First Three Letters of Last Name: | **TA Name:**

K	E	Y	

Hour Exam #1

5.12 Spring 2005

Organic Chemistry I

Printed name_____

Signature_____

ID#_____

Pre-requisite (circle one): 5.112 5.111 3.091

1. Make sure your exam has 9 numbered pages plus a periodic table.
2. Write your initials on each page.
3. Look over the entire exam before you begin to familiarize yourself with its length. Do what you know first, then attempt the harder problems.
4. Read the instructions carefully and budget your time.
5. Show all of your work. Partial credit receives points!

Page	Possible Points	Total
1	6	
2	16	
3	10	
4	10	
5	16	
6	12	
7	12	
8	18	
Total	**100**	
9	4	
XC	**104**	

1. (1 pt) What is the pKa of a *sp* hybrdized carbon atom?

(a) 25 b) 35 c) 45 d) 50

2. (2 pts) **a)** Circle the letter of the molecule with the lowest barrier to rotation (or ring-flip). **b)** Box the letter of the molelcule with the highest barrier to rotation (or ring-flip).

(a) ethane

b) propane

c) butane

[d] cyclohexane

3. (2 pts) Rank the following substituents in order of priority (1 = highest priority).

4 $-CH=CH_2$

2 $-CN$

3 $-CH_2NH_2$

1 $-CH_2Br$

4. (1 pt) If a chiral molecule has an absolute configuration of R, which direction does it rotate the plane of polarized light?

a) clockwise (dextroratory)

b) counterclockwise (levarotatory)

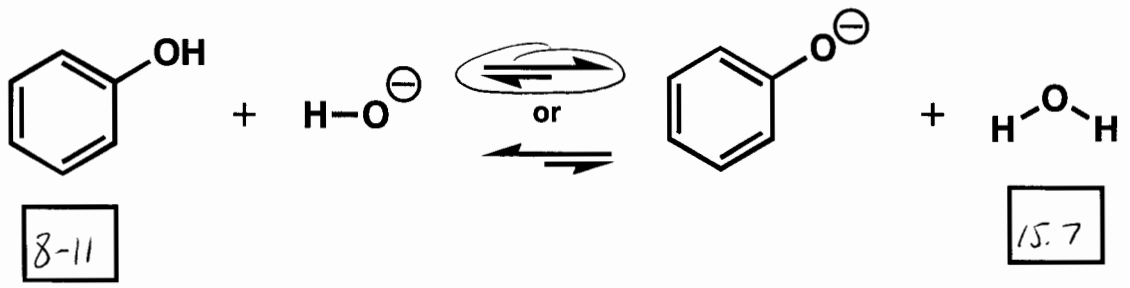
c) it doesn't rotate the plane of polarized light

(d) can't be determined from the information given

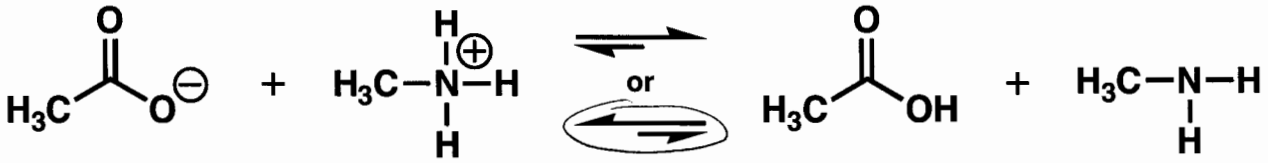
Initials

Points 6

5. (6 pts) **a)** Enter the pK_a value for each acid in the boxes below. **b)** Indicate whether the reactants or products will be favored at equilibrium by circling the appropriate set of equilibrium arrows (a longer arrow is drawn toward the species favored at equilibrium).

