

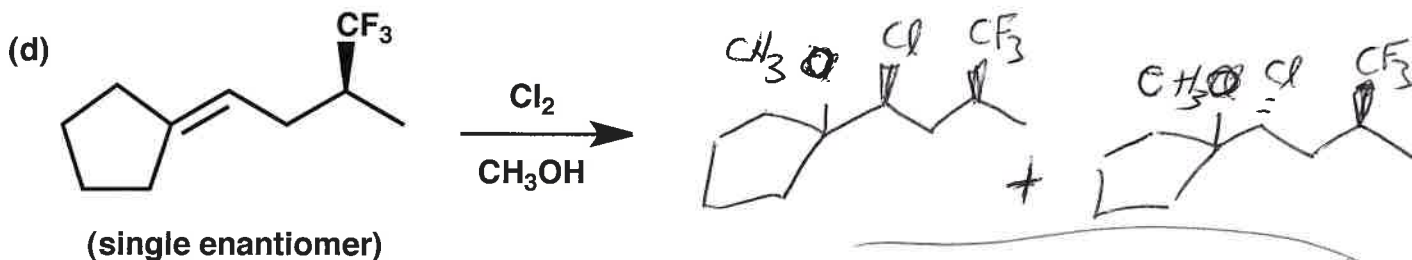
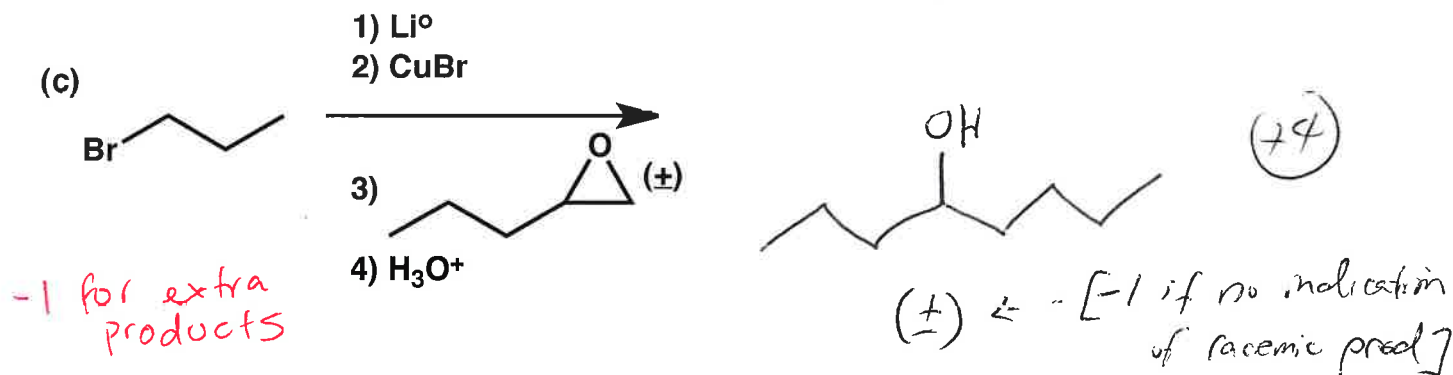
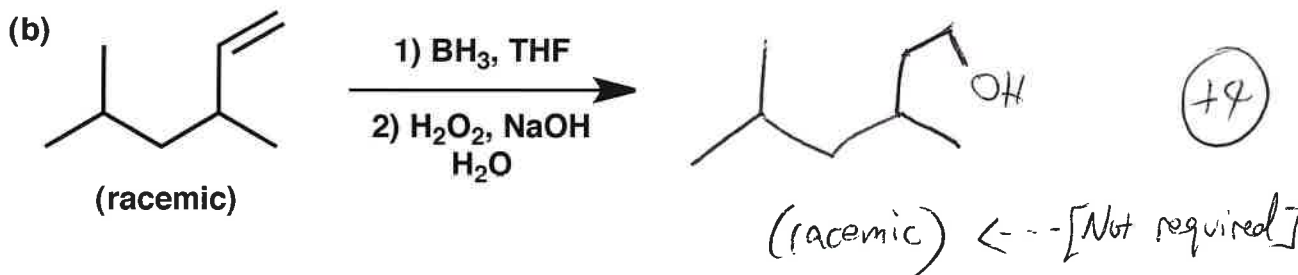
Last Name Answer

First Name Key

General Instructions:

- Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.
- Print your name on each page.
- Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (27 points) Show the major product or products expected from each reaction.



(continued on next page)

(+2 is no stereochem at new bonds)

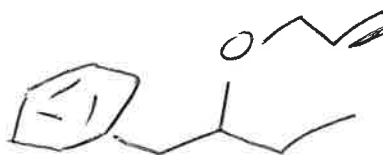
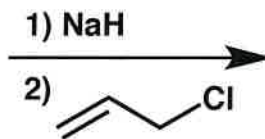
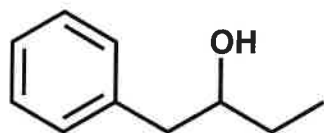
-3 for -OH instead of -OCH3

-5 for substituent reversal

1. (cont.)

