

Exam 3  
Chem 21  
Nov 19, 2009

Name Gary Snyder

page 1 (35) \_\_\_\_\_

2 (45) \_\_\_\_\_

3 (40) \_\_\_\_\_

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6 (25) \_\_\_\_\_

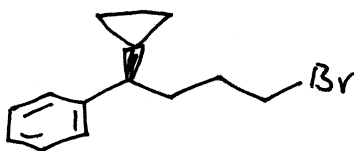
total (200)

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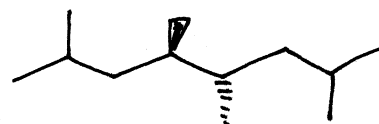
Please don't write in this space.

1. (19 points) Draw the following compounds. Show stereochemistry clearly.

8 (a) (*R*)-4-bromo-1-cyclopropyl-1-phenylbutane



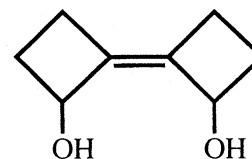
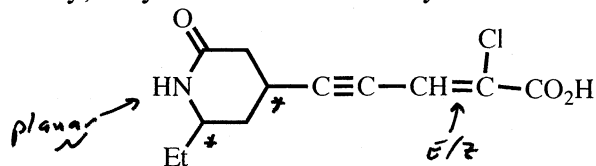
7 (b) *meso*-2,4,5,7-tetramethyloctane



4 (c) Draw the product of an  $S_N2$  reaction of the compound in part a with sodium borohydride,  $\text{NaBH}_4$ , in  $\text{Et}_2\text{O}$ .



2. (16 points) Consider the two compounds below. The structures below are not meant to imply any stereochemistry, only to show connectivity.



3 (a) How many stereoisomers of each compound can exist?

8

6

3 (b) How many stereoisomers are achiral?

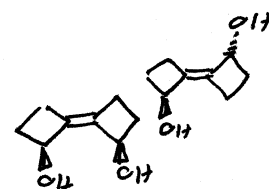
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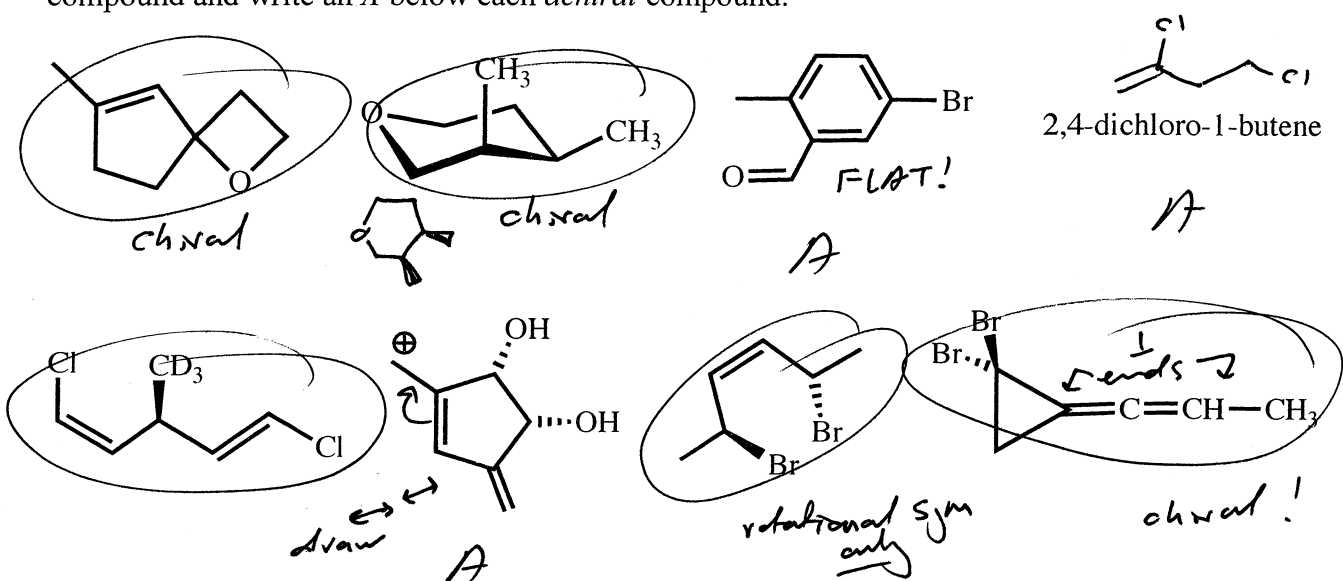
2 (c) How many tetrahedral stereocenters does each compound have?

