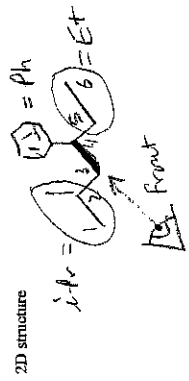




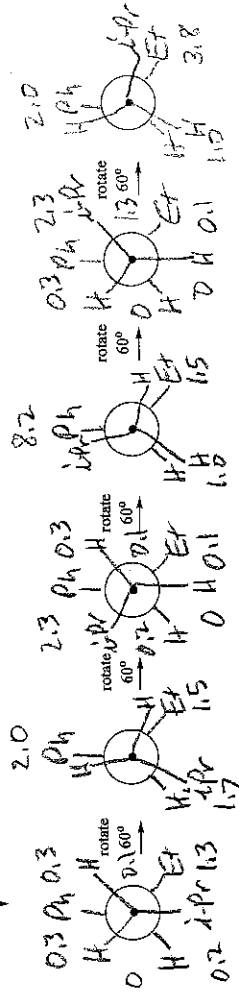
4. Use a Newman projection of the C3→C4 bond of 2-methyl-4-phenylhexane. Show the most stable conformation first. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. What are the relative percents of the most stable versus least stable 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. (25 pts)

$\frac{-\Delta G}{RT} = \ln K$   
 $K = 10^{2.303 \frac{-\Delta G}{RT}}$   
 $R = 2 \text{ cal/mol}\cdot\text{K}$   
 $T = 300 \text{ K}$

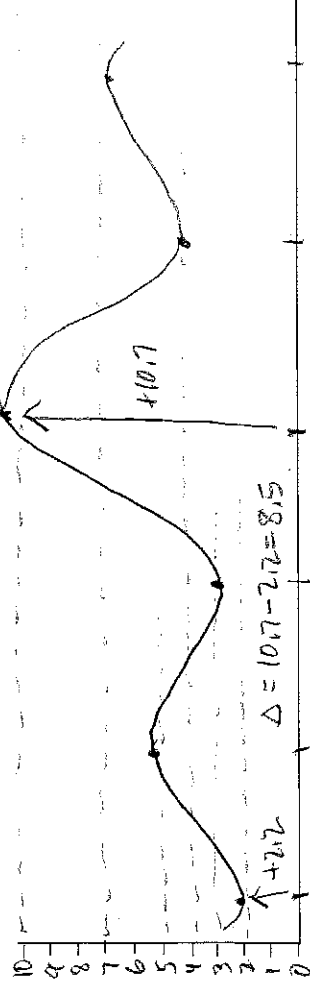
Approximate Eclipsing Energy Values (kcal/mole)		Approximate Gauche Energy Values (kcal/mole)									
H	Me	Et	i-Pr	t-Bu	Ph	H	Me	Et	i-Pr	t-Bu	Ph
0	0	0	0.1	0.2	0.3	0	0	0.1	0.2	0.5	0.3
1.4	2.5	2.7	3.0	3.5	3.3	0.1	0.9	1.1	1.5	2.7	1.4
1.5	2.7	3.3	3.8	10.0	4.5	0.2	1.1	1.3	2.0	3.8	2.3
1.7	3.0	3.8	7.8	13.0	8.2	0.5	2.7	3.0	3.8	8.2	4.1
2.0	3.3	4.5	8.2	14.1	8.7	0.3	1.4	1.7	2.3	4.1	2.7



