If you encounter any technical problems during the entire exam period, Zoom Jack Hayward Cooke at https://berkeley.zoom.us/j/93271902365
Label the final pdf file with your name and the words "3AExam2" (namely: Last Name, First Name, 3AExam2) and upload it to Gradescope.

To complete this page in AcrobatPro, click on "Comments" and use the "Text" function.

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, 2022

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 _____

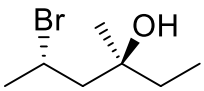
This test should have **13** numbered pages. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy entries. *Good Luck*!**

To answer the questions in AcrobatPro, click on the "Tools" tab in the top left, then scroll down and open the "Comments" tool, then use the "Text" or "Draw" functions, as applicable. For the latter, you will only need the "Line", "Rectangle", and "Oval" options. Keep saving your document as you complete it!

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

I. [30 Points] Name the following molecules, complete the drawing, or choose one given answer (as appropriate) according to the IUPAC rules.

a.

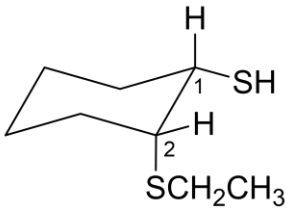


This enantiomer

(3*S*,5*S*)-5-Bromo-3-methylhexan-3-ol or
(3*S*,5*S*)-5-Bromo-3-methyl-3-hexanol

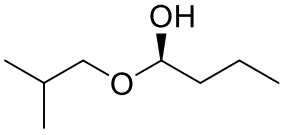
b.

(1*S*,2*R*)-2-(Ethylthio)cyclohexane-1-thiol



Place the missing substituents at the end of the dangling bonds

c.

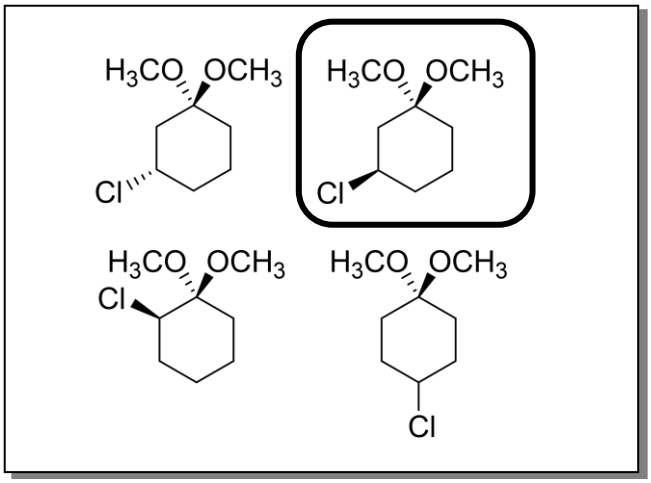


This enantiomer

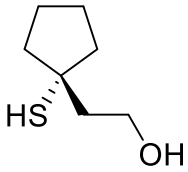
(*R*)-1-(2-Methylpropoxy)butan-1-ol or
(*R*)-1-(2-Methylpropoxy)-1-butanol

d.

(*R*)-3-Chloro-1,1-dimethoxycyclohexane



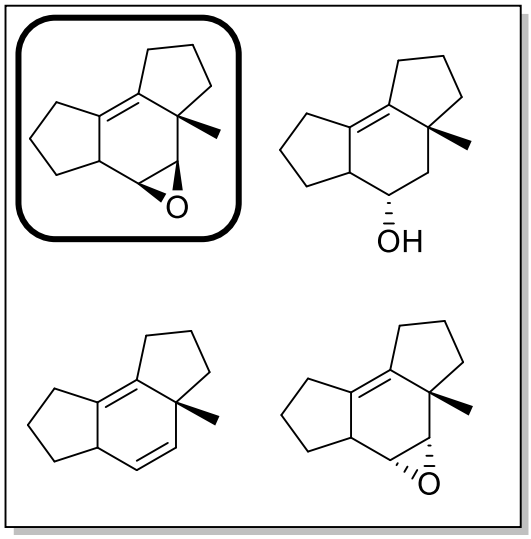
e.



