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 Label the final pdf file with your name and the words "Final Exam" (namely: Last Name, First Name, Final Exam) and e-mail it to your laboratory TA. If you are a lecture only student, send it to Justin: justin_jurczyk@berkeley.edu

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**FINAL EXAMINATION
Chemistry 3A**

Name: _____
 Print first name before second!
 Use capital letters!

SID #: _____
Make sure the number is correct!

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

**Peter Vollhardt
May 13, 2020**

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 _____

This test should have **20** numbered pages.

Please initial the box at the end of this pledge.

I pledge to maintain the integrity of this exam. As such, I pledge to abide by the exam instructions specified and to withhold communication through any means with anyone about the content of the exam until the entire class and I have completed it. I understand that breaking this pledge constitutes an academic transgression that will be reported to the office of student conduct and will result in dismissal from the university.

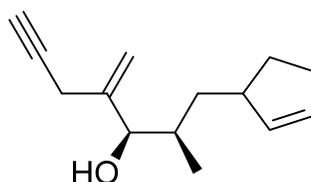
Initial this box using the "Text" tool

To answer the questions in AcrobatPro, click on “Comments” and use the “Text” or “Draw” functions, as applicable. For the latter, you will only need the “Line”, “Rectangle”, and “Oval” options.

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

- I. [60 Points] Name, complete the drawing, or choose one given answer, as appropriate, the following molecules according to the IUPAC rules.

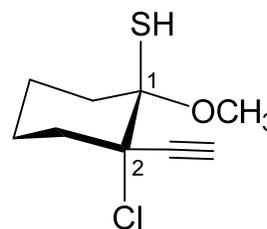
a.



This enantiomer

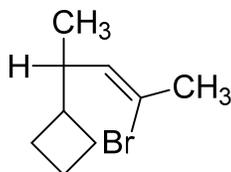
(2*R*,3*R*)-1-(2-Cyclopentenyl)-2-methyl-4-methylidenehept-6-yn-3-ol

- b. (1*R*,2*S*)-2-Chloro-2-ethynyl-1-methoxycyclohexane-1-thiol



Complete the stencil

c.

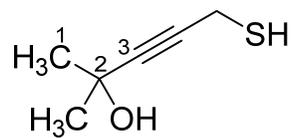


(This is a Fischer projection;
name this enantiomer)

(*S*,*Z*)-(3-Bromo-1-methyl-2-butenyl)cyclobutane

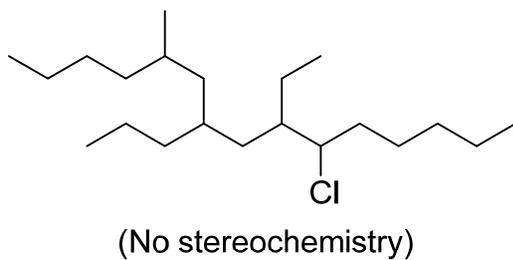
d.

5-Mercapto-2-methylpent-3-yn-2-ol



Complete the stencil

e.

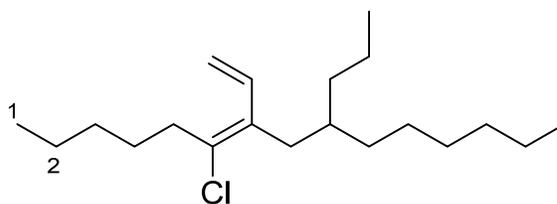


10-Chloro-9-ethyl-5-methyl-7-propylpentadecane

How many stereoisomers exist for this compound?

16

f.

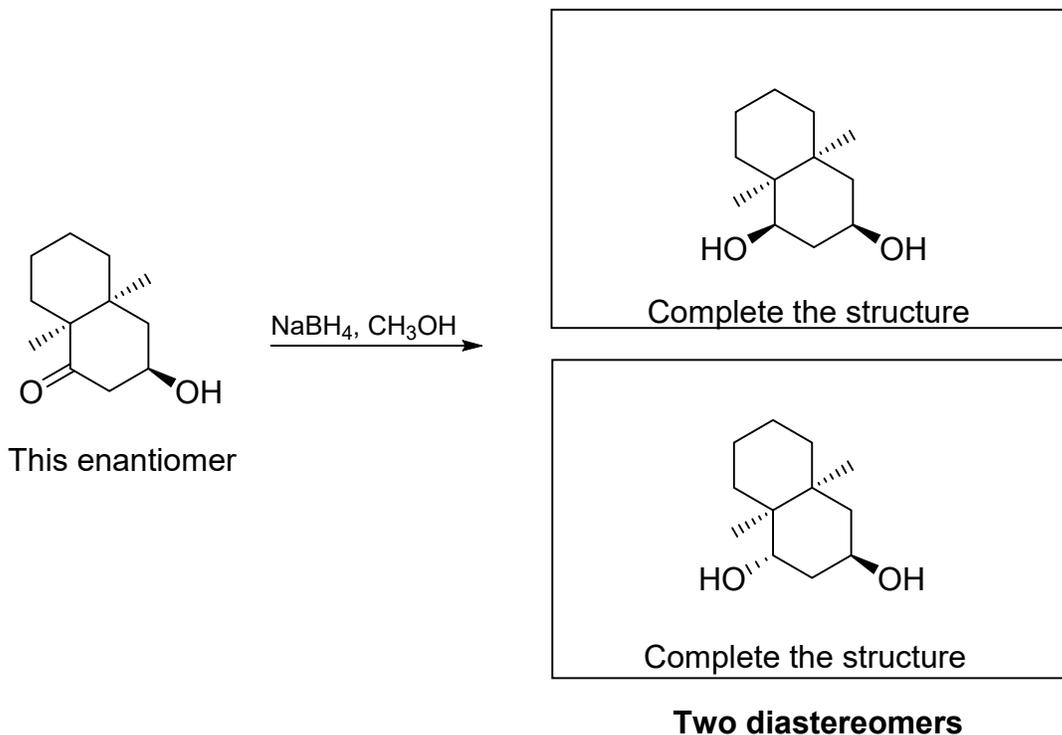
(E)-6-Chloro-7-ethenyl-9-propylpentadec-6-ene

Complete the stencil

II. [100 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). Don't forget **stereochemistry!**

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.

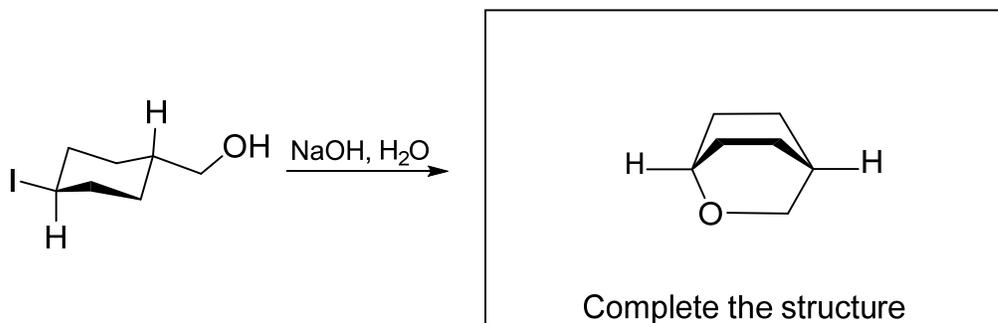
a.



