2 E1

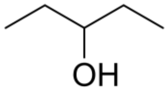
Omitting NaI from the starting mixture has one of the following effects:

Nothing happens [✓ The starting material equilibrates with its diastereomer]

E2 / E1 ratio increases S_N2 / E1 ratio increases

d.





Only the major product

Mechanism: S_N2 [✓ S_N1] E2 E1

Which of the following statements is correct?

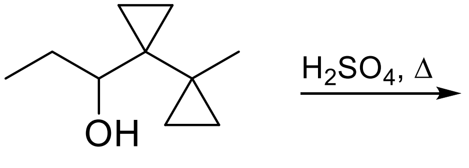
[✓ Doubling the concentration of starting iodide will double the rate of its disappearance]

Doubling the concentration of starting iodide will quadruple the rate of its disappearance

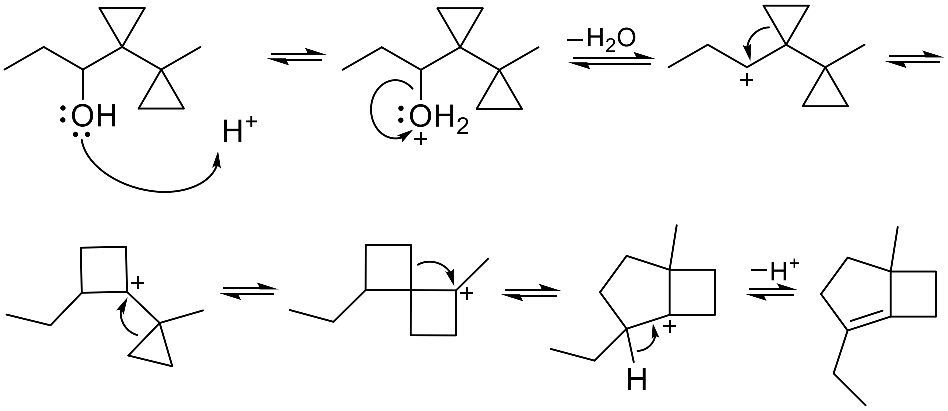
Doubling the concentration of starting iodide will not change the rate of its disappearance

IV. [40] Points]

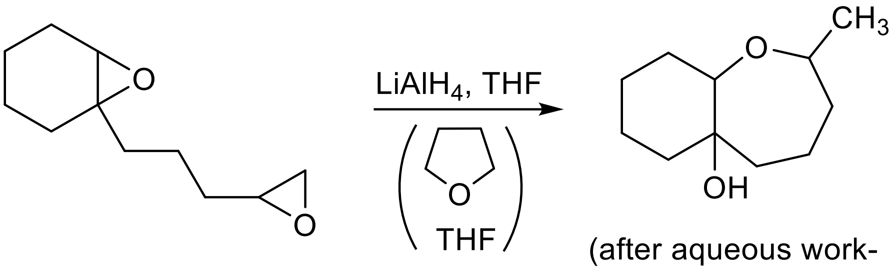
a. For the following reaction, provide a detailed mechanism (i.e., write a scheme with structures, arrow pushing, etc.) Do **not** *add* any reagents! This is not a synthesis!



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

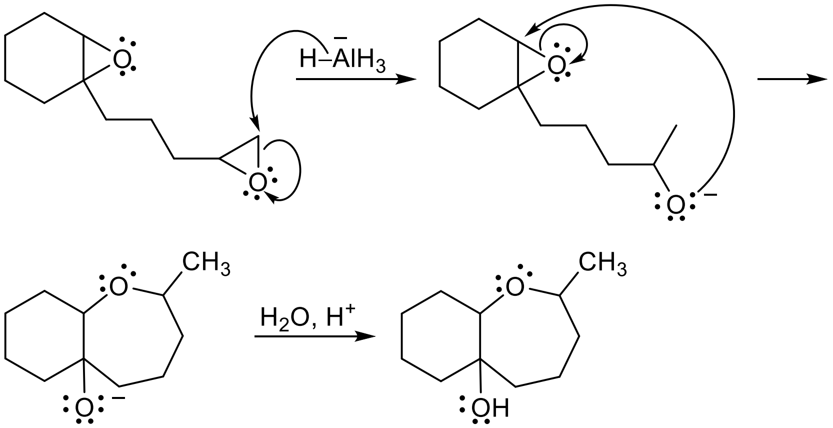


b. For the following reaction, provide a detailed mechanism (i.e., write a scheme with structures, arrow pushing, etc.) Do **not** *add* any reagents! This is not a synthesis!



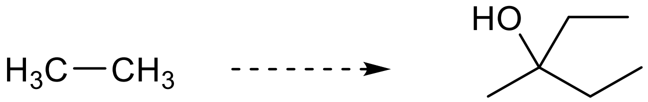
(after aqueous work-up; please write this step in your answer)

Work from left to right in the following spaces. There is more space than you will need. Do not worry about stereochemistry.