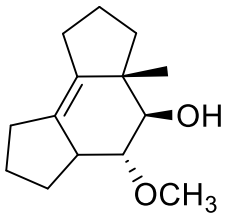
2-(1-Mercaptocyclopentyl)ethan-1-ol or
2-(1-Mercaptocyclopentyl)-1-ethanol

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

a.

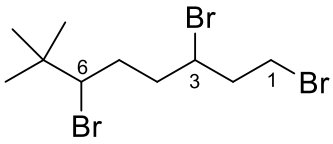


CH_3O^-, CH_3OH



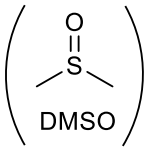
"Rectangle" your answer

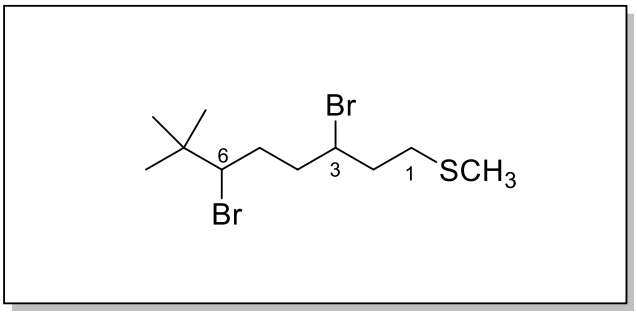
b.



No stereochemistry

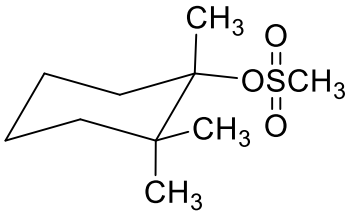
$NaSCH_3$ (1 equivalent), DMSO (solvent)





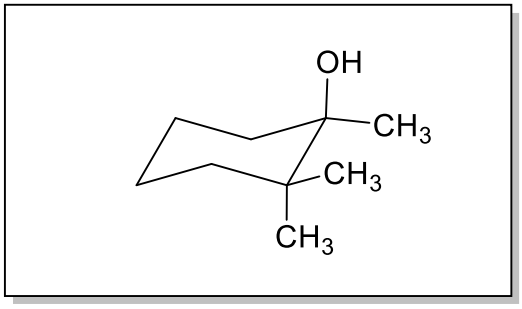
Place the missing substituents at the end of the dangling bonds of C1, C3, and C6

c.



This enantiomer

H_2O

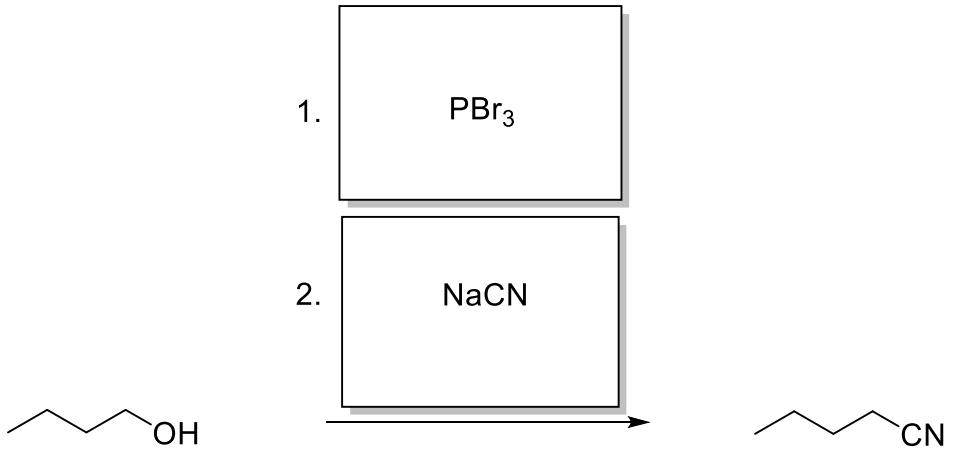


Draw the *more stable* conformer. Place the missing substituents at the end of the dangling bonds. Δ*G*° (equatorial→axial): CH_3, 1.70; OH, 0.94 kcal mol^{-1}.

