EXAMINATION 2
Chemistry 3A

If you encounter any technical problems during the exam period, Zoom Justin Jurczyk at https://berkeley.zoom.us/j/9291206889
E-mail the completed exam to your laboratory TA. If you are a lecture only student, send it to Justin: justin_jurczyk@berkeley.edu

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
April 4, 2020

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.

This test should have **12** 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*!**

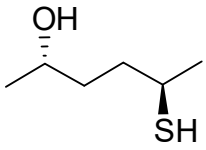
Please initial the box at the end of this pledge.
I pledge to maintain the integrity of this exam. As such, I pledge to abide by the exam instructions specified and to withhold communication through any means with anyone about the content of the exam until the entire class and I have completed it. I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

Please 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. This is deliberately low-tech.

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

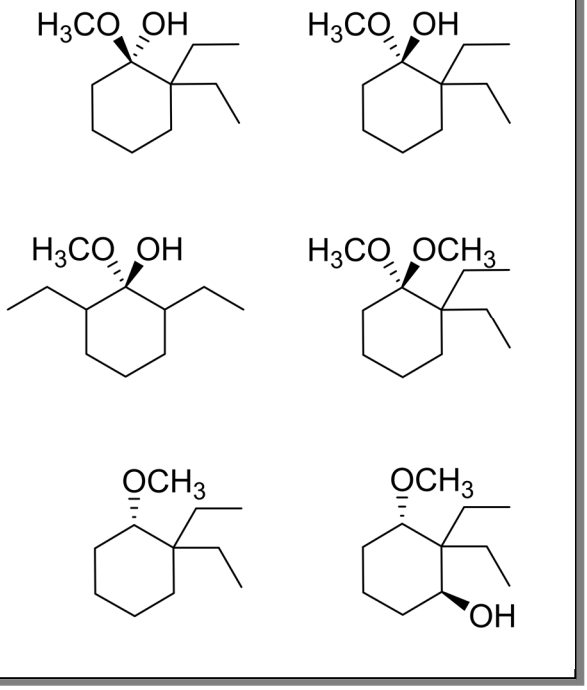
a.



This enantiomer

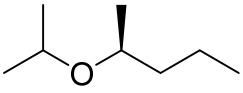
b.

(*S*)-2,2-Diethyl-1-methoxycyclohexan-1-ol



Use the "Rectangle" tool to enclose your answer

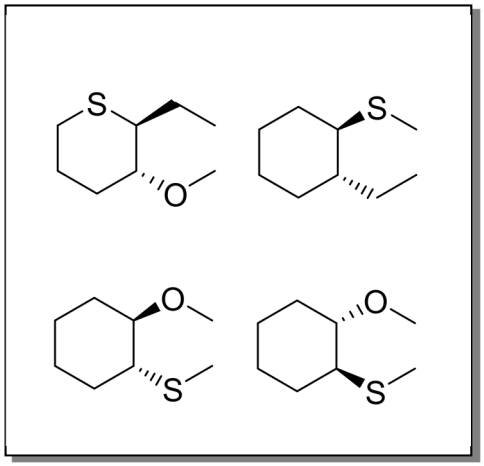
c.



This enantiomer

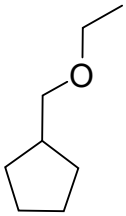
d.

(1*R*,2*R*)-1-Methoxy-2-methylthiocyclohexane



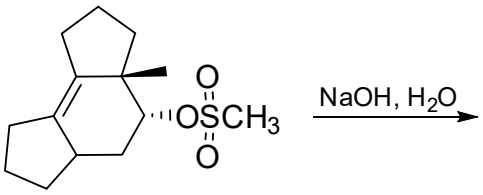
Use the "Rectangle" tool to enclose your answer

e.

