

Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. 2D Lewis structure (large structure with possible formal charge)	20	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	25	
4. Newman Projections, Conformational Energies	25	
5. Stereochemical Analysis	25	
6. 3D Structure, Resonance, Hybridization, Angles, Shapes, etc.	30	
7. Forces of Interaction and Physical Properties	20	
8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge (7)	42	
9. S _N /E Mechanisms, with all of the details (templates provided)	43	
10. Various Nucleophile/Electrophile Reactions, Predict the Products (30 reactions, 1.5 points each)	45	
11. Predicting RX compounds in S _N and E reactions, including stereochem details	20	
12. Fill in Arrow-Pushing Mechanistic Details, curved arrows, lone pairs, formal charge, one in acid and one in base	40	
Total	365	

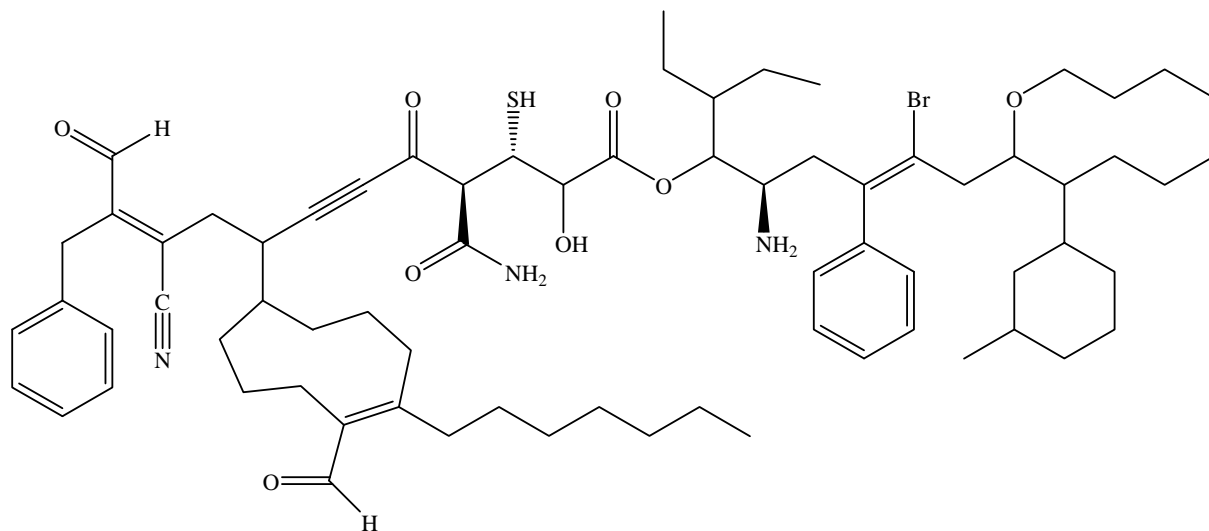
Points from Midterm Material: 175 points

Points from Newer Material: 190 points

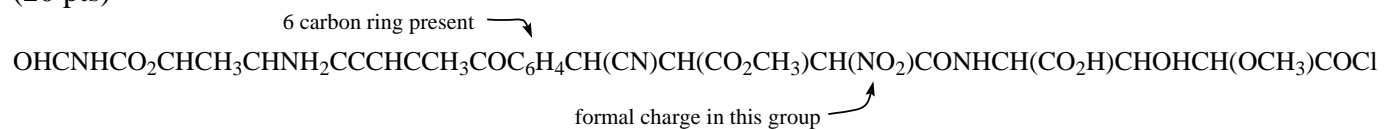
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron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

The best preparation for tomorrow is doing your best today. H. Jackson Brown

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



2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)



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→C₆ 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)



chair 1

chair 1

Newman
projection

$\frac{-\Delta G}{2.3RT}$
$K = 10$
$R = 2 \text{ cal/mol-K}$
$T = 300 \text{ K}$

show work



4. Use a Newman projection of the C4→C3 bond of 3-phenyl-2,4,4-trimethylhexane. **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)