Place an "X" mark into the box next to the correct statement (there is only one):

- 1 The products are identical
2. One product is meso
3. Both products are optically active and have the same $[\alpha]$ values
4. Both products are optically active and have different $[\alpha]$ values

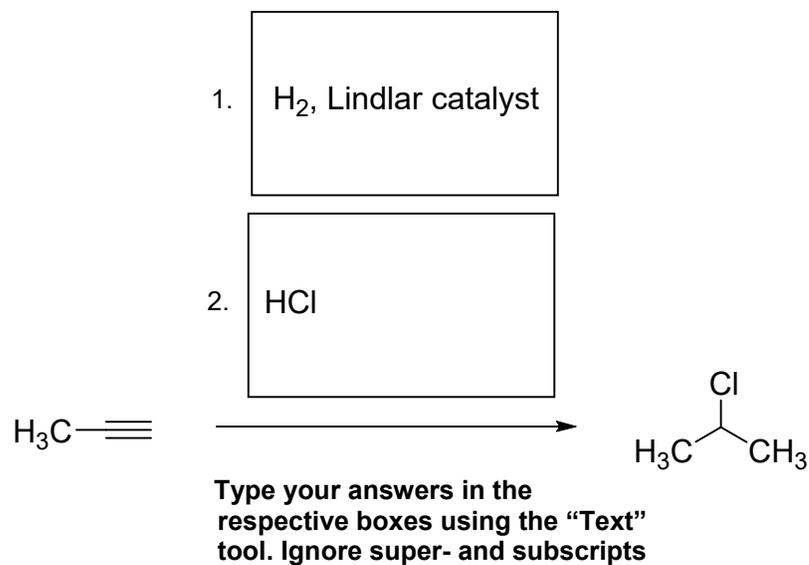
b.



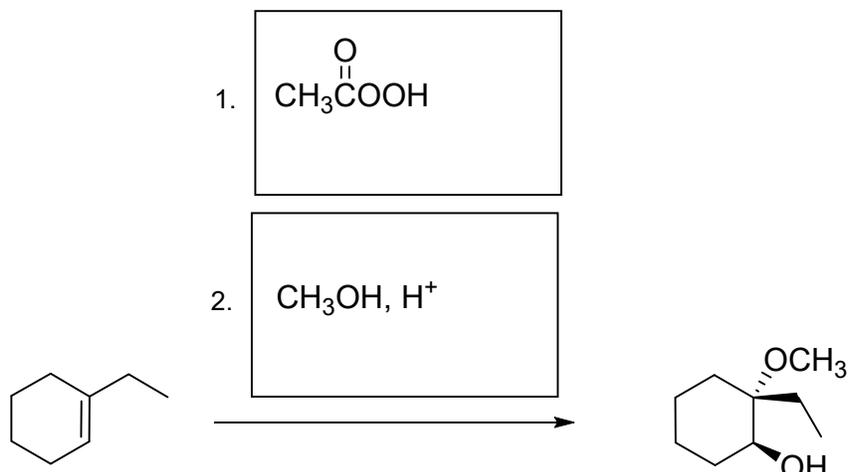
Place an "X" mark into the box next to the correct statement (there is only one):

1. The product is chiral
2. The product undergoes ring flip
3. In order to react, the starting material has to undergo partial ring flip to the half-chair conformation
4. Changing the base to NaH will slow the reaction

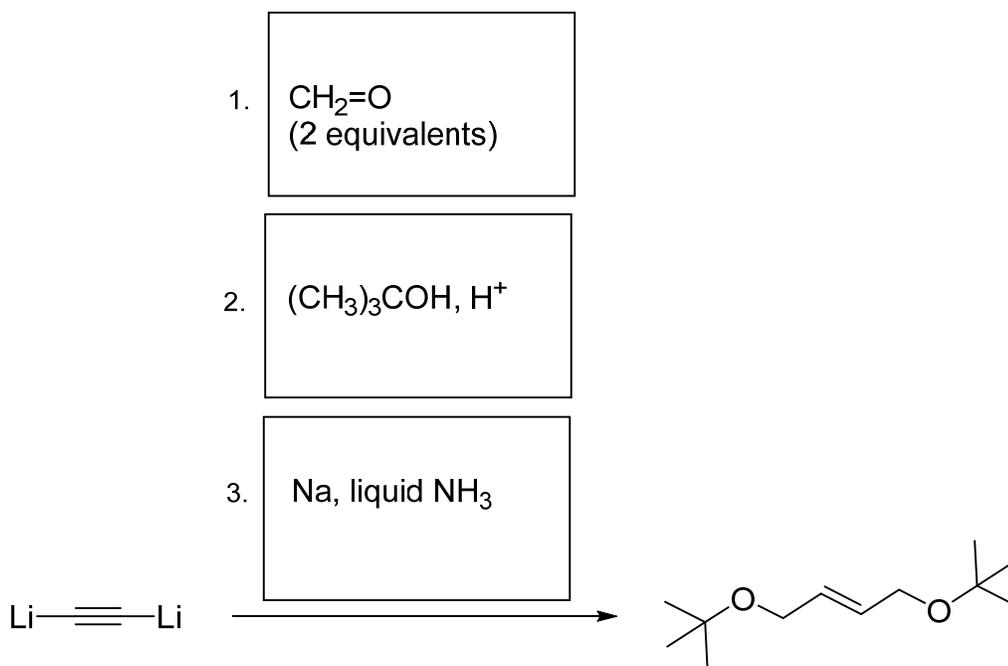
c.



d.

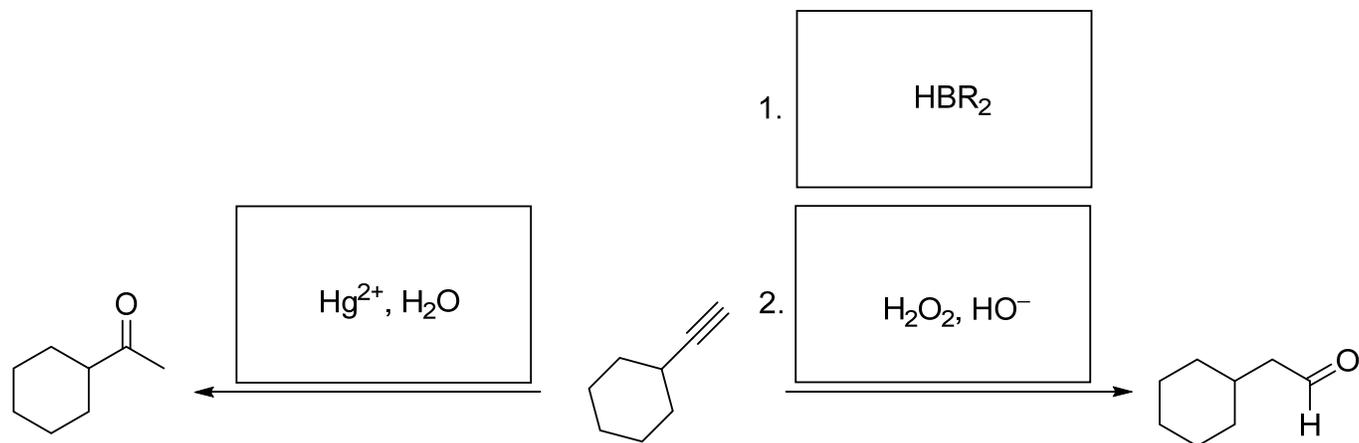


e.