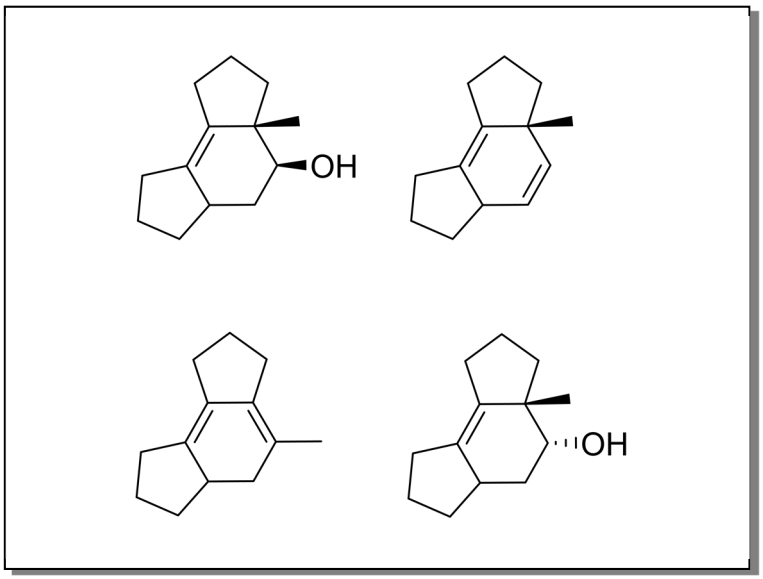


II. [80 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). **Caution:** Do not forget to consider ***stereochemistry***!

a.



This enantiomer



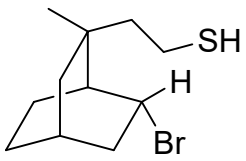
"Rectangle" your answer

For the following questions, "oval" your choice of an answer:

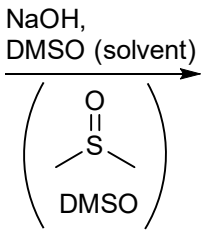
Is your chosen product chiral? Yes No

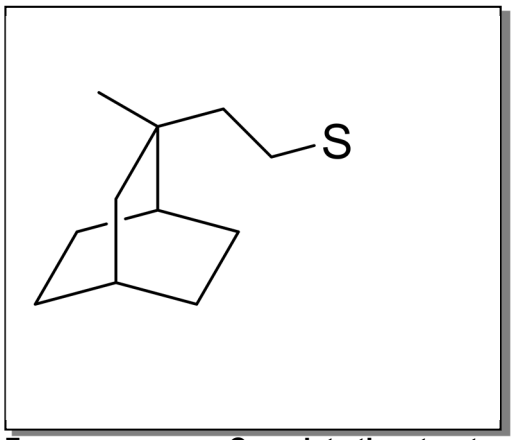
Is your chosen optically active? Yes No

b.



This enantiomer





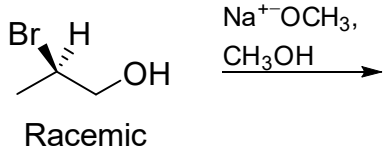
For your answer: Complete the structure by adding bonds ("Line" tool) and atoms ("Text" tool) as appropriate

For the following questions, "oval" your choice of an answer:

Is the product chiral? Yes No

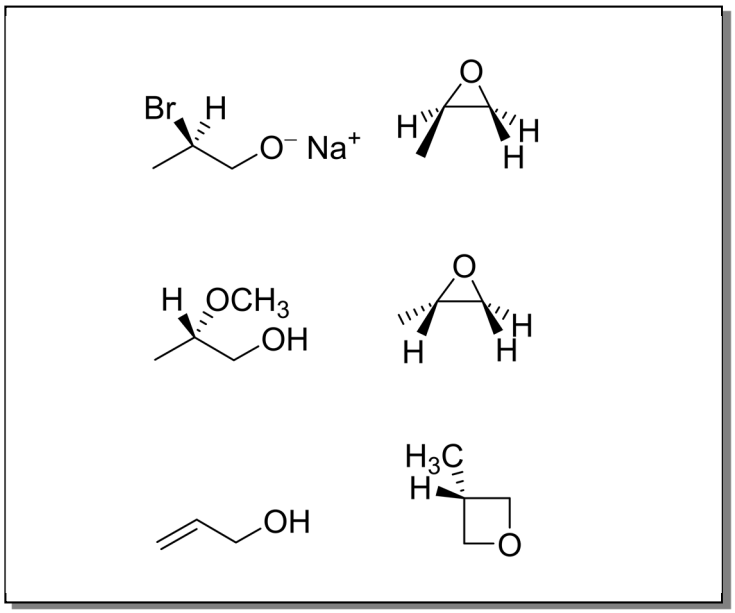
Is the product optically active? Yes No

c.



Racemic

$Na^{+-}OCH_3$, CH_3OH



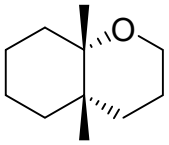
"Rectangle" your answer

For the following questions, "oval" your choice of an answer:

Is the product chiral? Yes No

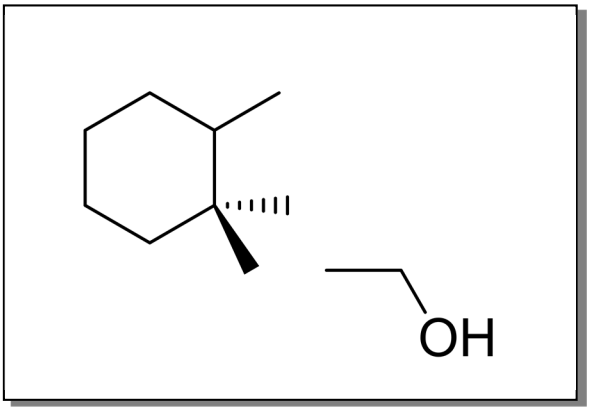
Is the product optically active? Yes No

d.



This enantiomer

Dilute H_2SO_4, H_2O, Δ



For your answer: Complete the structure by adding bonds ("Line" tool)

For the following questions, "oval" your choice of an answer:

Is the product chiral? Yes No

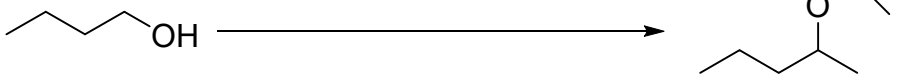
Is the product optically active? Yes No

e.

1.

2.

3.



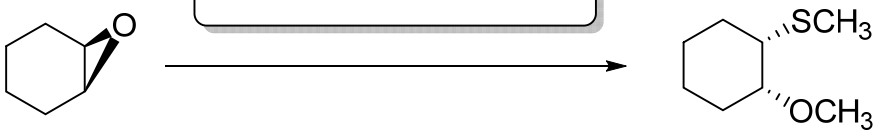
Type your answers in the respective boxes using the "Text" tool. Ignore super- and subscripts [as in, for example, tert-butyl cation = (CH3)3C+]

f.

1.

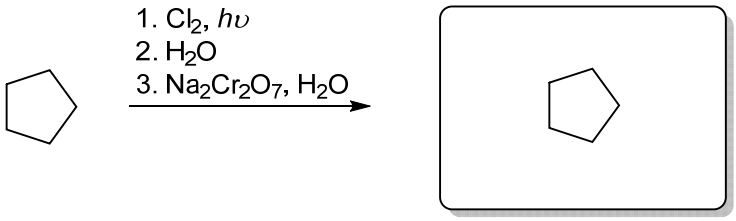
2.

3.