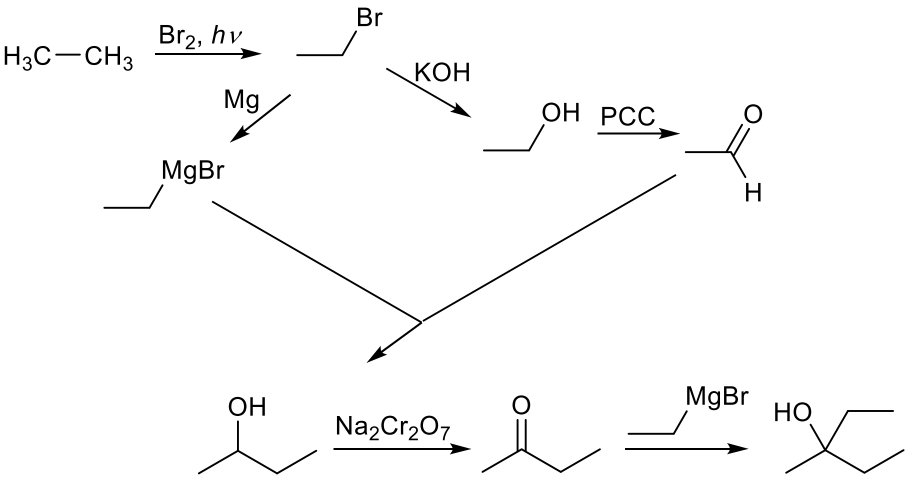


V. [40 Points]

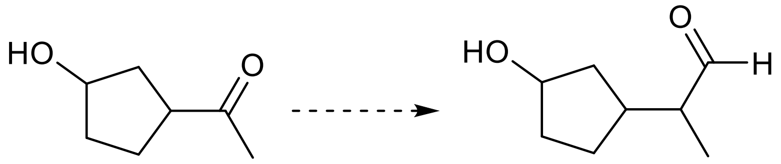
a. Provide a viable conversion of the starting material below as the only carbon source to the product. It will help you if you execute a retrosynthesis on the back of the preceding page (on your left). This problem should look familiar.



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

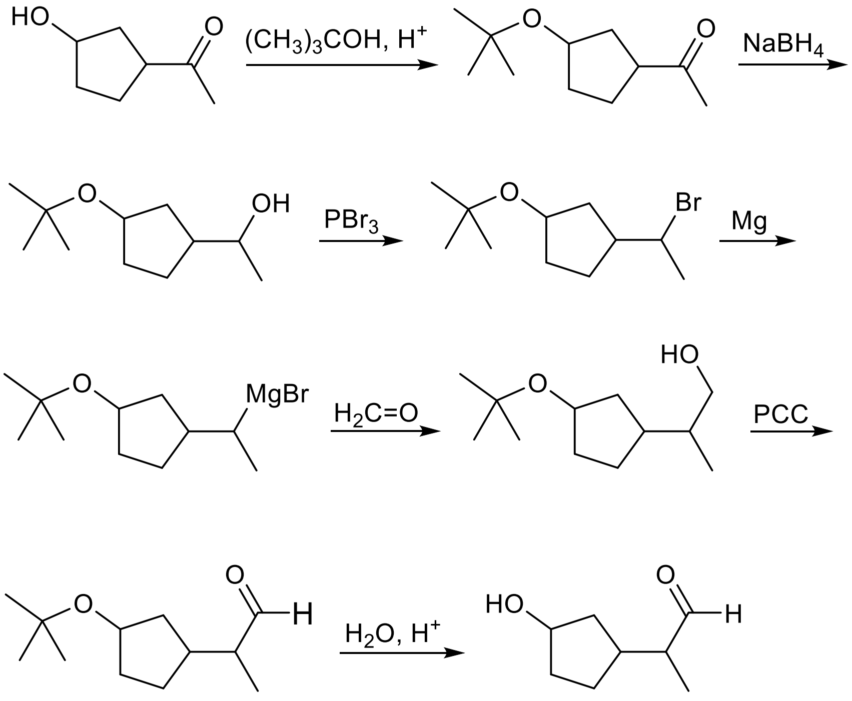


b. Provide a viable conversion of the starting material below to the product. You may use any additional organic compounds containing four carbons or less and any inorganic compounds in your scheme. It will help you if you execute a retrosynthesis on the back of the preceding page (on your left).



Do not worry about stereochemistry

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



VI. [20 Points]

a. We learned that the acidity if alcohols *decreases* when progressing from primary to secondary to tertiary, as shown in Table 8.2 below, because of increasing steric hindrance to solvation of the resulting conjugate base.