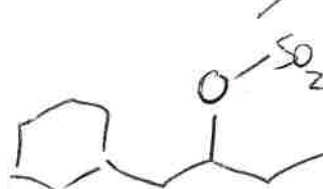
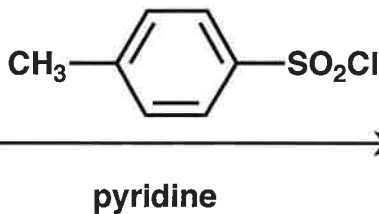
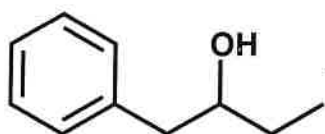
Name _____

(e)



(+4)

(f)



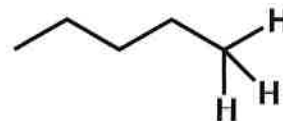
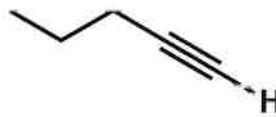
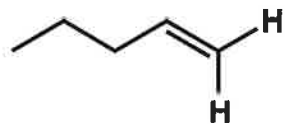
"15" ok

(+4)

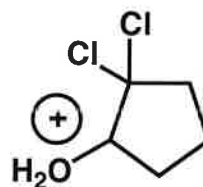
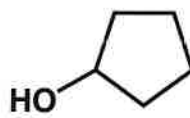
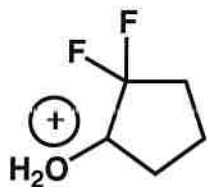
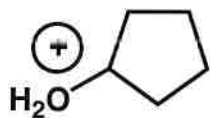
-2 for leaving Cl

2. (10 points) For each set of molecules below, redraw them in order based on expected pK_a of the indicated protons, with the highest pK_a on the left and the lowest on the right.

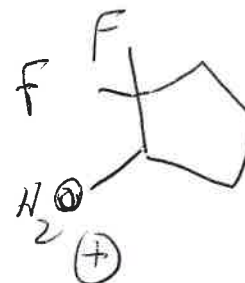
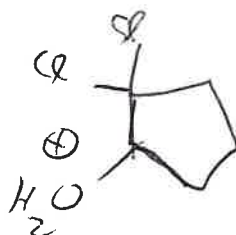
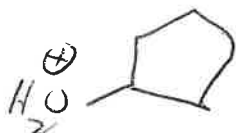
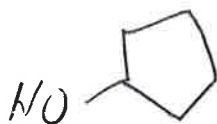
(a) H_2N-H



(b)



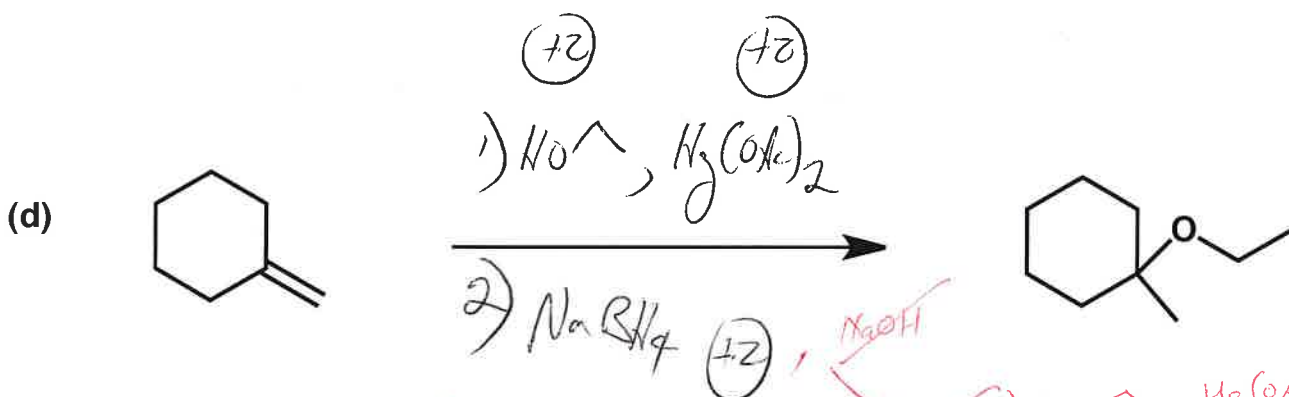
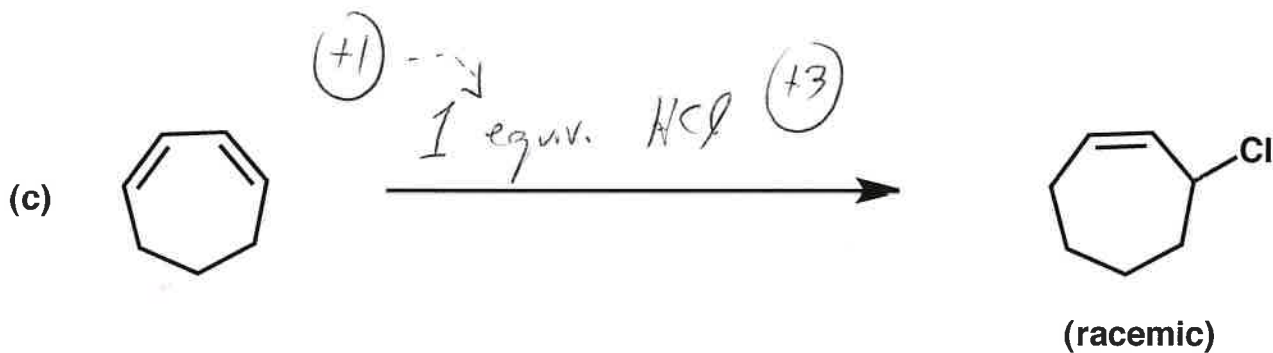
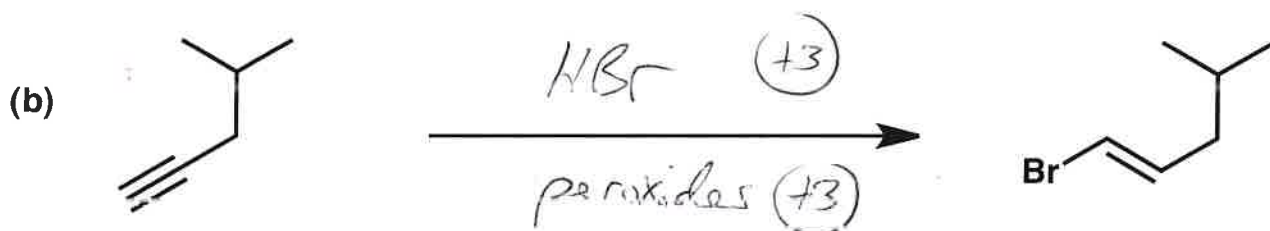
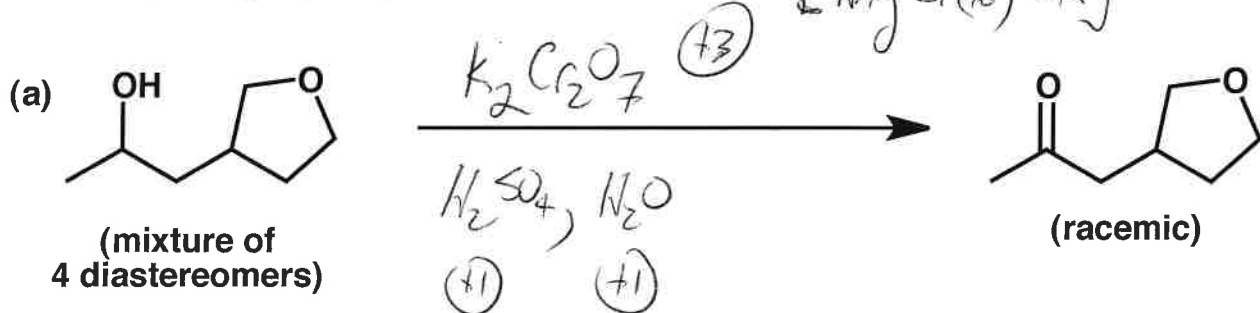
(+5 each)



