EXAMINATION 2
Chemistry 3A

Name:___Key_____________________ **SID #:**_____________________
Print first name before second!
Use capital letters!

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

Peter Vollhardt
March 29, 2016

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 _____

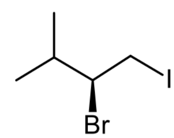
Please write the answer you wish to be graded in the boxed spaces provided.

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*!**

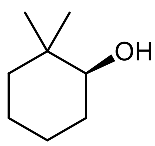
I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, *S*, or dashed/wedged lines).

a.

(*S*)-2-Bromo-1-iodo-3-methylbutane

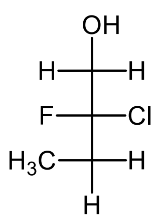


b.



(*S*)-2,2-Dimethylcyclohexanol

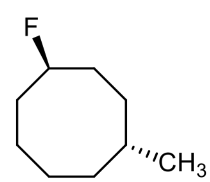
c.



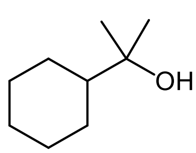
(*R*)-2-Chloro-2-fluoro-1-butanol

d.

(1*R*,4*R*)-1-Fluoro-4-methylcyclooctane



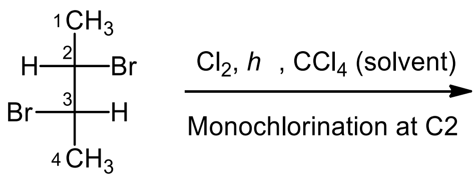
e.

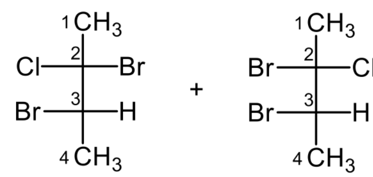


2-Cyclohexyl-2-propanol

II. [60 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). Don't forget ***stereochemistry***! Complete the stencils, when provided.

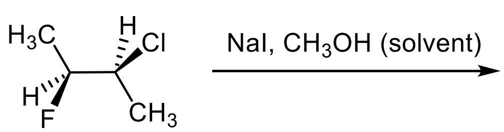
a.

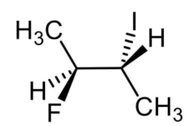




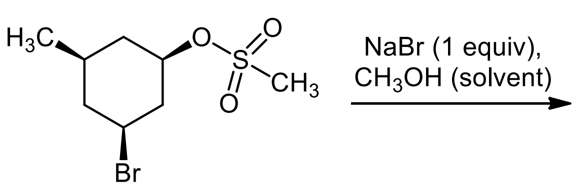
Hint: One or more products?

b.

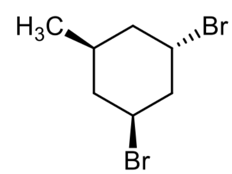




c.



Pure enantiomer

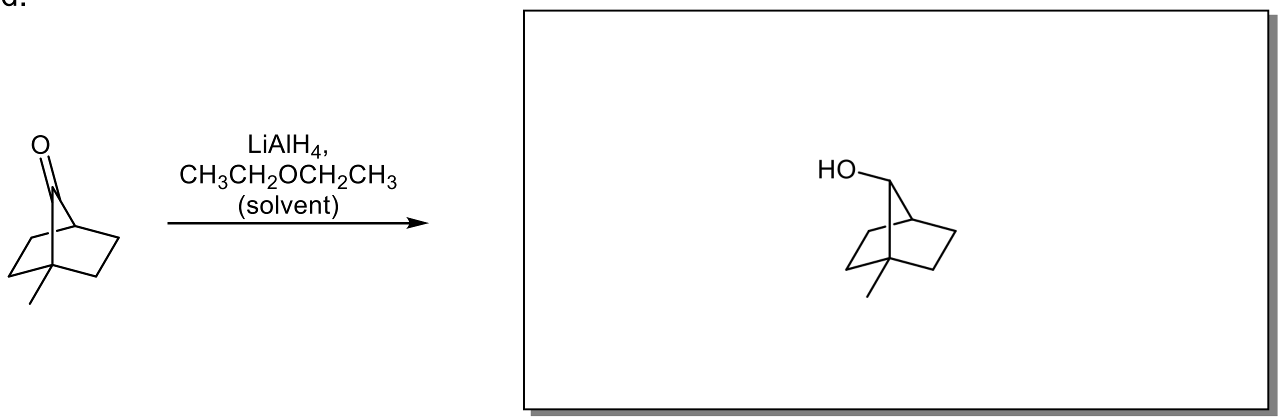


For the following questions, circle your choice of an answer:

Is the product chiral? Yes No

Is the product optically active? Yes No

d.