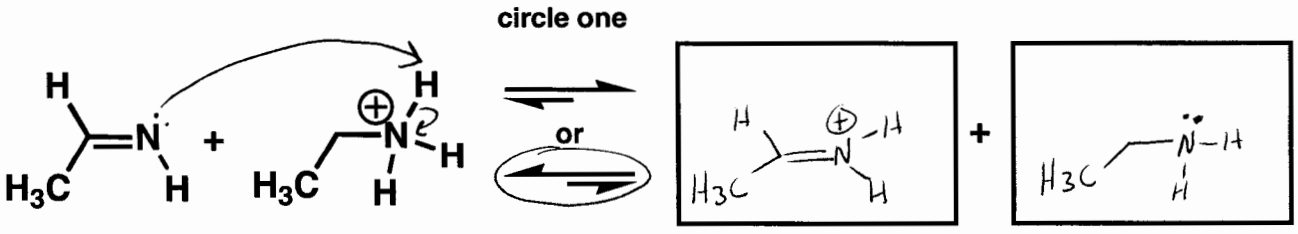


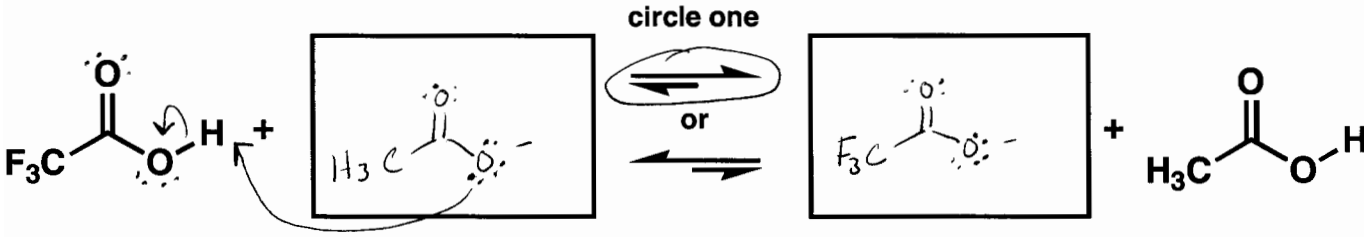
8-11 | 15.7



16-11 | 4-5

6. (10 pts) **a)** Provide structures in the boxes to complete the following acid-base (proton-transfer) reactions. **b)** For each set of reactants, draw in all lone pairs of electrons and show the electron movement by using curved arrows. **c)** Indicate whether the reactants or products will be favored at equilibrium by circling the appropriate set of equilibrium arrows.

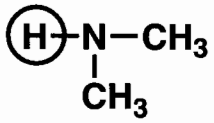




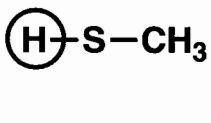
Initials | **Points**

16

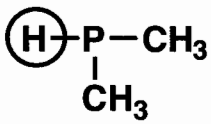
7. (10 pts) Rank the following sets of molecules in order of acidity (1 = most acidic).



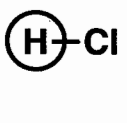
[4]



[2]



[3]



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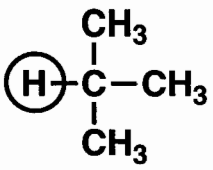
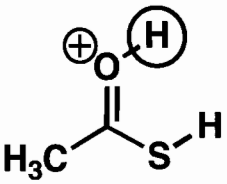
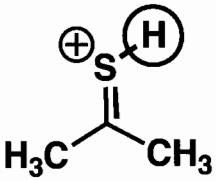


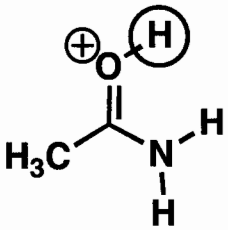
[5]



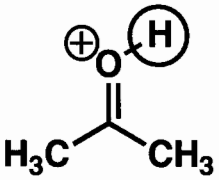
[3]



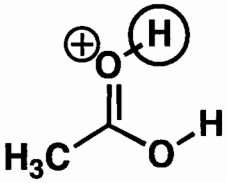
[1]



[5]



[2]



[4]