most stable conformation

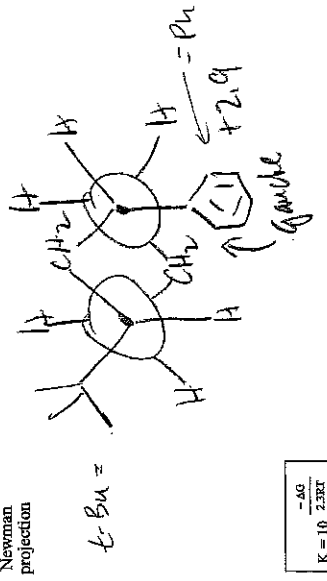
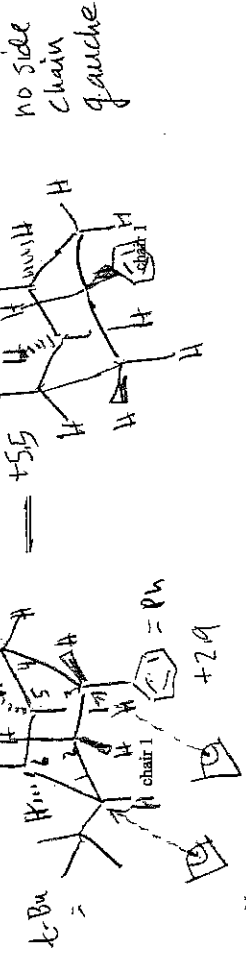


$\Delta H^{\ddagger} = 2.2$     $\Delta H^{\ddagger} = 5.2$     $\Delta H^{\ddagger} = 3.0$     $\Delta H^{\ddagger} = 10.7$     $\Delta H^{\ddagger} = 4.0$     $\Delta H^{\ddagger} = 6.8$



$K = 10^{\frac{-8500}{1380}} = 10^{-6.16} \approx \frac{0.000001}{1}$

3. Draw all possible chair conformations of trans-1-t-butyl-3-phenylcyclohexane. Draw C1 at the left-most side and number C2 towards the front. Show all axial and equatorial groups. Draw the most stable conformation first. Provide a reason for your choice. Draw a Newman projection of the more stable conformation using the C1→C2 and C3→C4 bonds to sight along. Point out any gauche interactions shown in your Newman projection. The axial energy of a t-butyl group is 5.5 kcal/mole and 2.9 kcal for a phenyl group. The gauche energy of phenyl/t-butyl is listed in a table on the next page, if necessary. What is the difference in energy between the chair conformations? What are the relative percents of each conformation? Show your work. Sketch an energy diagram that shows how the energy changes with the conformational changes. (25 pts)

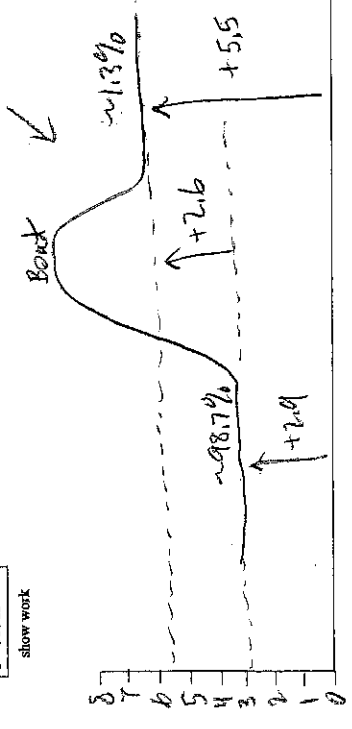


$\frac{-\Delta G}{RT} = \ln K$   
 $K = 10^{2.303 \frac{-\Delta G}{RT}}$   
 $R = 2 \text{ cal/mol}\cdot\text{K}$   
 $T = 300 \text{ K}$   
 show work

