

EXAMINATION 2  
Chemistry 3A

Name: KEY SID #: \_\_\_\_\_

Print first name before second!  
Use capital letters!

GSI (if you are taking Chem 3AL): \_\_\_\_\_

Peter Vollhardt  
April 11, 2017

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* \_\_\_\_\_

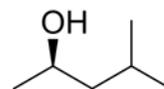
***Please write the answer you wish to be graded in the boxed spaces provided.***

***Do scratch work on the back of the pages.*** This test should have **13** 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!**

- I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, *S*, or dashed/wedged lines).

a.

(*R*)-4-Methyl-2-pentanol



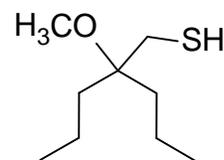
b.



*cis*-3-Propylcyclobutanol

c.

2-Methoxy-2-propyl-1-pentanethiol



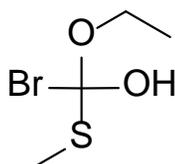
d.



(This enantiomer)

(1*S*,2*S*)-2-Mercaptocyclopropanol

e.

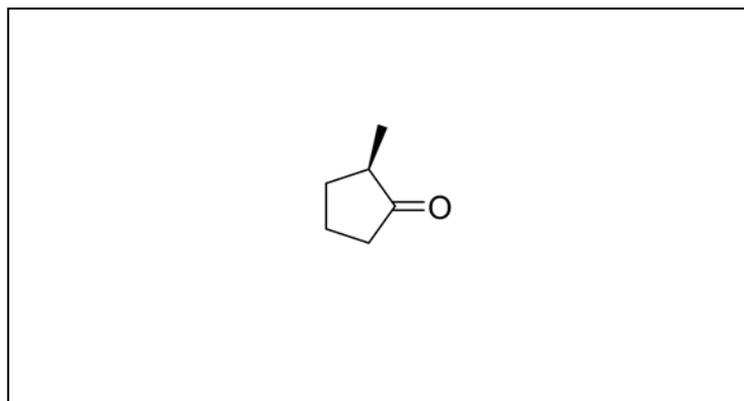
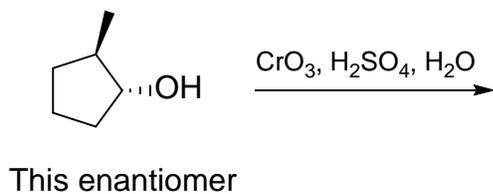


(Fischer projection: this enantiomer)

(*R*)-Bromo(ethoxy)(methylthio)methanol

II. [70 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). **Caution:** Do not forget **stereochemistry!**

a.



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

Is the product chiral?

Yes

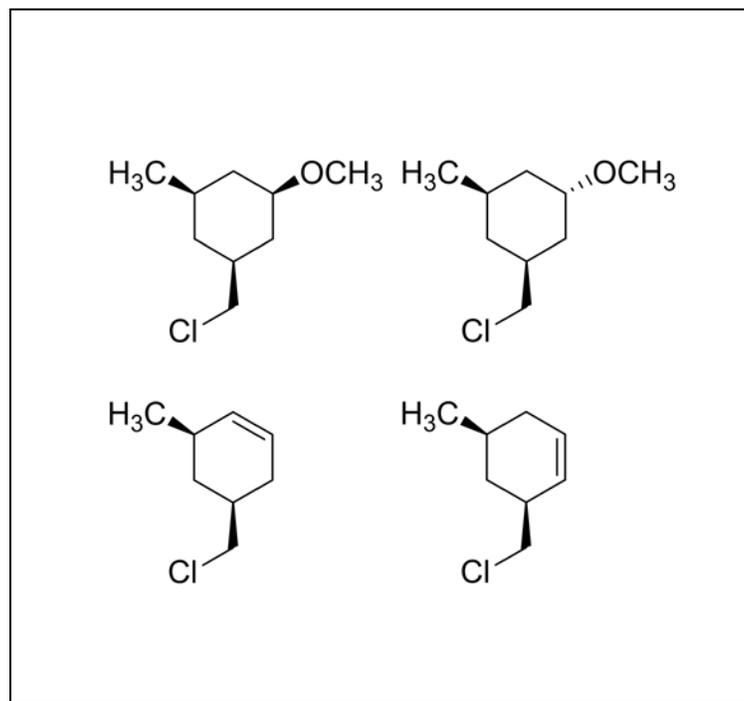
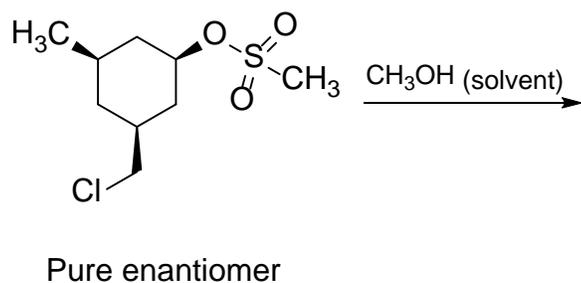
No

