Chem 201 Final
Winter, 2018 Name _____
Beauchamp

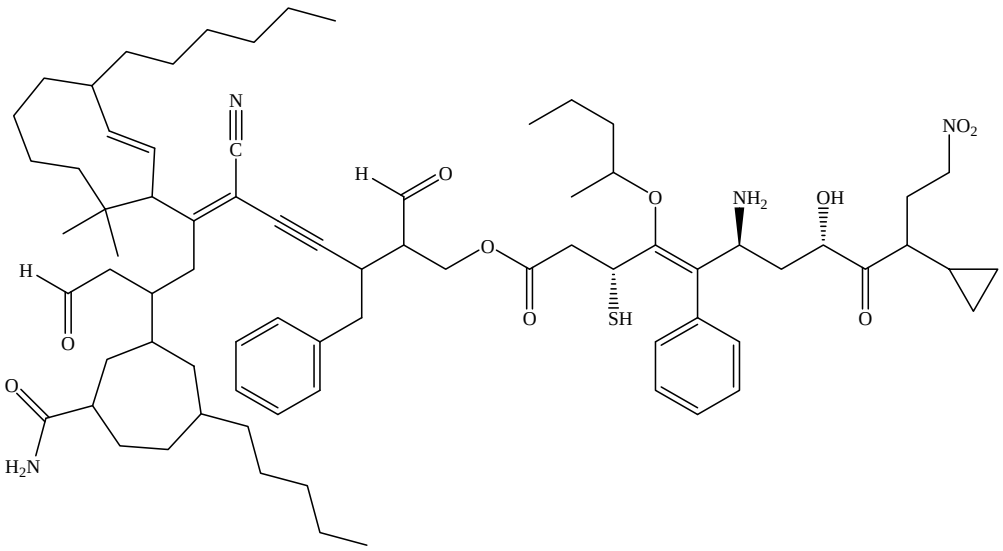
Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Lewis Structures, Resonance, Formal Charge	18	
3. Cyclohexane Conformations, 2 substituents, Newman Projections, Relative Energies	30	
4. Newman Projections, Conformational Energies, K_{eq} Calculation	30	
5. Stereochemical Analysis	30	
6. 2D Resonance Structures, 3D Structure, Hybridization, Angles, Shapes	30	
7. Dipole Moments and Inductive versus Resonance Effects	15	
8. Quantitative Acid/Base Equation, Identify Conjugate Acid and Base and Calculate $K_{equilibrium}$, Supply Curved Arrows.	15	
9. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge, Qualitative Equilibrium (7)	35	
10. S_N/E 3D Mechanisms, with all of the details, Templates Provided	43	
11. Various Reactions, predict the products (20 reactions)	30	
12. Fill in all mechanistic details, curved arrows, lone pairs, formal charge,	15	
13. SN/E Mechanism, Carbocation Reactions	15	
14. Free Radical Substitution Problem – Predict Possible Products, How Much, Stereochemistry and Provide a Mechanism For Major Product	30	
Total	366	

Premidterm material = 183
Postmidterm material = 193

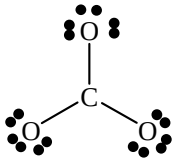
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron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

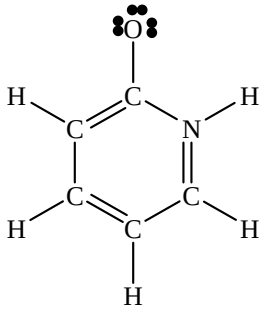
"Change your thoughts and you change your world." – Norman Vincent Peale

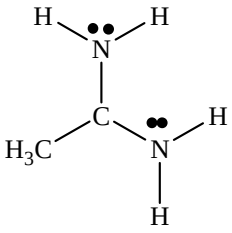
1. Provide an acceptable name for the following molecule. (30 pts)



2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw a best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or that they are equivalent. (18 pts)







3. Draw all possible chair conformations of trans-1- t-butyl-3-ethylcyclohexane. Make the left most ring carbon C1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projections of the most stable conformation using the $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a t-butyl group is 5.5 kcal/mole and the axial energy of an ethyl group is 1.8 kcal/mole and a t-butyl/ethyl gauche interaction is 3.0 kcal/mole, what is the ratio of the two conformations at equilibrium? Show your work. Sketch an energy diagram that shows how the energy changes (lower to higher) with the conformational changes and estimate the ratio of the two conformations at equilibrium. (30 pts)