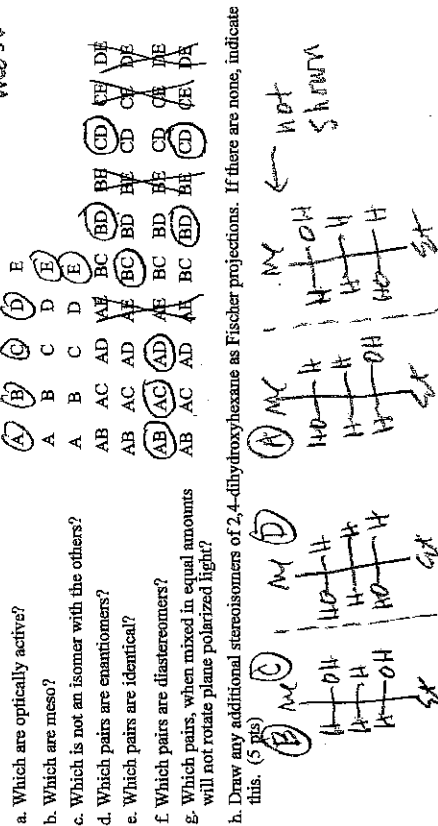
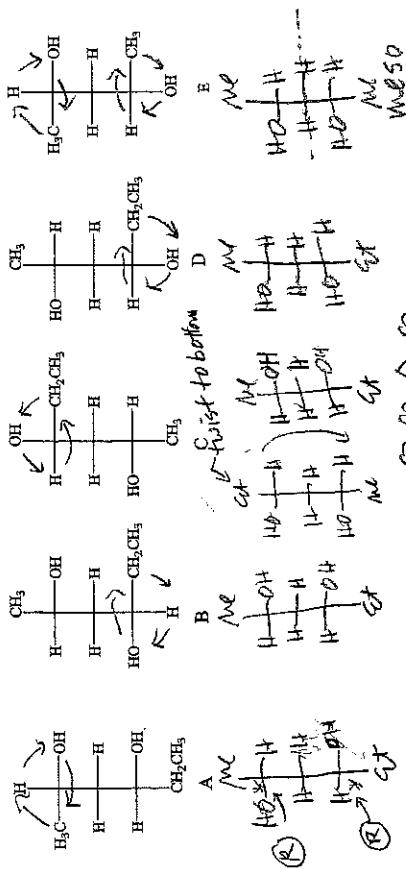
$K = 10^{\frac{-2600}{1380}} = 10^{-1.88}$

$\frac{\text{product}}{\text{reactant}} = \frac{0.013}{1}$

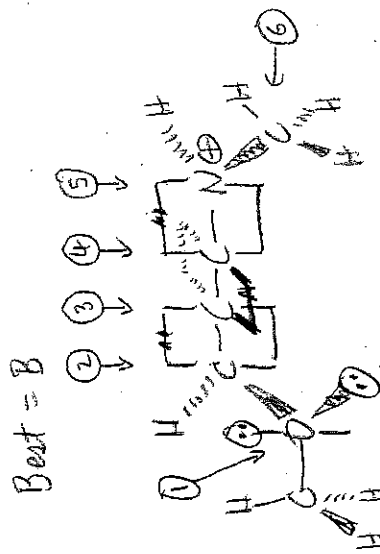
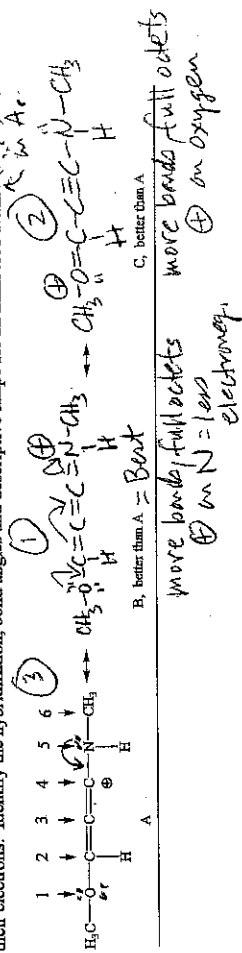
$\% \text{ prod} = \frac{0.013}{1.013} \times 100 \approx 1.3\%$



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)



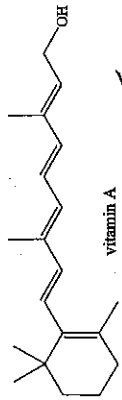
6. Draw two additional "better" 2D resonance structures of the given structure. Which structure is best and why? Draw a 3D structure for the best resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals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



Use given structure A to fill in this table.