[+1 for correct compound at the very left; no other partial credit.]

Name _____

3. (21 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)," "2)," etc. over the arrow. [Any Cr(+6) ok]



+2 1) H₂SO₄, H₂O

+2 2) NaH

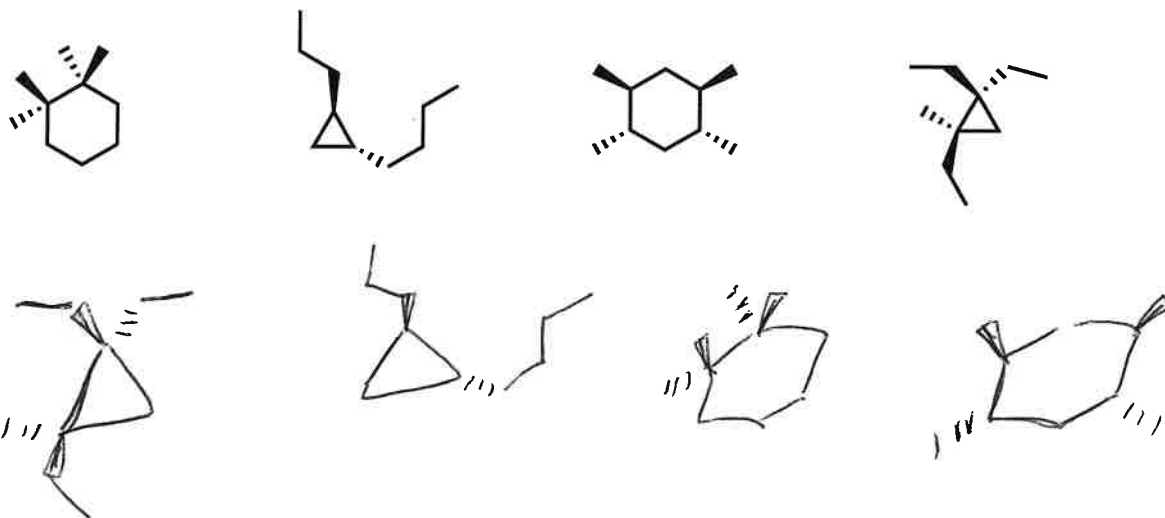
+2 3) I₂

+3 { 1) Hg(OAc)₂, NaOH
 2) NaBH₄
 and then 3, 4, 5 steps.

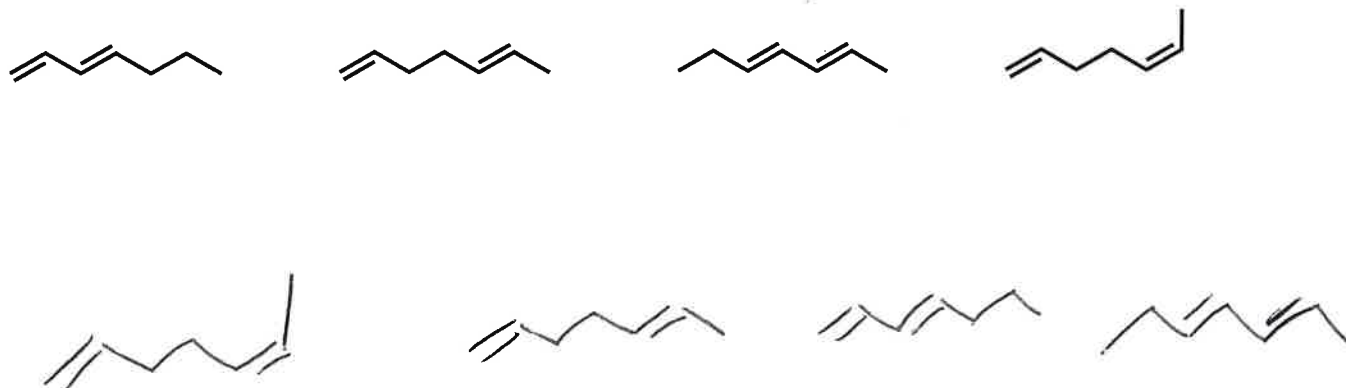
Name _____

4. (10 points)

(a) Redraw the isomeric molecules below ordered according to heat of combustion, with the one that would give the largest heat of combustion (absolute value) on the left, and the one that would give the smallest heat of combustion on the right.