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

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

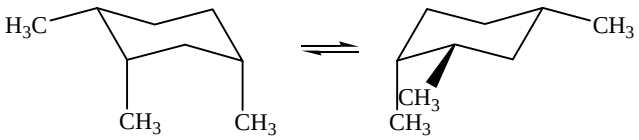
(15 pts)

chair 1 ⇌ chair 2

b. Newman projection ($C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$) – most stable, point out any gauche interactions with the substituent(s)

c. Energy diagram (lower to higher) and relative percents (K_{eq} = ?) (5 pts)

d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq}. (Assume R = 2 cal/mol-K and T = 300 K.) Use energy values provided in the box. Show your work. (5 pts)



One axial methyl group = +1.7 kcal/mole,
Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
Three axial methyl groups, on the same side = +12.9 kcal/mole and
1,2 gauche methyl groups = 0.8 kcal/mole.

ΔH ≈

K_{eq} ≈

4. Use a Newman projection of the C4→C3 bond of 2-methyl-3-phenylhexane 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. Calculate a ratio of least stable to most stable based on ΔH values. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection, then decide your line of sight. (25 pts)

2D structure (3 pts)

Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.0	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.0	10.0	3.8	3.1
i-Pr	1.6	3.0	4.0	7.8	13.0	8.1	3.6
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2
Br	1.6	2.8	3.1	3.6	9.1	4.2	3.0

$\Delta G \approx \Delta H$

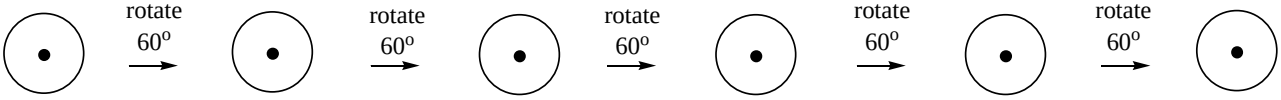
$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

Approximate Gauche Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.6	3.0	1.5	1.3
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1	1.6
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9	3.3
Ph	0.2	1.4	1.5	2.1	3.9	2.3	1.9
Br	0.1	1.0	1.3	1.6	3.3	1.9	1.1

most stable conformation

(14 pts)

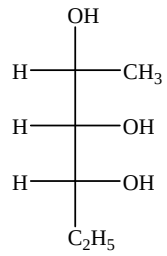


$\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$

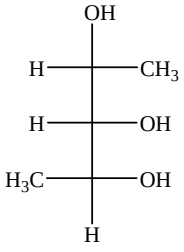
(4 pts)

$K_{calculation}$ (4 pts)

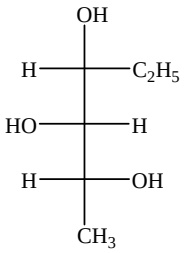
5. Use the following set of Fischer projections to answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (30 pts)



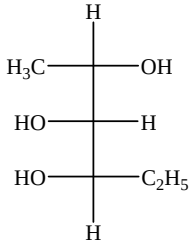
(3 pts)
A



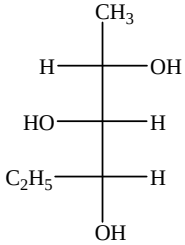
B



C



D



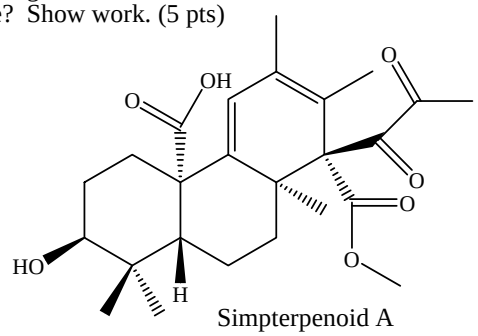
E

(17 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

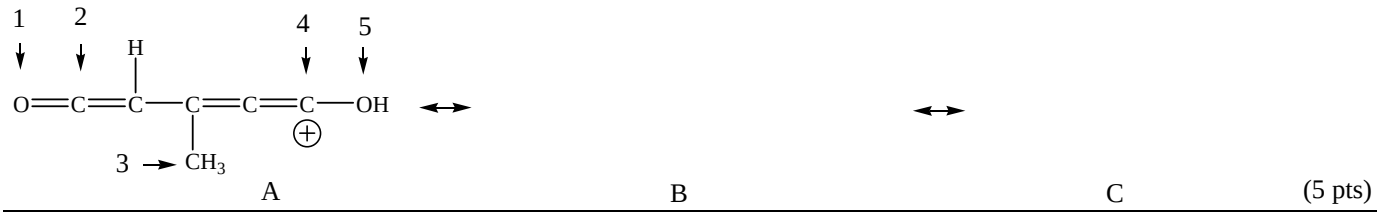
h. Draw any stereoisomers of hexan-2,3,4-triol as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)