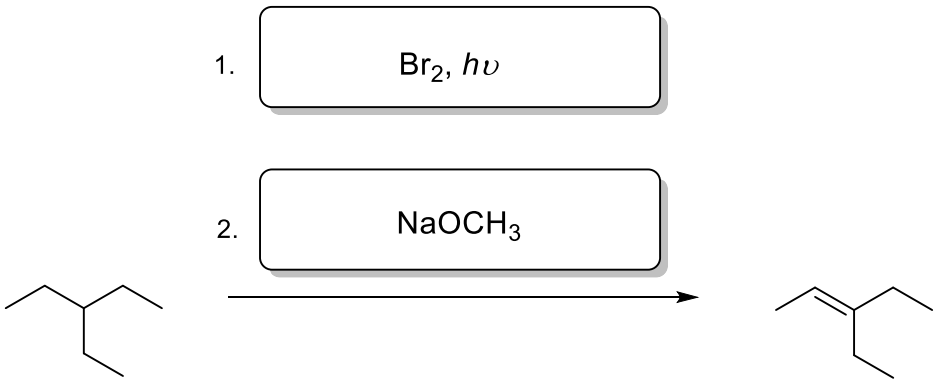
"Oval" your choice of an answer: Is the product optically active? Yes (No)

For the following d.–h., type your answers in the respective boxes using the "Text" tool. Ignore super- and subscripts, if applicable [as in, for example, tert-butyl cation = (CH3)3C+]. For *hv* use hv.

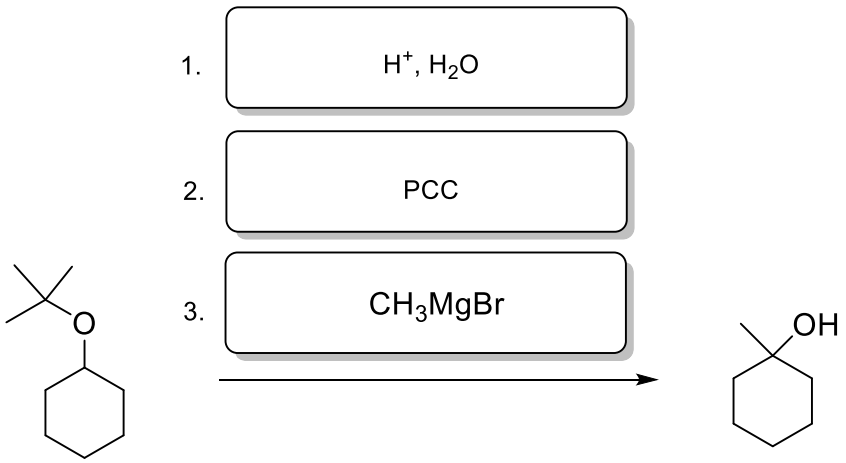
d.



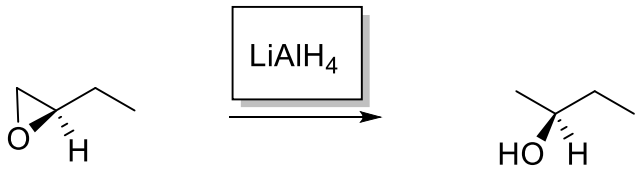
e.



f.



g.



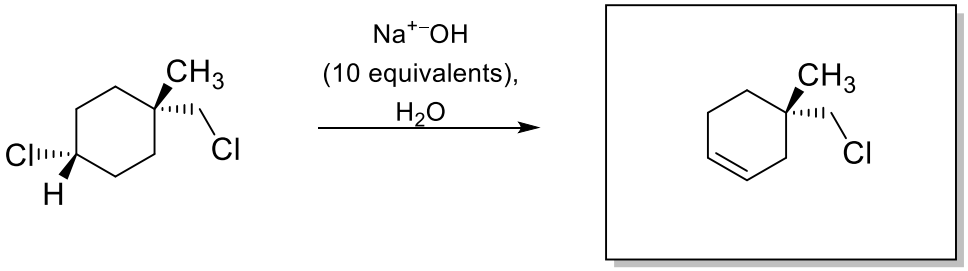
This enantiomer

"Oval" your choice of an answer:

Is the product chiral? (Yes) No

Is the product optically active? (Yes) No

h.