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

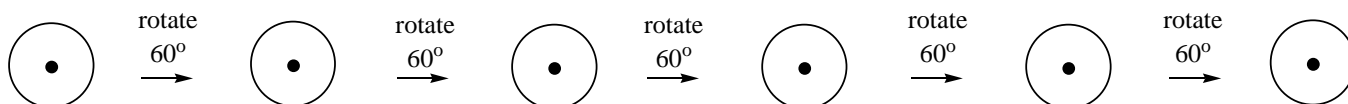
R = 2 cal/mol-K
T = 300 K

2D structure

Approximate Eclipsing Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.7	3.0	2.0
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	3.8	10.0	4.5
i-Pr	1.7	3.0	3.8	7.8	13.0	8.2
t-Bu	3.0	8.5	10.0	13.0	23.0	14.1
Ph	2.0	3.3	4.5	8.2	14.1	8.7

Approximate Gauche Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.3
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.3	3.0	1.7
i-Pr	0.2	1.1	1.3	2.0	3.8	2.3
t-Bu	0.5	2.7	3.0	3.8	8.2	4.1
Ph	0.3	1.4	1.7	2.3	4.1	2.7

most stable conformation
↓



$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

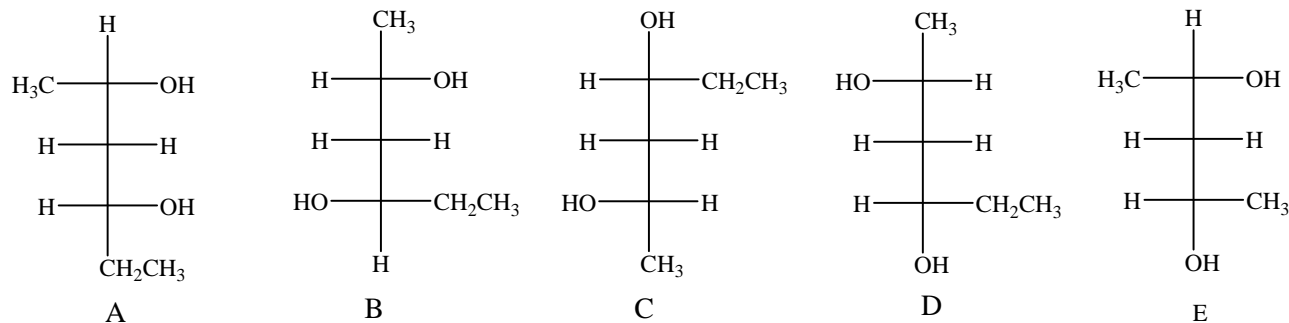
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

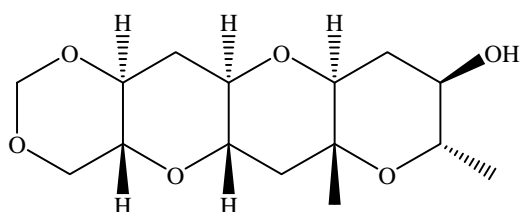


5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (25 pts)



- | | |
|---|---|
| a. 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 additional stereoisomers of 2,4-dihydroxyhexane as Fischer projections. If there are none, indicate this. (5 pts) | |

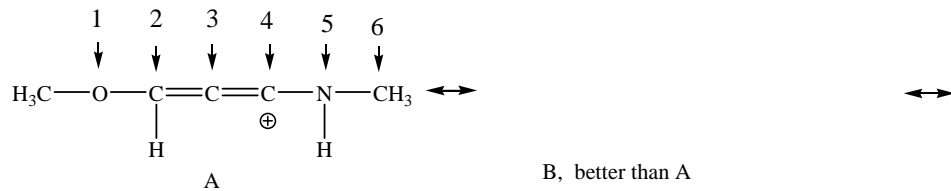
- i. A recent Organic Letters paper presented an approach for making 'ladder ethers' found in toxins common among dinoflagellate algae that cause toxic red tides (Org. Lett. p.774, 2015). Circle all chiral centers and any other stereochemical features, and calculate the maximum number of stereoisomers possible. (5 pts)



Number of stereogenic centers = _____

Maximum number of stereoisomers = _____

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. **Using structure A**, identify the hybridization, bond angles and descriptive shape for all numbered atoms. (30 pts)



