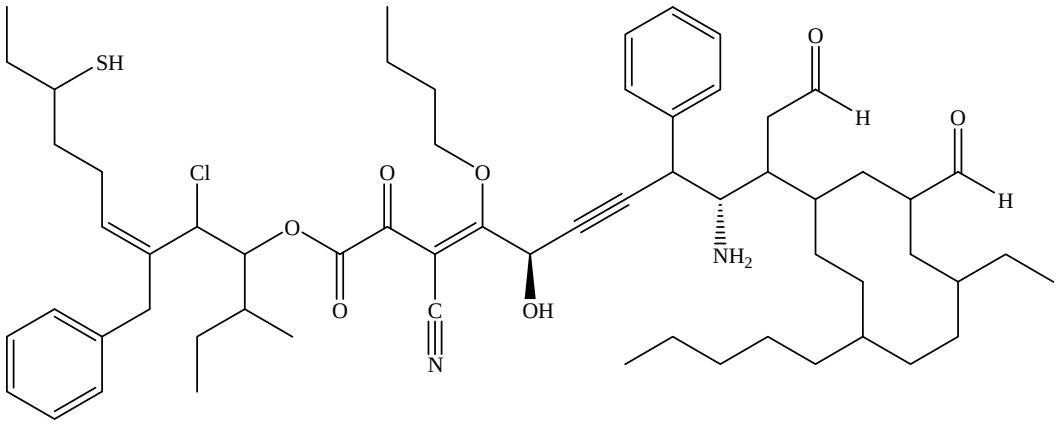
Chem 201 Final
Fall, 2012 Name _____
Beauchamp

Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure) (R/S and E/Z too)	30	
2. Types of Isomers, Degrees of Unsaturation	25	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	25	
4. Newman Projections, Conformational Energies	25	
5. Stereochemical Analysis	30	
6. 3D Structure, Hybridization, Angles, Shapes	25	
7. Forces of Interaction and Physical Properties	15	
8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge	30	
9. S_N/E Mechanisms, with all of the details	37	
10. S_N/E Mechanisms, predict the products	32	
11. Miscellaneous Reactions, predict the products	45	
12. Fill in all mechanistic details, curved arrows, lone pairs, formal charge, (One in acid and one in base)	30	
Total	349	

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.

The important thing is this: To be able at any moment to sacrifice what we are for what we could become.
Charles DuBois

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



2. Use the formula $C_6H_{13}NO$ to draw examples for each type of isomerism indicated. This will require that you draw at least two structures to show these differences. What is the degree of unsaturation? (25 pts)

skeletal isomers	positional isomers	functional group isomers
conformational isomers	enantiomers	diasteromers

3. Draw all possible chair conformations of trans-1-ethyl-2-methylcyclohexane. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the less 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 methyl group is 1.7 kcal/mole and 1.9 kcal for an ethyl group and a methyl/ethyl gauche interaction is 0.9 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

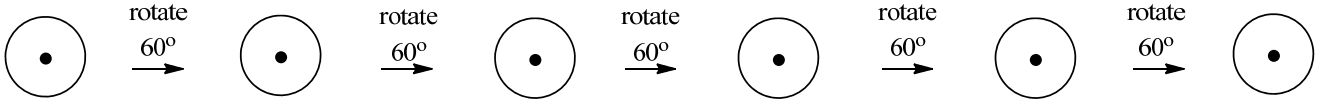
4. Use a Newman projection of the C4→C3 bond of 2,3-dimethylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table sbelow, calculate the relative energies of the different conformations. Plot 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. (25 pts)

2D structure

Eclipsing Energy Values (kcal/mole)	
H/H	+1.0
H/CH_3	+1.4
H/ethyl	+1.5
H/isopropyl	+1.6
CH_3/ethyl	+2.7
isopropyl/ethyl	+4.5

Gauche Energy Values (kcal/mole)	
CH_3/H	+0.0
ethyl/H	+0.1
isopropyl/H	+0.2
CH_3/ethyl	+0.9
ethyl/isopropyl	+1.6

most stable conformation



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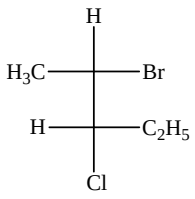
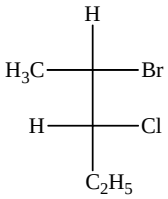
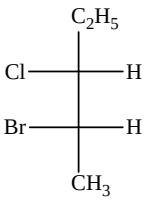
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify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



