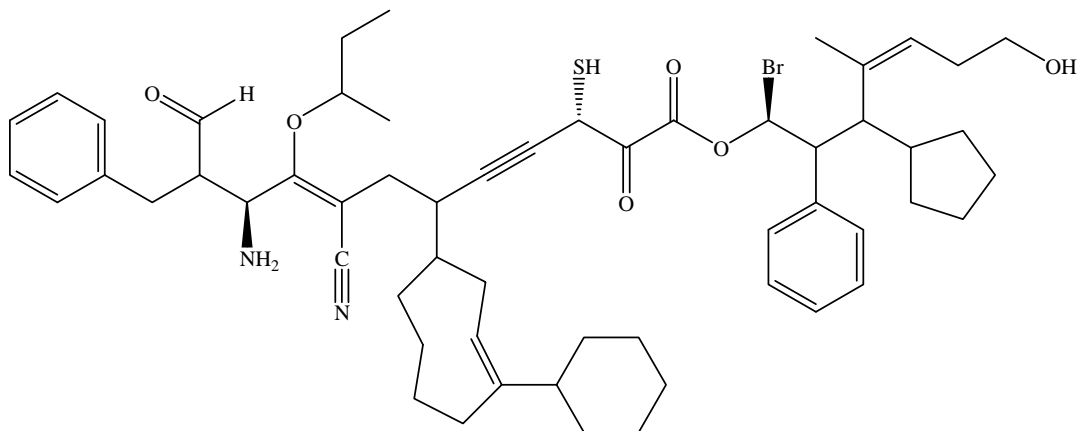


Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Types of Isomers, Degrees of Unsaturation	25	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	25	
4. Newman Projections, Conformational Energies	30	
5. Stereochemical Analysis	25	
6. 3D Structure, Hybridization, Angles, Shapes	30	
7. Forces of Interaction and Physical Properties	24	
8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge	30	
9. S <sub>N</sub> /E Mechanisms, with all of the details	43	
10. Various Reactions, predict the products	30	
11. Fill in all mechanistic details, curved arrows, lone pairs, formal charge	30	
Total	322	

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

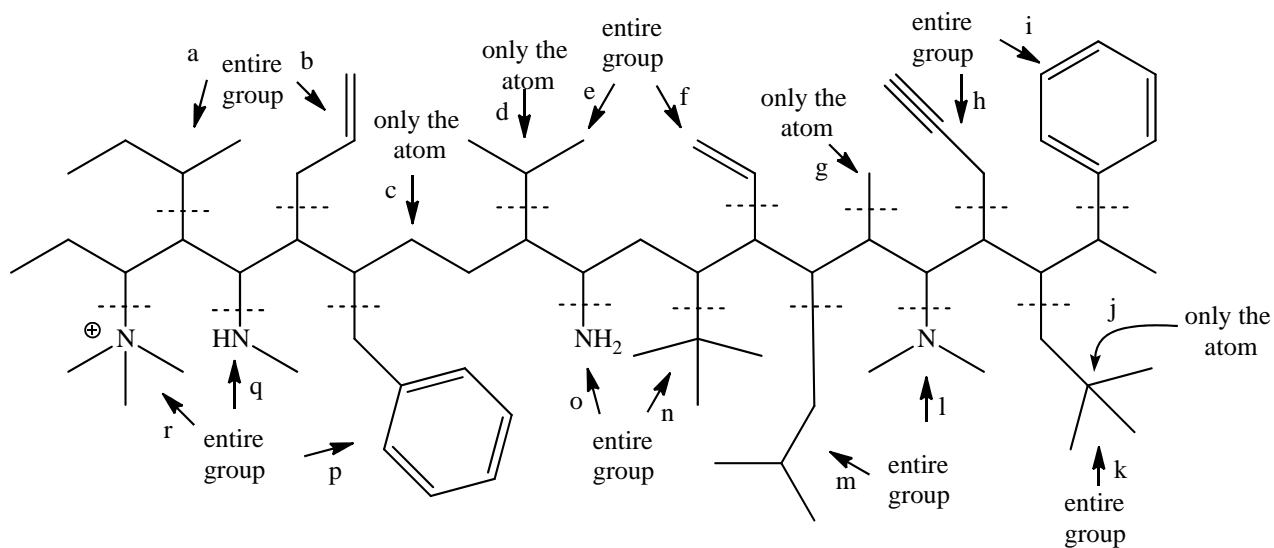
*To live a creative life, we must lose our fear of being wrong. -- Joseph Pearce*