Atom	Shape	Hybridization	Bond Angles	#σ bonds	# π bonds	# lone pairs
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1

2

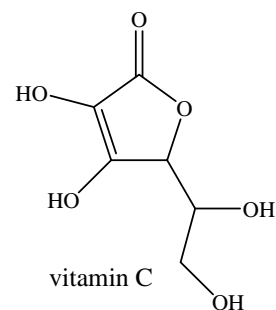
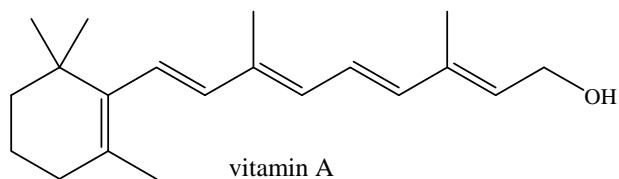
3

4

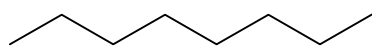
5

6

7. a. 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)

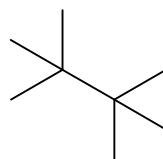


- b. The melting points and boiling points for the following two compounds are: -57°C , 101°C , 106°C and 126°C . Match those temperatures with the structures below and provide a possible explanation for the differences. (10 pts)



$T_{\text{bp}} =$

$T_{\text{mp}} =$

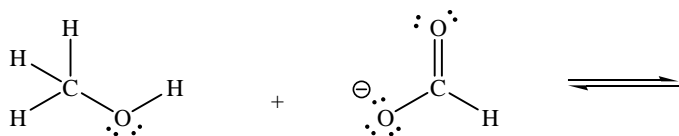


$T_{\text{bp}} =$

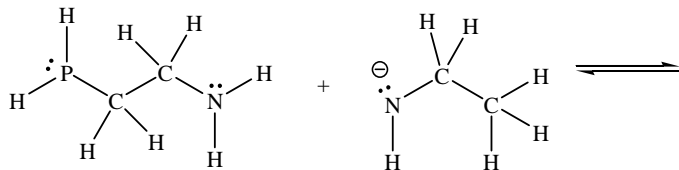
$T_{\text{mp}} =$

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)

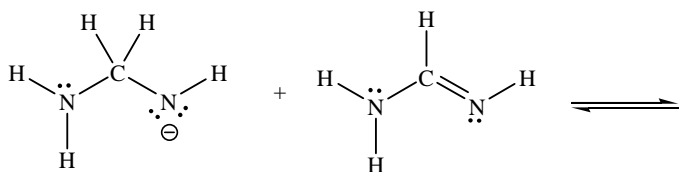
a.



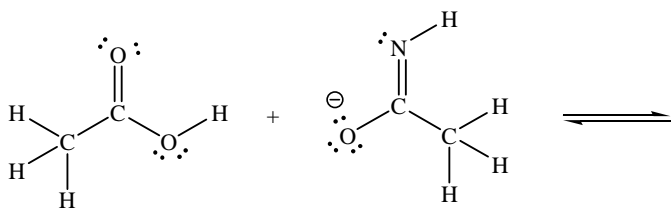
b.



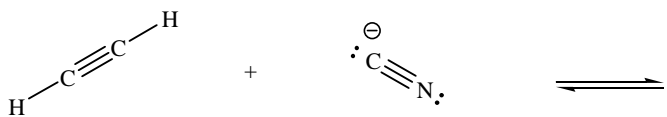
c.



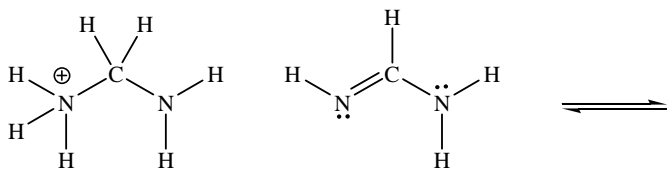
d.



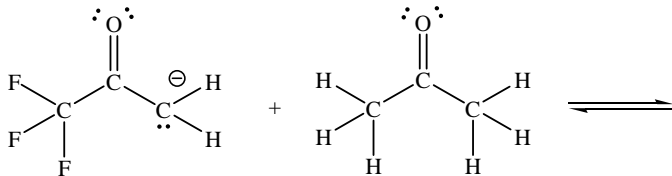
e.



f.



g.