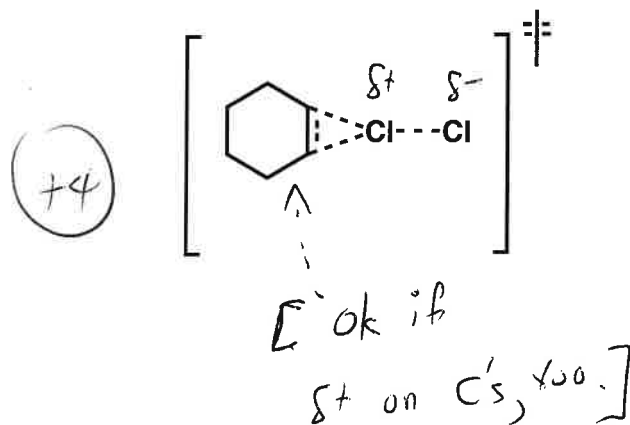
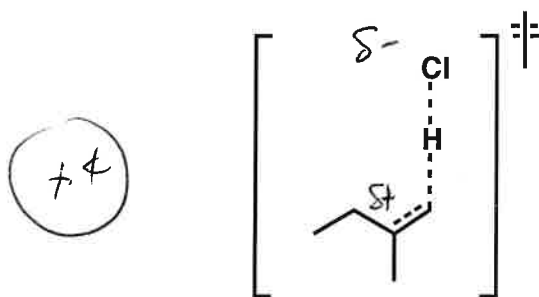
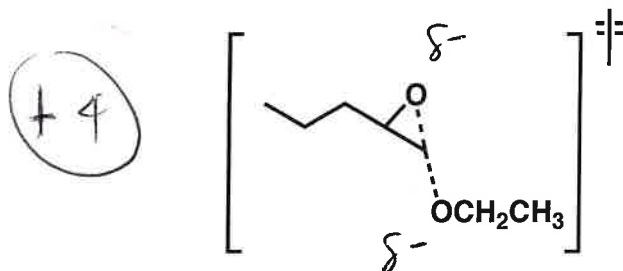
(b) Redraw the isomeric molecules below ordered according to heat of hydrogenation, with the one that would give the largest heat of hydrogenation (absolute value) on the left, and the one that would give the smallest heat of hydrogenation on the right.



*5 each

5. (12 points) Shown below are transition states for reaction mechanisms that we have discussed in class. Add $\delta+$ and/or $\delta-$ at the appropriate position(s) in each case.

NOTE: It is possible that some of the transition states have a net charge, but no counterions are shown.



6. (30 points)

Indicate isomeric relationships to the structure drawn in each box among the structures drawn around the boxed structure. Follow the directions below. (Conformational differences are not relevant to this question.)

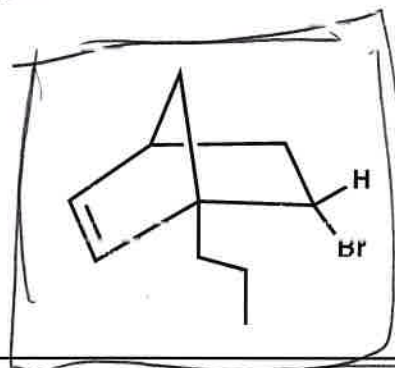
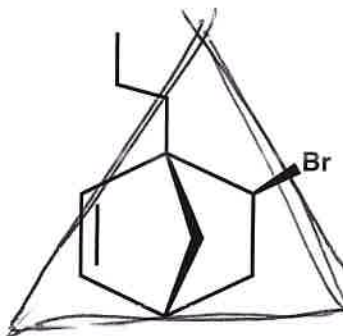
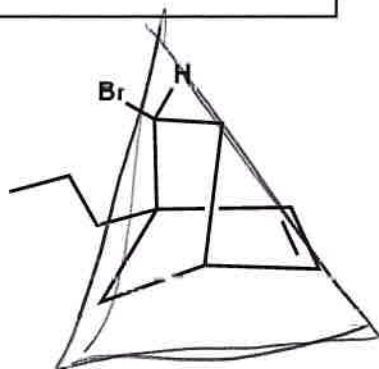
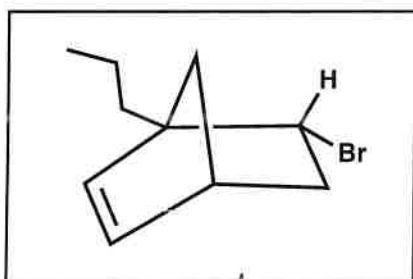
Put a **CIRCLE** around any structure that corresponds to boxed structure (i.e., a different drawing of the same molecule).

Put a **SQUARE** around any structure that corresponds to the **ENANTIOMER** of the boxed structure.

Put a **TRIANGLE** around any structure that corresponds to a **DIASTEREOMER** of the boxed structure.