1. Provide an acceptable name for the following molecule. (30 pts)



2. Match the arrows with the terms. Some arrows may be associated with more than one term. (25 pts)

- |                    |                     |                         |                           |
|--------------------|---------------------|-------------------------|---------------------------|
| 1. methyl _____    | 7. quaternary _____ | 13. vinyl _____         | 19. secondary amine _____ |
| 2. methylene _____ | 8. isopropyl _____  | 14. allyl _____         | 20. tertiary amine _____  |
| 3. methine _____   | 9. isobutyl _____   | 15. propargyl _____     | 21. quaternary ammonium   |
| 4. primary _____   | 10. sec-butyl _____ | 16. phenyl _____        | ion _____                 |
| 5. secondary _____ | 11. t-butyl _____   | 17. benzyl _____        |                           |
| 6. tertiary _____  | 12. neopentyl _____ | 18. primary amine _____ |                           |



3. Draw all possible chair conformations of cis-1-ethenyl-2-t-butylcyclohexane. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the more stable conformation using the  $C_1 \rightarrow C_2$  and  $C_5 \rightarrow C_4$  bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a ethenyl group is 1.7 kcal/mole and 5.0 kcal for an t-butyl group and a ethenyl/t-butyl gauche interaction is 1.4 kcal/mole, what is the difference in energy between the chair conformations? What are the relative percents of each conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes. (25 pts)

$$K = 10^{\frac{-\Delta G}{2.3RT}}$$

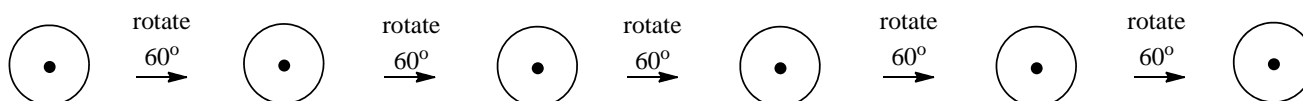
R = 2 cal/mol-K  
T = 300 K

4. Use a Newman projection of the C1→C2 bond of 1-phenyl-2,3,3-trimethylbutane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (30 pts)

2D structure

Gauche Energy Values (kcal/mole)		Eclipsing Energy Values (kcal/mole)	
H/H	+0.0	H/H	+1.0
H/CH <sub>3</sub>	+0.0	H/CH <sub>3</sub>	+1.4
H/t-butyl	+0.5	H/t-butyl	+3.0
H/phenyl	+0.2	H/phenyl	+1.7
CH <sub>3</sub> /phenyl	+1.4	CH <sub>3</sub> /phenyl	+3.3
CH <sub>3</sub> /t-butyl	+2.7	CH <sub>3</sub> /t-butyl	+8.5
phenyl/t-butyl	+3.9	phenyl/t-butyl	+13.5

most stable  
conformation  
↓



$\Delta H^\circ =$

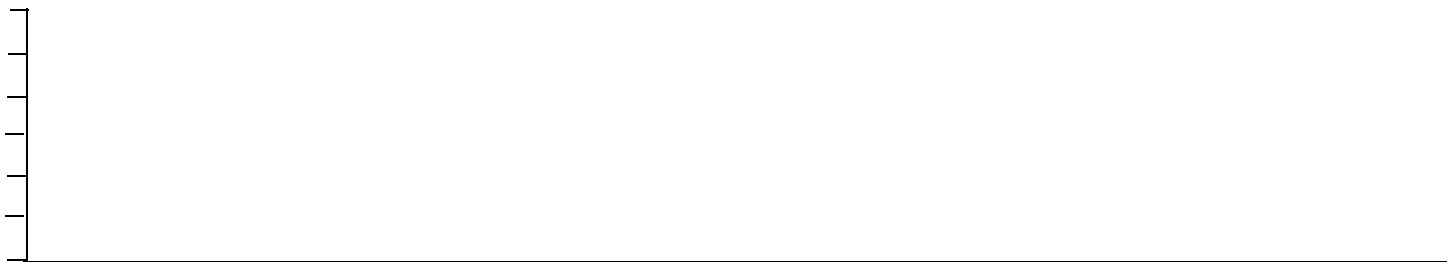
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