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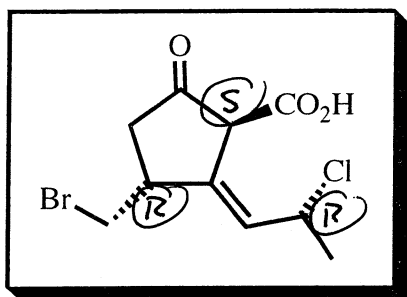


3. (24 points) Which of the following compounds are chiral? Please **circle** each **chiral** compound and write an **A** below each **achiral** compound.

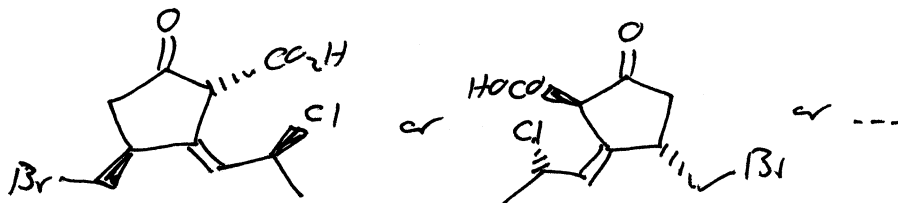


4. (21 points) (a) Label each stereocenter of the compound in the box below as R or S.

6



enantiomer:

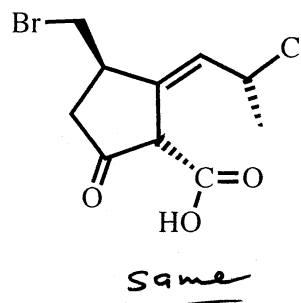
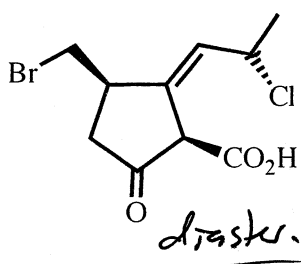
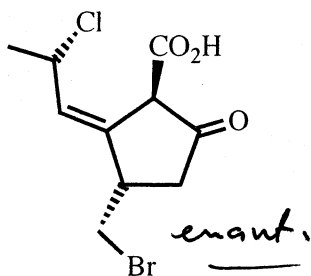


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(b) Draw the enantiomer of the compound in the space provided above.

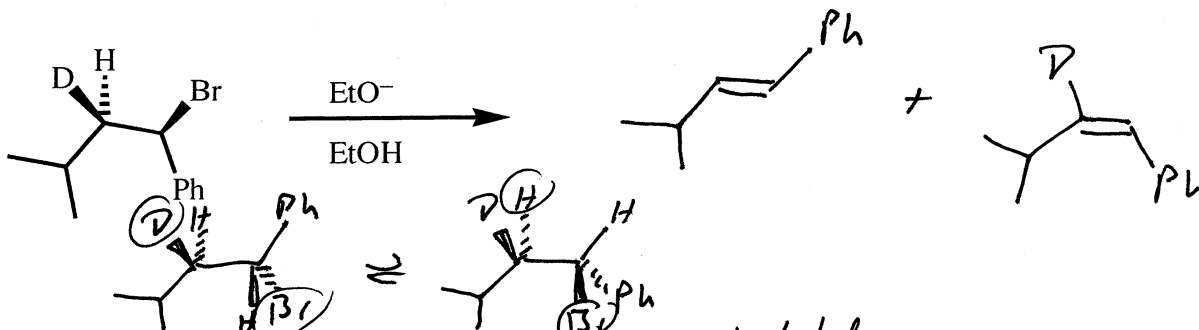
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(c) Look carefully at the compounds below, then label each one as: the **same** as, the **enantiomer** of, a **diastereomer** of, a **resonance structure** of, or a **constitutional isomer** of the compound in the box.



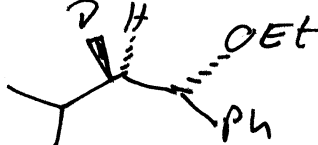
5. (18 points) The following E2 reaction forms two alkenes — one contains deuterium and the other does not. Draw them below, showing their stereochemistry clearly.