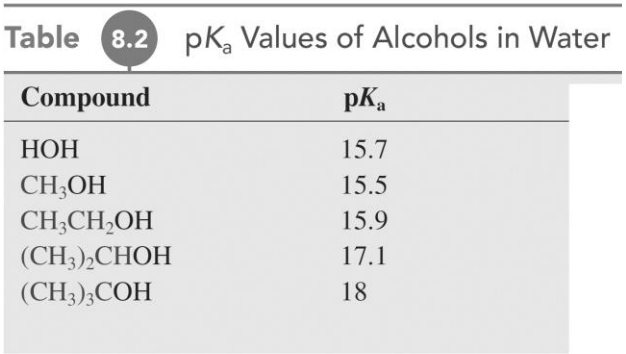


Table 8.2 pK_a Values of Alcohols in Water

Compound	pK_a
HOH	15.7
CH_3OH	15.5
CH_3CH_2OH	15.9
$(CH_3)_2CHOH$	17.1
$(CH_3)_3COH$	18

In contrast, Table 8.3 in your book shows that the acidities of alkyloxonium ions *increase* when progressing from primary to secondary to tertiary.

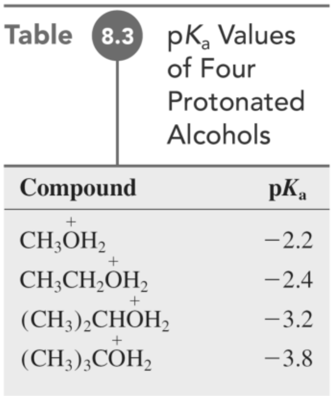


Table 8.3 pK_a Values of Four Protonated Alcohols

Compound	pK_a
$CH_3\overset{+}{O}H_2$	−2.2
$CH_3CH_2\overset{+}{O}H_2$	−2.4
$(CH_3)_2CH\overset{+}{O}H_2$	−3.2
$(CH_3)_3C\overset{+}{O}H_2$	−3.8

Place an ***X mark*** in the box preceding the most reasonable explanation for this finding.

☐ Along the series (primary to secondary to tertiary), hyperconjugation increases.

☐ Along the series (primary to secondary to tertiary), the alcohols resulting from proton dissociation are increasingly better solvated.

☒ Along the series (primary to secondary to tertiary), the oxonium ions suffer increasing steric hindrance to solvation.

☐ Along the series (primary to secondary to tertiary), the oxonium ions suffer decreasing inductive stabilization.

b. The following four problems list pairs of statements. For each, place an ***X mark*** in the box preceding the correct one.

1. ☒ Electronegativity increases to the right and up the periodic table.

   ☐ Electronegativity increases to the right and down the periodic table.

2. ☒ Nucleophilicity in protic solvents increases down the periodic table.

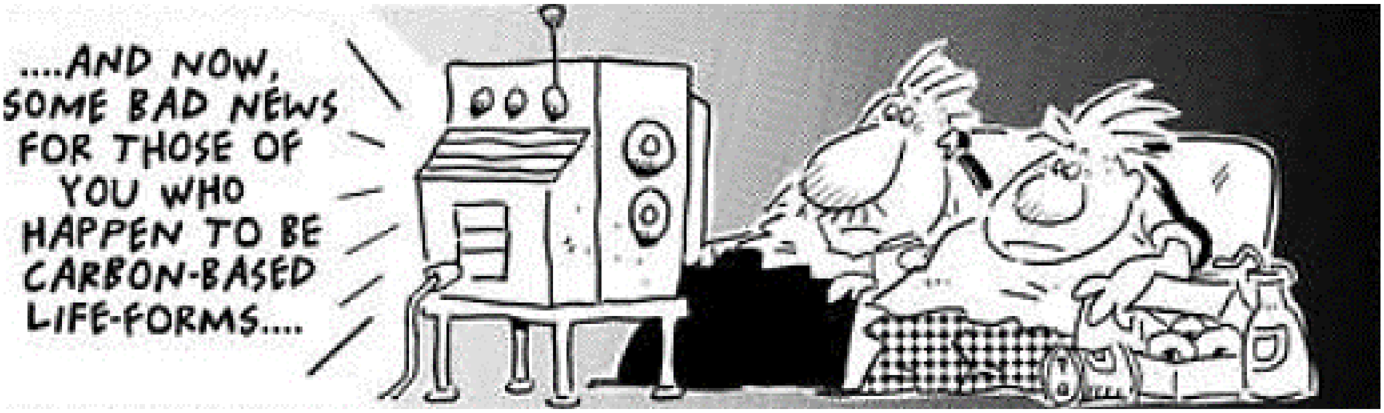
   ☐ Nucleophilicity in aprotic solvents increases down the periodic table.

3. ☒ Leaving group ability increases to the right and down the periodic table.

   ☐ Leaving group ability increases to the right and up the periodic table.

4. ☐ The S_N2 reaction of oxacyclopropanes is possible because the ring carbon is relatively unhindered.

   ☒ The S_N2 reaction of oxacyclopropanes is possible because ring strain is released.



* The End *