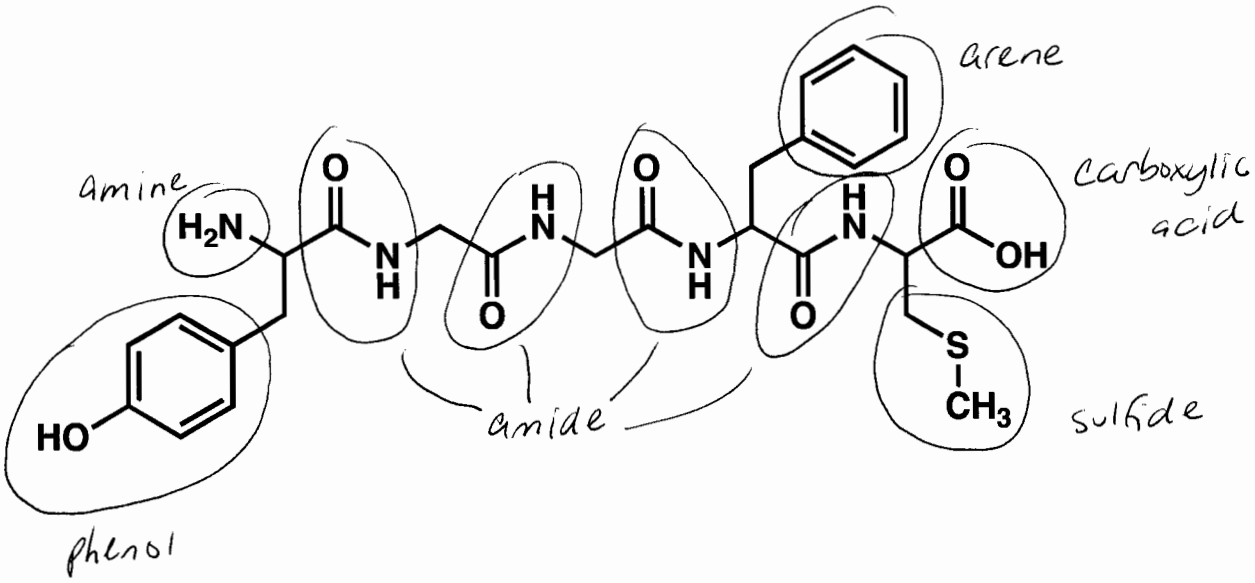
Initials

[ ]

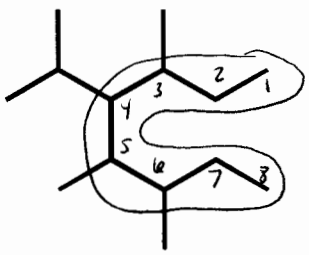
Points

[10]

8. (6 pts) Met-enkephalin, an endorphin, serves as a natural pain reliever that changes or removes the perception of nerve signals. Label all of the functional groups present in Met-enkephalin.

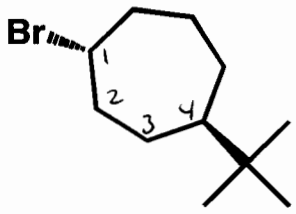


9. (4 pts) Name the following molecules.