10



(b) Would you expect an S<sub>N</sub>2 reaction to occur also? *absolutely*  
 If so, draw the product(s) below. If not, write "none".

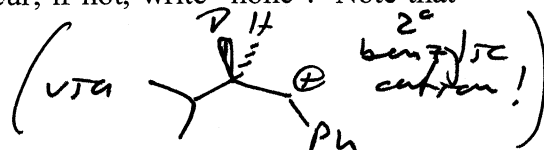
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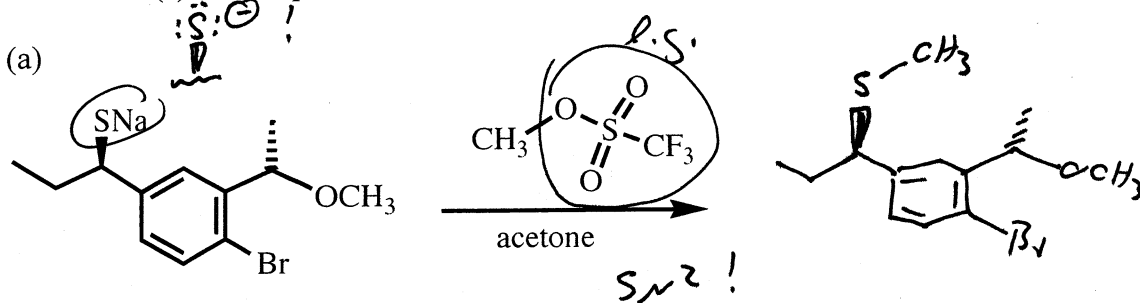
(c) If the compound above were solvolyzed in ethanol (with no ethoxide), would you expect a reaction to occur? If so, state what type of reaction would occur; if not, write "none". Note that you are **not** asked to draw products this time.

*S<sub>N</sub>1/E1*

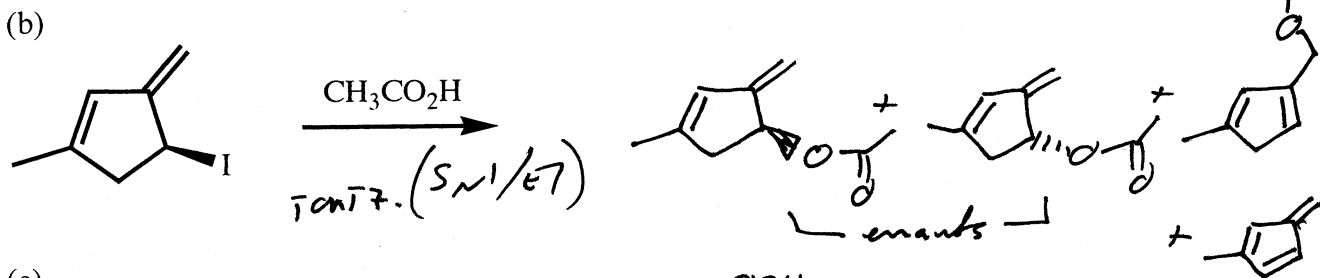


6. (22 points) The reactions below may proceed by S<sub>N</sub>2, E2, or S<sub>N</sub>1/E1 pathways, or not at all. Draw the organic products, showing stereochemistry where necessary, and indicate which reaction mechanism(s) is/are operative. Or, if no reaction occurs, write NR.