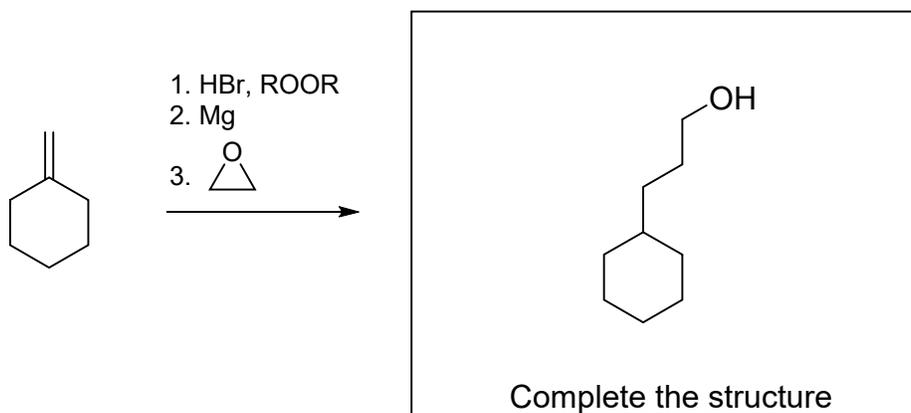
Type your answers in the
respective boxes using the "Text"
tool. Ignore super- and subscripts

f.

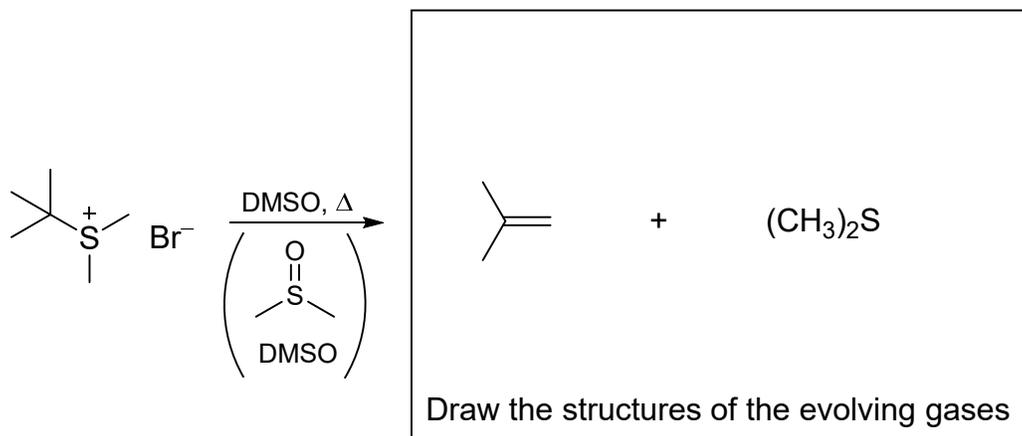


Type your answers in the respective boxes using the "Text" tool. Ignore super- and subscripts

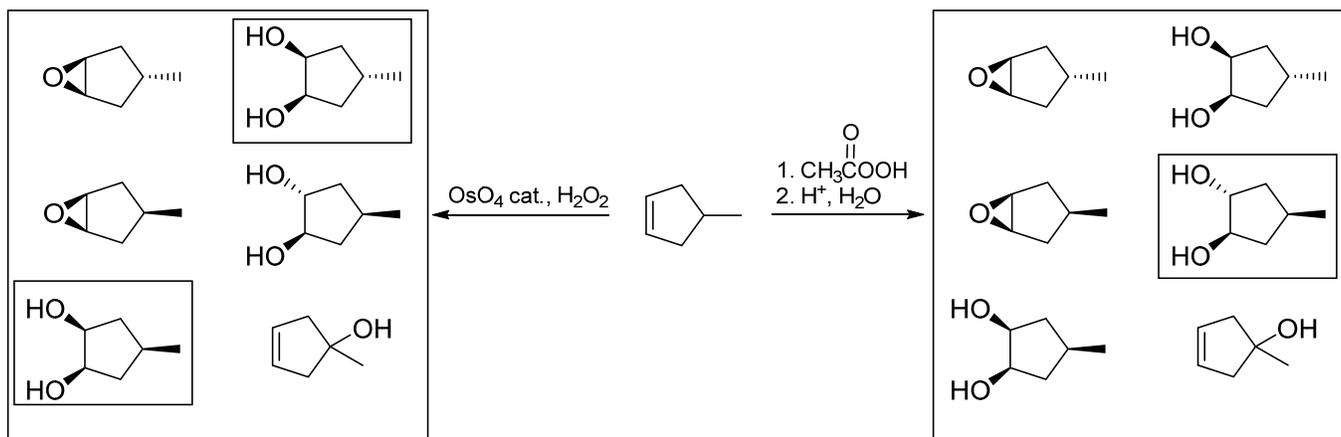
g.



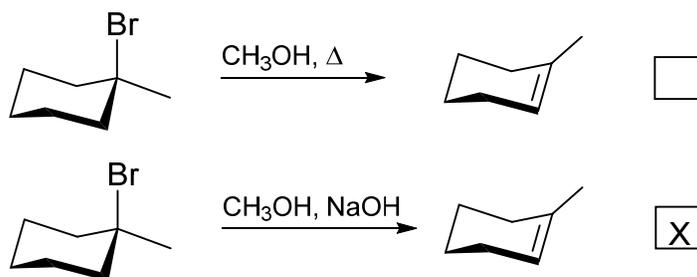
h.



i. Use the rectangle tool to select your choices of products of the two reactions shown below. There may be more than one product in each case.

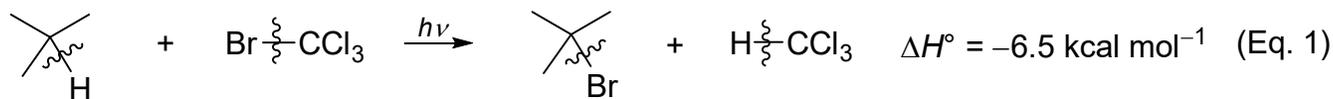


j. Place an "X" mark in the box next to the elimination reaction that will be faster.



