California State Polytechnic University, Pomona

Chem 315
Midterm Exam **Name: _____**
Fall, 2015
Beauchamp

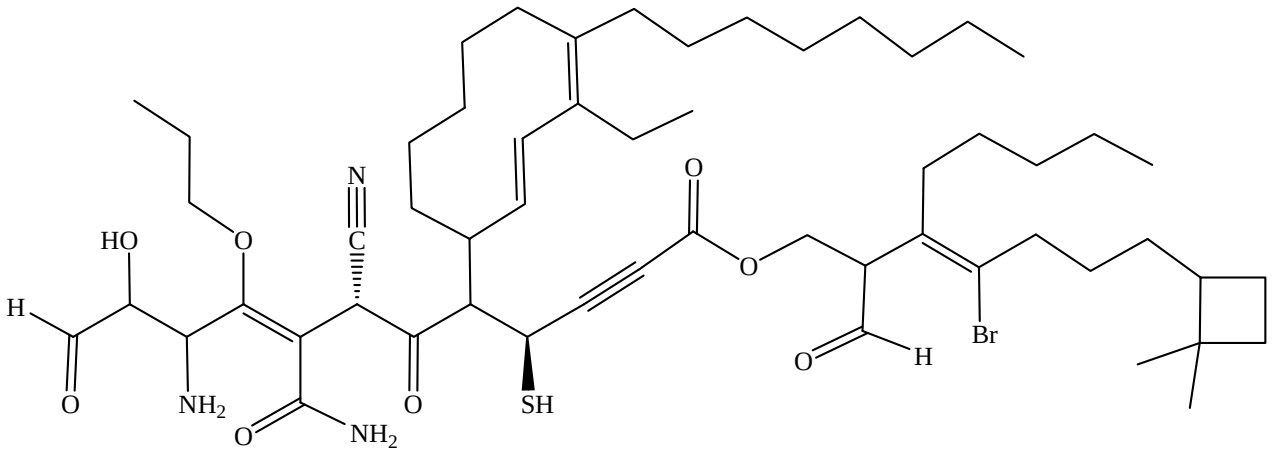
Topic	**Total Points**	**Credit**
1. Nomenclature (1)	30	
2. Relative reactivity of C=O functional groups	20	
3. Reactions Page (10 x 3 = 30 reactions)	30	
4. Tautomeric mechanisms, arrow pushing, proton transfers, resonance, one in acid and one in base	30	
5. Multistep syntheses using the reactions learned thus far in the course (2 target molecules, use organometallics)	30	
6. Complete details of S_N1/E1 and S_N2/E2 reactions. Stereochemistry, arrow pushing, carbocations,	34	
7. Two Arrow-Pushing Mechanisms, one in acid and one in base	30	
Total	204	

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. In mechanism problems, draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. When resonance is present, draw at least two resonance structures, including the best one. Only write answers in the space available. Do your best to show me what you know in the time available.

"Do not dwell on the past, do not dream of the future, concentrate the mind on the present moment."
Buddha

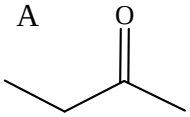
California State Polytechnic University, Pomona

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

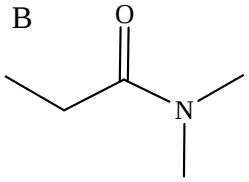


2. What is the relative order of reactivity of the following functional groups? Explain your answers. Predict the expected product when reacted with an appropriate amount of methyl lithium, followed by normal workup. (20 pts)

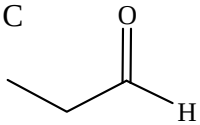
A



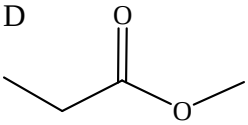
B



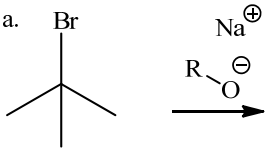
C

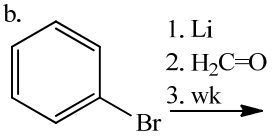


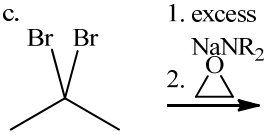
D

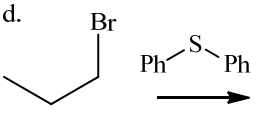


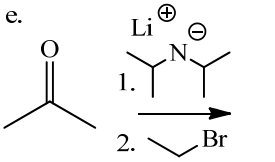
3. Fill in the missing product or reagent, as needed, for each reaction below. Do not waste time by writing mechanisms or thinking too much on any one part. (30 pts)

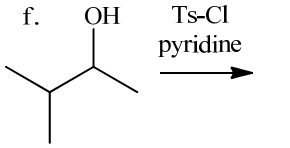
a. 