Is the product optically active?

Yes

No

b.



There may be more than one product.

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

Is/are the product(s) chiral?

Yes

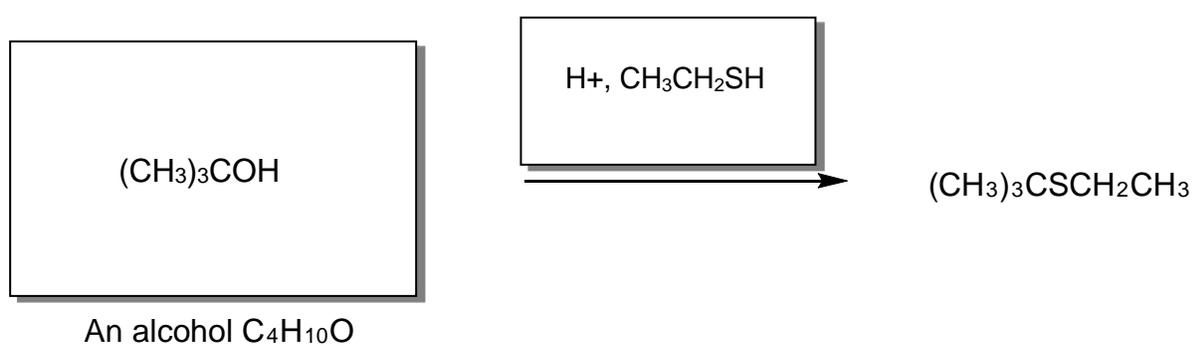
No

Is/are the product(s) optically active?