III. [35 Points] Treatment of 2-methylpropane with bromotrichloromethane in the presence of light results in 2-bromo-2-methylpropane and trichloromethane (chloroform) (Eq. 1).

a. Using the C–H bond dissociation energy DH° of chloroform (96 kcal mol⁻¹) and the $\Delta H^\circ_{\text{reaction}} = -6.5$ kcal mol⁻¹ given below, in addition to Table 3-1, enter the missing DH° values below the equation (fill in the boxes).



96.5

64

71

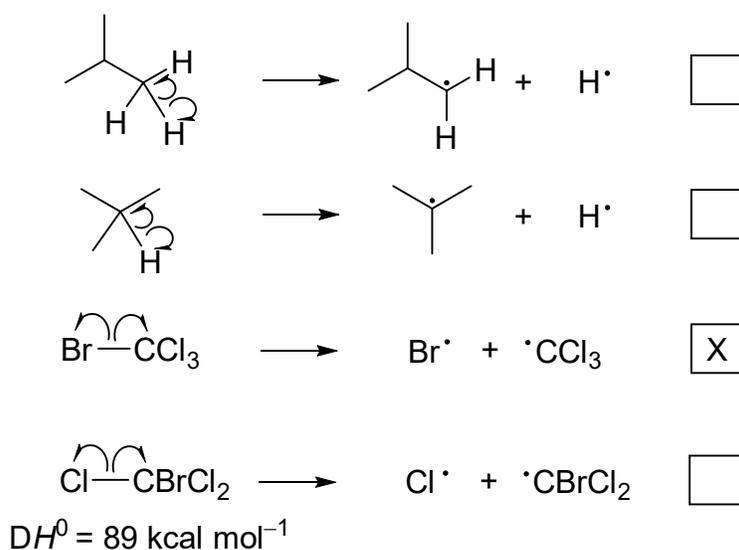
96

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)

Note: (a) $DH^\circ = \Delta H^\circ$ for the process A–B → A· + ·B. (b) These numbers are being revised continually because of improved methods for their measurement. (c) The trends observed for A–H bonds are significantly altered for polar A–B bonds because of dipolar contributions to DH° .

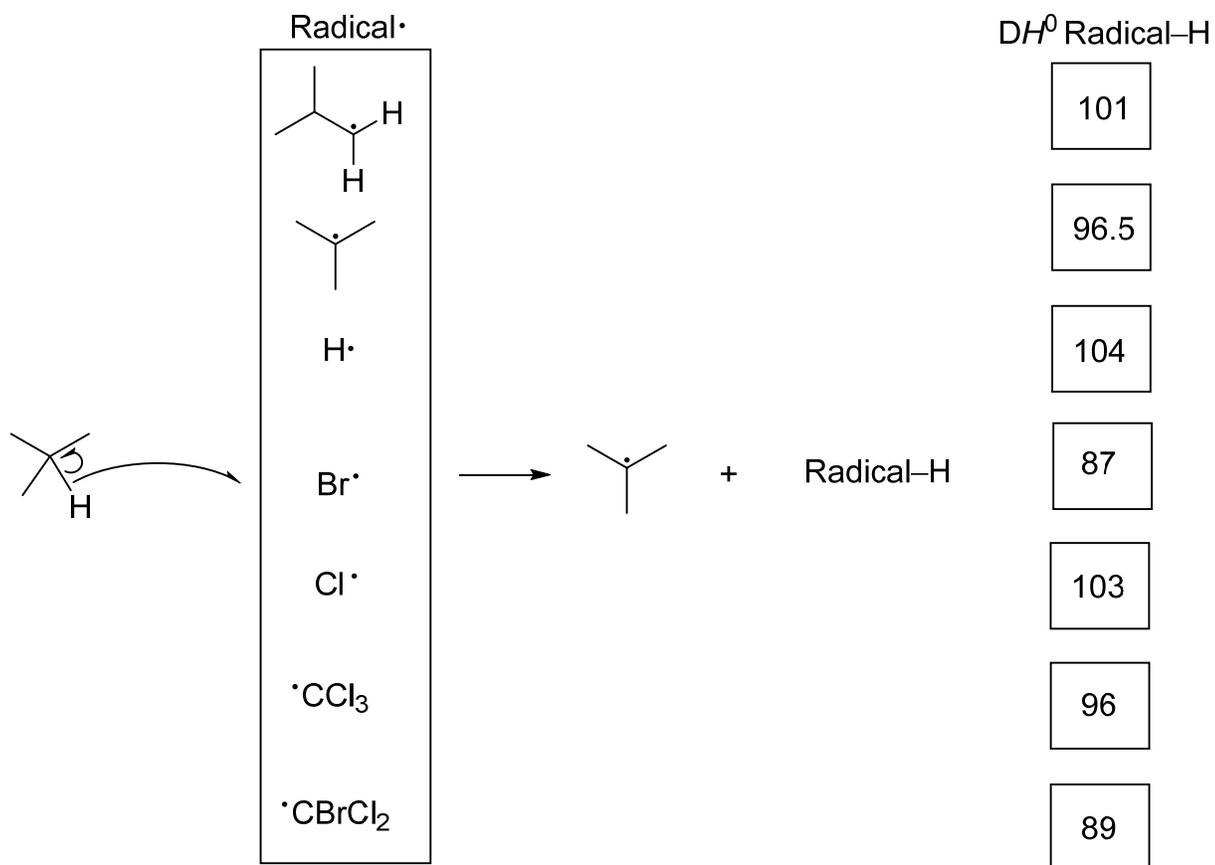
b. Place an “X” mark in the box next to the correct initiation step.



c. In the following larger box, give a one-sentence explanation for your choice.

The Br—CCl₃ bond is the weakest of all bonds in the starting materials.

d. The first propagation step of the mechanism of Eq. 1 is the abstraction of the tertiary hydrogen atom in 2-methylpropane by one of the seven radical species (labelled "Radical•" below) depicted in b. and generating a Radical–H bond. Using the information in a., enter the corresponding Radical–H bond dissociation energies into the boxes below (kcal mol⁻¹; the value for the H–CBrCl₂ bond is given).



e. In the unlikely scenario of all of these radicals competing in d., which one would win (enter in the box below)?