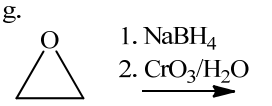
b. 

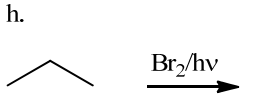
c. 

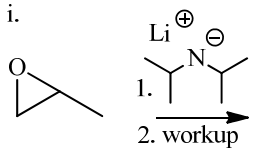
d. 

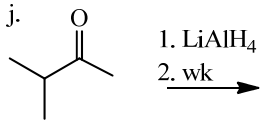
e. 

f. 

g. 

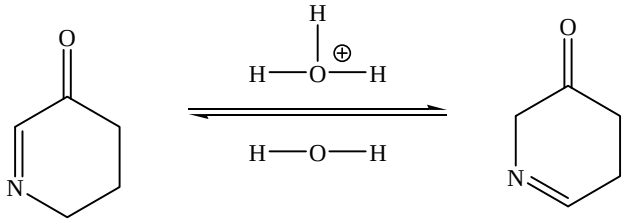
h. 

i. 

j. 

4. Provide a complete arrow-pushing mechanism for the following transformations (curved arrows, lone pairs, formal charge and at least 2 resonance structures, including the "best" one). Restrict your tautomeric changes to keto or enol portions of the molecules, not isolated carbon-carbon double bonds. (30 pts)

a.



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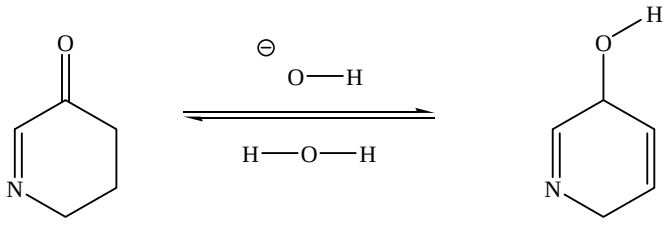
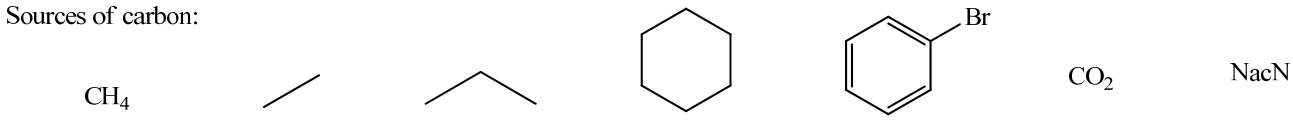
b.

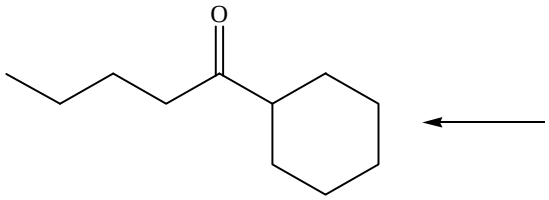


5. Propose a reasonable synthetic method to accomplish the following transformations using the given structures and any additional materials available from our course. Show a reaction arrow with appropriate reagents and the product for each step of your synthesis. Do not show mechanisms. (15 pts each)

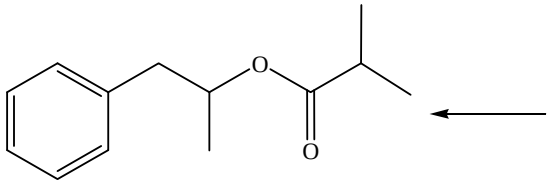
Sources of carbon:



a.

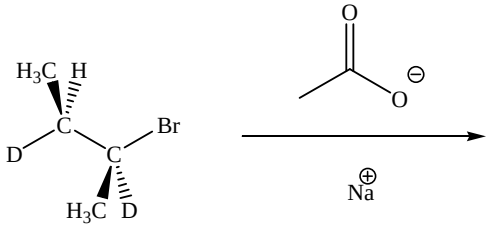


b.