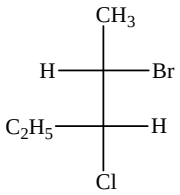
A



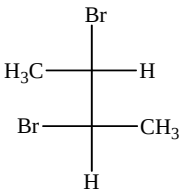
B



C



D



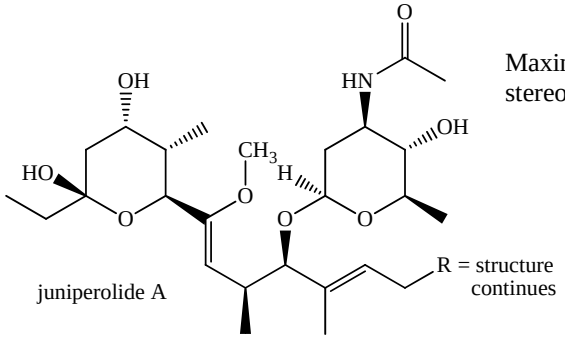
E

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 2-bromo-3-chloropentane as Fischer projections, which are not shown above. If there are none, indicate this.

i. Would anything change if, in compound D, the Br was replaced with a Cl group? How if a Br was replaced with a Cl in compound E?

j. A novel polyketide, juniperolide A, was isolated from a species of streptomyces and its structure determined. 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. 2012, Nov. ASAP article)

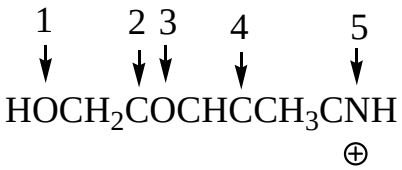


juniperolide A

Maximum possible stereoisomers = _____

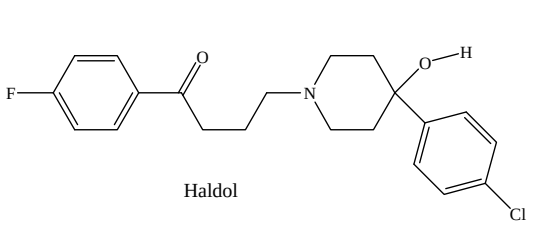
The complete formula is $C_{39}H_{67}NO_{10}$.
What is the degree of unsaturation?

6. Draw a 3D structure for the following molecule. 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. (25 pts)

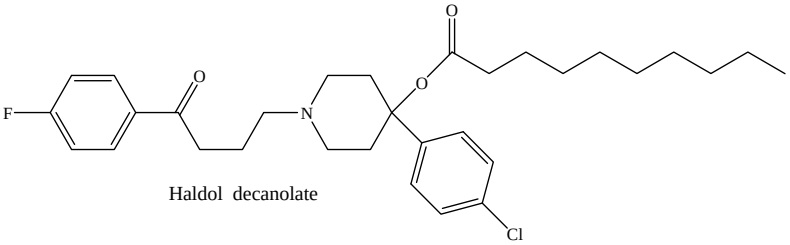


Atom	Shape	Hybridization	Bond Angles	# σ bonds	# π bonds	# lone pairs
1						
2						
3						
4						
5						

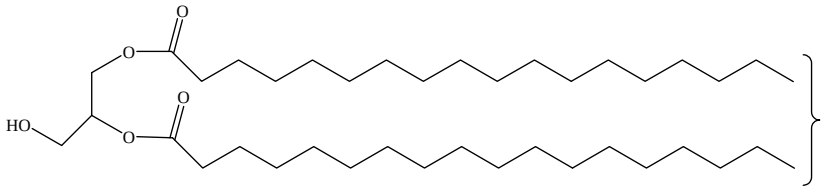
7. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. It has also been used in birds, such as parrots who continually pluck out their feathers. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). A decanoate ester prodrug was prepared to increase Haldol's lifetime in the body. (Cell membranes are composed of a lipid bilayer having large amounts of diglyceride alkane-like fatty acid chains.) When injected intramuscularly haldol decanoate's anti-psychotic activity lasts about 1 month. Provide an explanation for its longer lifetime. (15 pts)