i. In the most recent Organic Letters, 2018, 20, 1465-8, a new natural product was isolated, Simpterpenoid A, from a fungal source in the south China Sea. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)



Simpterpenoid A

6. Draw two additional "**better**" 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets except for + carbon. Add in any necessary lone pairs and use proper curved arrows. Which structure(s) is(are) 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 in the **<u>given</u>** structure. (30 pts)



(5 pts)

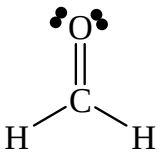
(15 pts)

Use the given (first) Lewis structure to answer this part.

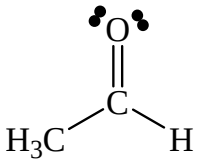
Atom	Shape	Hybridization	Bond Angles	#σ bonds	# π bonds	# lone pairs
1						
2						
3						
4						
5						

(10 pts)

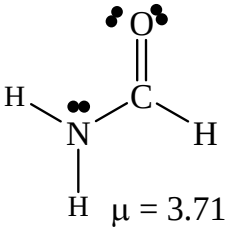
7. Explain what the following dipole moments suggest about inductive effects and resonance effects. You will need to draw additional structures to help your explanation. (15 pts)



μ = 2.3 D

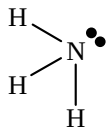


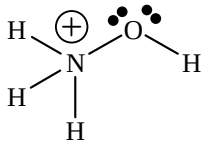
μ = 2.68 D

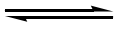


μ = 3.71 D

8. Only the reactant acid and base are drawn below. Decide which is which and draw a mechanism to show formation of the conjugate base and acid. The two acids have pK_a's of 10 and 8 (K_a values are 10^{-10} and 10^{-8}). Match the K_a values with the proper acid, write a $K_{equilibrium}$ expression and calculate a quantitative $K_{equlibrium}$ value for the reaction. Show your work. Provide an explanation for your value of $K_{equilibrium}$. (15 pts)



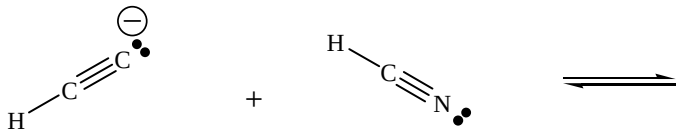




$K_{equilibrium}$ =

9. 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. (35 pts)

a.



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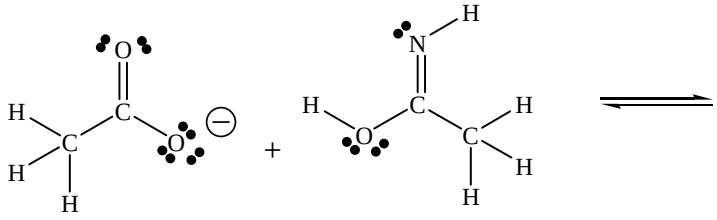
b.



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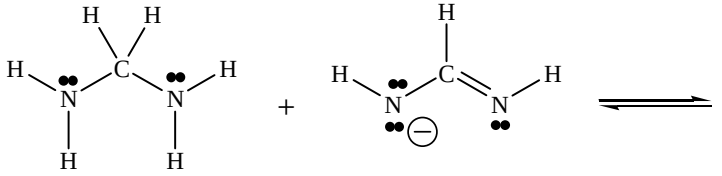
c.



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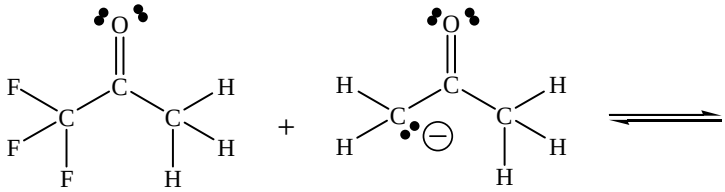
d.