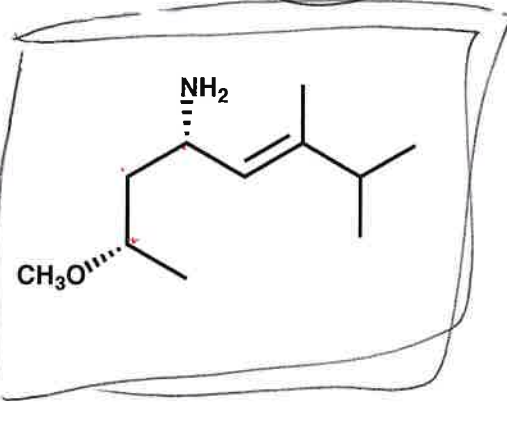
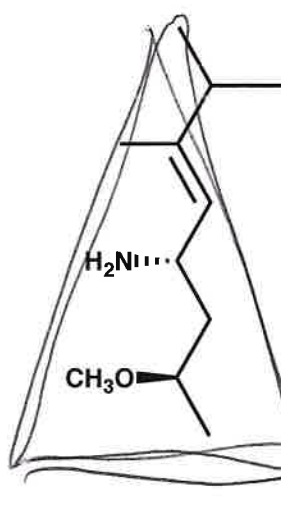
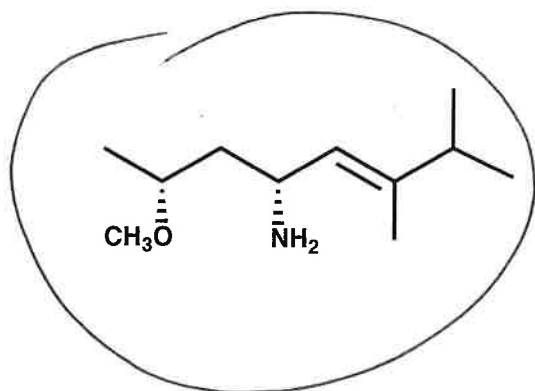
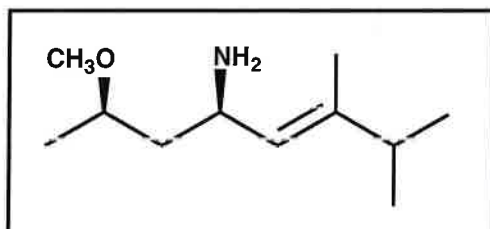
Put an **X** across any structure that corresponds to a **CONSTITUTIONAL ISOMER** of the boxed structure.

(a)



15 each

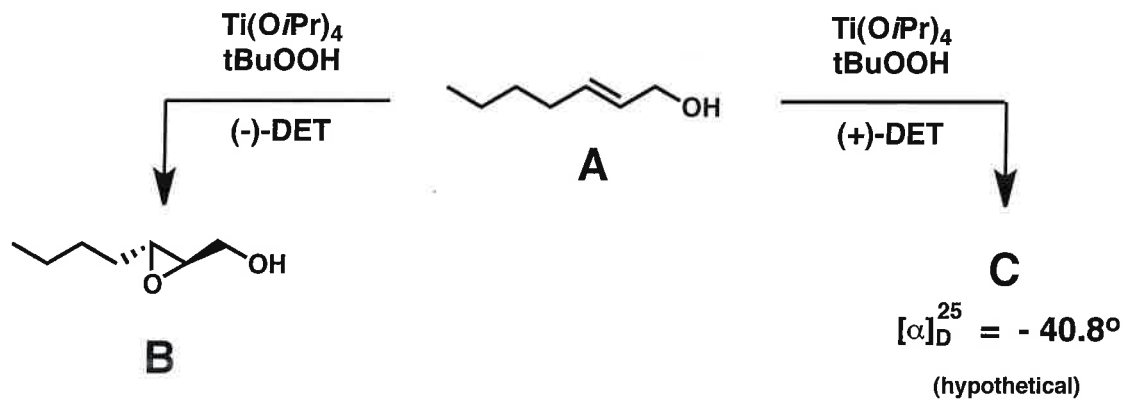
(b)



15 each

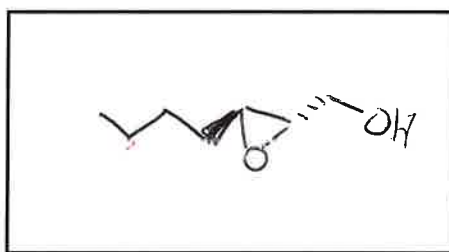
Name _____

7. (6 points) When molecule A is allowed to react as indicated below, either molecule B or molecule C is produced. In light of the information about B and C shown below, answer the questions below.



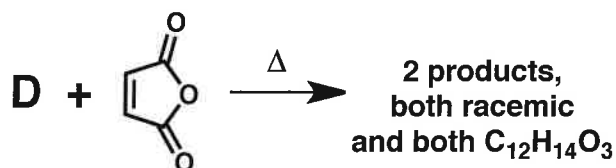
(a) For B, $[\alpha]_D^{25} =$ +40.8 $^\circ$

(b) The structure of C =

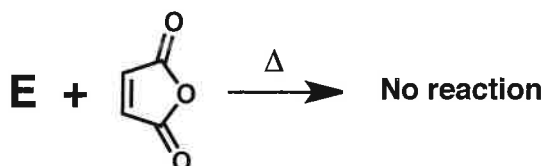


Name _____

8. (12 points) Two isomers, D and E, have the formula C_8H_{12} . Both react with two equivalents of H_2 in the presence of Pd/C to form ethylcyclohexane. However, exposing these isomers to the reaction conditions shown below gives divergent results.

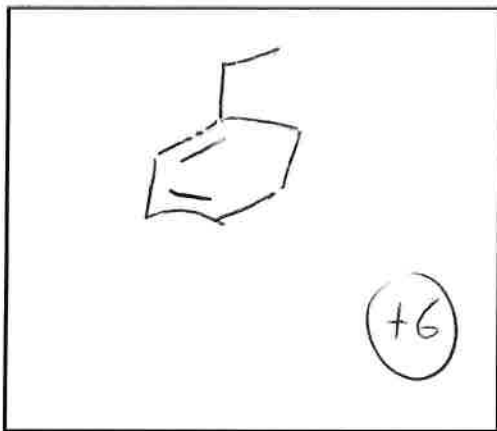


VS.