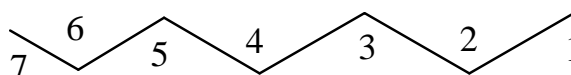


9. Use (2*S*,3*R*)-2-bromo-3-deuterioheptane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If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

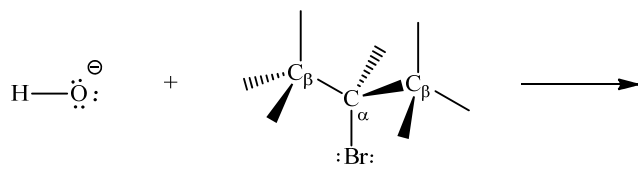
2D structure

3D structure



(2*S*,3*R*)-2-bromo-3-deuterioheptane

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

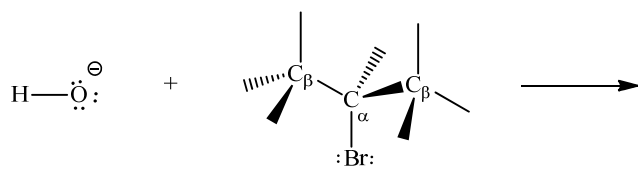


mechanism



configuration
in product

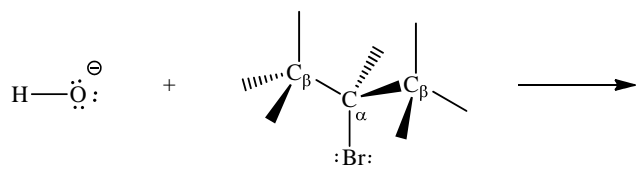
c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (13 pts)



mechanism



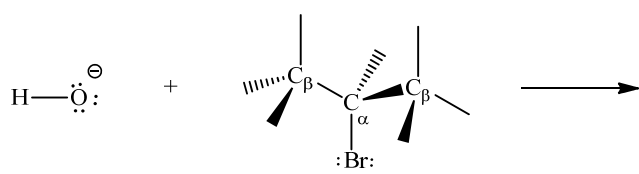
configuration
in product



mechanism



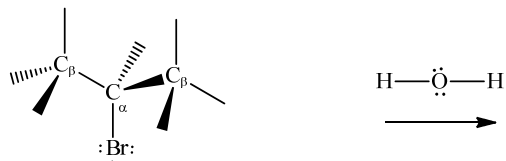
configuration
in product



mechanism

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_{α} center in your product(s). (10 pts)