Complete the structure

"Oval" your choice of an answer:

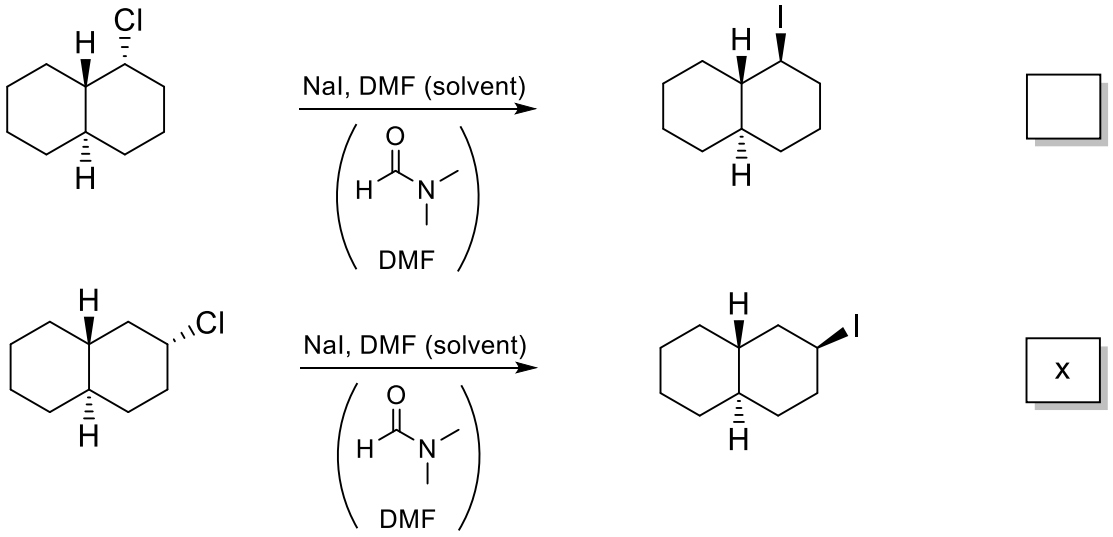
Is the product chiral? (Yes) No

Is the product optically active? Yes (No)

III. [40 Points] For each pair of reactions shown below, mark the box on the right with an "X" indicating which will go faster and “rectangle” the mechanism by which it proceeds (e.g. S_N2, S_N1, E2, E1). In one sentence, provide a brief explanation for the rate acceleration in each case in the bottom box provided.

a.

1.



x

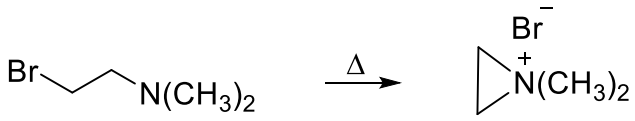
2. Mechanism: (SN2) SN1 E2 E1

3. Explain your choice of the faster reaction in one sentence.

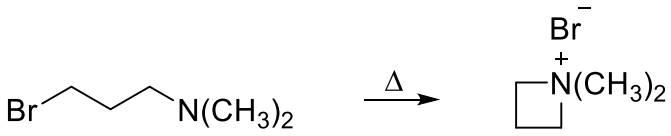
The second reaction is faster because it encounters less steric hindrance.

b.

1.



x



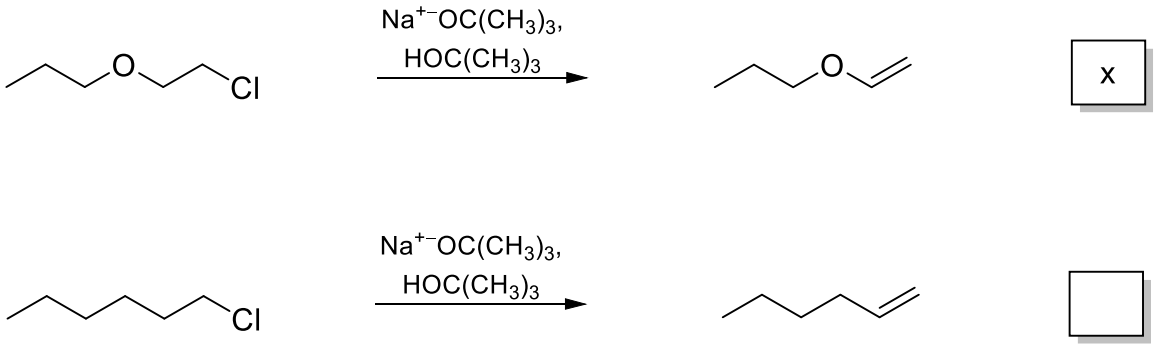
2. Mechanism: (SN2) SN1 E2 E1

3. Explain your choice of the faster reaction in one sentence.

In intramolecular S_N2 reactions, three-membered rings form faster than four-membered rings.

c.