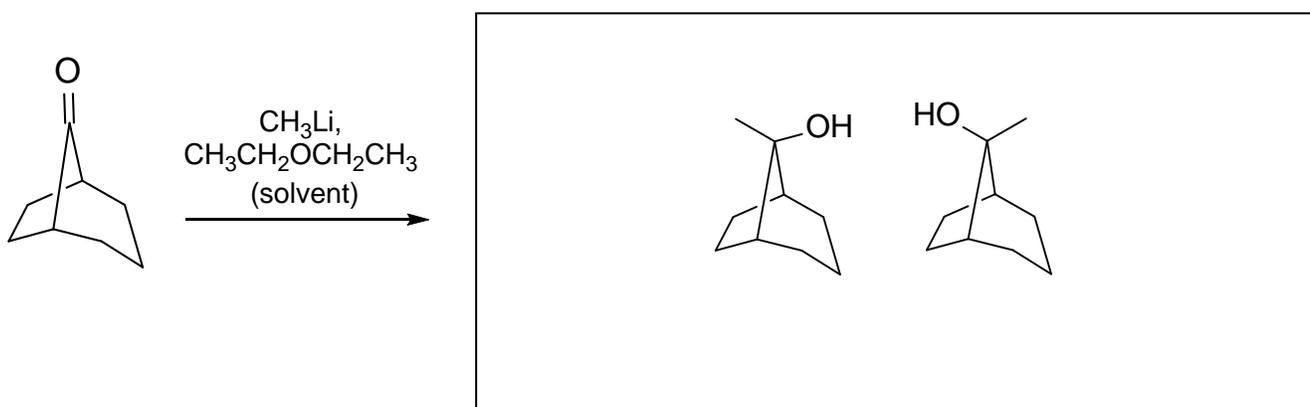
Yes

No

c.



d. Complete one or more of the stencils provided.



There may be more than one product.  
There are more stencils than you will need.

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

Is/are the product(s) chiral?

Yes

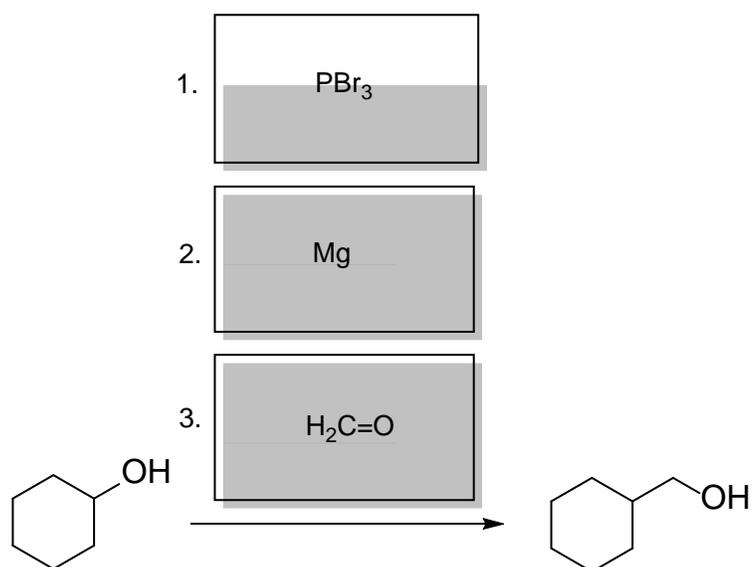
No

Is/are the product(s) optically active?

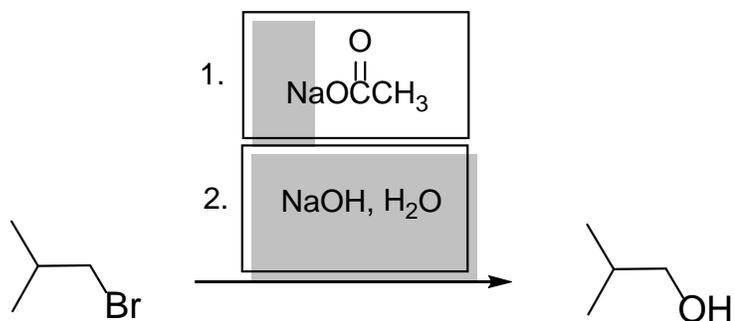
Yes

No

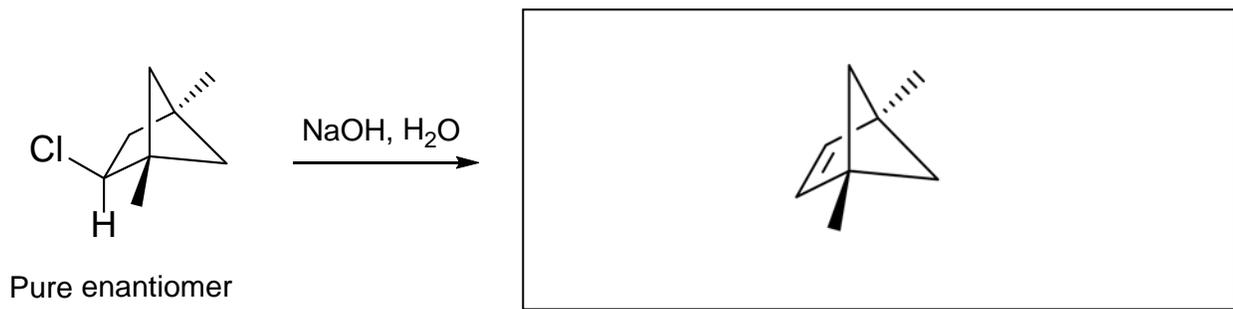
e.