octane
3-methyl
4-isopropyl
5-methyl
6-methyl
4-isopropyl-3,5,6-trimethyl

4-isopropyl-3,5,6-trimethyloctane

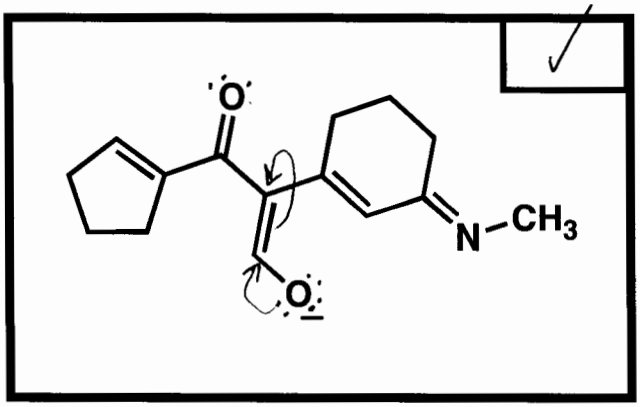


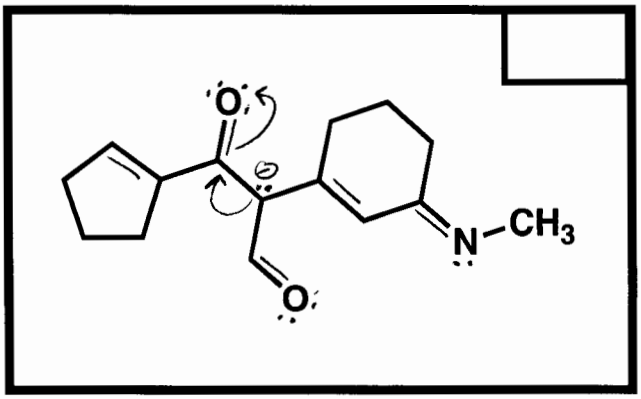
trans-1-bromo-4-tert-butylcycloheptane

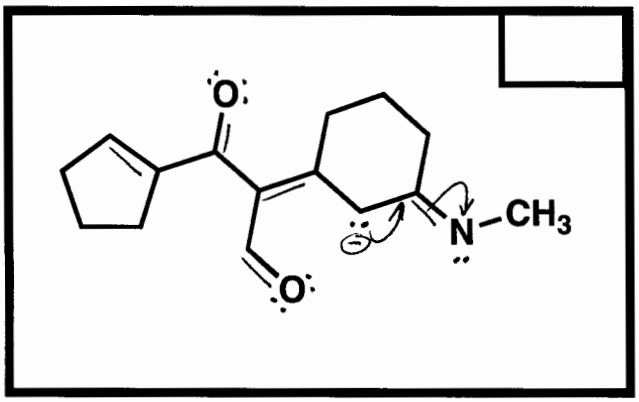
Initials

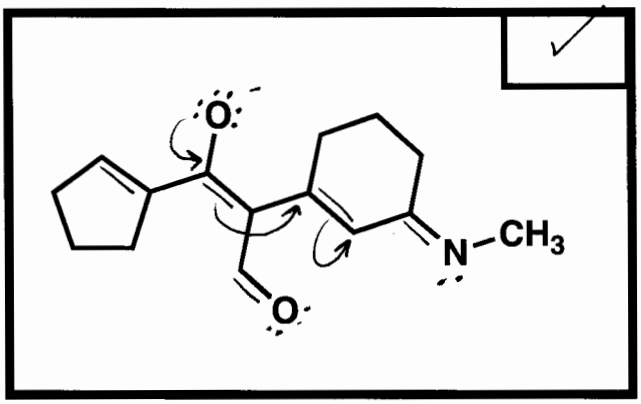
Points 10

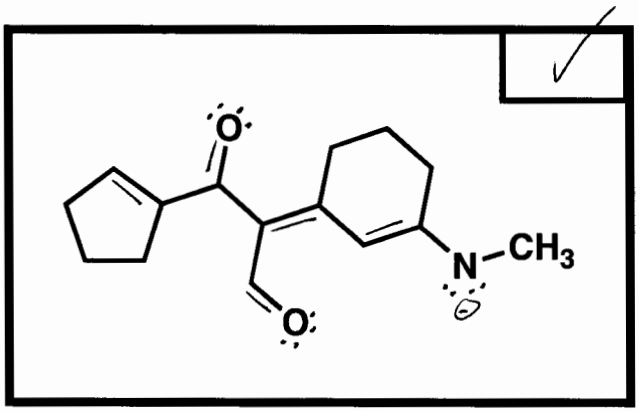
10. (16 pts) **a)** Draw the 4 major resonance contributors for the molecule shown in the first box. Partially completed structures are provided as a time-saver. **Do not generate any additional charges. b)** Draw in all lone pairs of electrons and use arrows to show the movement of electrons within the structure. **c)** Place a checkmark in the small boxes of the three structures that contribute the most to the resonance hybrid. **d)** Circle all the nucleophilic atoms in the structure at the bottom of the page.