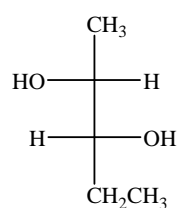
$\Delta H^\circ =$

$\Delta H^\circ =$

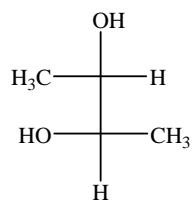


5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical

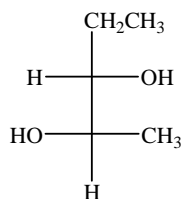
direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (25 pts)



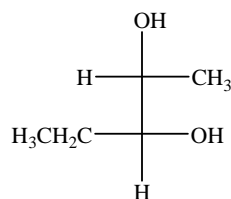
A



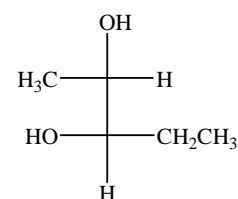
B



C



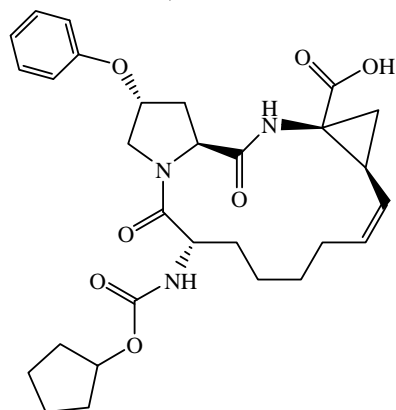
D



E

- a. Which are optically active?                    A    B    C    D    E
- b. Which are meso?                                    A    B    C    D    E
- c. Which is not an isomer with the others?    A    B    C    D    E
- d. Which pairs are enantiomers?                AB AC AD AE BC BD BE CD CE DE
- e. Which pairs are identical?                    AB AC AD AE BC BD BE CD CE DE
- f. Which pairs are diastereomers?             AB AC AD AE BC BD BE CD CE DE
- g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?    AB AC AD AE BC BD BE CD CE DE
- h. Draw any stereoisomers of pentane-2,3-diol as Fischer projections, which are not shown above. If there are none, indicate this.

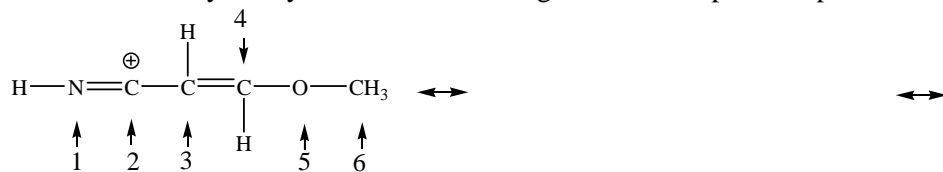
- j. An anti-hepatitis C drug was recently synthesized. Part of its structure is shown below. Circle all chiral and E/Z centers. How many stereoisomers are possible from the stereogenic centers shown? (Org. Lett. 2013, Vol 15, 1016-1019)



Maximum possible stereoisomers = \_\_\_\_\_

The complete formula is  $C_{29}H_{37}N_3O_7$   
What is the degree of unsaturation?