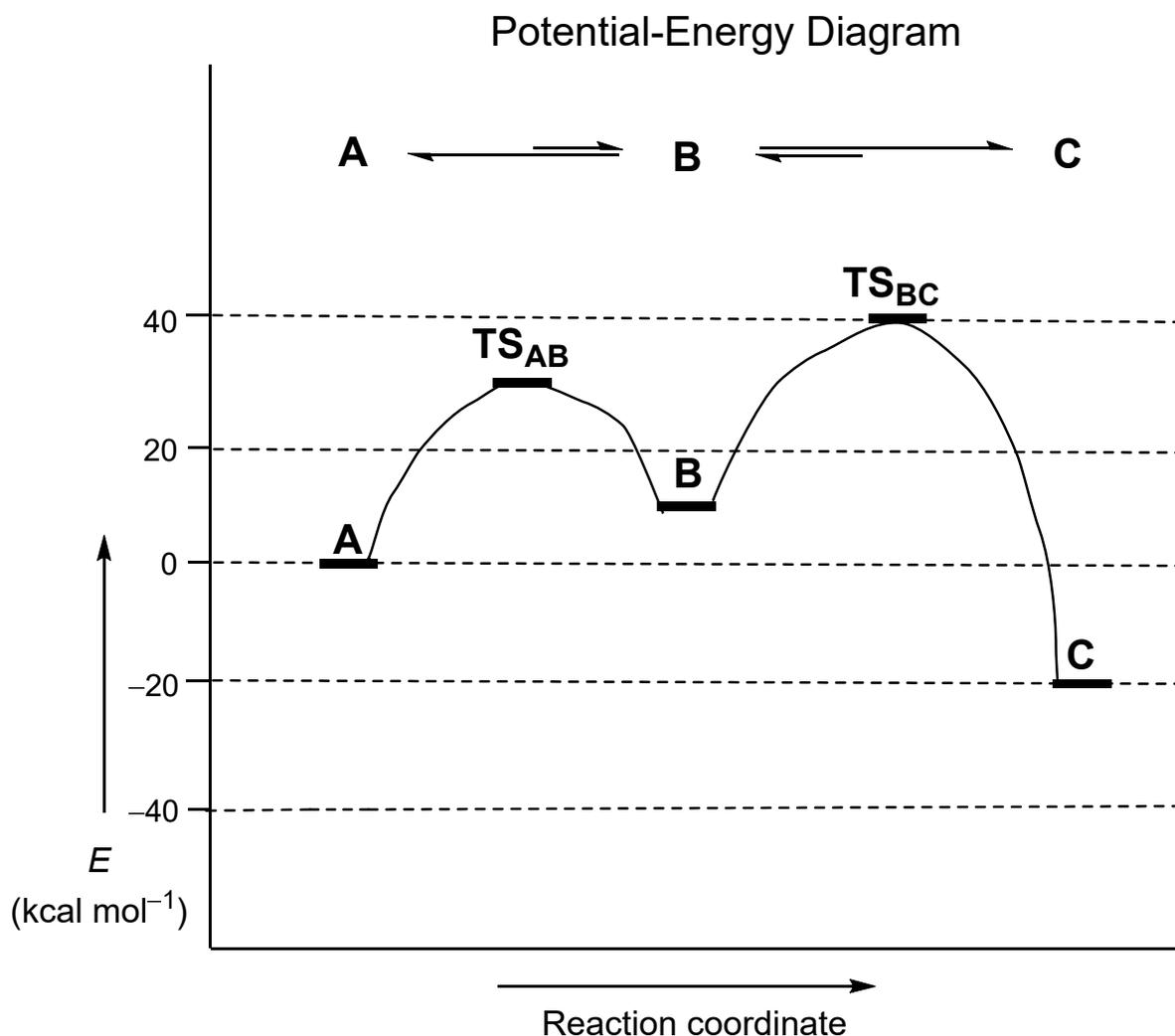
H•

IV. [20 Points] Compound **A** enters into a preequilibrium with **B**, before proceeding **C**. The associated thermodynamic and kinetic data are given in the equation shown:

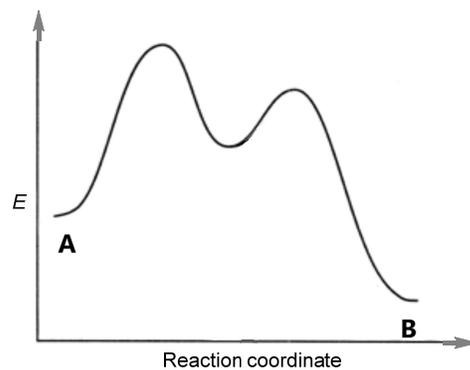
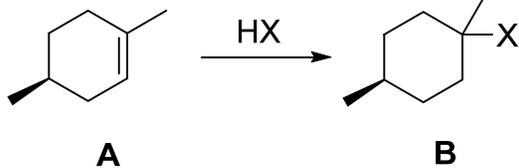


Complete the energy diagram below as follows:

- Starting with **A** positioned at level "0" (black bar), indicate the respective positions of **B** and **C** along the reaction coordinate (use bars and label them with the respective letters).
- Show the positions of the two respective transition states (bars) that reflect the activation energies of the two steps. Label them "**TS_{AB}**" and "**TS_{BC}**", respectively.



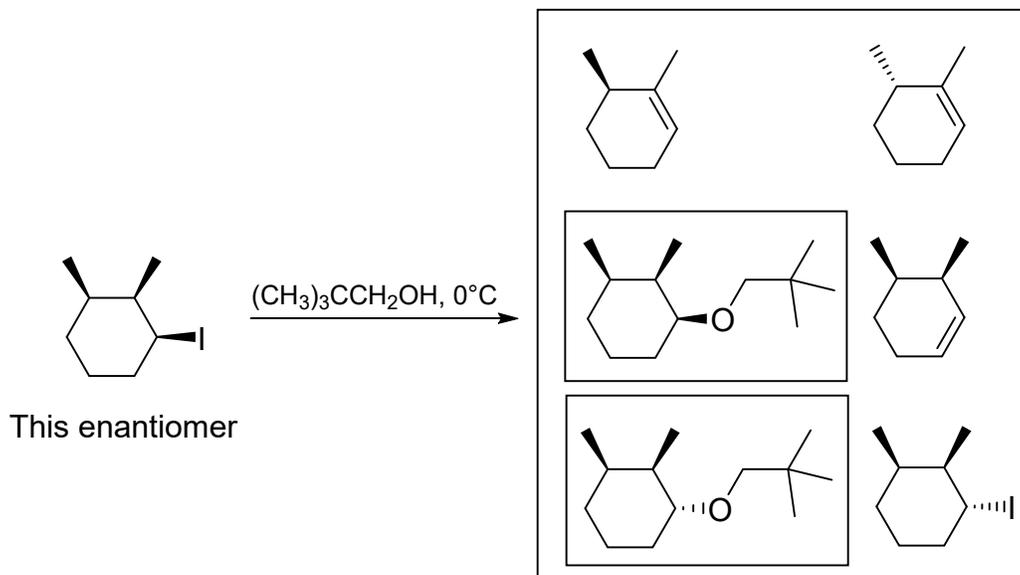
V. [30 Points] Using key words or a short sentence, list three observations that support the mechanism of hydrohalogenation of **A** to **B**.



1. Stereochemistry: diastereomers
2. Rate increases with increasing $[\text{H}^+]$
3. Rate is independent of concentration of $[\text{X}]$
4. Rate is independent of nature of X
5. Regioselectivity (Markovnikov)

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

a.