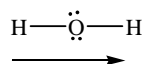
mechanism

configuration
in product

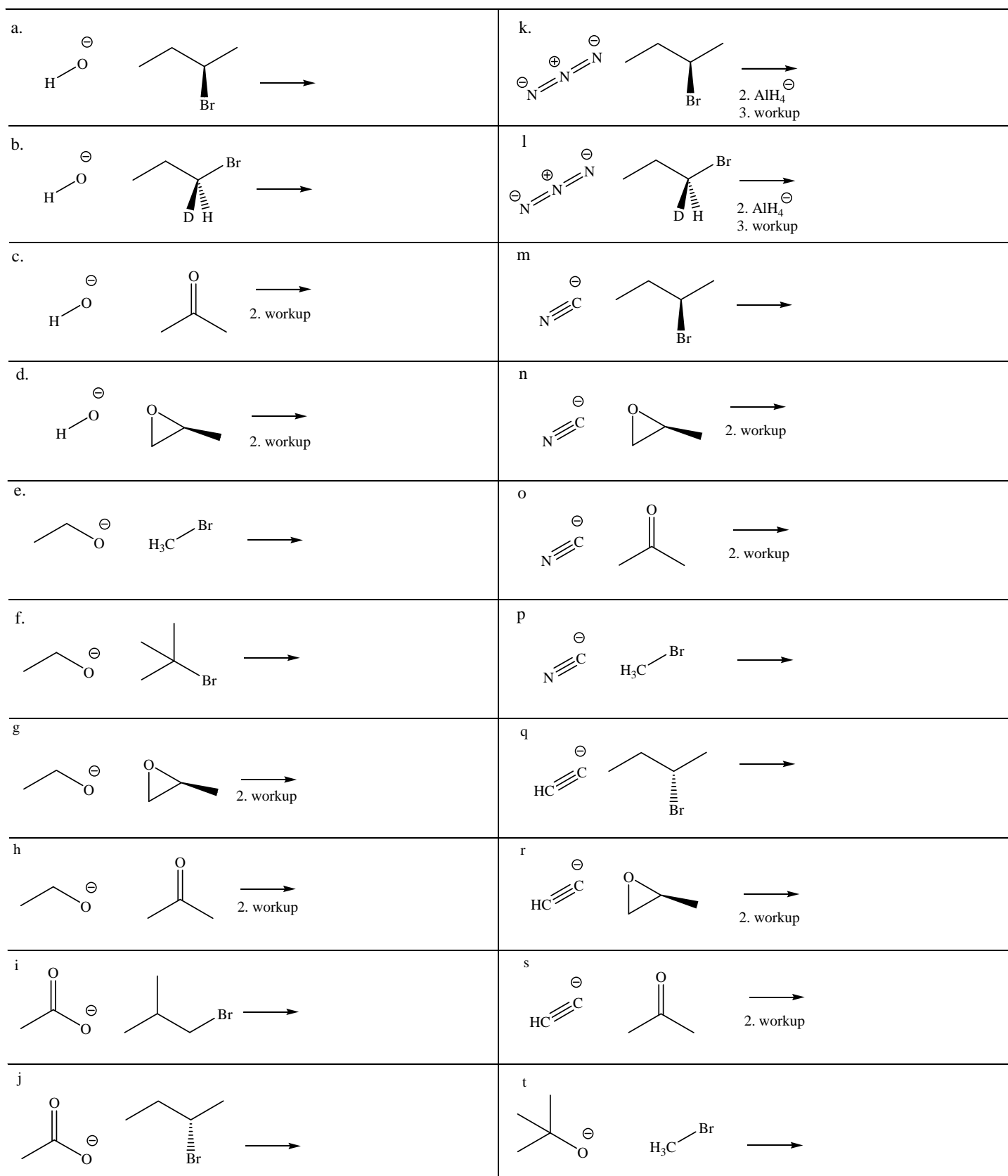
e. Redraw the intermediate used in 8d above to show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism for those two atoms and just draw the additional possible products. (10 pts)