6. Draw two additional “better” 2D resonance structures of the given structure. Which structure is best and why? Draw a 3D structure for the given resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms. (30 pts)



Atom	Shape	Hybridization	Bond Angles	# $\sigma$ bonds	# $\pi$ bonds	# lone pairs
------	-------	---------------	-------------	------------------	---------------	--------------

1

2

3

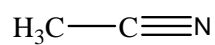
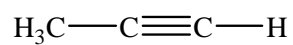
4

5

6

7. a. Which solvent do you suspect would dissolve NaCl better, methanol, CH<sub>3</sub>OH or benzene, C<sub>6</sub>H<sub>6</sub>? Explain your choice using structures? (8 pts)

- b. Match the boiling point with the structure below and provide an explanation for the difference. (8 pts)

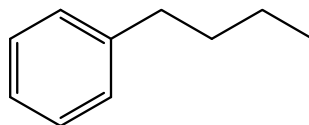
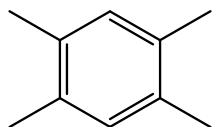


bp = +82 °C

bp = -23 °C

ΔT = \_\_\_\_\_

- c. Match the melting point with the structure below and provide an explanation for the difference. (8 pts)

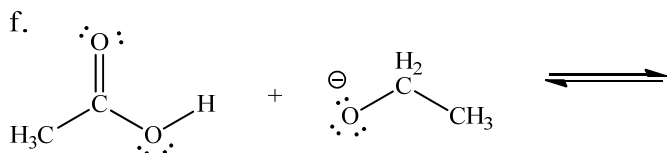
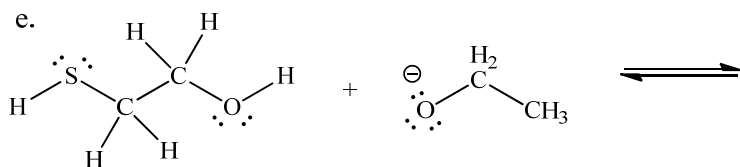
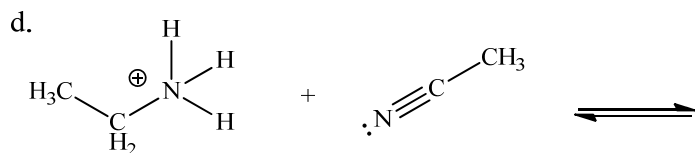
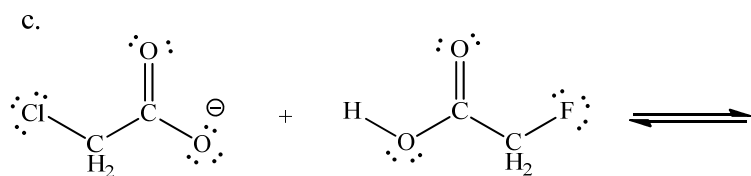
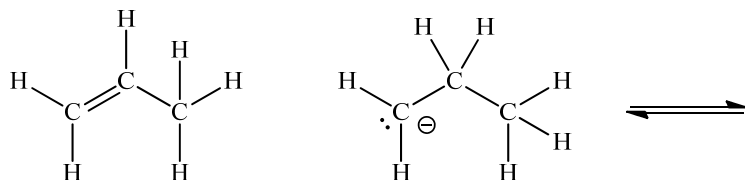
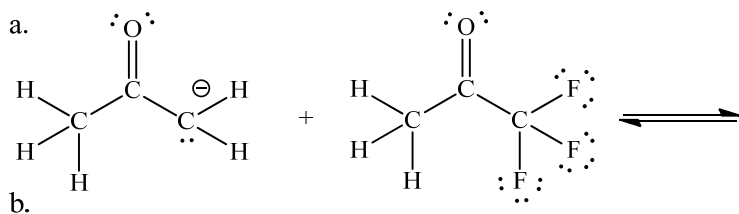


mp = +79 °C

mp = -88 °C

ΔT = \_\_\_\_\_

8. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the "right" or to the "left". Also, very briefly explain your reasoning. (30 pts)



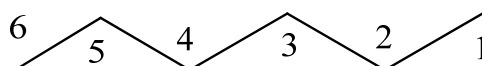


9. Use (2R,3S)-3-bromo-2-deuteriohexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. Do not consider carbocation rearrangement possibilities. You can abbreviate (simplify) parts of the molecule that are not part of a reaction. (43 pts)

a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)