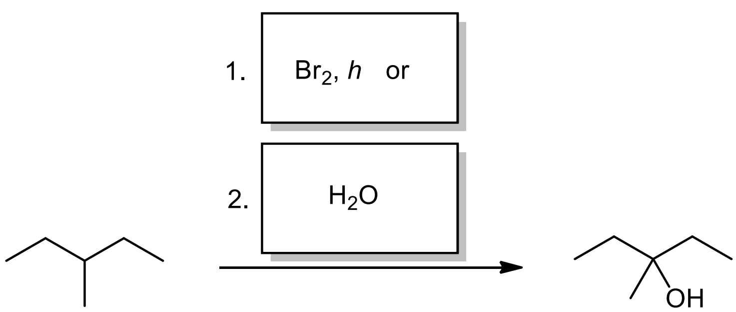


For the following questions, circle your choice of an answer:

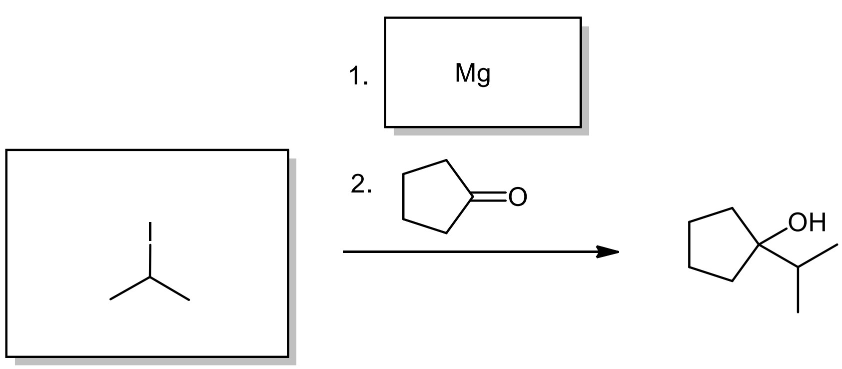
Is the product chiral? Yes No

Is the product optically active? Yes No

e.

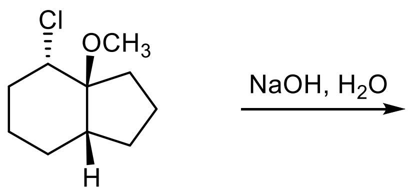


f.

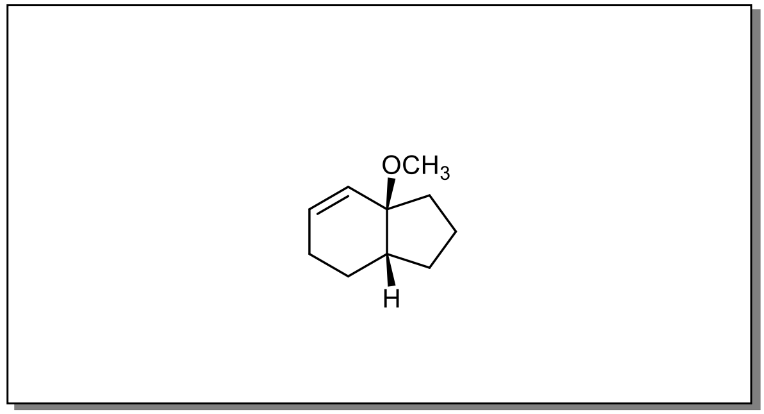


An iodoalkane

g.