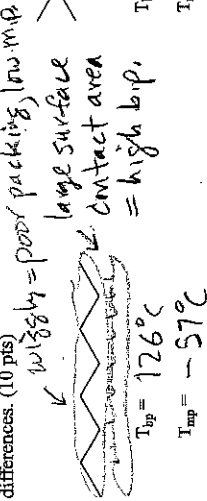
Atom	Shape	Hybridization	Bond Angles	# sigma bonds	# pi bonds	# lone pairs
1	trig. planar	sp <sup>2</sup>	120°	2	0	2
2	trig. planar	sp <sup>2</sup>	120°	3	1	0
3	linear	sp	180°	2	2	0
4	linear	sp	180°	2	1	0
5	trig. planar	sp <sup>2</sup>	120°	3	0	0
6	tetrahedral	sp <sup>3</sup>	109°	4	0	0

7. The structures of vitamin A and vitamin C are shown below. If they are taken in large daily amounts one is toxic and one is not. Explain why this observation is reasonable? (10 pts)



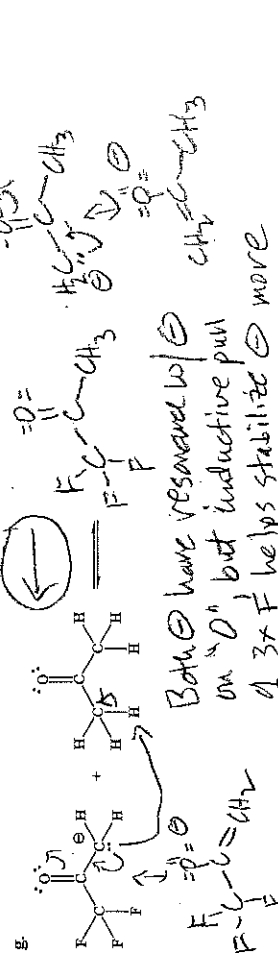
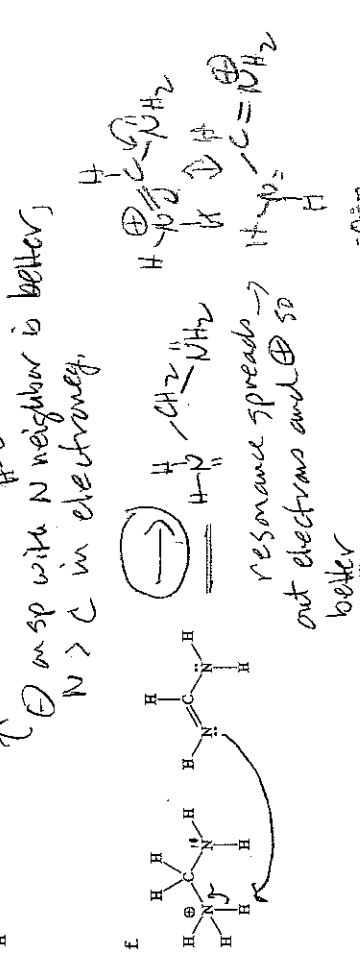
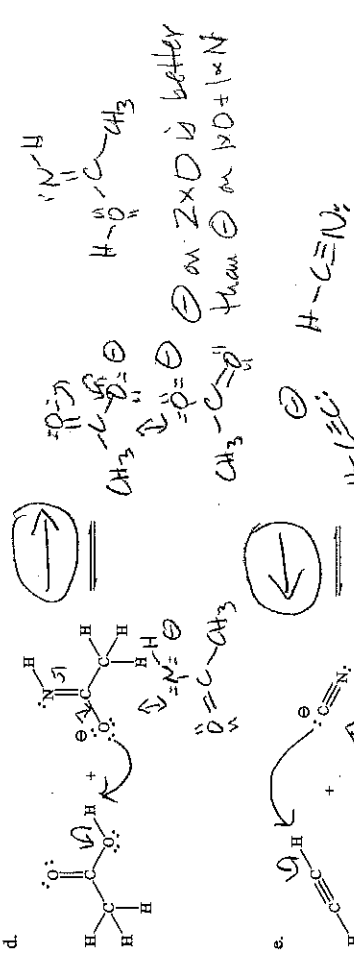
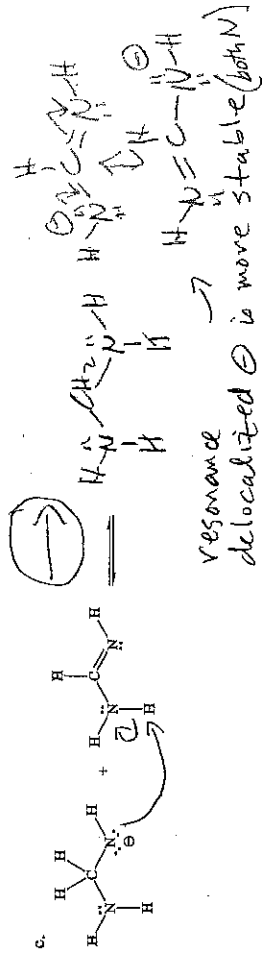
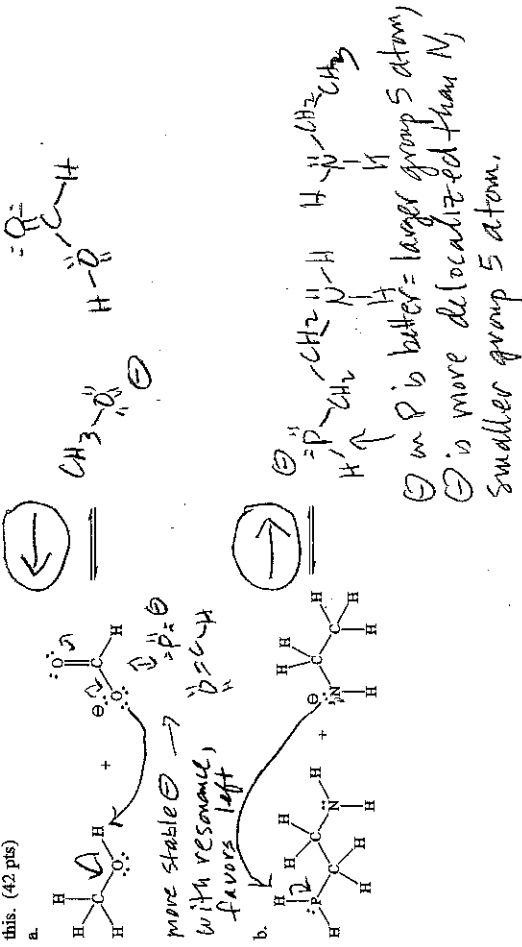
hydrophobic, dissolved in membranes, trapped in body, levels build up to toxic amounts