Mechanism:

S_N2

S_N1

E2

E1

When using $(CH_3)_3CSH$ instead of $(CH_3)_3CCH_2OH$, which one of the following ratios will increase:

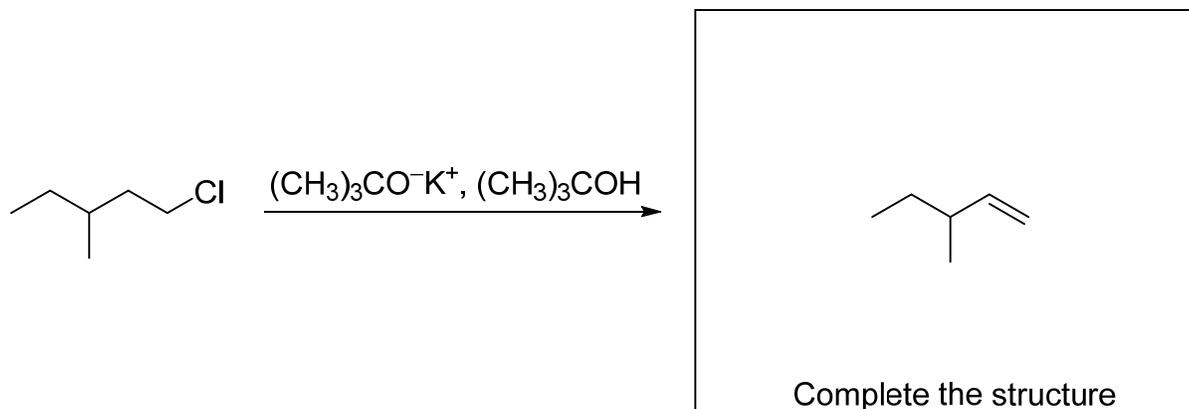
S_N2 / S_N1

E1 / S_N1

E2 / S_N2

E1 / E2

b.



Mechanism:

S_N2

S_N1

E2

E1

When using $CH_3O^-K^+$, CH_3OH instead of $(CH_3)_3CO^-K^+$, $(CH_3)_3COH$, which one of the following ratios will increase:

S_N2 / S_N1

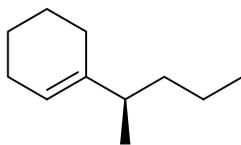
$S_N1 / E1$

$S_N2 / E2$

E1 / E2

VII. [70 Points]

a. Consider the hydrochlorination (HCl) of the alkene enantiomer shown below. How many product isomers do you expect?

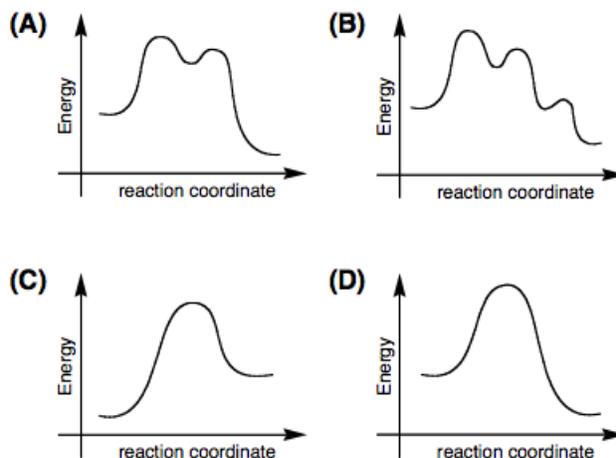
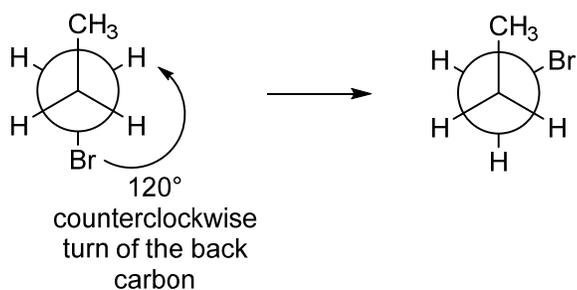


(*R*)-1-(1-methylbutyl)cyclohex-1-ene

Place an "X" mark next to your answer (there is only one that is correct).

- one enantiomer
 two diastereomers
 a meso compound
 two isomers
 two enantiomers

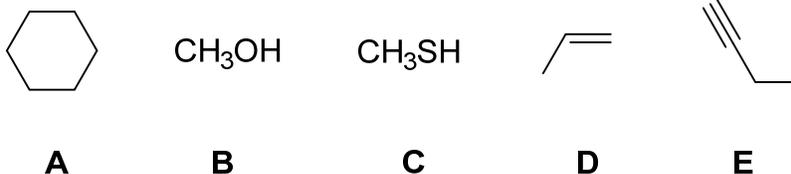
b. Which of the following potential energy diagrams describes the isomerization depicted below left? Give your answer (**A**, **B**, **C**, or **D**) in the box provided.



Answer:

C

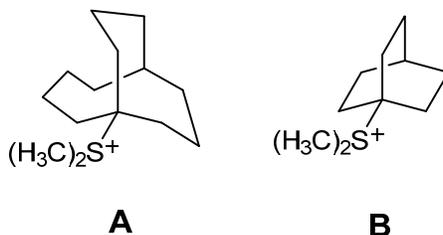
c. Rank the following species in the order of increasing acidity:



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

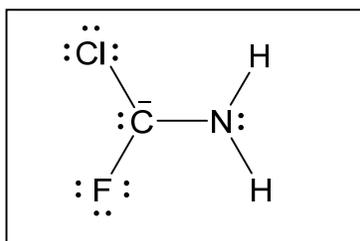
d. Solvolysis of both **A** or **B** is very slow, but that of **B** much more so than that of **A**. Why?



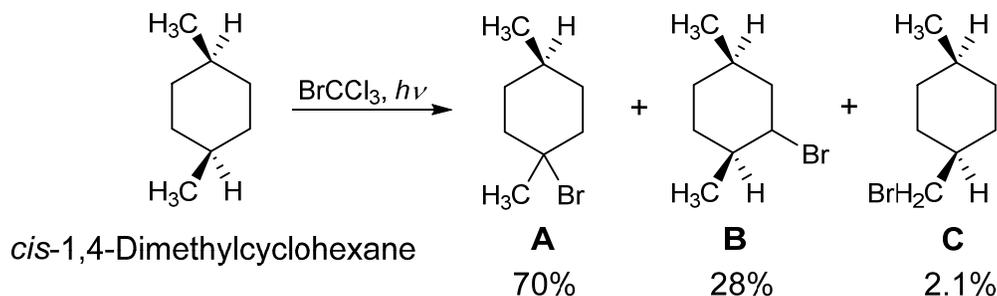
Place an "X" mark next to your answer (there is only one that is correct).

- B** is more sterically hindered.
 A is more sterically hindered.
 B is better solvated.
 Planarization of the resulting carbocation is more difficult for **B**.

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



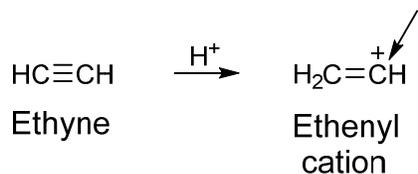
f. *cis*-1,4-Dimethylcyclohexane has tertiary, secondary, and primary hydrogens. Bromination with bromotrichloromethane in the presence of light (see Problem III) gave **A**, **B**, and **C** in the yields indicated below.