Haldol



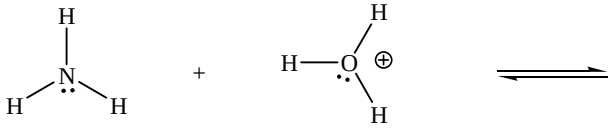
Haldol decanolate



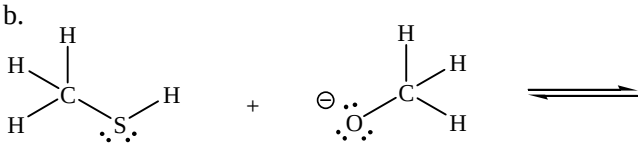
Typical membrane lipid

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)

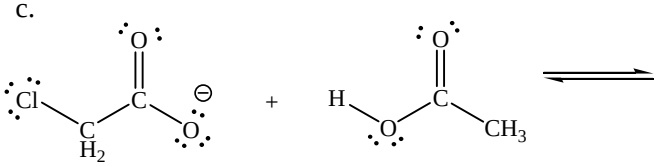
a.



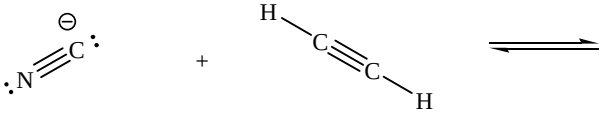
b.



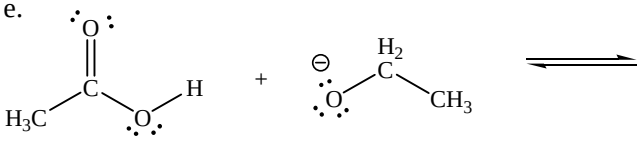
c.



d.

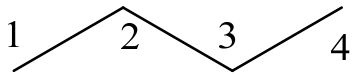


e.



9. Use (2S,3R)-2-bromo-3-deuteriobutane 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. (37 pts)

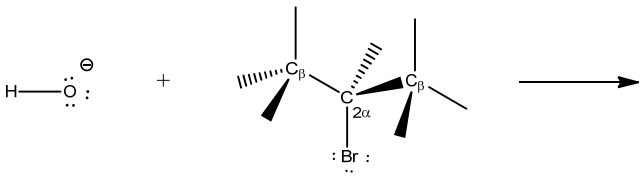
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (2 pts)



2D structure

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

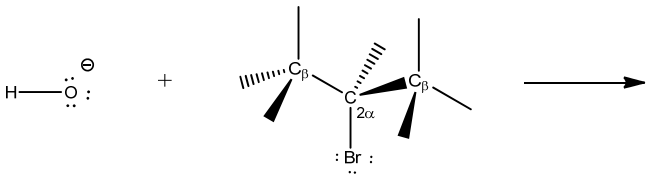
b. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (5 pts)



mechanism

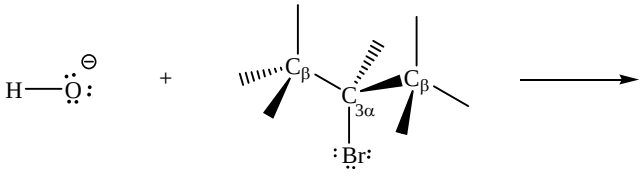
configuration in product

c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (10 pts)

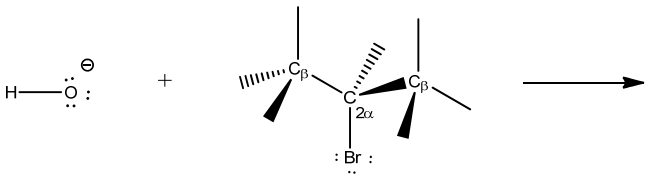


mechanism

configuration in product

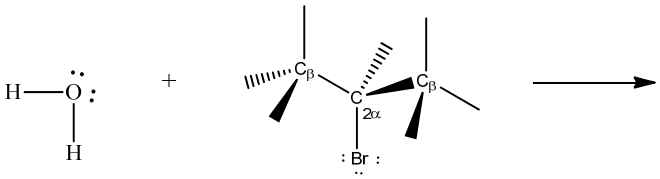


configuration in product



configuration in product

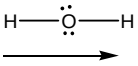
d. Show the S_N reaction (what kind?). You can use one intermediate to show all possible mechanistic S_N possibilities. Indicate absolute configuration(s) of the C_α center in your product(s). (10 pts)



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 and just draw the additional possible products. (10 pts)