Pure enantiomer

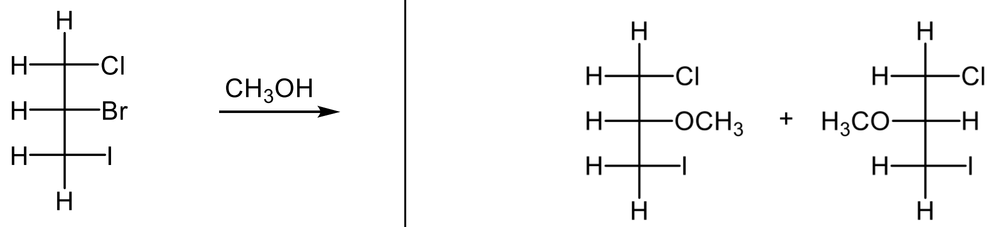


For the following question, circle your choice of an answer:

Is the product optically active? Yes No

III. [50 Points] The following reactions proceed (predominantly) by S_N2, S_N1, E2, or E1 pathways, respectively. Give the major product(s) in each case and answer the questions by ***circling*** the most applicable statement.

a.



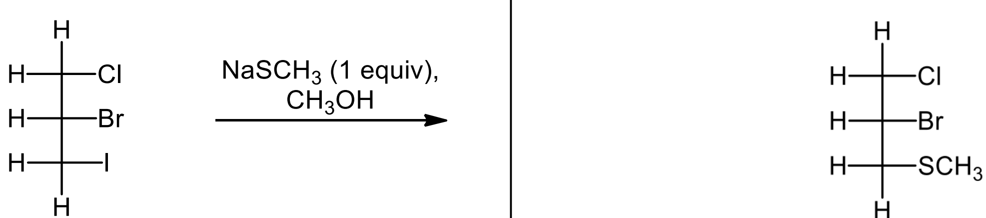
Use Fischer stencils

Mechanism: S_N2 S_N1 E2 E1

At lower temperatures, which one of the following ratios will increase:

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

b.



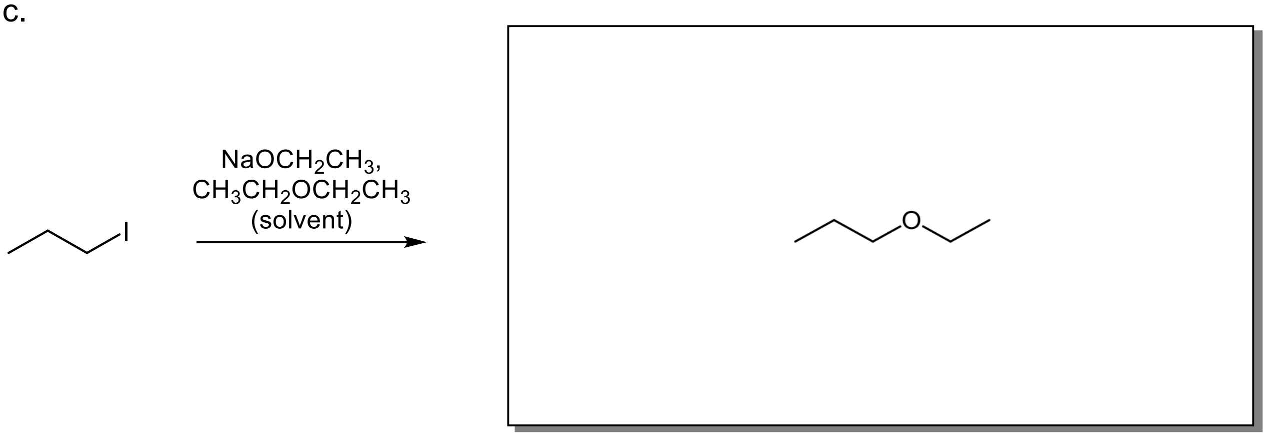
Use Fischer stencils

Mechanism: S_N2 S_N1 E2 E1

When using $NaOCH_3$ instead of $NaSCH_3$, which one of the following ratios will increase:

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

c.