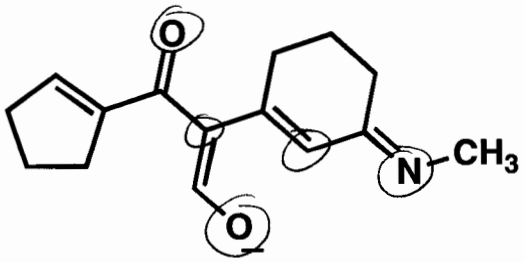








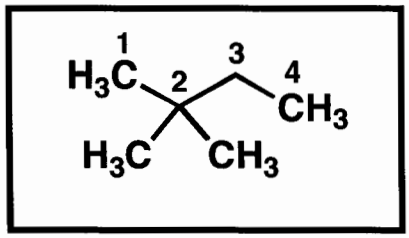
Circle all of the nucelophilic atoms in the molecule below.

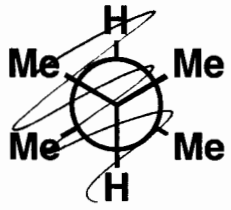


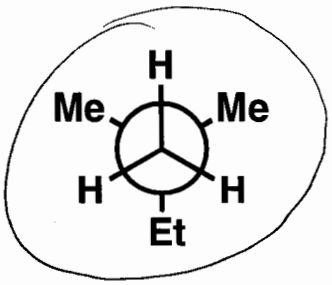
Initials

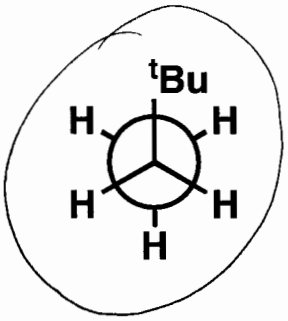
Points 16

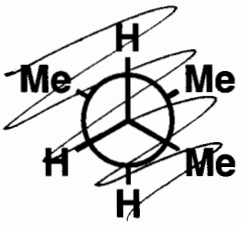
11. (12 pts) **a**) Circle the structures that represent a conformation of 2,2-dimethylbutane sighting along **any** C-C bond.



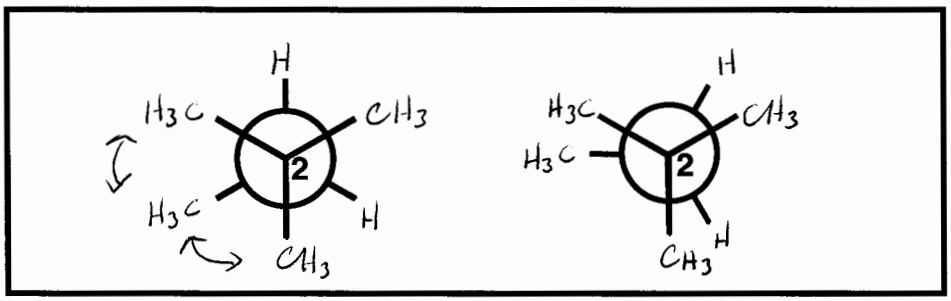








b) Complete each of the Newman projections below to show the most stable and least stable conformations of 2,2-dimethylbutane, sighting along the C_2-C_3 bond.



2 gauche: $E_{rel} = 2(0.9) = 1.8$ kcal/mol

H/me eclipsing 1.4 kcal/mol
H/me eclipsing 1.4 kcal/mol
me/me eclipsing 2.6 kcal/mol
E_{rel} = 5.4 kcal/mol

c) Use the above Newman projections to calculate the barrier to rotation of 2,2-methylbutane sighting along the C_2-C_3 bond.