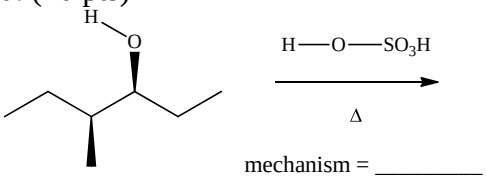


mechanism

E or Z

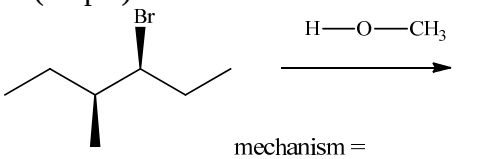
10. Indicate the major reaction mechanism in each reaction below and write an arrow-pushing mechanism (include the usual mechanistic details). If a certain 3D arrangement is required for the reaction to proceed, show it. If multiple products form by one type of mechanism, just show the mechanistic sequence for the major product and draw the other expected products. Do not consider rearrangements. (32 pts)

a. (10 pts)



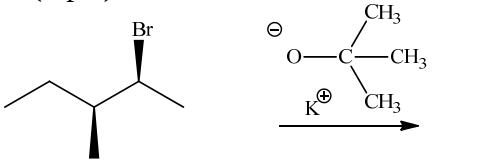
mechanism = _____

b. (10 pts)



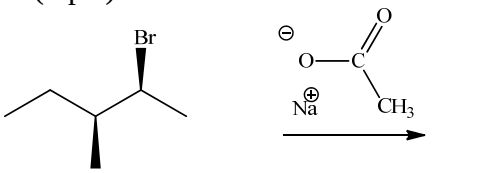
mechanism = _____

c. (6 pts)



mechanism = _____

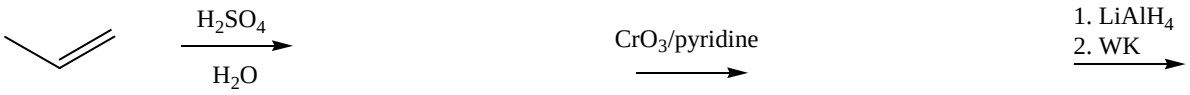
d. (6 pts)



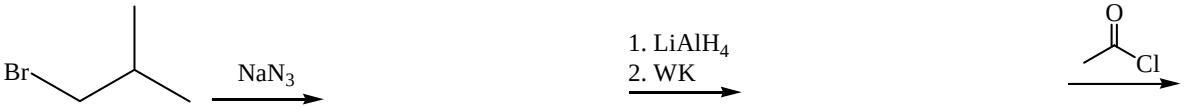
mechanism = _____

11. Provide the expected product for each of the following reactions. Do NOT show mechanisms. WK = workup (45 pts)

a.



b.



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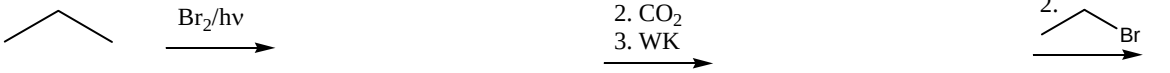

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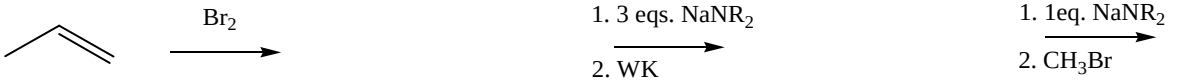
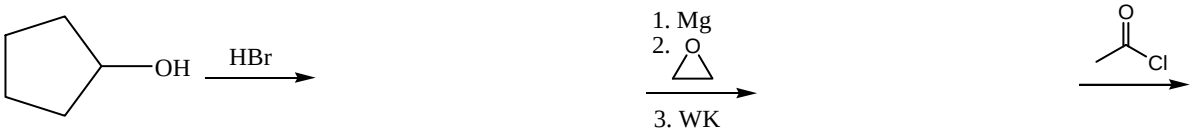
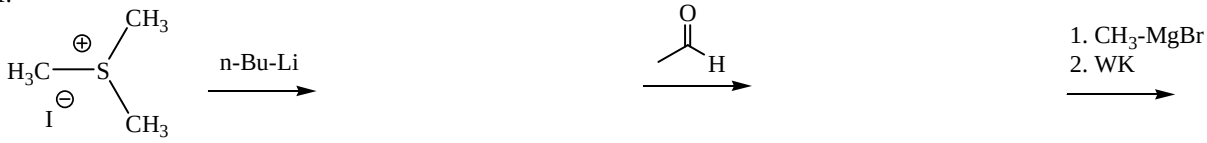