b. The melting points and boiling points for the following two compounds are:  $-57^{\circ}\text{C}$ ,  $106^{\circ}\text{C}$  and  $10^{\circ}\text{C}$ ,  $106^{\circ}\text{C}$  and  $126^{\circ}\text{C}$ . Match those temperatures with the structures below and provide a possible explanation for the differences. (10 pts)



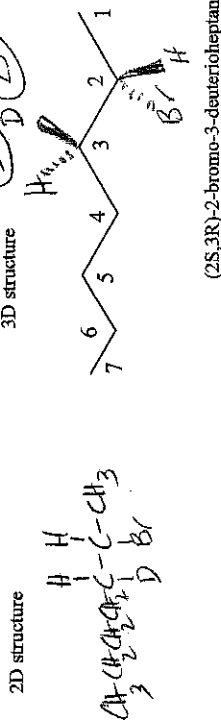
Very H<sub>2</sub>O soluble, washes out of body in urine, no buildup

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". Very briefly explain your reasoning. If resonance is important, show this. (42 pts)

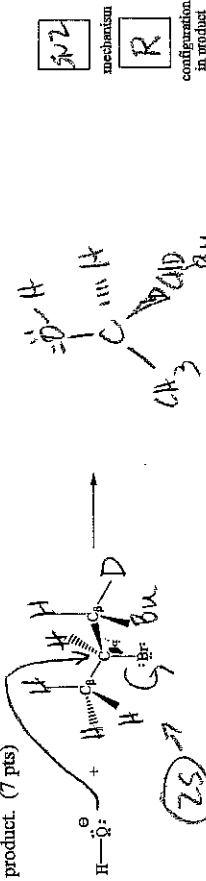


9. Use (2S,3R)-2-bromo-3-deuterioheptane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants 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)

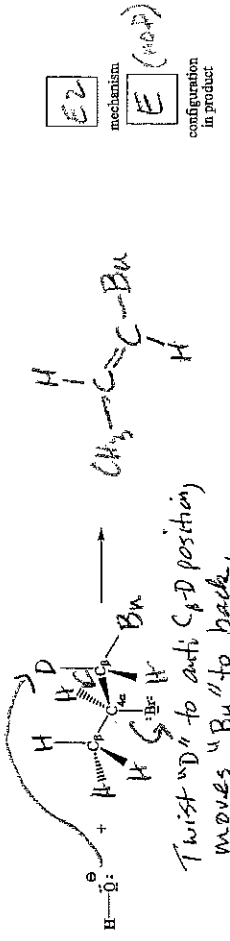
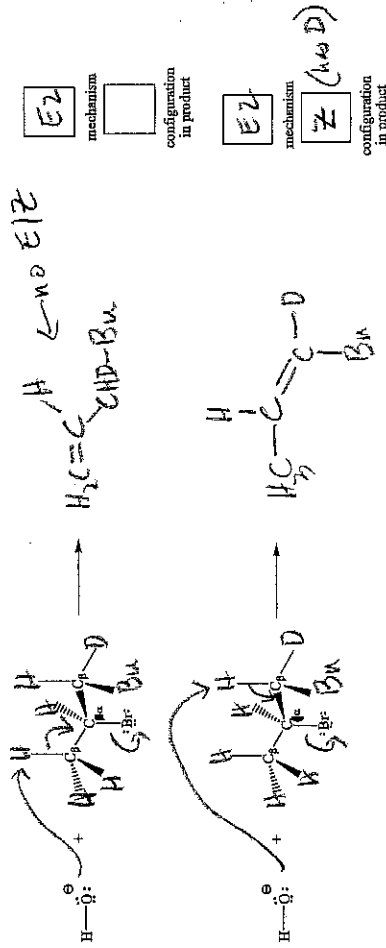
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



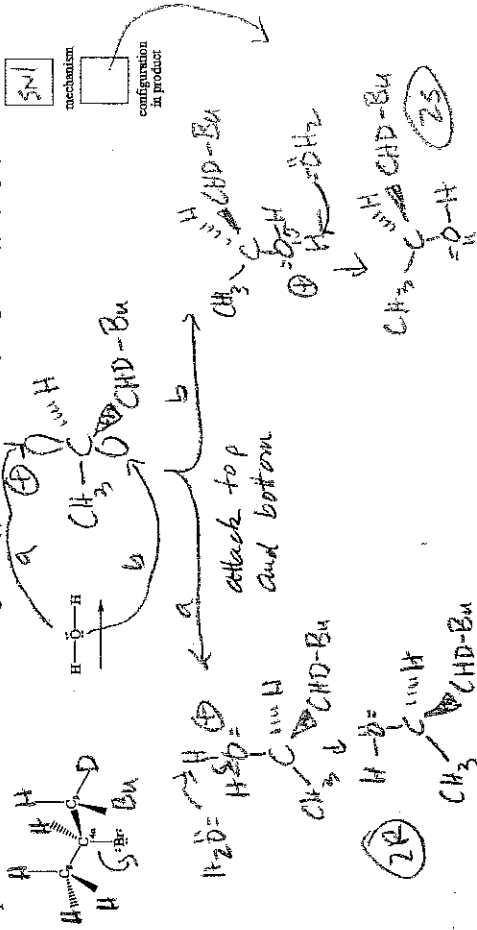
b. Show the  $S_N1$  reaction (what kind?), indicate the absolute configuration(s) of the  $C_2$  center in the product. (7 pts)