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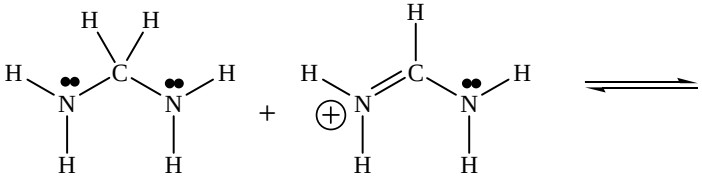
e.



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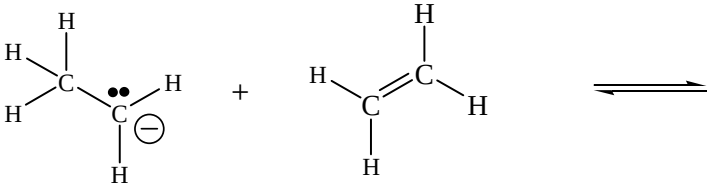
f.



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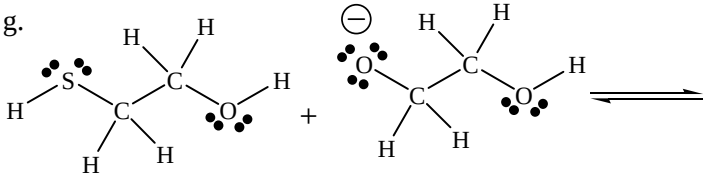
g.

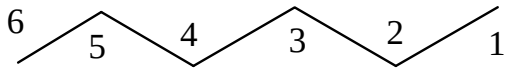


10. Use (2R,3R)-3-bromo-2-deuteriohexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants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

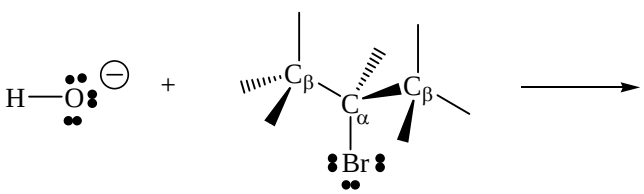
2D structure

3D structure



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

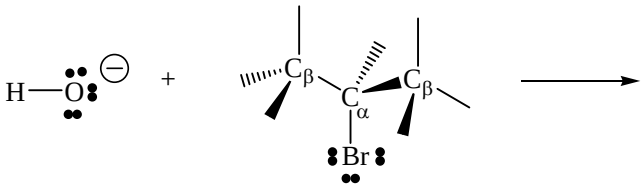
b. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (7 pts)



mechanism

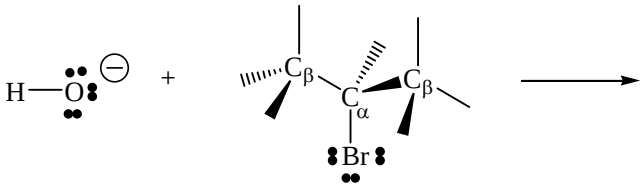
configuration in product

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



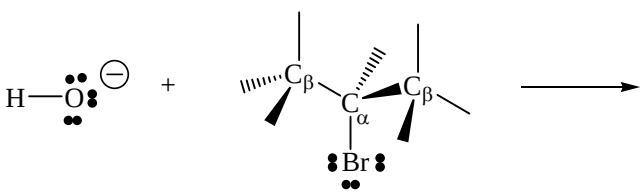
mechanism

configuration in product



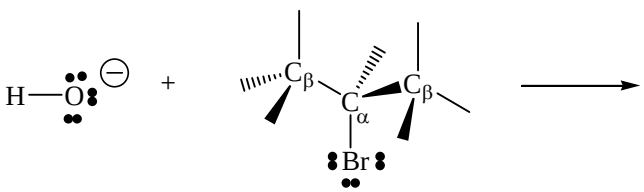
mechanism

configuration in product



mechanism

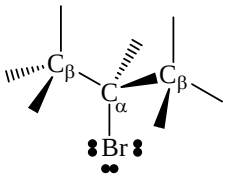
configuration in product

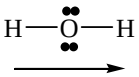


mechanism

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)