Indicate your estimate of the relative reactivity of the primary : secondary : tertiary C–H positions in this reaction by placing an “X” into one of the boxes provided.

- 2.1 : 28 : 70
- 3 : 2 : 1
- 6 : 8 : 2
- 1 : 10 : 100

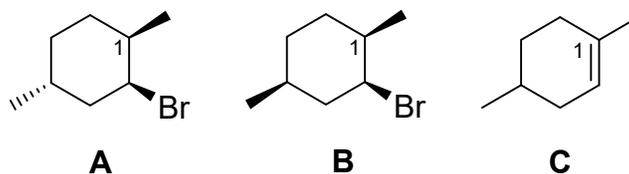
g. Protonation of ethyne engenders the ethenyl cation:



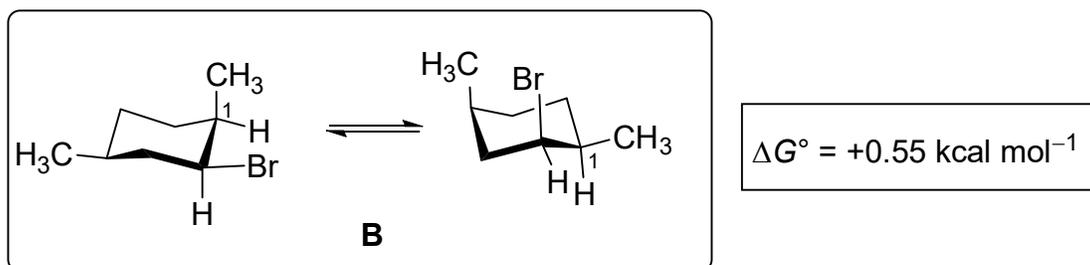
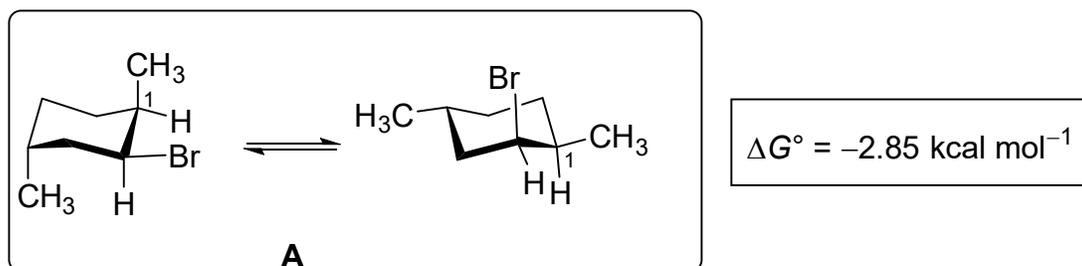
Indicate the hybridization (or lack thereof) of the positively charged carbon (arrow) by placing an “X” in the box next to your answer (there is only one that is correct).

- sp*
- sp*²
- sp*³
- p*
- s*
- unhybridized

VIII. [25 Points] On treatment with NaOH, racemic **A** and its diastereomer **B** both undergo Saytzev elimination to give 1,4-dimethylcyclohex-1-ene **C**. However, **A** does so faster than **B**. Why?



1. To find the answer, draw the two chair conformers of **A** and **B** using the stencils in the boxes below. Add H, CH₃, or Br to the ends of the dangling bonds.



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

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 ₃ CH ₂	1.75 (7.32)	Br	0.55 (2.30)
(CH ₃) ₂ CH	2.20 (9.20)	I	0.46 (1.92)
(CH ₃) ₃ C	≈ 5 (21)	HO	0.94 (3.93)
	1.41 (5.90)	CH ₃ O	0.75 (3.14)
	1.29 (5.40)	H ₂ N	1.4 (5.9)

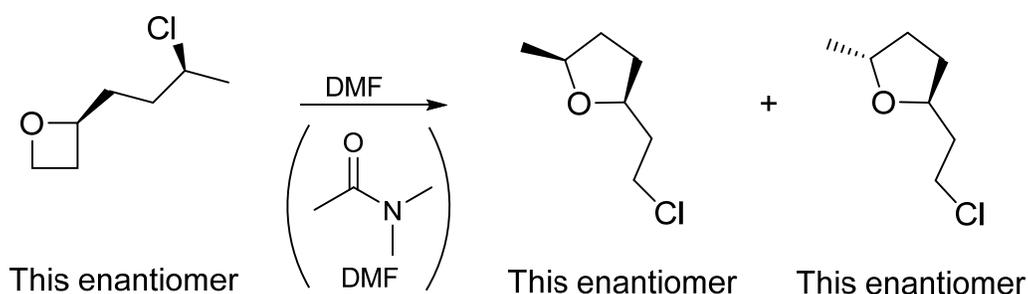
3. Armed with the results of the above analysis, why does **A** react faster than **B**? Explain in one sentence in the box below.

The more stable conformer of **A** contains the axial Br necessary for anti elimination. The more stable conformer of **B** first needs to undergo unfavorable ring flip to reach such a conformation.

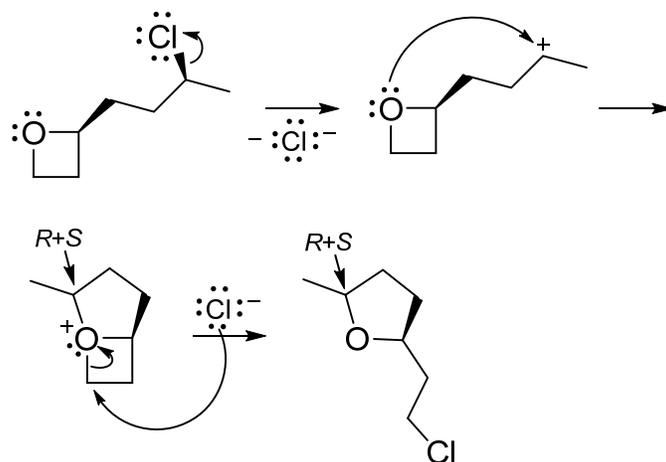
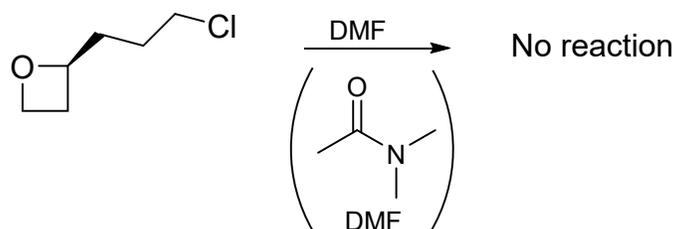
The following five problems contained in Sections VIII and IX should be answered on five separate pages of hard copy white paper using a dark (at least #2) pencil. Ascertain that your drawings are clearly visible. When you are finished, scan the five pages with your device, save the document as a pdf file, and add its contents to this exam file, using the "Combine Files" feature in AcrobatPro. Make sure to set up the correct order of the two; the combined file should feature your scanned pages at the end, in the sequence of the questions posed in the exam. Label the final pdf file with your name and the words "Final Exam" (namely: Last Name, First Name, Final Exam) and e-mail it to your designated TA.