f.



g. Complete the stencil provided.



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

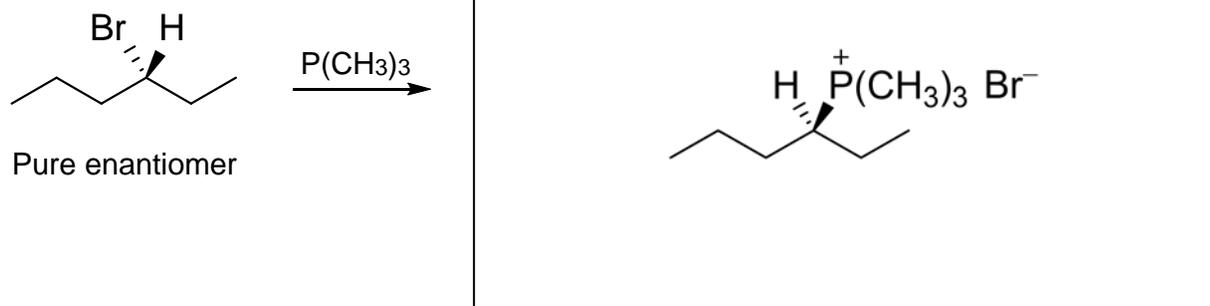
Is the product optically active?

Yes

No

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

a.



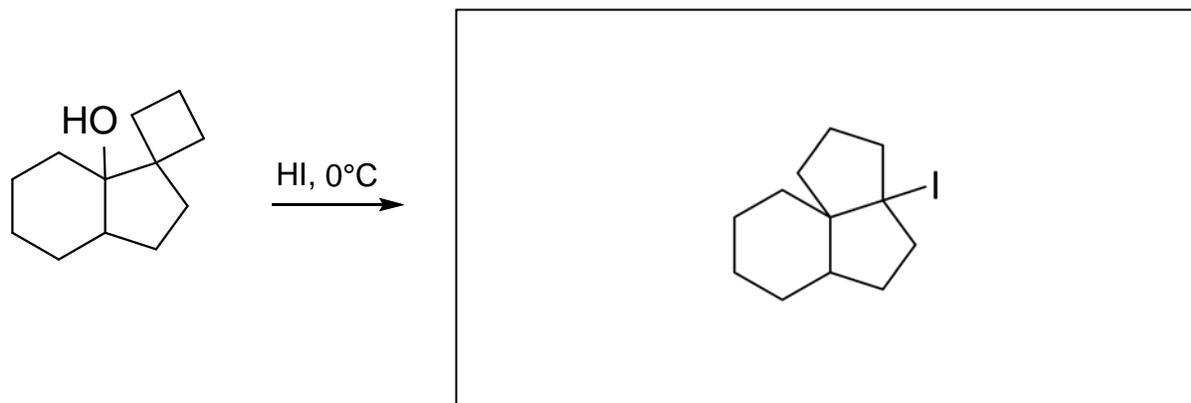
Mechanism:

  $S_N2$   $S_N1$  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.