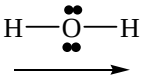




mechanism

configuration in product

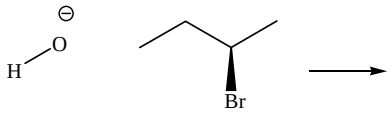
e. Redraw the intermediate used in 8d above to show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show the possibilities for a single hydrogen atom and just draw the additional possible "E" products. (10 pts)

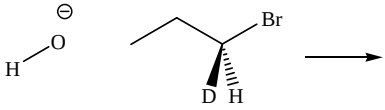


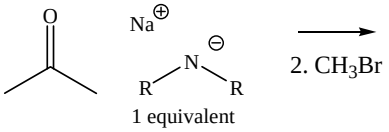
mechanism

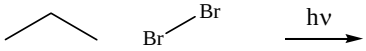
E or Z

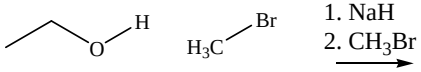
11. Indicate the **major** product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (30 pts)

a. 

b. 

c. 

d. 

e. 

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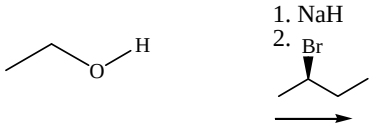
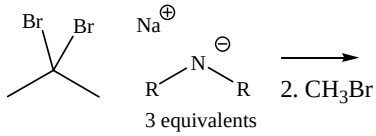
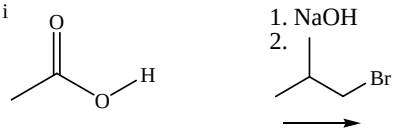
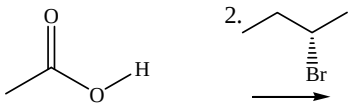
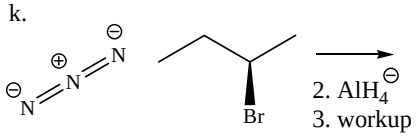
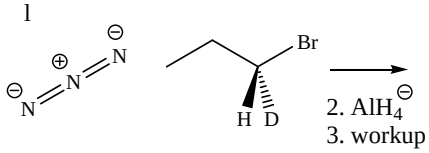
g. 

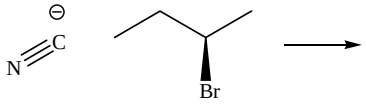
h. 

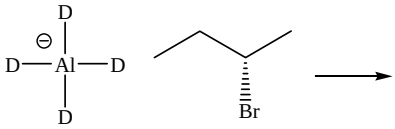
i. 

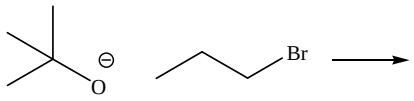
j. 

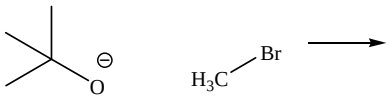
k. 

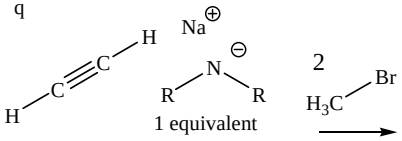
l. 

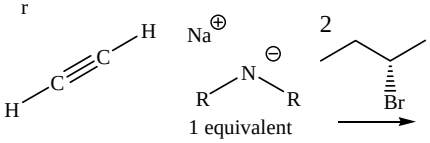
m. 

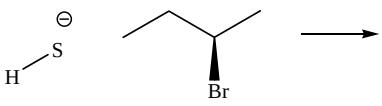
n. 

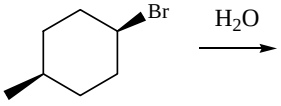
o. 

p. 

q. 