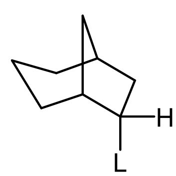


Mechanism: S_N2 S_N1 E2 E1

When using $NaOC(CH_3)_3$ instead of $NaOCH_2CH_3$, one of the following ratios will increase:

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

d. Consider the reaction of **A** with a negatively charged nucleophile/base in methanol.



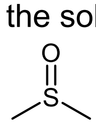
A

Circle your answer –"yes" or "no"– to the following statements:

The rate of E1 will increase along the series L = F, Cl, Br, I. Yes No

The rate of S_N2 will increase with temperature. Yes No

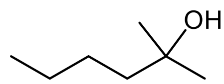
The rate of S_N2 will increase when switching the solvent to DMSO. Yes No



DMSO

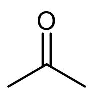
The rate of E2 will increase along the series L = F, Cl, Br, I. Yes No

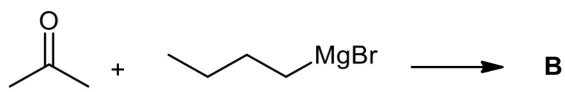
IV. [40 Points] Suggest four different syntheses of 2-methyl-2-hexanol **B**. Each scheme should start with the compound given in the respective box. In addition, you can use any other reagents. You do not need to include aqueous work-up steps.



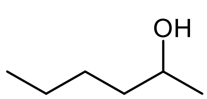
B

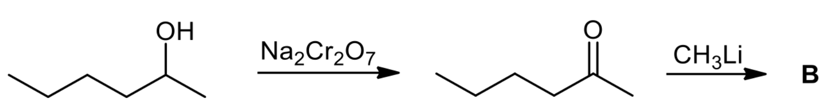
a.

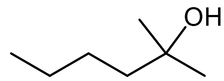




b.

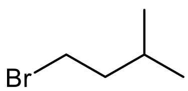


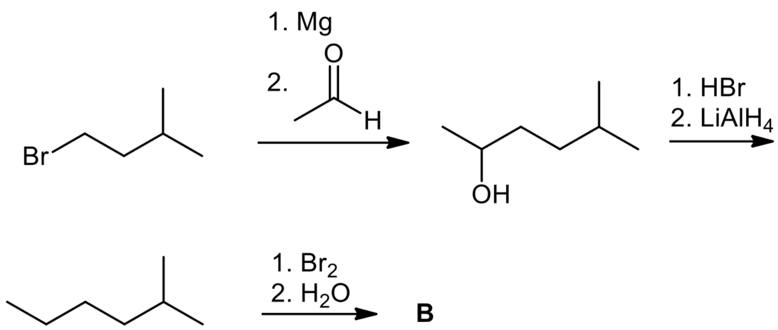



OH

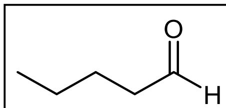
B

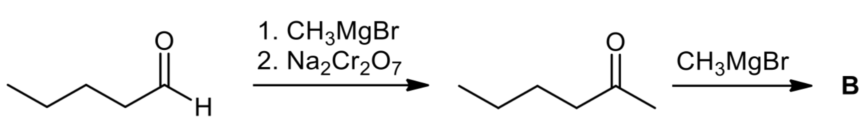
c.