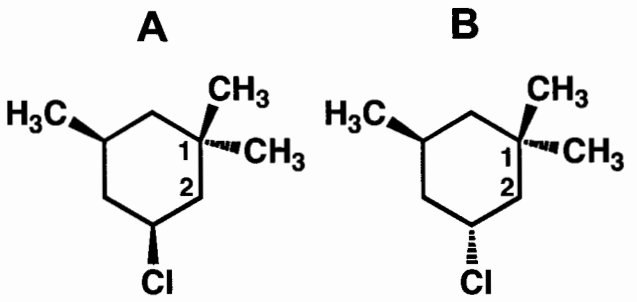
Barrier to Rotation = 5.4 kcal/mol - 1.8 kcal/mol = 3.6 kcal/mol

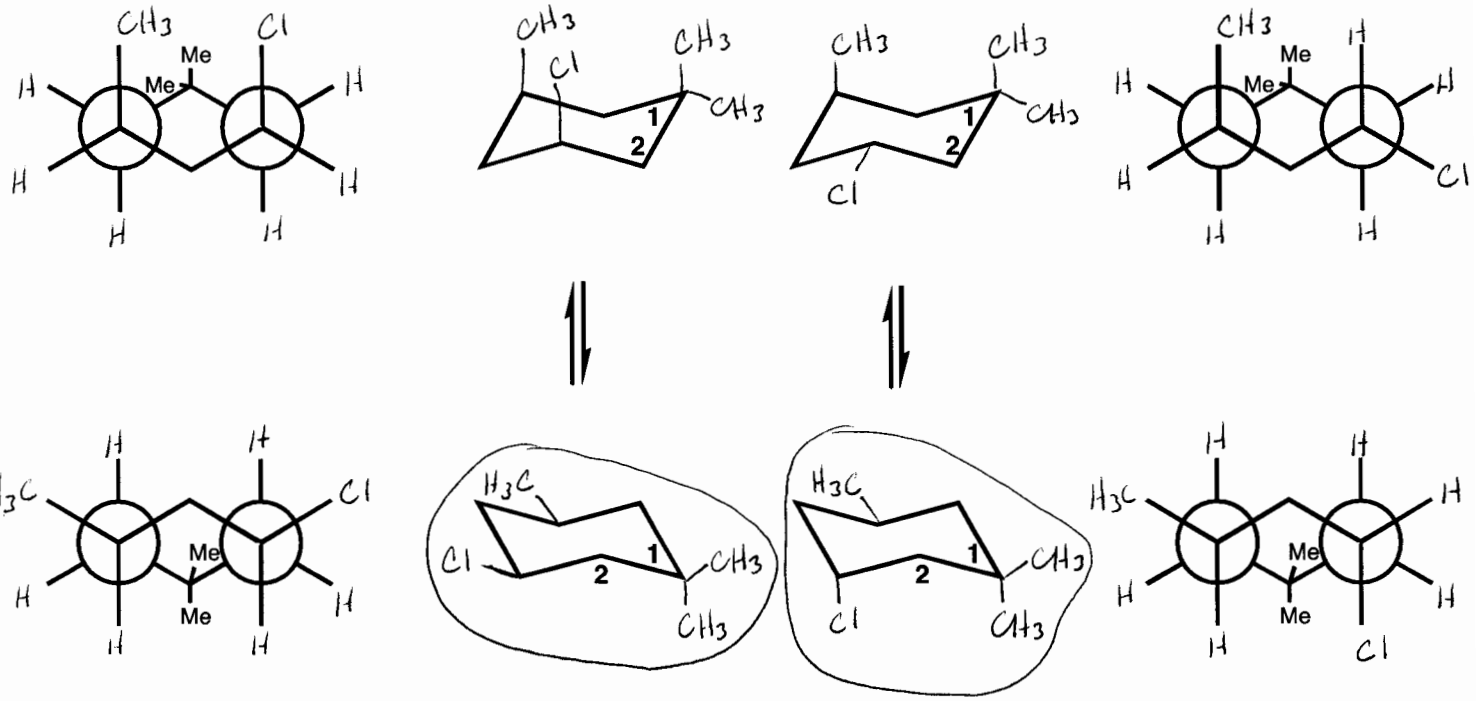
Initials

Points

12

12. (12 pts) **a)** Draw in the substituents on the ring flipped conformers of each molecule (**A** and **B**) to predict which molecule is lower in energy. **b)** Show the Newman projection for each ring-flipped conformer, sighting along the C_5-C_6 and C_3-C_2 bonds.





c) Circle the chair conformation that is lower in energy for each molecule.