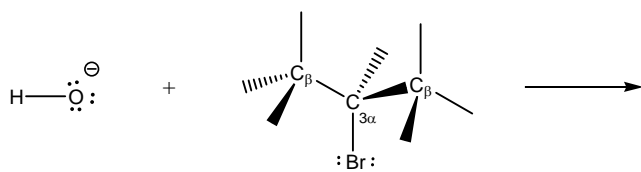
2D structure

3D structure



(2R,3S)-3-bromo-2-deuteriohexane

b. Show the  $S_N$  reaction (what kind?), indicate the absolute configuration(s) of the  $C_\alpha$  center in the product. (7 pts)

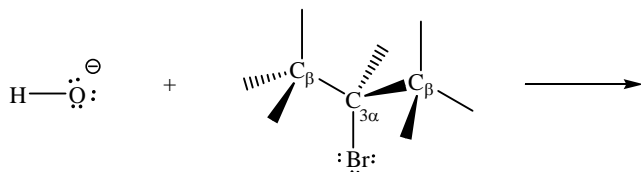


mechanism



configuration  
in product

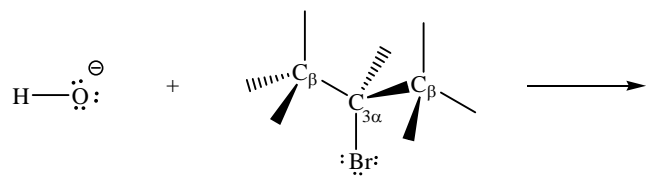
c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (13 pts)



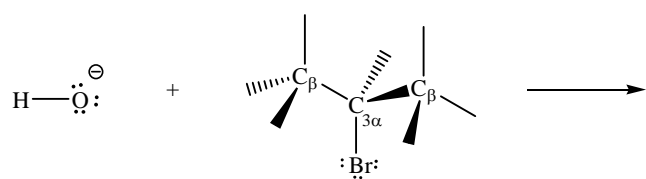
mechanism



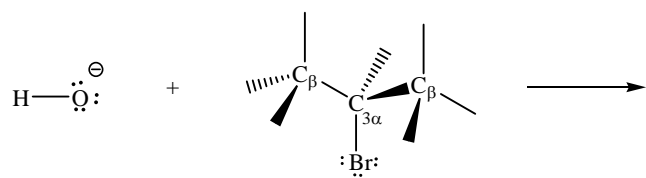
configuration  
in product



configuration  
in product

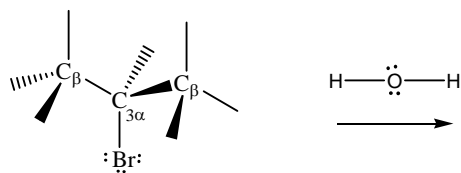


configuration  
in product



configuration  
in product

d. Show the  $S_N$  reaction (what kind?). You can use one intermediate to show all possible mechanistic  $S_N$  possibilities. Indicate absolute configuration(s) of the  $C_\alpha$  center in your product(s). (10 pts)



mechanism



configuration  
in product

e. Redraw the intermediate used in 8d above to show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism and just draw the additional possible products. (10 pts)