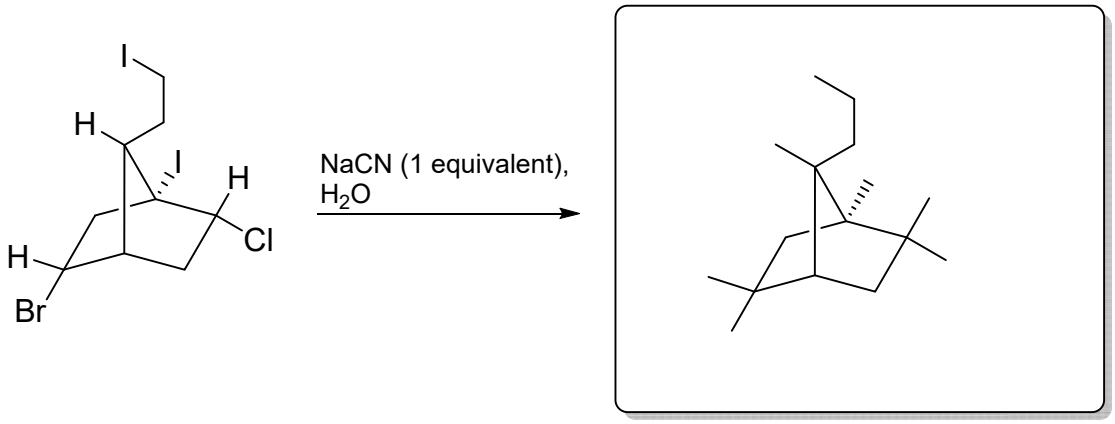
Type your answers in the respective boxes using the "Text" tool, as in e.

g.



For your answer: Complete the structure by adding bonds ("Line" tool) and atoms ("Text" tool) as appropriate

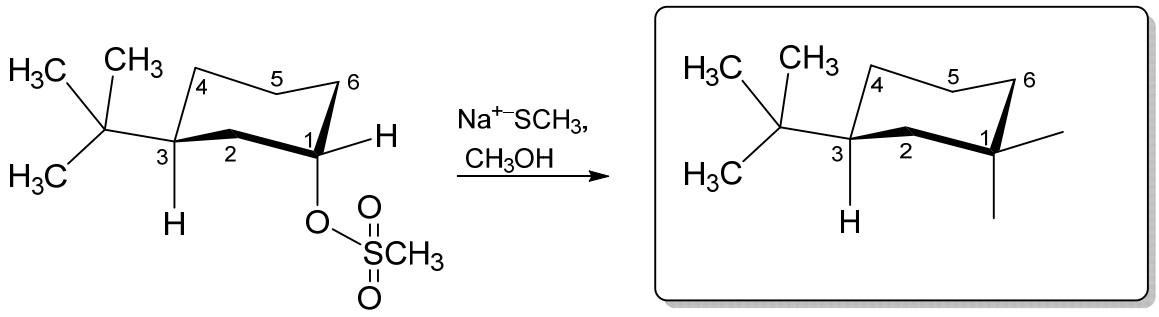
h.



Complete the stencil in the box by adding the missing substituents using the "Text" tool

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.