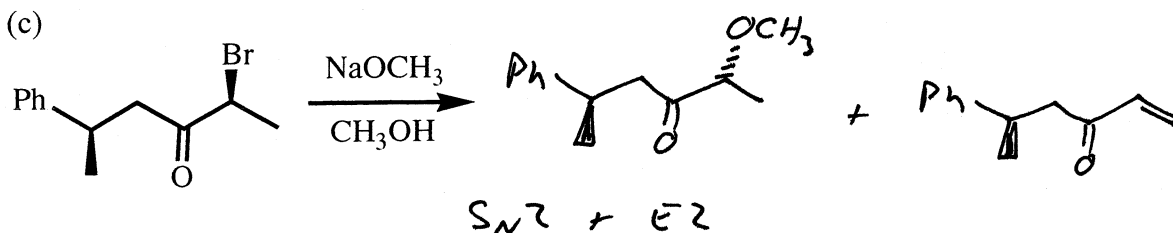
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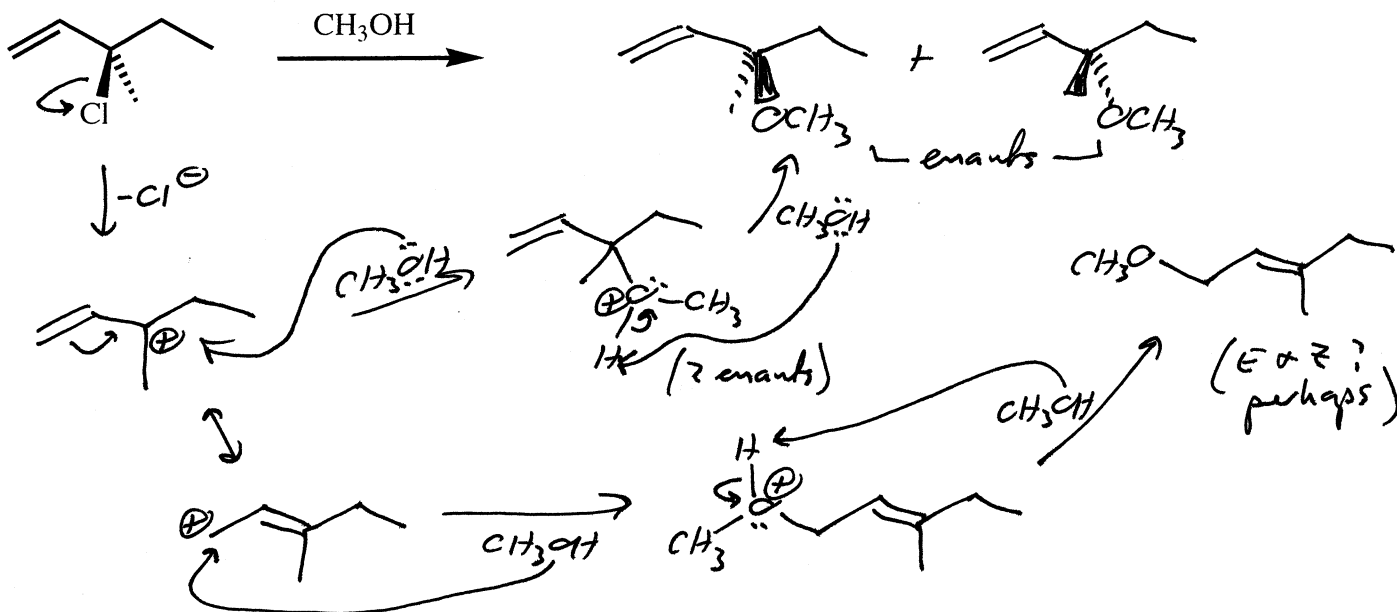