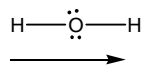
\_\_\_\_\_



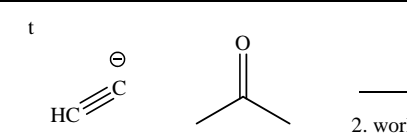
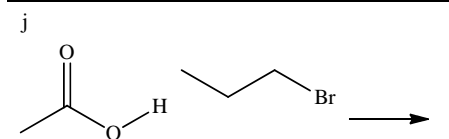
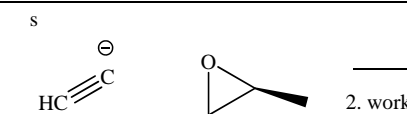
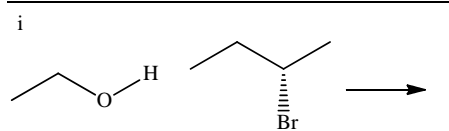
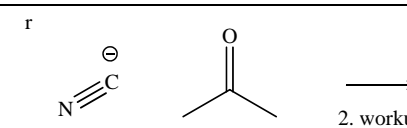
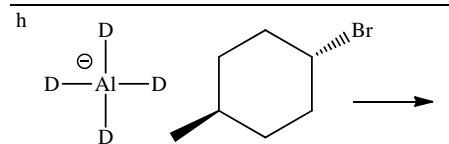
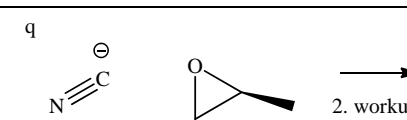
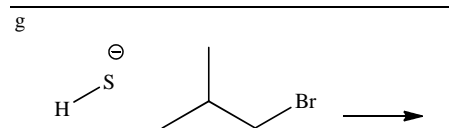
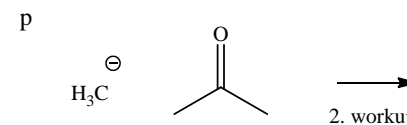
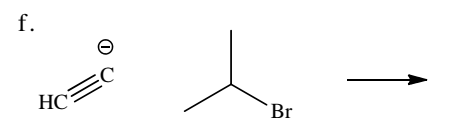
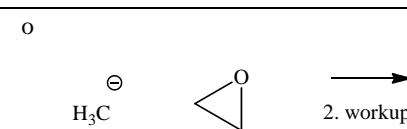
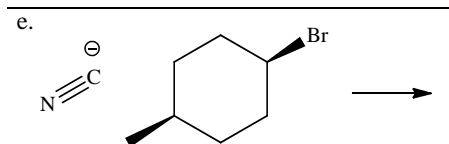
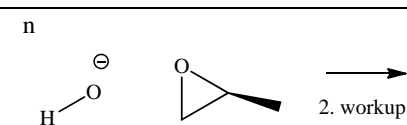
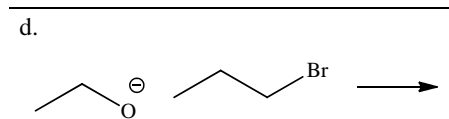
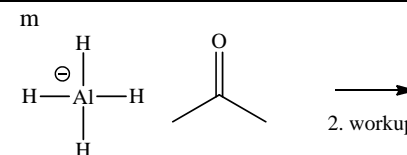
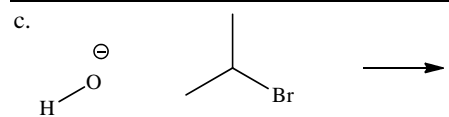
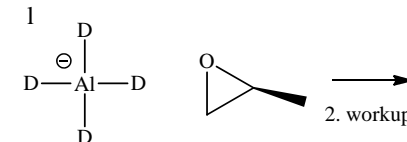
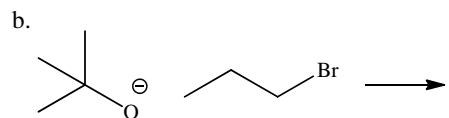
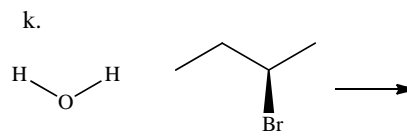
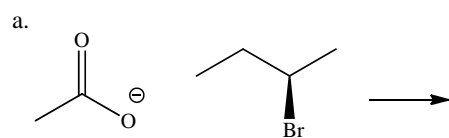
mechanism