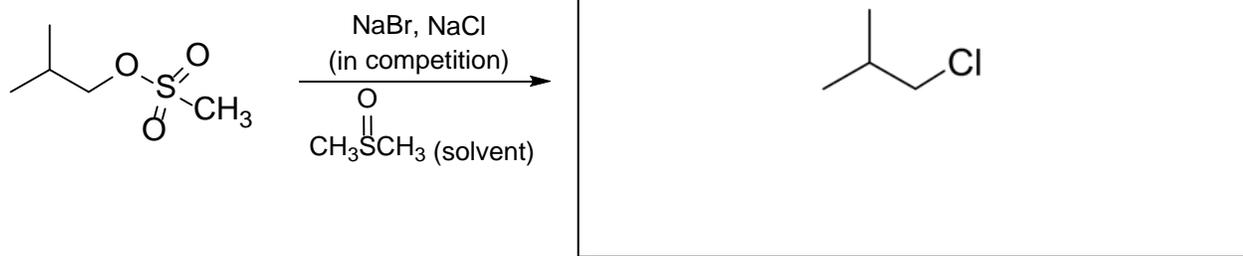
Mechanism:

  $S_N2$   $S_N1$  E2 E1

When using  $H_2SO_4$  instead of HI, which one of the following ratios will increase:

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

c.

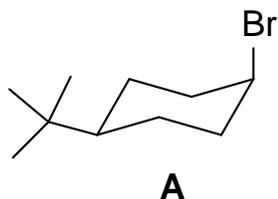


Mechanism:

 S<sub>N</sub>2 S<sub>N</sub>1 E2 E1

When changing the solvent to CH<sub>3</sub>OH, one of the following changes will occur:

Rate decreases

CH<sub>3</sub>OH will outcompete NaBr NaBr will outcompete NaClThe E1 / S<sub>N</sub>1 ratio will increased. Consider the bromide **A** in methanol at room temperature.

Circle your answer to the following statements, in the form of “yes” or “no”.

Addition of NaOH will cause E2 to take place.

 Yes No

Addition of NaI will cause E1 to take place.

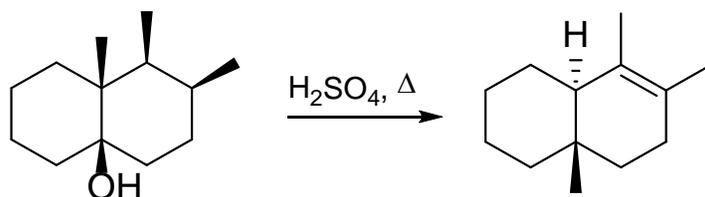
 Yes No

Increasing the temperature will increase its rate of disappearance.

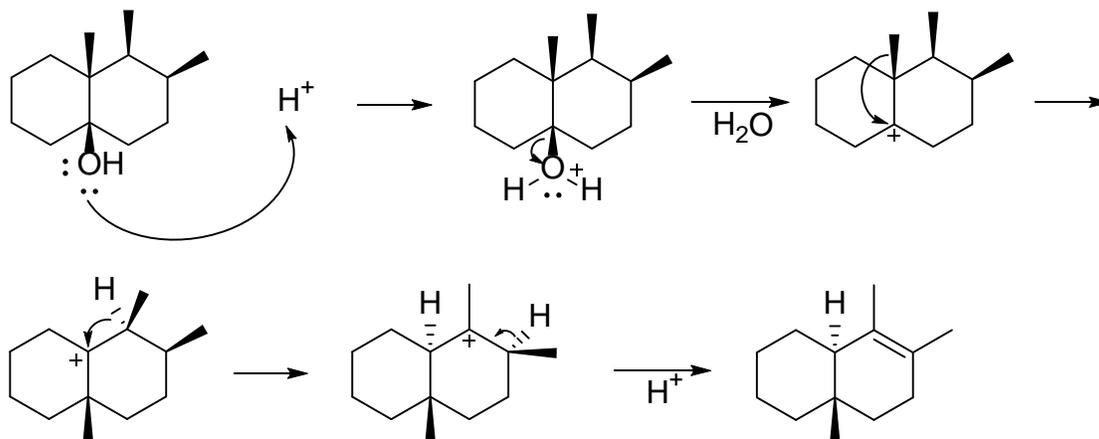
 Yes NoAdding acetone will increase the S<sub>N</sub>1 / E1 ratio. Yes No

IV. [40] Points] Explain the following observations (on this and the next page) by a detailed mechanism (i.e., write a scheme with structures, arrow pushing, etc.)