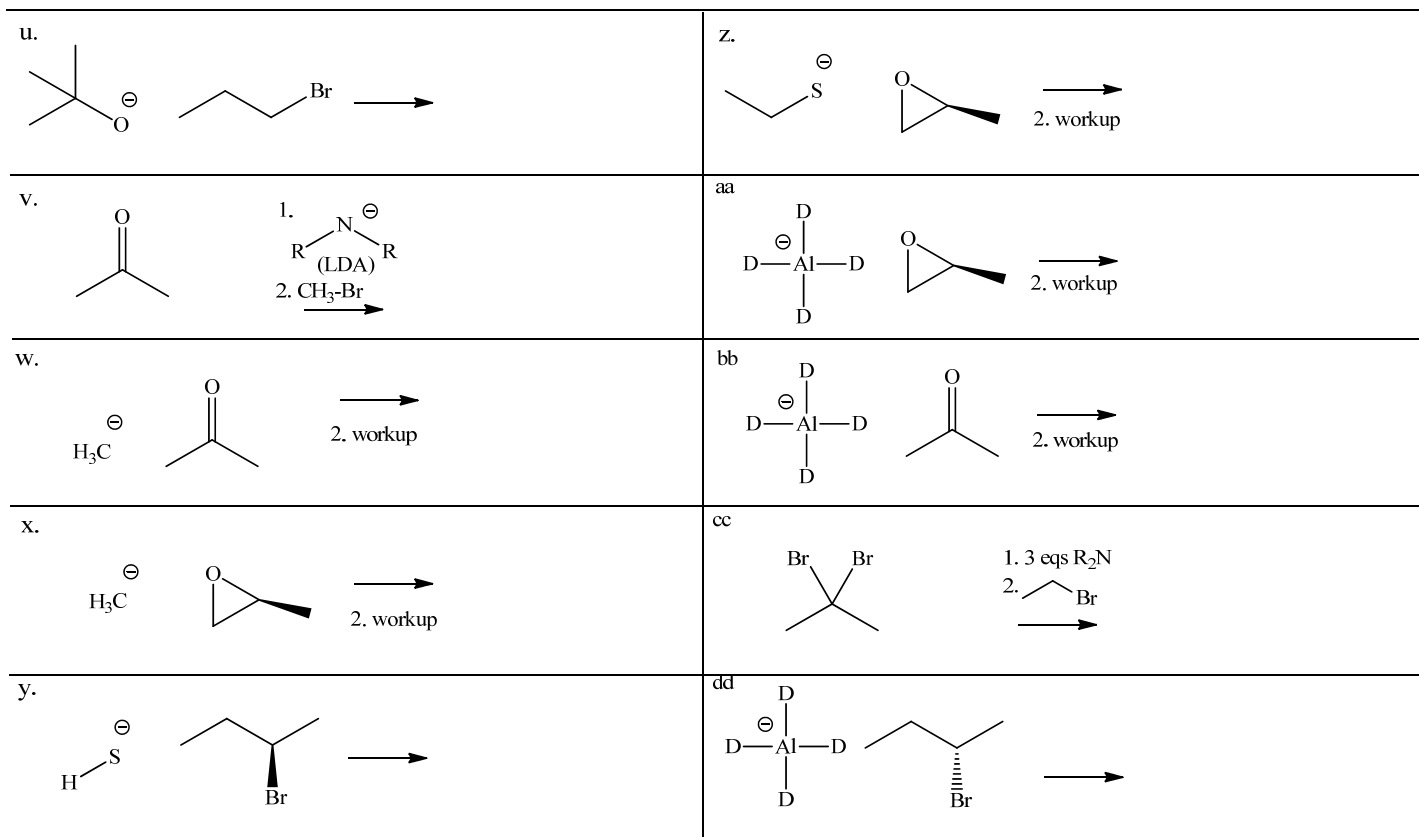
mechanism

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) (45 pts)





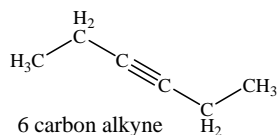
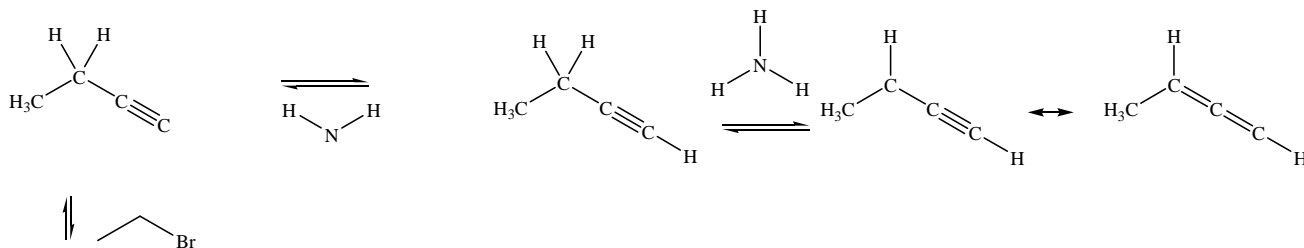
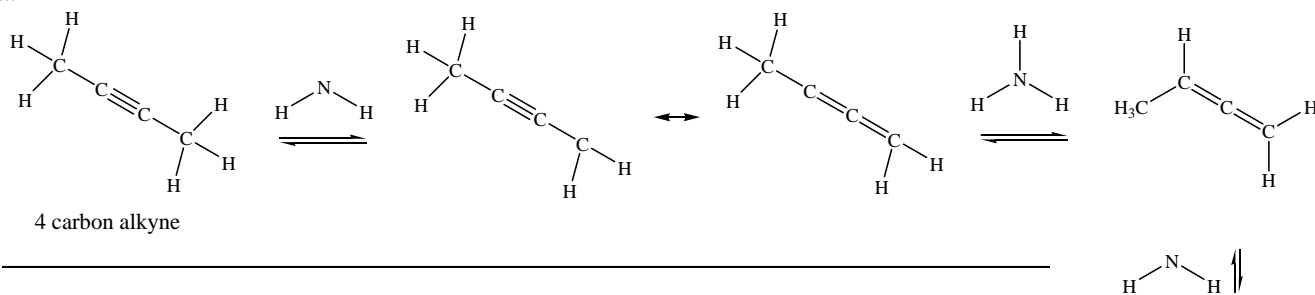
11. Using the given formula, $C_8H_{15}Br$, draw an isomer which satisfies each given statement. **Do not use any given isomer more than one time.** If stereochemistry is important make sure you draw your structure so that its three dimensional nature is clearly indicated. Point out the feature of your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