E or Z

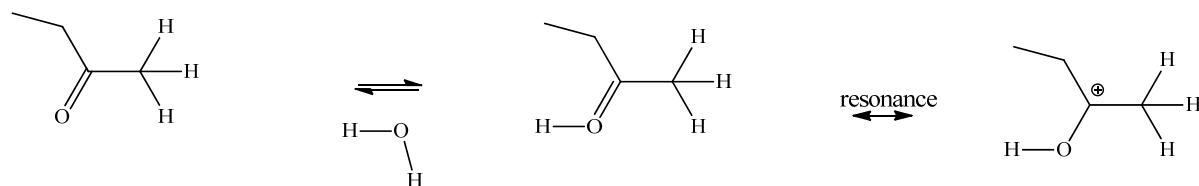
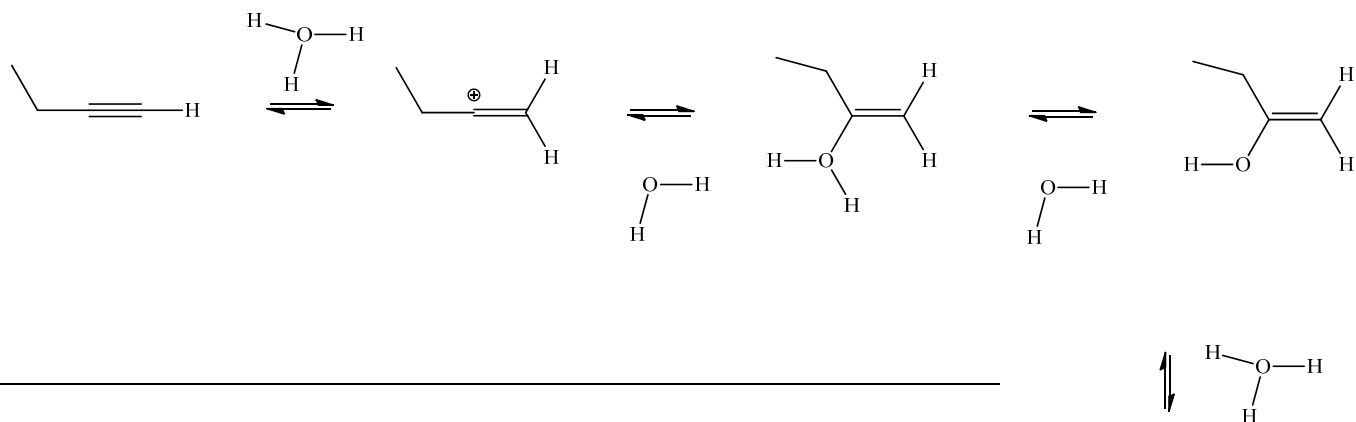


10. Indicate the major product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (30 pts)

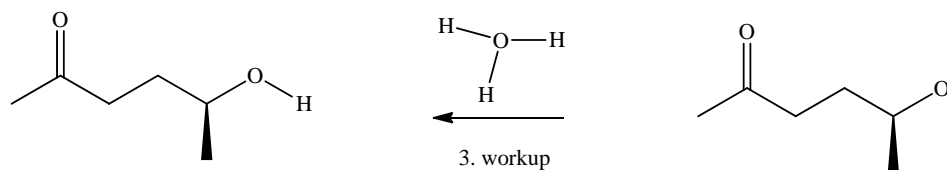
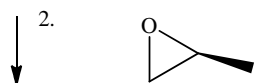
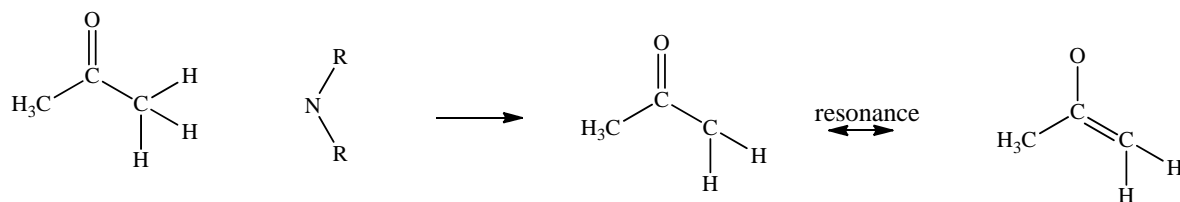


11. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations, one in acid and one in base. Assume all nonhydrogen atoms have full octets unless a positive charge is written by the atom. (30 pts)

a.



b.



*The highest result of education is tolerance. - Helen Keller*