1.



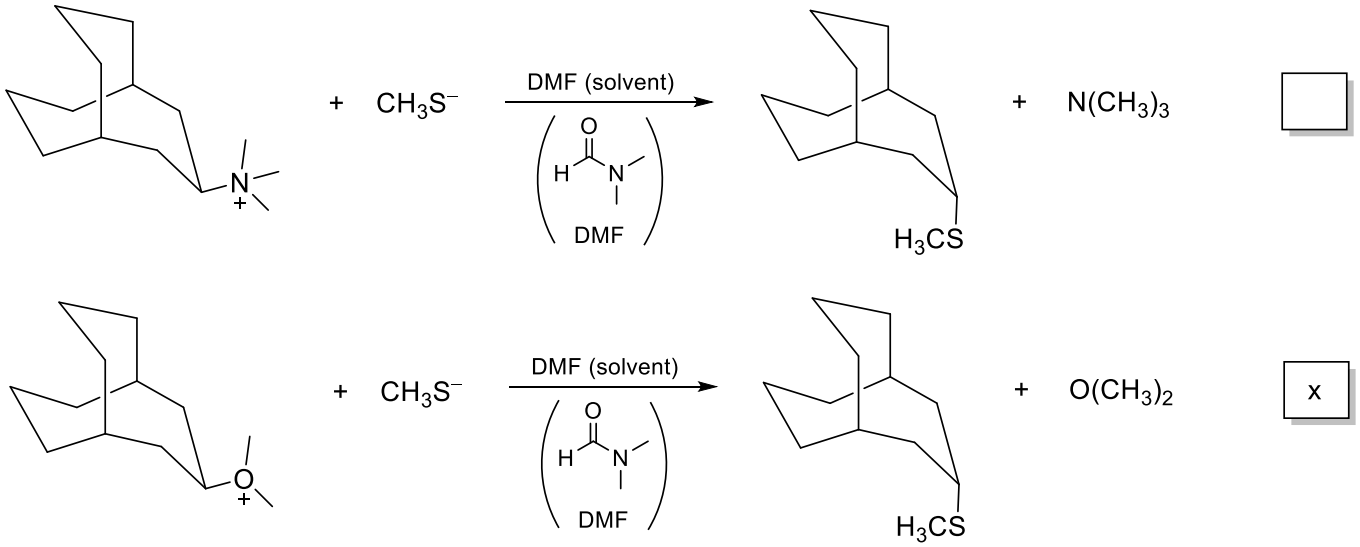
2. Mechanism: S_N2 S_N1 E2 E1

3. Explain your choice of the faster reaction in one sentence.

The larger electronegativity of O relative to that of C makes the hydrogens next to O more acidic.

d.

1.



x

2. Mechanism: (SN2) SN1 E2 E1

3. Explain your choice of the faster reaction in one sentence.

$(CH_3)_2O$ is a better leaving group because O is more electronegative than N.

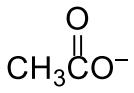
IV. [20 Points]

a. Place an ***X mark*** (“Text” tool) in the box preceding a true statement. There will be several such statements. Leave blank those that you deem untrue. Note: An incorrect X mark will count against your total score, but the minimum is zero (i.e., no negative points).

[ ] Along the cation series–primary to secondary to tertiary–hyperconjugation decreases.

[X] Transferring an electron from a 1*s* orbital to a 2*s* orbital costs energy.

[ ] A compound with two stereocenters bearing the same substituents on each center is always meso.

[ ]  is a better leaving group than CH_3O^- because it is larger.