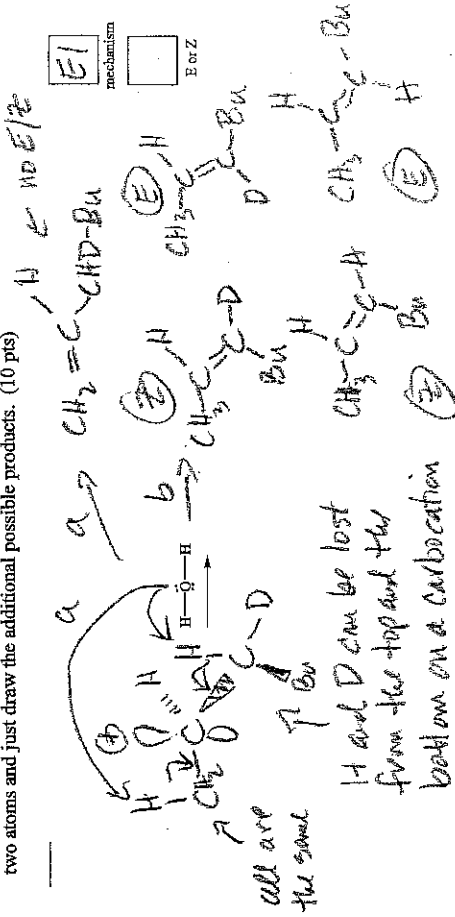
c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (13 pts)



d. Show the  $S_N1$  reaction (what kind?). You can use one intermediate to show all possible mechanistic  $S_N1$  possibilities. Indicate absolute configuration(s) of the  $C_2$  center in your product(s). (10 pts)