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*S<sub>N</sub>2 + E2*

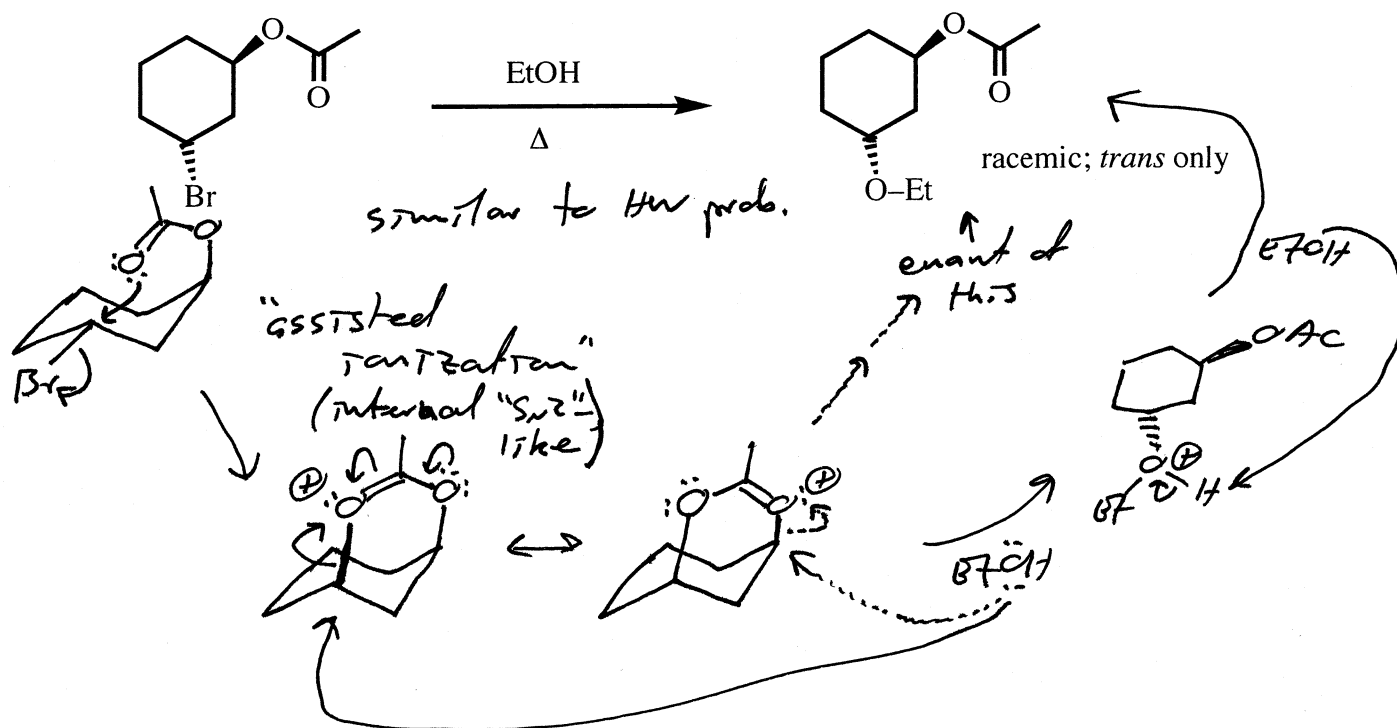
7. (18 points) Write the mechanism of the  $S_N1$  solvolysis of the optically active alkenyl chloride below, illustrating each step clearly with curved arrows, and draw the product(s), showing stereochemistry where relevant.



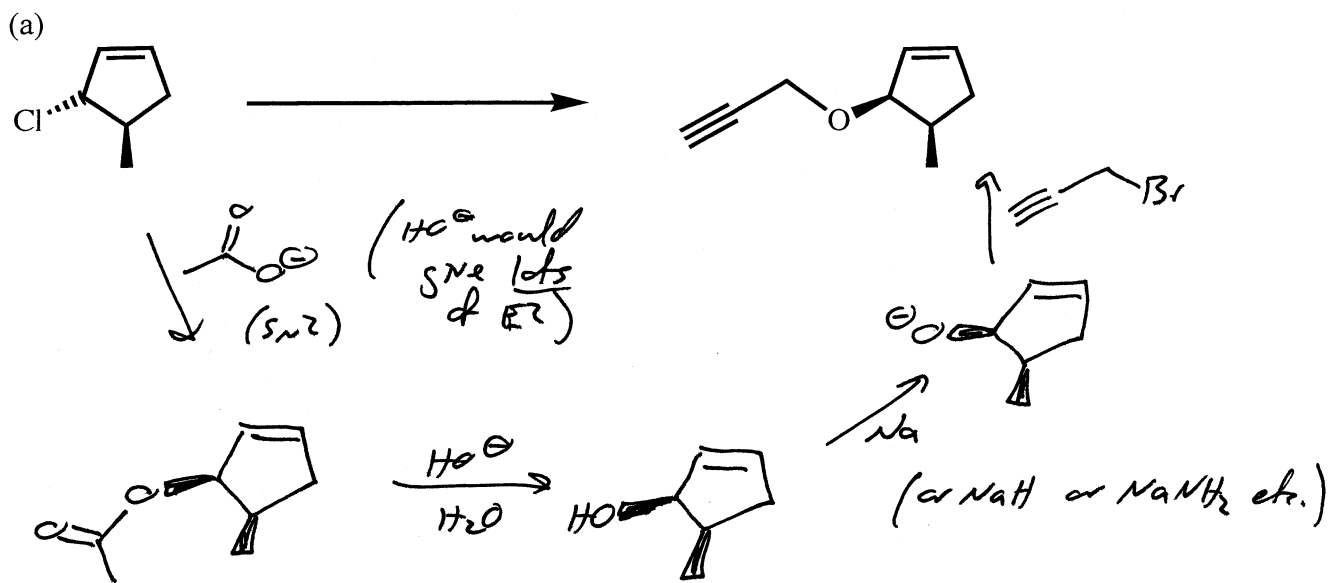
(b) Based on your mechanism, would you expect the product mixture to be optically active or inactive?

inactive - cation intermediate is achiral.