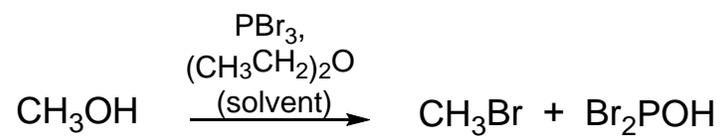
a.



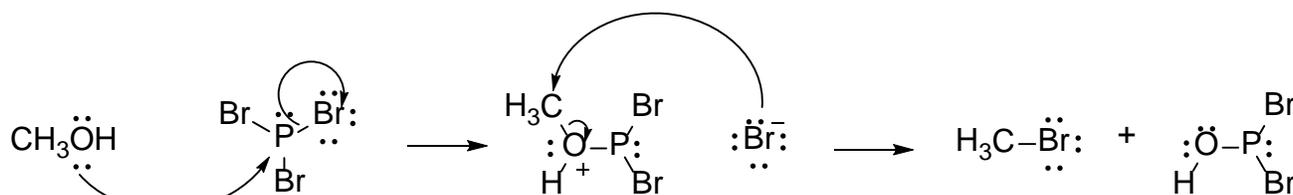
Work from left to right in the following spaces. There is much more space than you will need.



b.

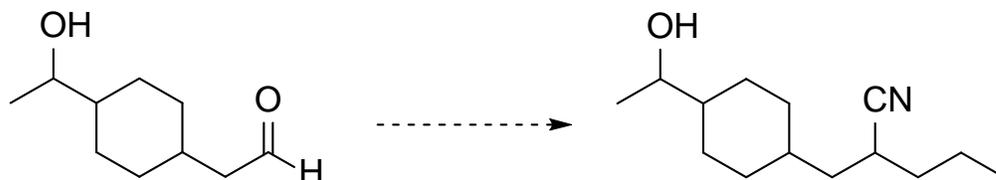


Work from left to right in the following spaces. There is much more space than you will need.



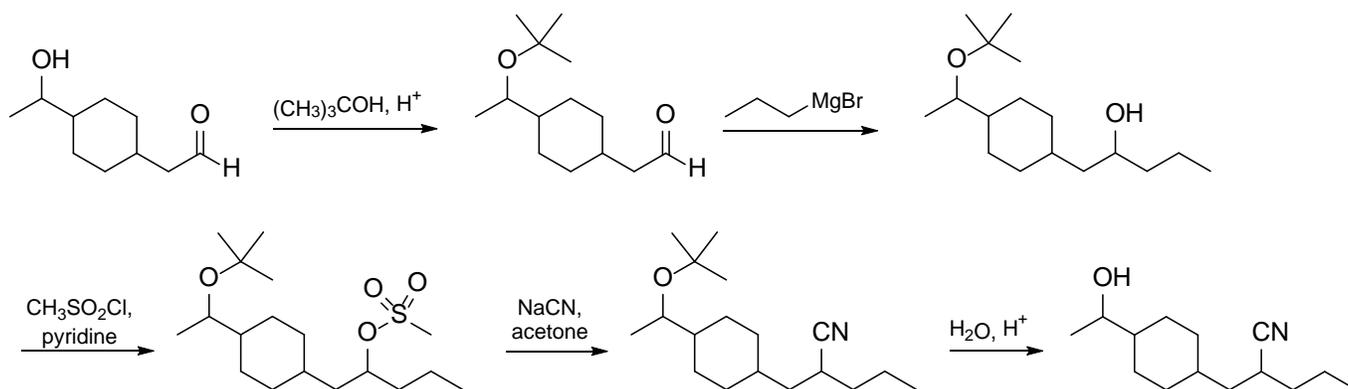
- V. [50 Points] Provide a viable conversion of starting materials on this and the next page to the respective products. You may use any additional organic or inorganic compounds in your scheme. It will help you if you execute a retrosynthesis on the back of the preceding page (on your left).

a.