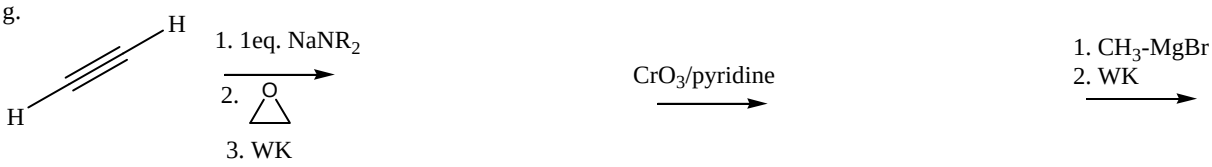
e.



f.

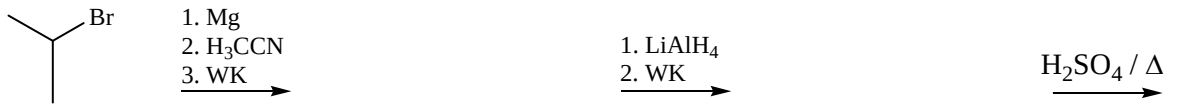


g.

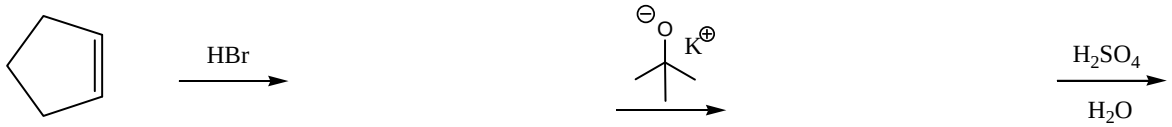


h.

i.