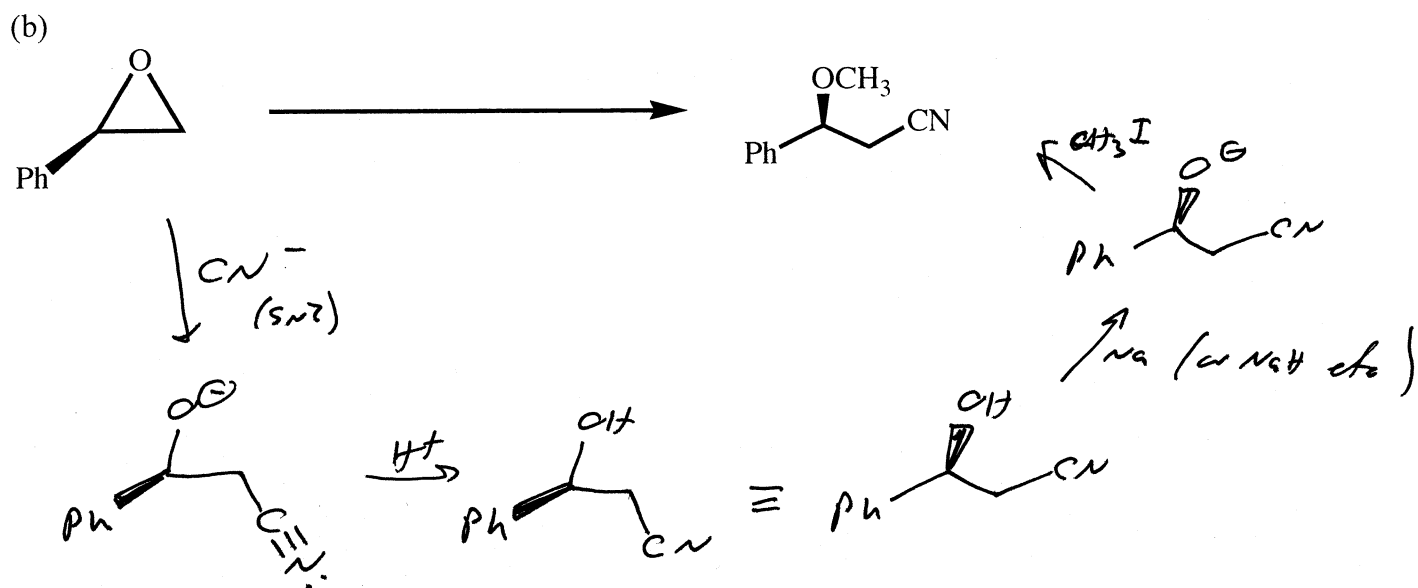
8. (17 points) When the optically active bromo-acetate below is solvolyzed in ethanol, only racemic *trans* product is formed. Furthermore, the *trans* bromo-acetate reacts much faster than the *cis* stereoisomer. Suggest a mechanism that is consistent these observations.



9. (25 points) Suggest a synthetic route for carrying out each of the following transformations in good yield. Pay attention to stereochemistry. As long as you start with the compound shown, you can use any other organic or inorganic compounds you need.

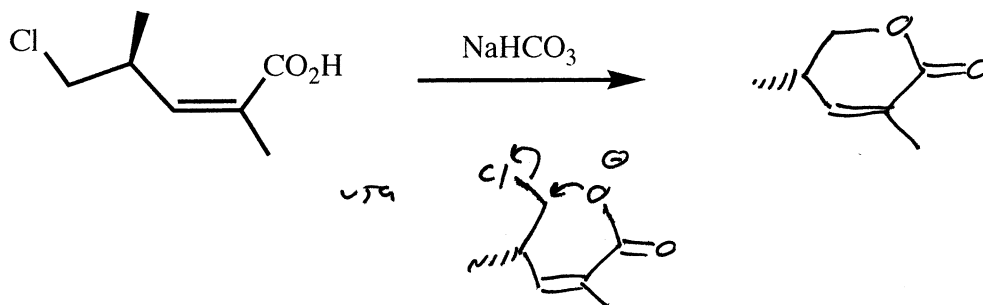


other routes may also be possible.