degrees of unsaturation = _____ (2 pts)

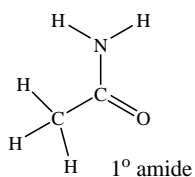
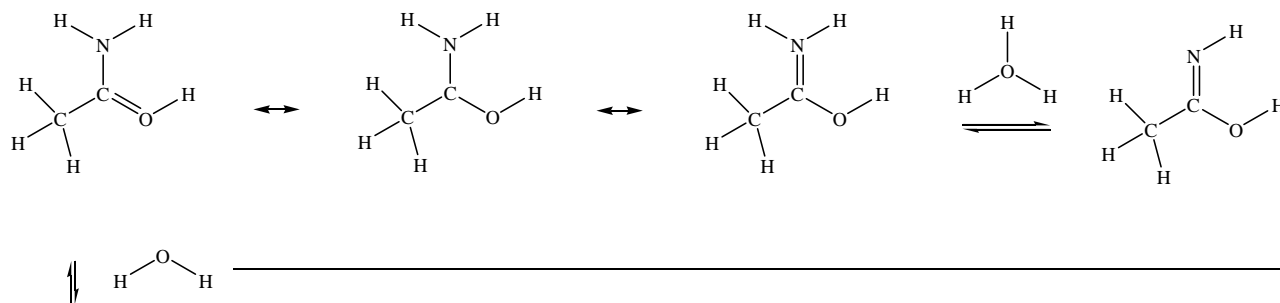
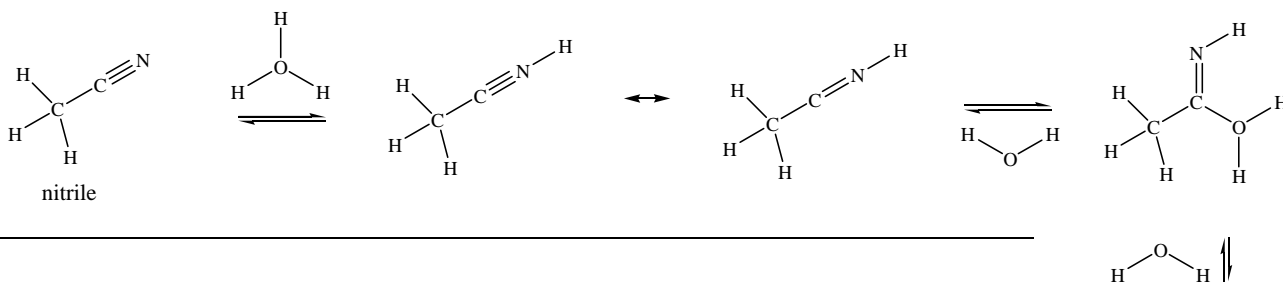
a. Undergoes E2 reaction, but not S_N2 reaction in HO^-/H_2O . Show a possible product too. (4 pts)	b. Does not react by S_N1 or E1 reaction. (2 pts)
c. Can reasonably react by all four mechanisms (S_N2 , E2, S_N1 , E1). (2 pts)	d. Undergoes fast S_N1 reaction with H_2O . Show the product(s) too. (4 pts)
e. Undergoes fast S_N2 reaction with HO^-/H_2O . Show the product(s) too. (4 pts)	f. Write a possible E1 product from part d. (2 pts)

12. 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. Those details were deliberately left out. (40 pts)

a.



b.



The secret of getting ahead is getting started. Mark Twain