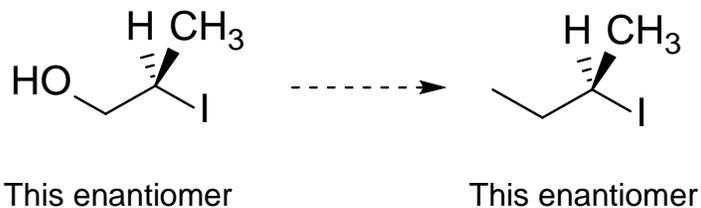


Do not worry about stereochemistry.

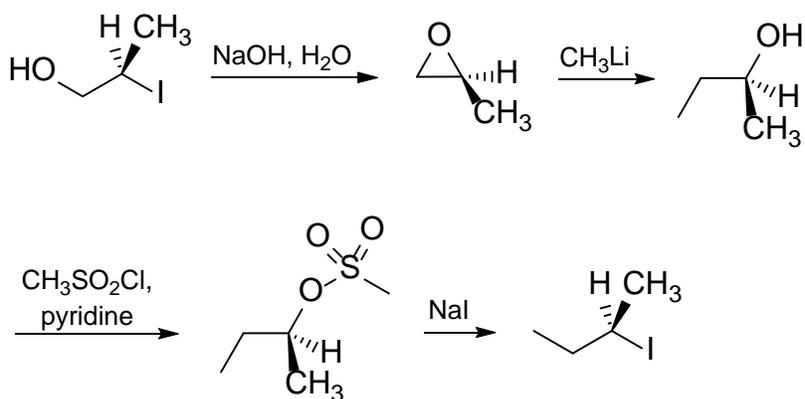
Work from left to right in the following spaces. There is much more space than you will need.



b.

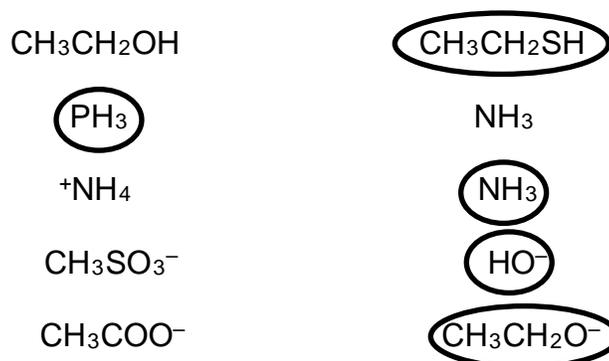


Work from left to right in the following spaces. There is much more space than you will need. It will help you if you execute a retrosynthesis on the back of the preceding page (on your left).



VI. [20 Points]

a. In each pair of nucleophiles shown below, circle the stronger one (in H<sub>2</sub>O).



b. Place an **X mark** in the box preceding the most accurate statement. Only one answer is allowed.

The nucleophilicity of the anions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> in CH<sub>3</sub>OH increases along the series, because

- the atoms get heavier
- their electronegativity increases
- the atoms are increasing less solvated
- the atoms are increasing less polarizable

On NaBH<sub>4</sub> reduction, a chiral racemic ketone cannot give

- a chiral alcohol
- an optically active alcohol
- a meso compound
- diastereomers

Along the series  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{OH}_2$ ,  $\text{FH}$ ,

- bond strengths increase
- acidity decreases
- electronegativity decreases
- basicity increases