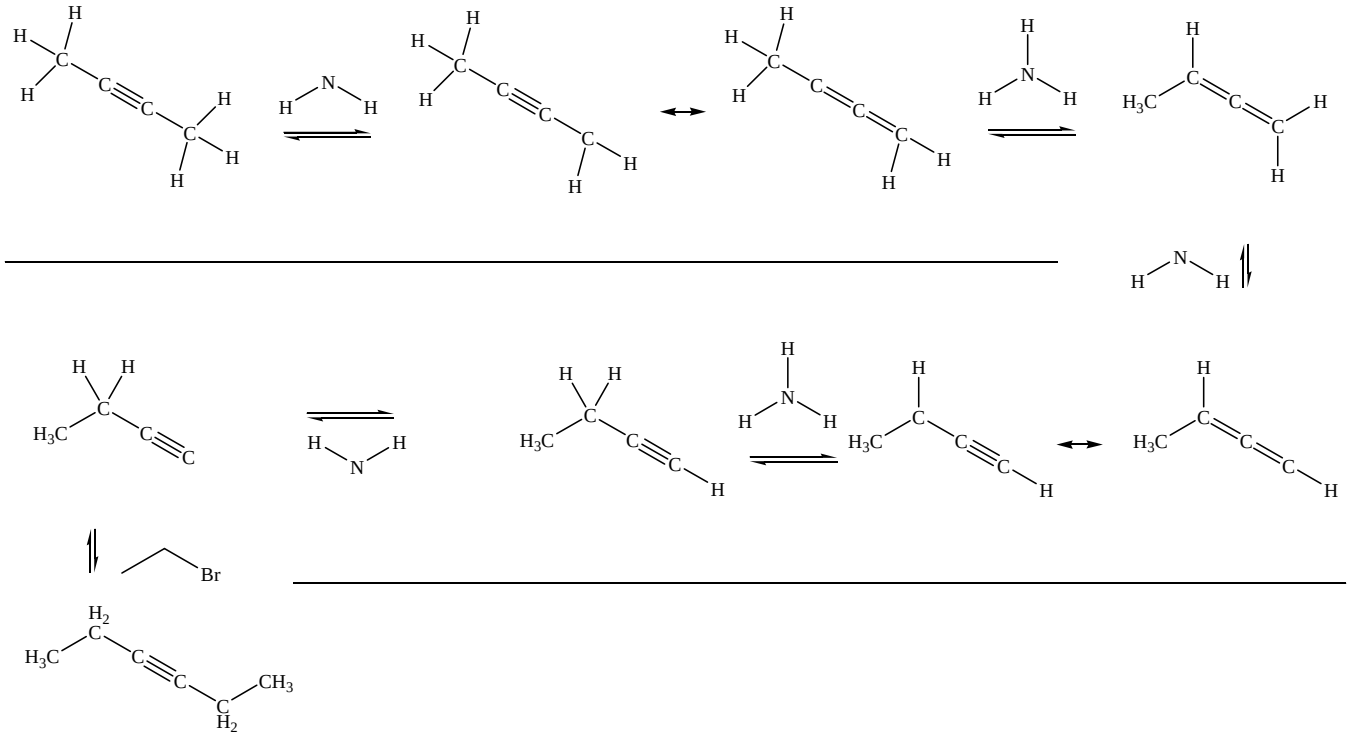
r. 

s. 

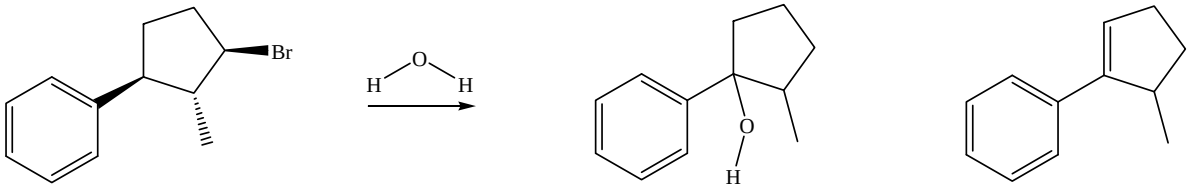
t. 

12. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformation. Assume all nonhydrogen atoms have full octets unless a positive charge is written by a carbon atom. (15 pts)

a.



13. Provide a complete arrow-pushing mechanism for the following transformations (lone pairs, formal charge and curved arrows). (15 pts)



14. a. Show all possible products when 2R-chlorobutane is brominated with Br_2/hv? Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp^3 C-H bond are: primary = 1, secondary = 80, tertiary = 1600 and C-H on a carbon with chlorine = 2000. Identify any stereoisomers as enantiomers, diastereomers or meso structures. Specify the absolute configuration of any chiral centers(15 pts)

b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (15 pts)

Br—Br	46
H—Br	87
Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92
Cl-C-H	90
Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67
Cl-C-Br	67

Talent is God given. Be humble. Fame is man-given. Be grateful. Conceit is self-given. Be careful...
John R. Wooden