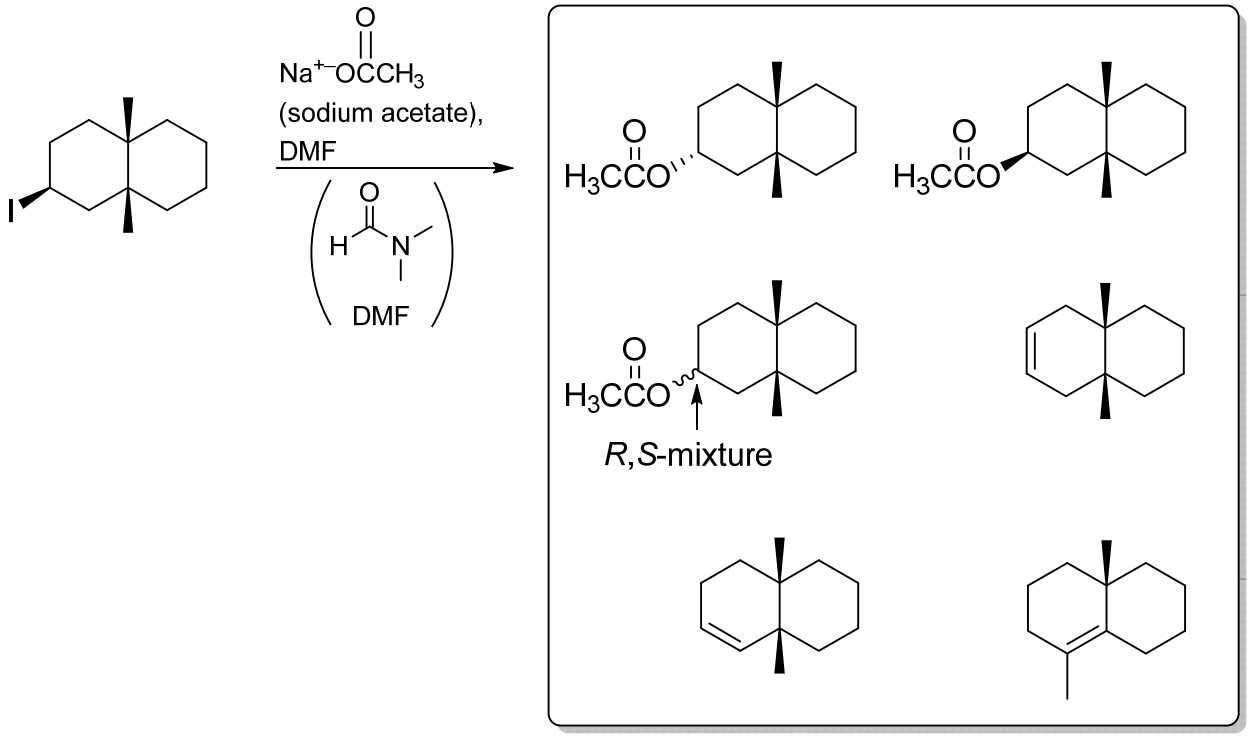
Complete the stencil in the box by adding the missing substituents at C1 using the "Text" tool

Mechanism: S_N2 S_N1 E2 E1

When using $Na^{+}{-}OCH_3$ instead of $Na^{+}{-}SCH_3$, which one of the following ratios will increase:

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

b.

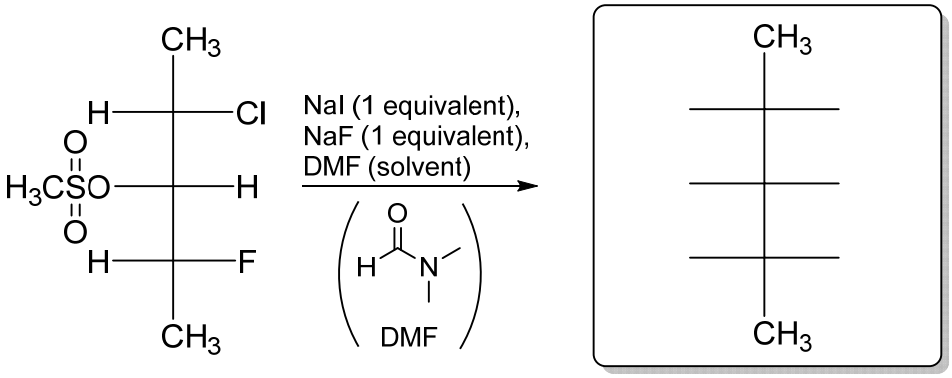


Mechanism: S_N2 S_N1 E2 E1

Changing the reagent from sodium acetate to lithium amide ($Li^{+}\ {-}NH_2$) has one of the following effects:

E2 / S_N2 increases S_N1 / E1 increases No effect Rate decreases

c.



Complete the stencil in the box by adding all missing substituents using the "Text" tool

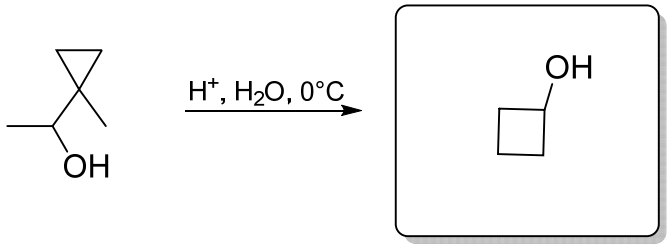
Mechanism: S_N2 S_N1 E2 E1

Changing the solvent to CH_3OH has one of the following effects:

Starting material stays unchanged Starting material equilibrates with its diastereomer

I / F ratio of S_N2 increases E2 / E1 ratio increases

d.