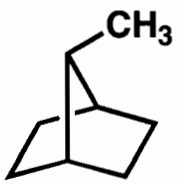
d) Which structure is lower in energy (circle one)? (**A**) or **B**

e) Briefly explain your choice: A has fewer 1,3-diaxial interactions in its lowest energy conformation

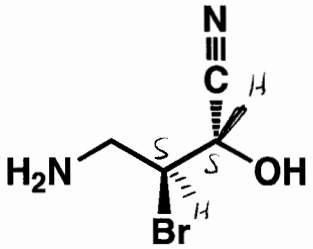
Initials [ ]

Points [12]

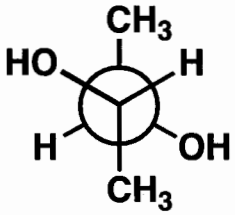
13. (9 pts) **a)** Label each molecule as chiral (**C**), achiral (**A**), or achiral/meso (**M**). **b)** Designate each chirality center as **R** or **S**.



A



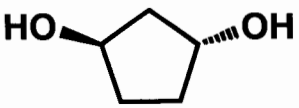
C



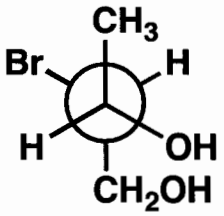
S- front
R- back

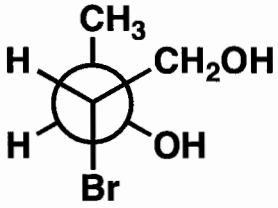
M

14. (9 pts) Indicate the relationships between the two molecules as enantiomers (**E**), diastereomers (**D**), or same molecule (**S**).

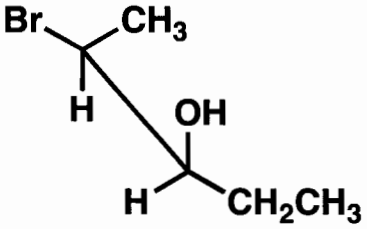


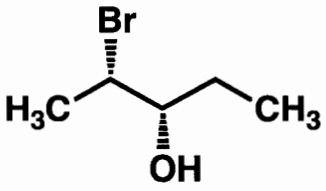
E





E





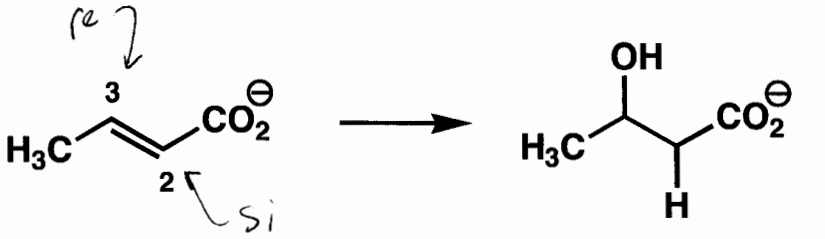
D

Initials

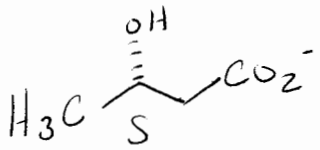
Points 18

EXTRA CREDIT

(4 pts) One of the steps in fat biosynthesis is the hydration of crotonate to yield 3-hydroxybutyrate. The reaction occurs by addition of -OH to the *si* face at C_3, followed by protonation at C_2, also from the *si* face. **a)** Label the top face of each alkene carbon atom as *re* or *si*. **b)** Show the stereochemistry of the product and **c)** label C_3 as R or S.



crotonate **3-hydroxybutyrate**



Initials

Points 4