[X] If the rate of the reaction A + B → C + D is proportional to only the concentration of A, it is called unimolecular.

[ ] If the reaction of two achiral starting materials leads to a chiral product, the product will be optically active.

[ ] The ability of an attached atom and its substituents to leave a carbon chain decreases from left to right across a row of the periodic table.

[X] An axial substituent in the cyclohexane chair suffers from transannular strain.

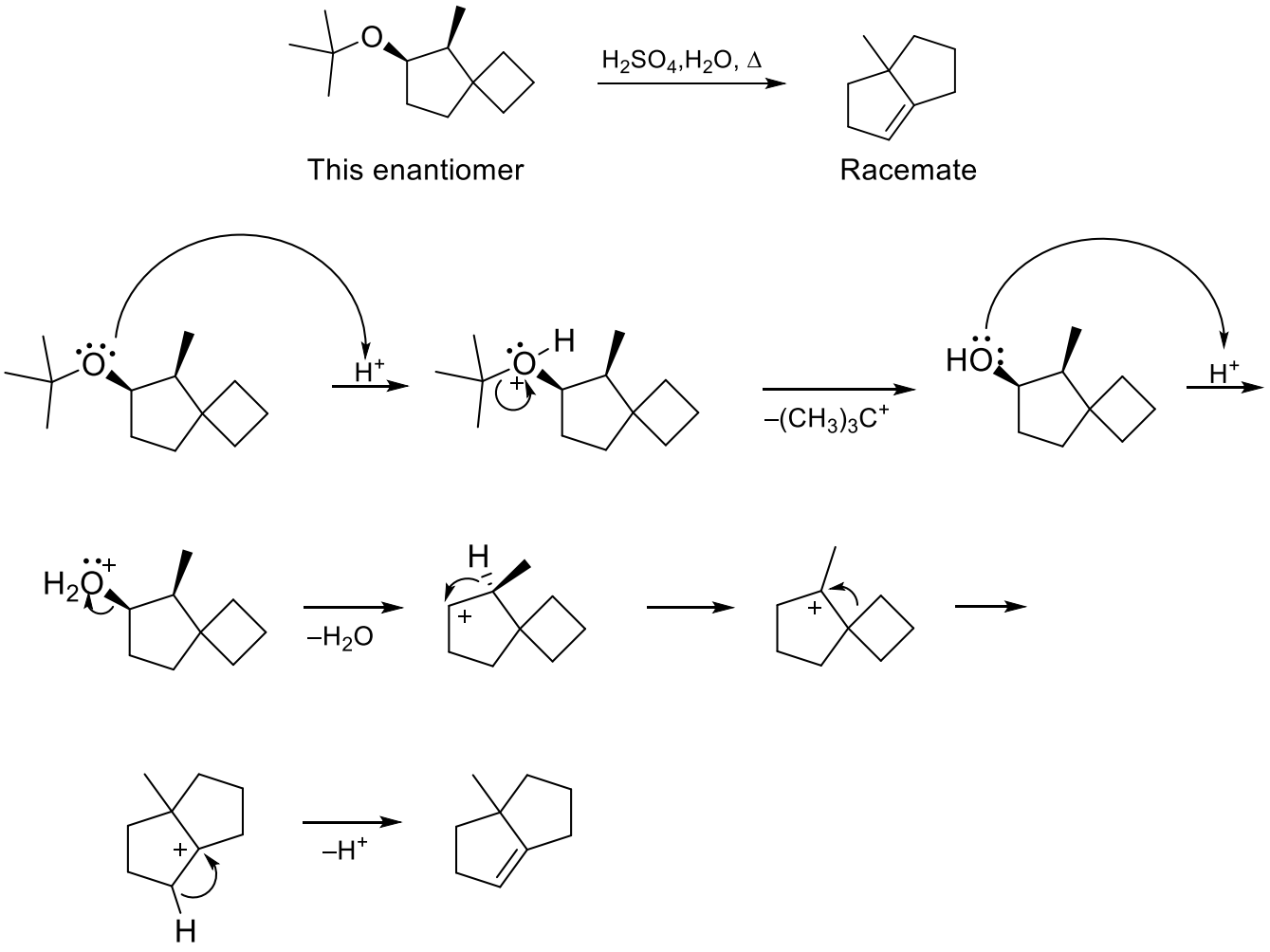
[X] The E2 reaction speeds up with better leaving groups.