IX. [50 Points] For each of the following reactions, provide a detailed mechanism (i.e., write a scheme with structures, arrow pushing, etc.) Do not add any reagents! These are not synthesis problems!

a.

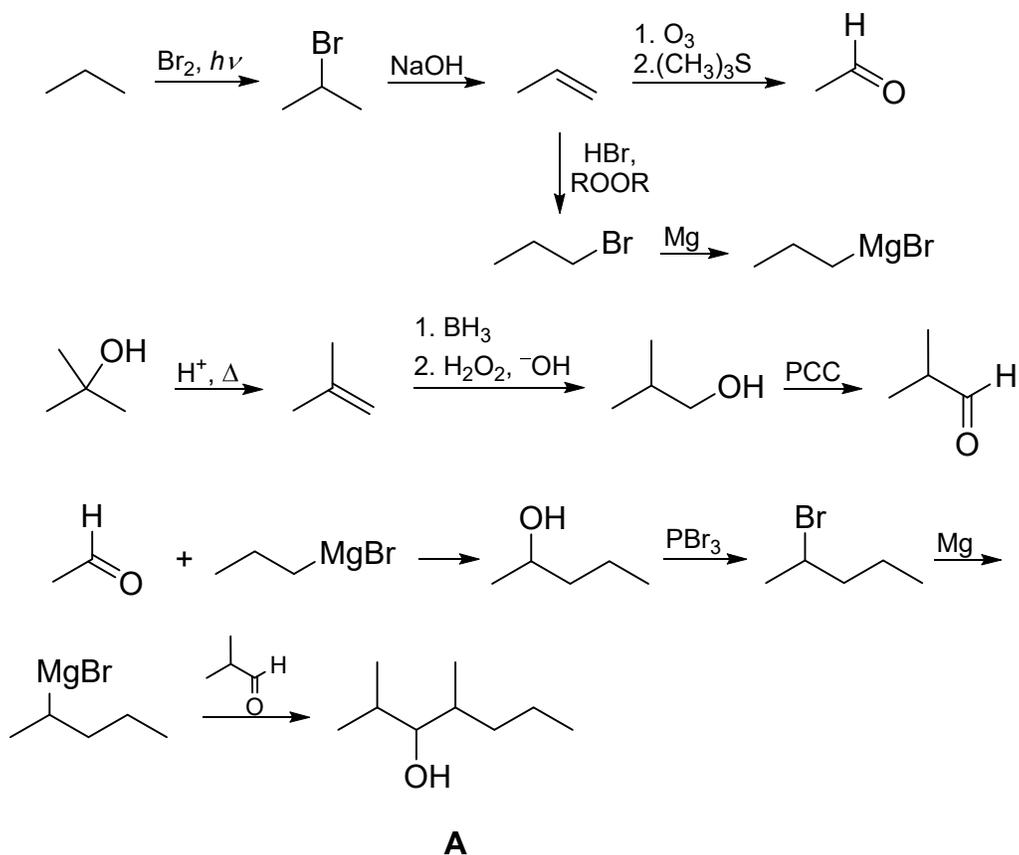
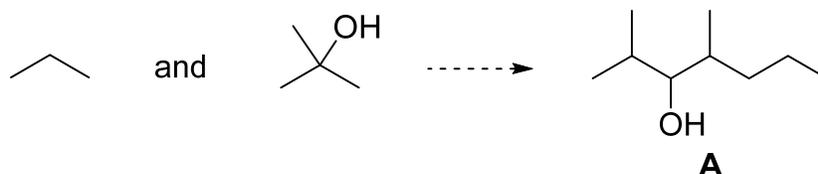


Hint:

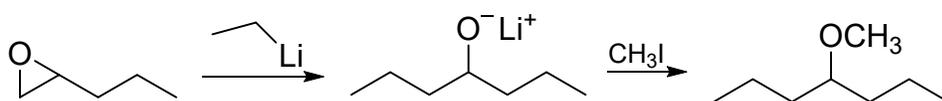
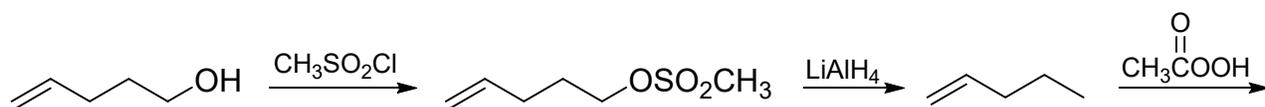
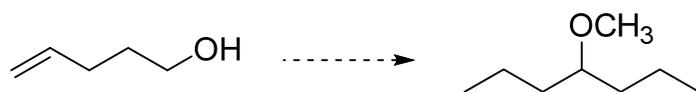


X. [90 Points] Show synthetic **forward connections** (reagents, intermediates; no mechanisms!) between the following starting materials and the final products. Note: several steps are required in each case; there may be several solutions to each problem, but you should show only one. It is best to work backwards (retrosynthetically), on a separate sheet of paper, to enable you to dissect the products into less complex precursors. However, the answer to be graded should be a *forward* scheme.

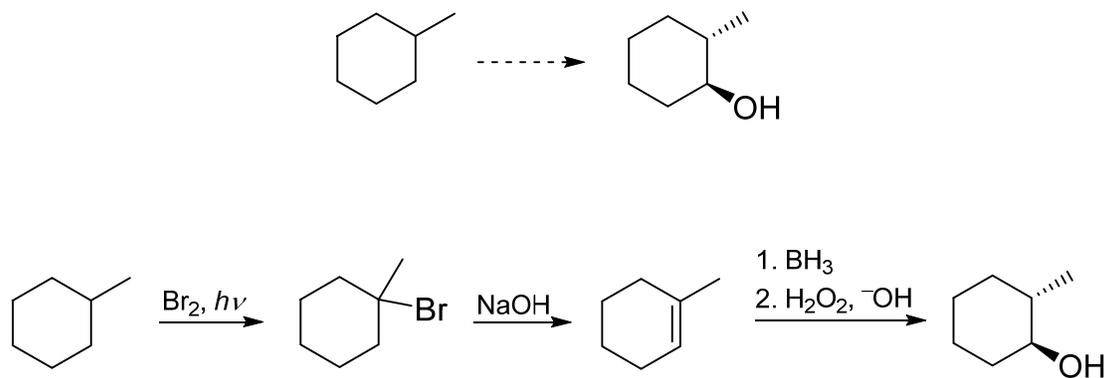
a. Starting from propane and 2-methyl-2-propanol (*tert*-butyl alcohol) as the only carbon containing materials, propose a synthesis of **A**.



b. For the synthetic conversion below, you may use any other reagents containing three carbons or less.



c. For the synthetic conversion below, you may use any other reagents.



* The End *

*Have a
great
summer!*