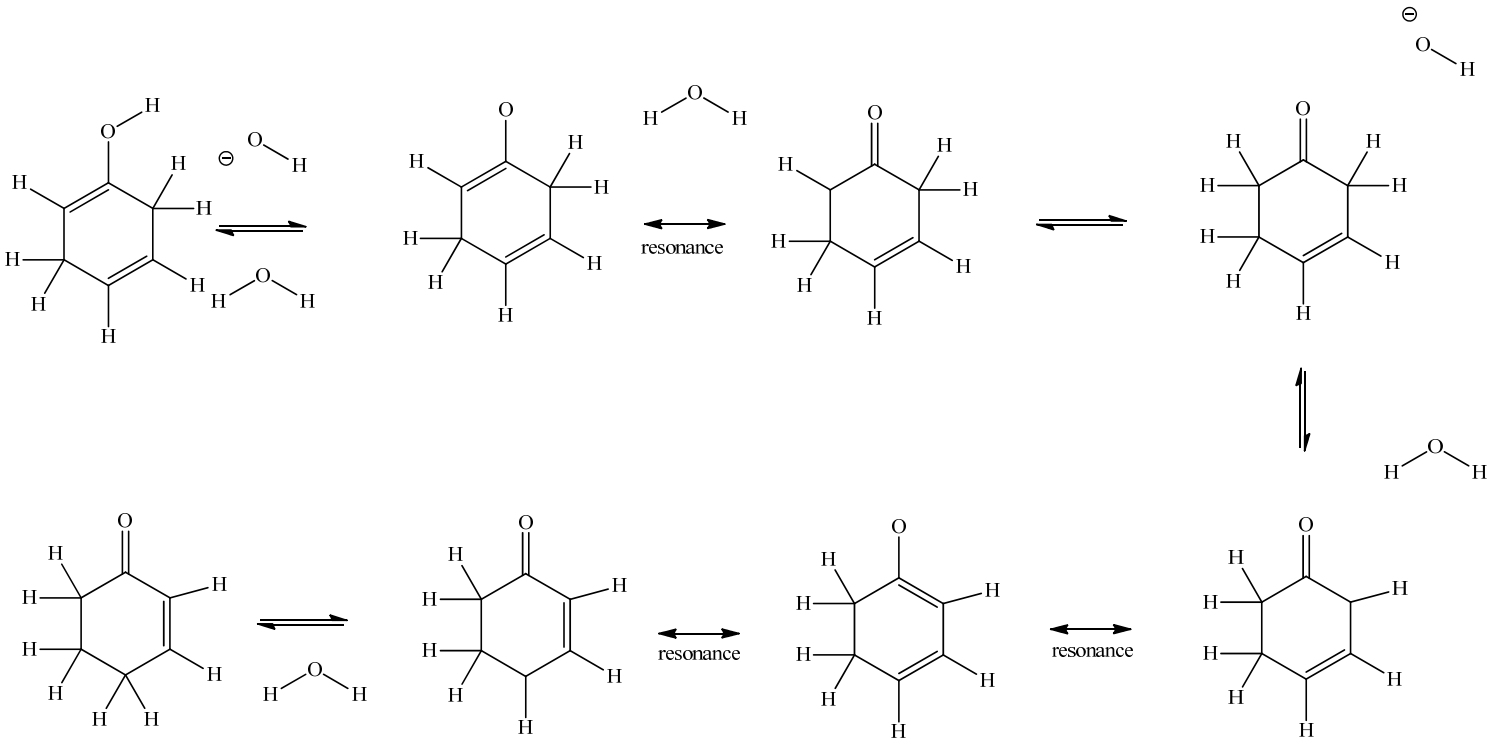


j.



12. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations. (30 pts)

a.



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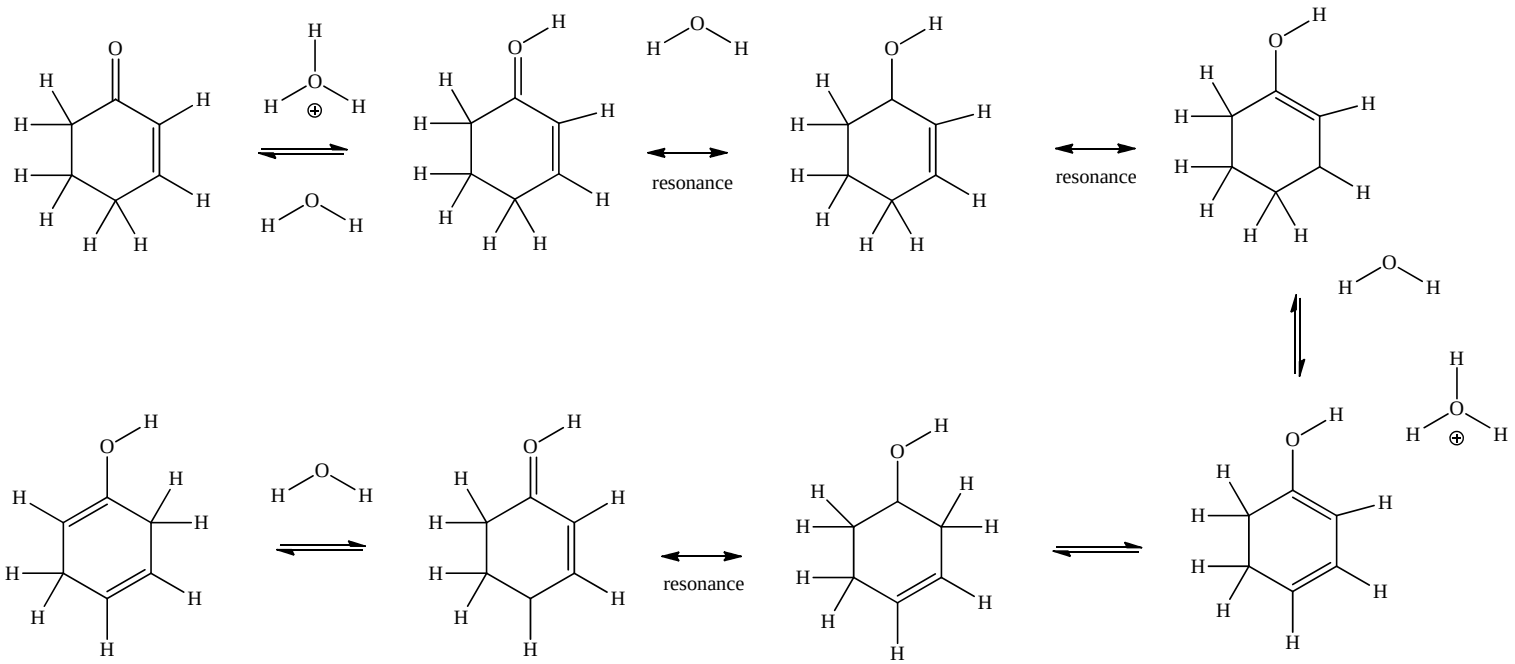
b.



Nothing is easy to the unwilling. - Nikki Giovanni