[X] Secondary chloroalkanes may undergo all four modes of reaction: S_N2, E2, S_N1, and E1.

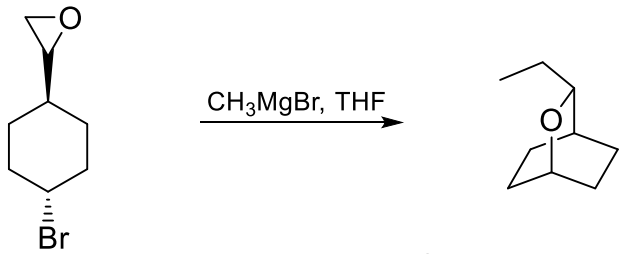
The following four problems should be answered on *four* separate pages of hard copy white paper using a dark (at least #2) pencil. Label these pages "V.a", "V.b", "VI.a", and "VI.b". Ascertain that your drawings are clearly visible. When you are finished, scan the four pages on your device with a suitable scanning app (do not use CamScanner) in the order V.a →VI.b, save the document as a pdf file, and add its contents to this file, using the "Combine Files" feature on AcrobatPro. Make sure to set up the correct order of the two; the combined file should feature your scanned pages at the end.
Label the final combined pdf file with your name and the words "3AExam 2" (namely: **Last Name, First Name, 3AExam 2) and upload it to Gradescope.**

V. [40] 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!

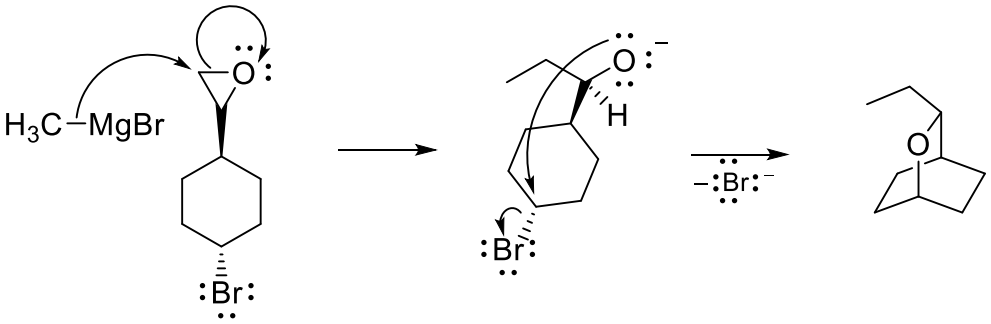
a.



b.

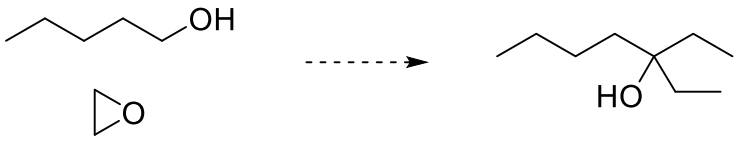


After aqueous work-up



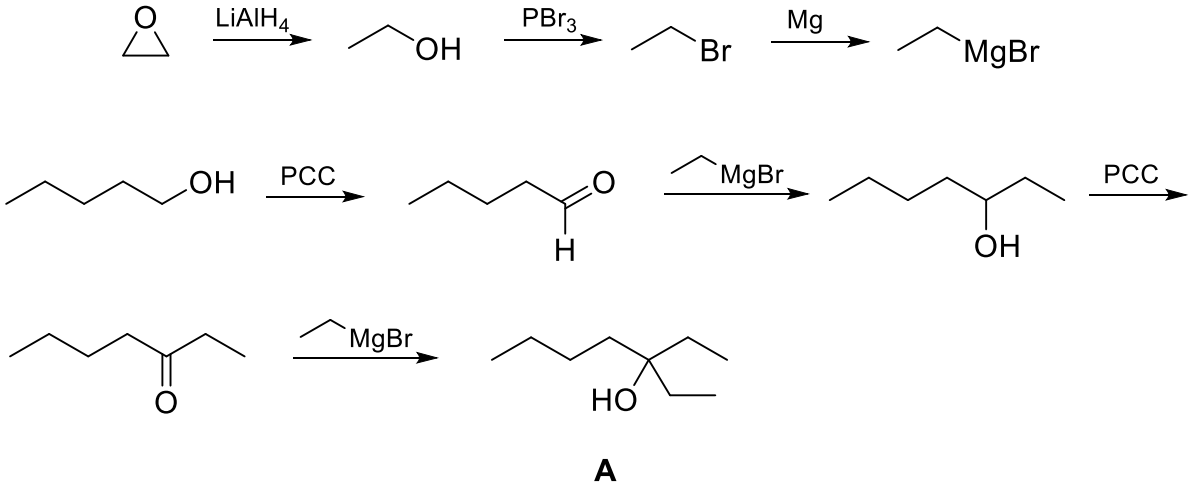
VI. [40 Points]