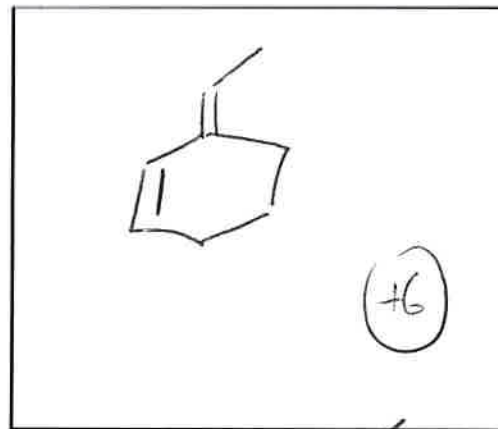
Propose a structure for D and a structure E below (there may be more than one correct answer in each case).

D =



OK, but technically incorrect

E =

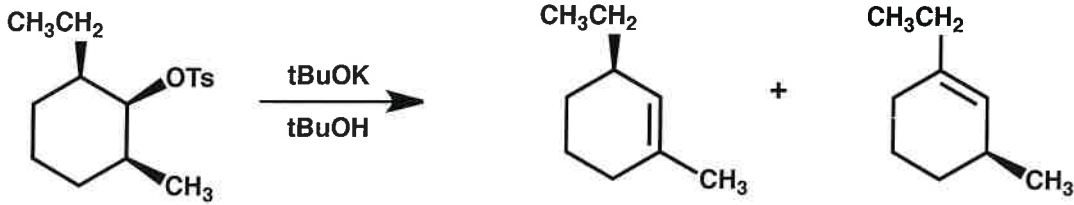


etc.



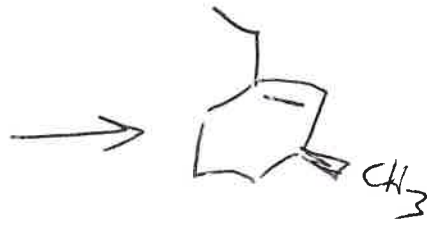
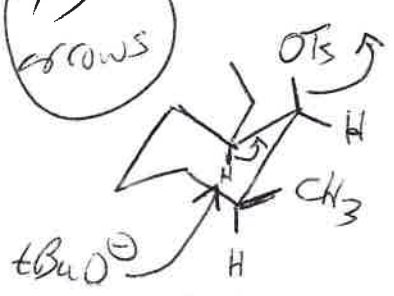
9. (20 points)

(a) Provide a conformationally accurate drawing of the starting material below, and use that drawing as the starting point for a mechanism (curved arrows) that show how the products are formed. Be sure to show any intermediates.



+2 for ~~ex. eq.~~ material chair

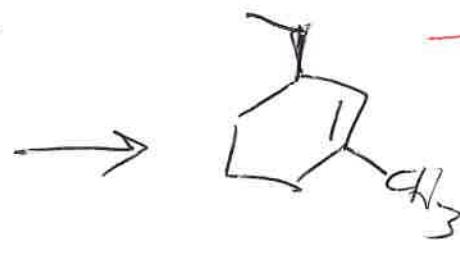
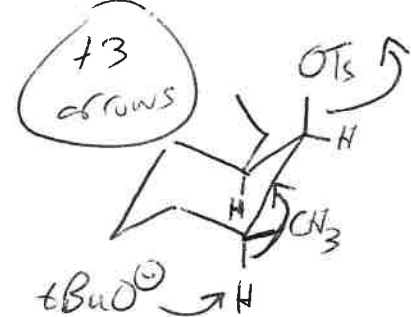
+3 arrows



+10 total

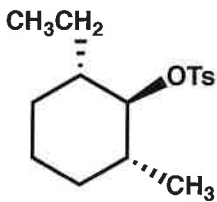
2 separate mechanisms -2

+4 for one correct chair

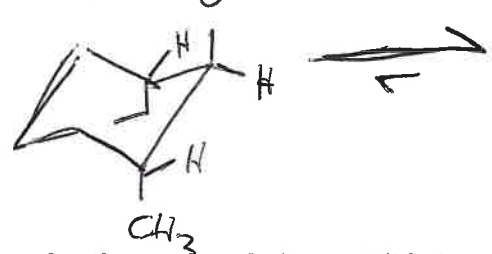


-6 if E1

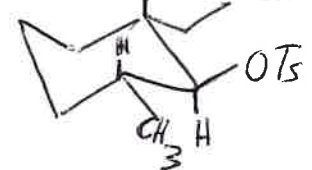
(b) Provide a conformationally accurate drawing of the molecule shown below. Your drawing will provide the basis of your answer to part (c); it may be helpful to show more than one conformation.



+4 for either



+1 for second



(c) In a single sentence, explain why the molecule in part (b) does not undergo any reaction when treated with the reagents used in part (a), i.e., when this molecule is treated with potassium *t*-butoxide in *t*-butanol.

+2 E2 requires antiperiplanar H and OTs (leaving group), which is not possible for molecule in part (b).