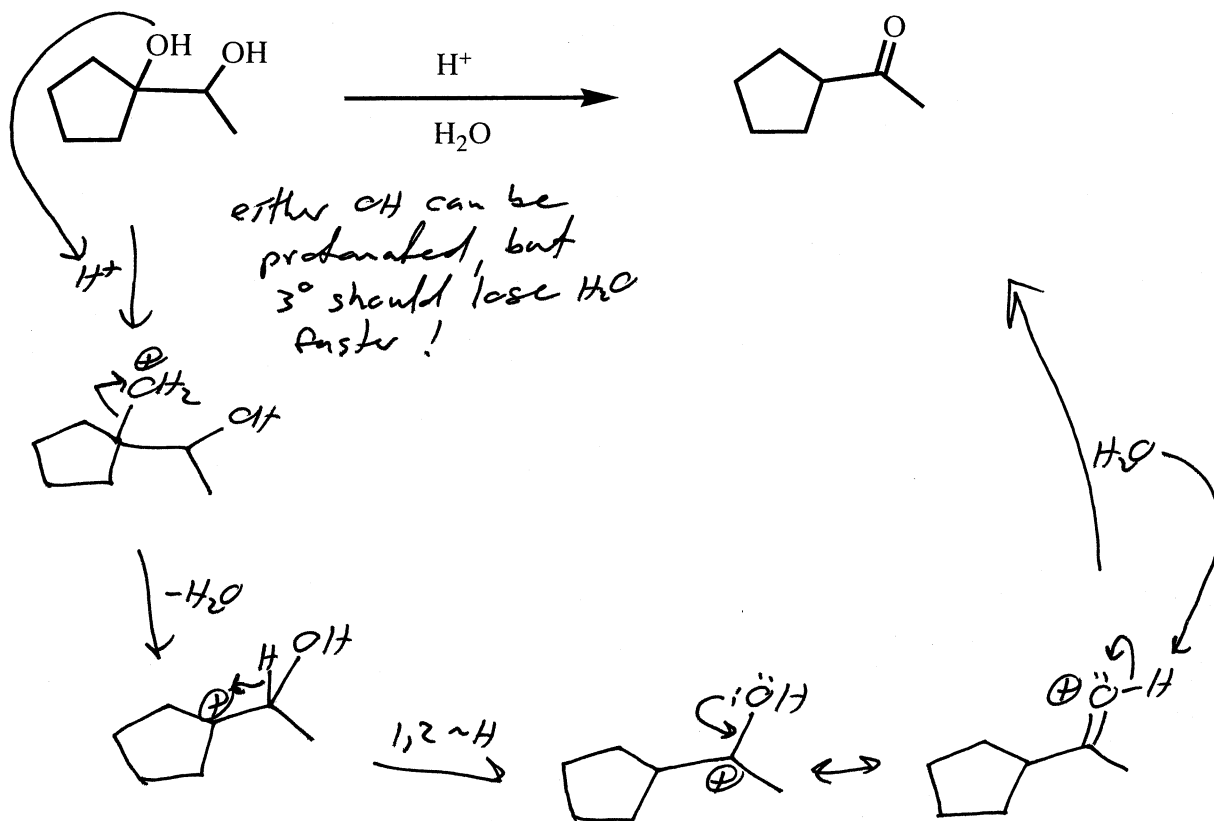


other routes may also be possible.

10. (8 points) Upon treatment with  $\text{NaHCO}_3$ , the (*Z*)-chloro-carboxylic acid below undergoes an acid-base reaction, followed by a rapid intramolecular " $\text{S}_{\text{N}}2$ " cyclization. Draw the product, showing its *structure* and stereochemistry clearly.



11. (17 points) The reaction below is one you haven't seen before, but you are familiar with all the steps of the mechanism. Write the mechanism, showing each step clearly with curved arrows.



this is called a "pinacol rearrangement".