a. Devise the synthesis of compound **A** below, using only 1-pentanol and oxacyclopropanes as building blocks. It will help you if you execute a retrosynthesis on a separate page (not to be submitted).



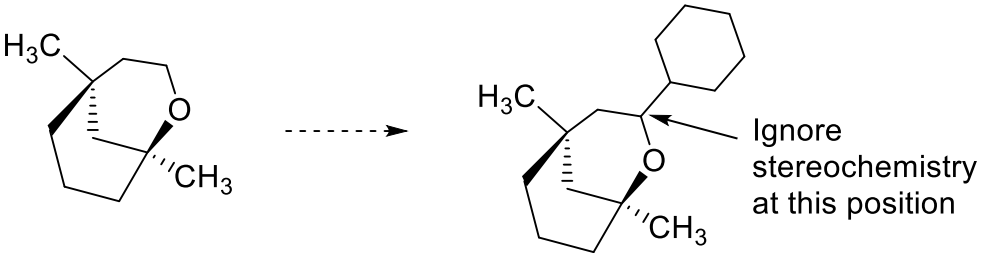
Only carbon containing building blocks

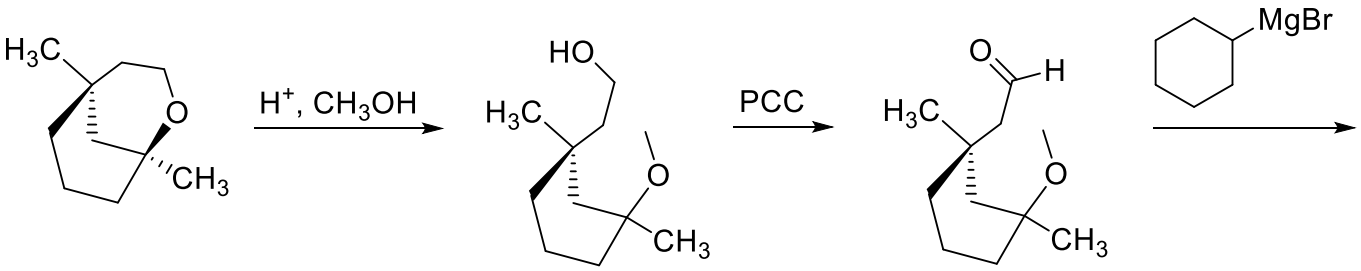
A

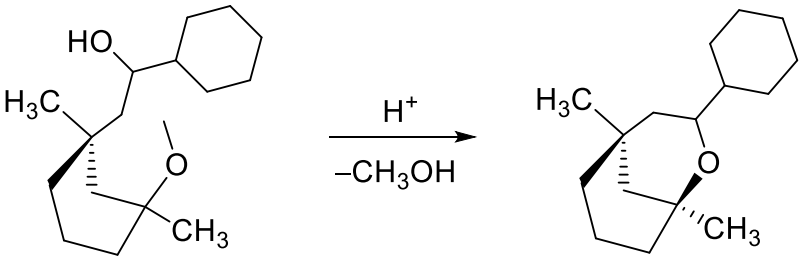


A

b. Provide a viable conversion of the starting material below to the product. You may use any additional compounds and reagents. It will help you if you execute a retrosynthesis on a separate page (not to be submitted).







♫ The End ♫