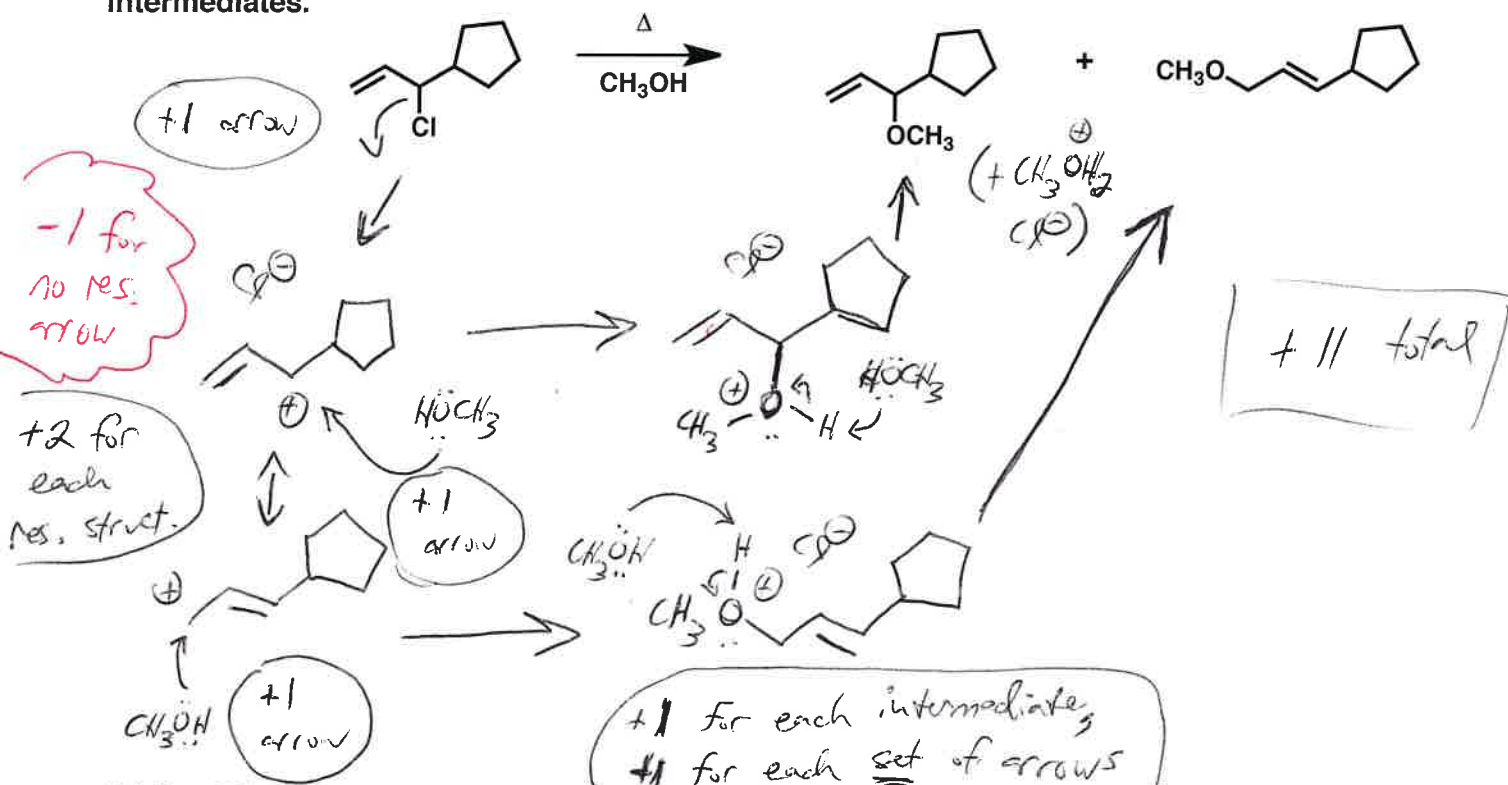
+3

-1 if they said trans instead of anti

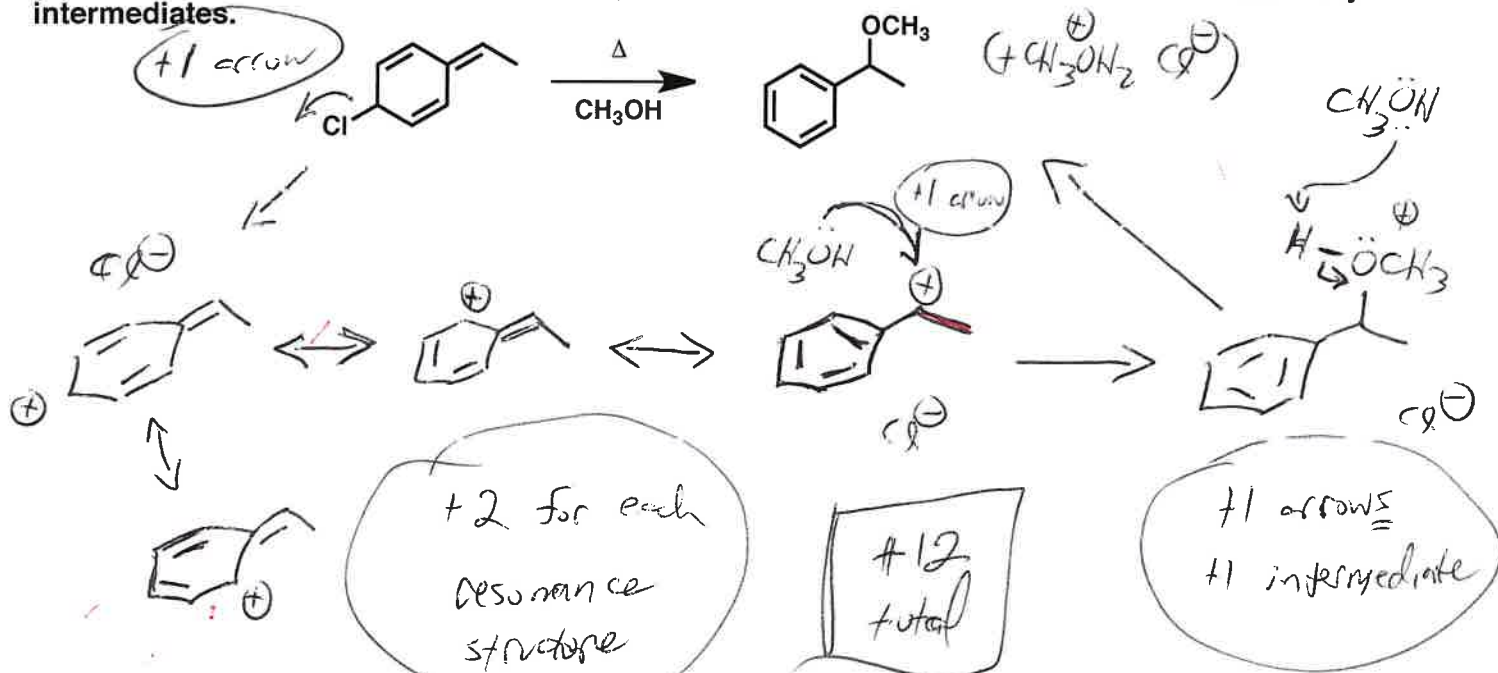
10. (28 points)

Name _____

(a) Provide a mechanism (curved arrows) for the reaction shown below. Be sure to show any intermediates.