Br

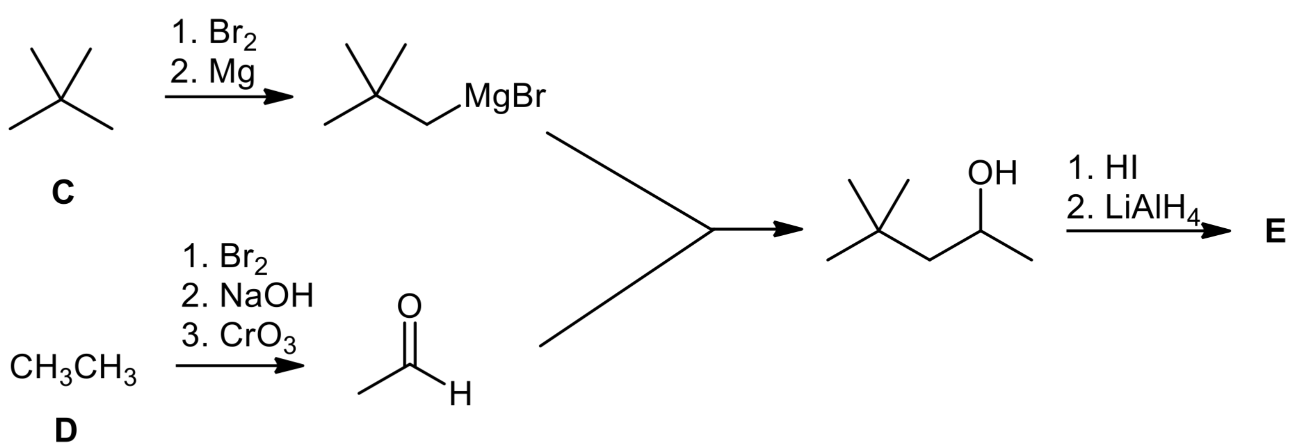

1. Mg
2.
O
H
Br
OH
1. HBr
2. $LiAlH_4$
1. Br_2
2. H_2O
B

d.

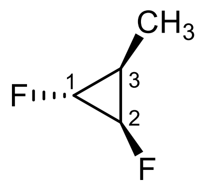

O
H


O
H
1. CH_3MgBr
2. $Na_2Cr_2O_7$
O
CH_3MgBr
B

V. [30 Points] Outline a synthetic sequence that leads to hydrocarbon **E** using **C** and **D** as the sources of the carbon atoms in the product. **Hint**: work backwards (retrosynthetically), on the back of the preceding page.

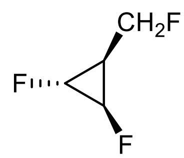


VI. [20 Points] Give all possible products of the **mono**fluorination (with F_2; remember: nonselective) of the enantiomer of 1,2-difluoro-3-methylcyclopropane shown below. You will lose points if you depict redundant structures. Complete the stencils provided (**including H atoms**). **Caution**: *There may be more stencils drawn than you will need.* To avoid ambiguity, do not use any extra stencils for practice, but do so on the back of the preceding page.

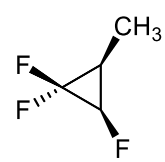


(1*R*,2*R*)-1,2-Difluoro-3-methylcyclopropane

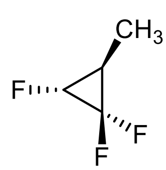
Reaction at CH_3



Reaction at C1



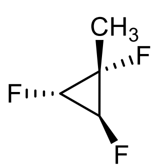
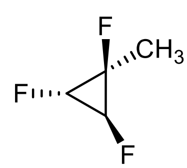
Reaction at C2



Circle your answer to the following question. Are the products of reaction at C1 and C2:

Identical   Enantiomers   Diastereomers ?

Reaction at C3

 Note: This is identical to 

VI. [20 Points]

a. In each pair of acids shown below, circle the stronger one (in H_2O).

CH_3CH_2OH	CH_3CH_2SH
HCl	HCN
$^+NH_4$	NH_3
CH_3SO_3H	H_2O
CH_3COOH	CH_3CH_2OH

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

The basicity of the anions CH_3^-, NH_2^-, OH^-, and F^- decreases from left to right in the periodic table, because

☐ the atoms that are being protonated get heavier

☒ X the atoms that are being protonated get more electronegative

☐ the atoms that are being protonated become more polarized

☐ solvation is impeded by protic solvents

A compound with two asymmetric carbon centers bearing the same substituents (such as 2,3-dibromobutane) can exist as

☐ 4 diastereomers

☐ 8 stereoisomers

☒ X Two enantiomers and an achiral meso diastereomer

☐ Only the *R*,*R*- and *S*,*S*-stereoisomers

Nucleophilicity of anions in CH_3OH increases from top to bottom in a column of the periodic table, because

- [X] they become increasingly less solvated
- [ ] their polarizability decreases
- [ ] they are increasingly sterically hindered
- [ ] their basicity increases

"It says he led the attack on the tert-butyl bromide with hydroxide ion."

* The End *