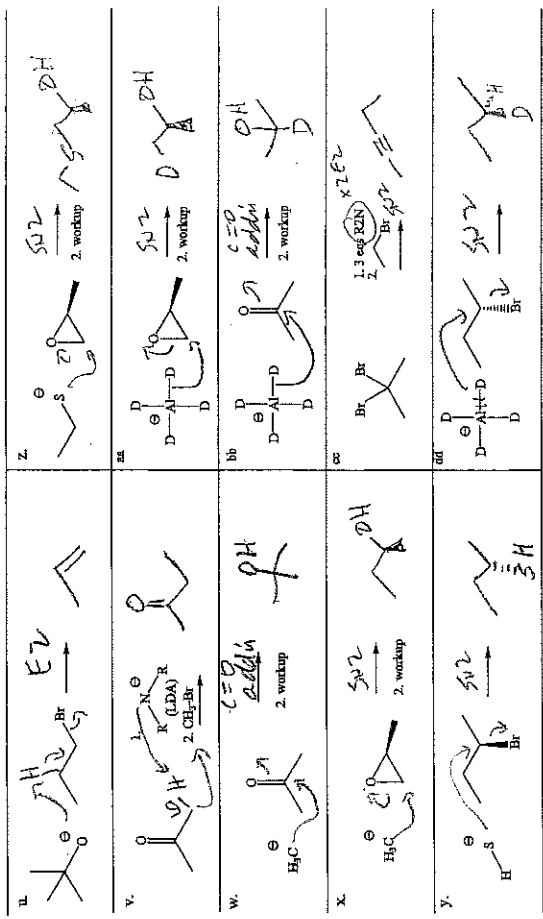
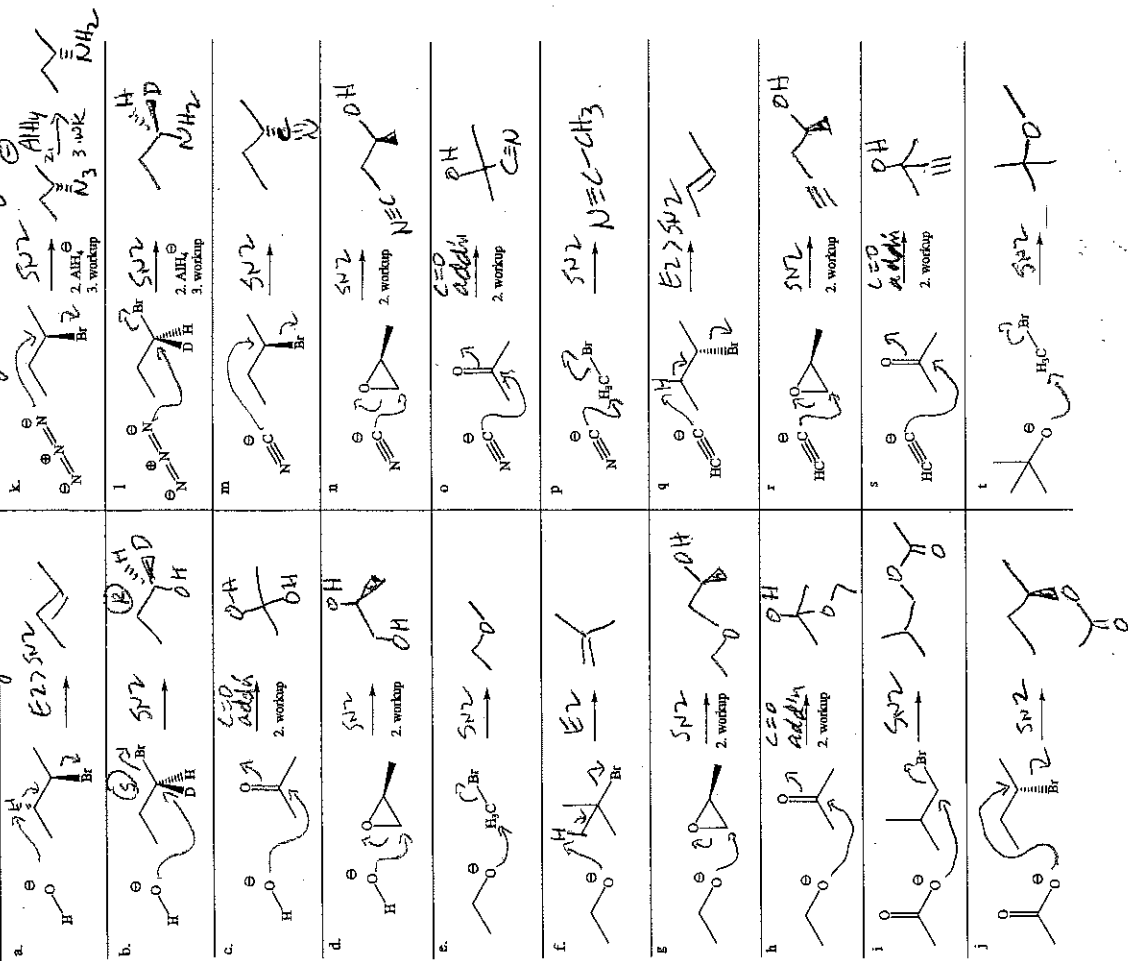


e. Redraw the intermediate used in 8d above to show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism for those two atoms and just draw the additional possible products. (10 pts)



10. Indicate the major product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (45 pts)

*Arrows are added to give hints about mechs. They are NOT required*



11. Using the given formula,  $C_8H_{15}Br$ , draw an isomer which satisfies each given statement. Do not use any given isomer more than one time. If stereochemistry is important make sure you draw your structure so that its three dimensional nature is clearly indicated. Point out the feature of your structure that makes it consistent with the given statement. How many degrees of unsaturation are there? (show work) (20 pts)

degrees of unsaturation =  $10 - \frac{2(8) + 2}{2} = 10 - 10 = 0$  (1 bond or ring)