(b) Provide a mechanism (curved arrows) for the reaction shown below. Be sure to show any intermediates.



(c) In a single sentence, explain why there is only one product (actually, a racemic pair) from the reaction shown in part (b).

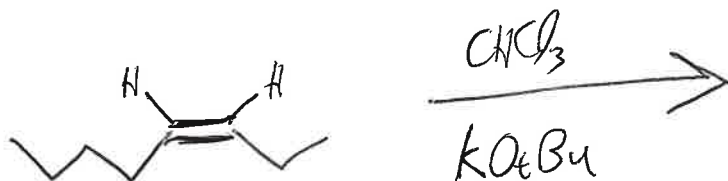
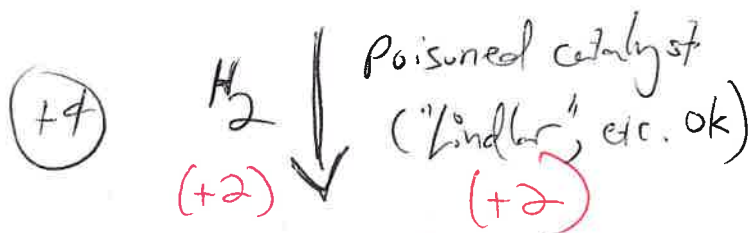
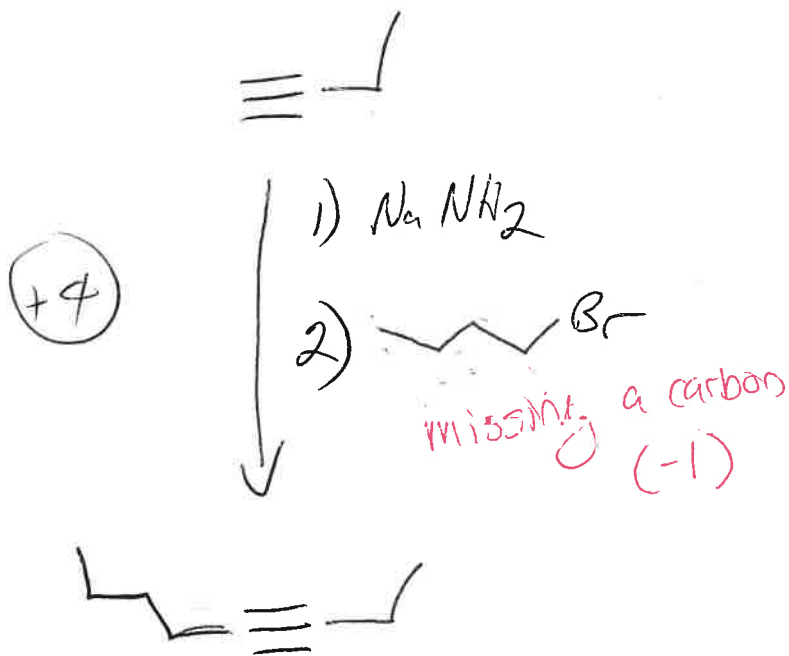
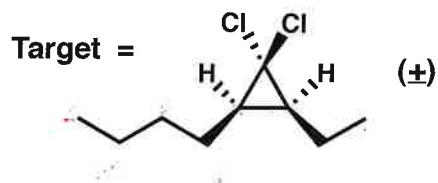
Attack of CH_3OH at any other site of \oplus among the resonance structures would lead to a non-aromatic product.

+5 (circled)

11. (24 points)

(a) Devise a synthetic route from the indicated starting material(s) to the indicated target. The route should be as short and as selective as possible. You may use any inorganic reagents in your synthetic plan. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)

Starting materials = Any organic molecule(s) with 4 or fewer carbons



(+4)

-- cont. on next page --

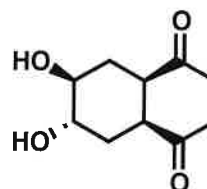
Grades based on reagents (so long as structures make sense).

11. (cont.)

(b) Devise a synthetic route from the indicated starting material to the indicated target. The route should be as short and as selective as possible. You may use any other organic molecules and any inorganic reagents in your synthetic plan. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)

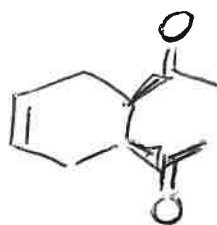
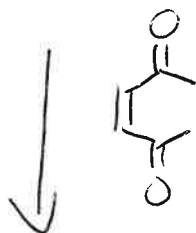
Starting material = C=CC=C

Target =



(racemic)

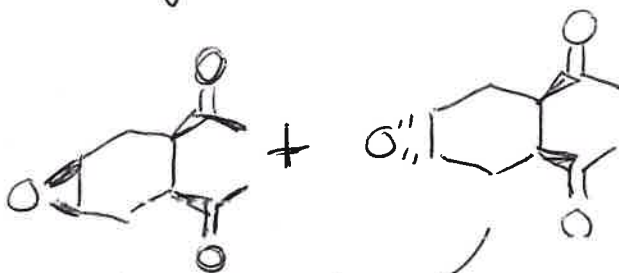
+4



+4

(Any "peracid" indication ok)

mCPBA



-2 not separating both steps!

+4

NaOH, H₂O

or

H₂SO₄, H₂O

"Target"

Grades based on reagents (i.e. how many reagents make sense).