Complete the product structure in the box by adding missing substituents using the "Line" and "Text" tools. Do not worry about stereochemistry.

Mechanism: S_N2 S_N1 E2 E1

Which of the following statements is correct?

Doubling the concentration of starting alcohol will double the rate of its disappearance

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

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

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.

☐ Along the carbocation series–primary to secondary to tertiary–hyperconjugation increases.

☐ Leaving group ability decreases from left to right in the periodic table, because bond strengths increase.

☐ Leaving group ability increases down the periodic table, because bond strengths decrease.

☐ Leaving group ability increases along the series HO^-, $CH_3\overset{\overset{O}{\|}}{C}O^-$, $CH_3SO_3^-$, because the oxygen becomes more electropositive.

☐ In competition with S_N1, E1 wins out at high temperatures, because the entropy (ΔS) of the E1 reaction is negative.

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

☐ Nucleophilicity of charged nucleophiles in aprotic solvents decreases down the periodic table.

☐ CH_3SH is more acidic than CH_3OH, partly because the S–H bond is weaker than the O–H bond.

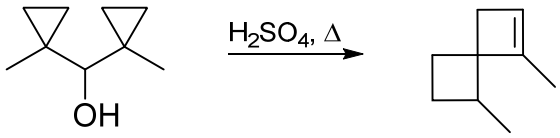
☐ The intramolecular Williamson ether synthesis is faster in aprotic solvents, compared to those in protic solvents.

☐ Electron withdrawing groups next to the proton that is being removed accelerate the E2 reaction.

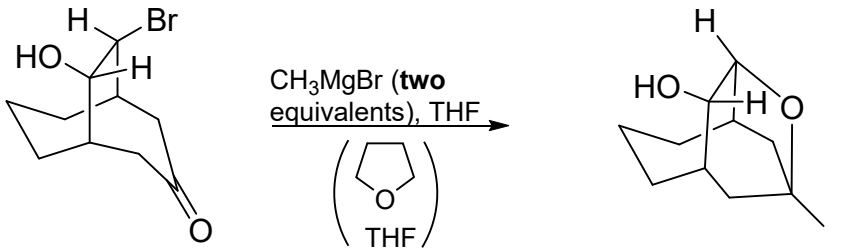
The following four problems should be answered on four separate pages of hard copy white paper using a dark (at least #2) pencil. Ascertain that your drawings are clearly visible. When you are finished, scan the four pages on your device, save the document as a pdf file, and add its contents to this 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, in the order of the questions posed in the exam. Label the final pdf file with your name and the words "Exam 2" (namely: **Last Name, First Name, Exam 2) and e-mail it to your designated TA.**

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.



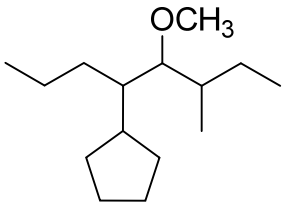
b.



(after aqueous work-up; please add this step in your scheme)

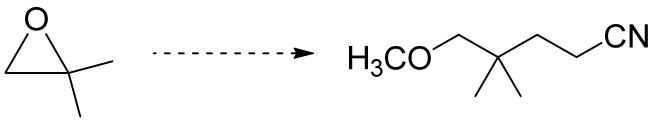
VI. [40 Points]

a. Devise the synthesis of compound **A** below, starting with building blocks containing five carbons or less as the only carbon sources. It will help you if you execute a retrosynthesis on a separate page (not to be submitted).



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).



"I do feel a lot better since we switched to the trans-fat free oil."

*** The End ***