6. Indicate the major reaction mechanism in each reaction below and write an arrow-pushing mechanism, using 3D structures. Assume that if a more stable intermediate can form, it will generate the major product(s). If multiple products form the most stable intermediate, just show the mechanistic sequence for the major product and draw the other expected products. Specify R/S and/or E/Z in parts a and b. (30 pts)

a. (7 pts)



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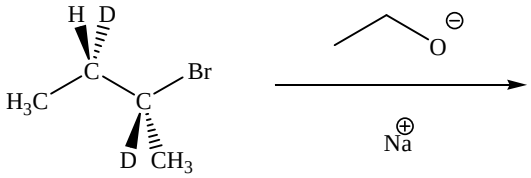
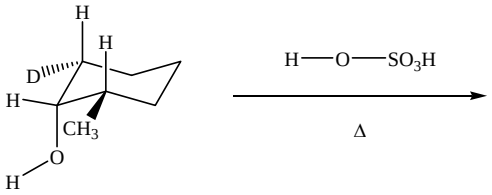


c. (10 pts)



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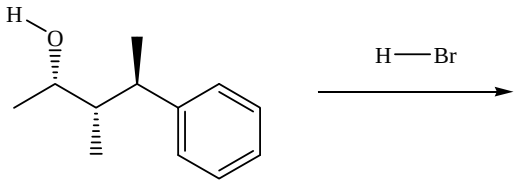
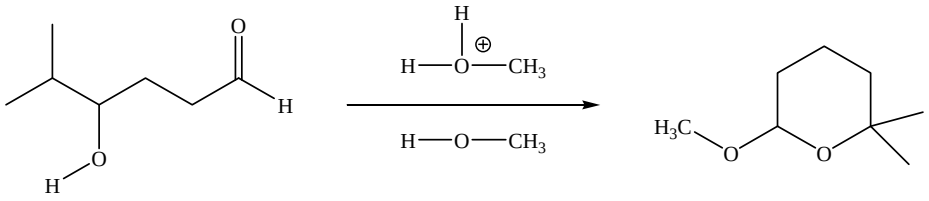


6. a. Write a complete mechanism for each of the following reactions. Be careful where you begin. It might help if you number the carbons to see where changes have occurred. (15 pts each)



b. State what side each equilibrium lays and state a very brief explanation for your answer. Add in any necessary arrow pushing details to complete the reaction and show how the reaction occurs. (10 pts)

"Believe you can and you're halfway there." Theodor Roosevelt

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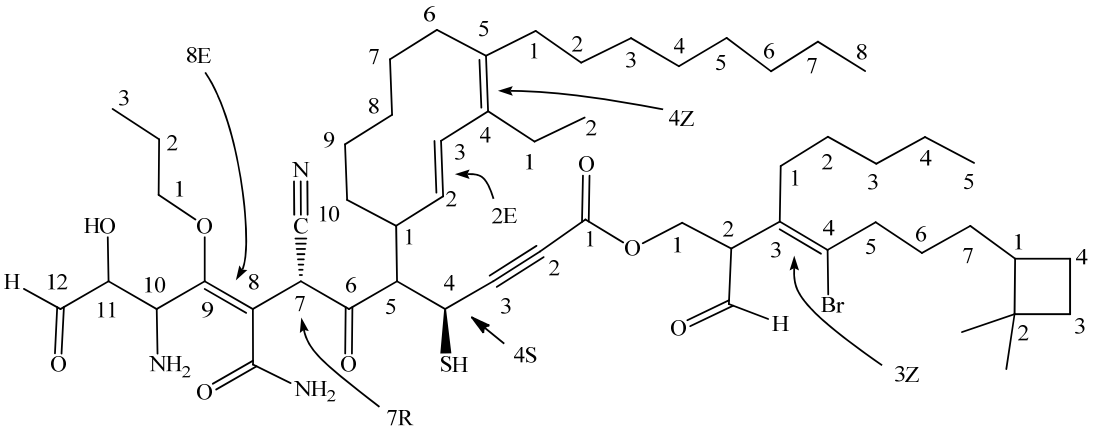
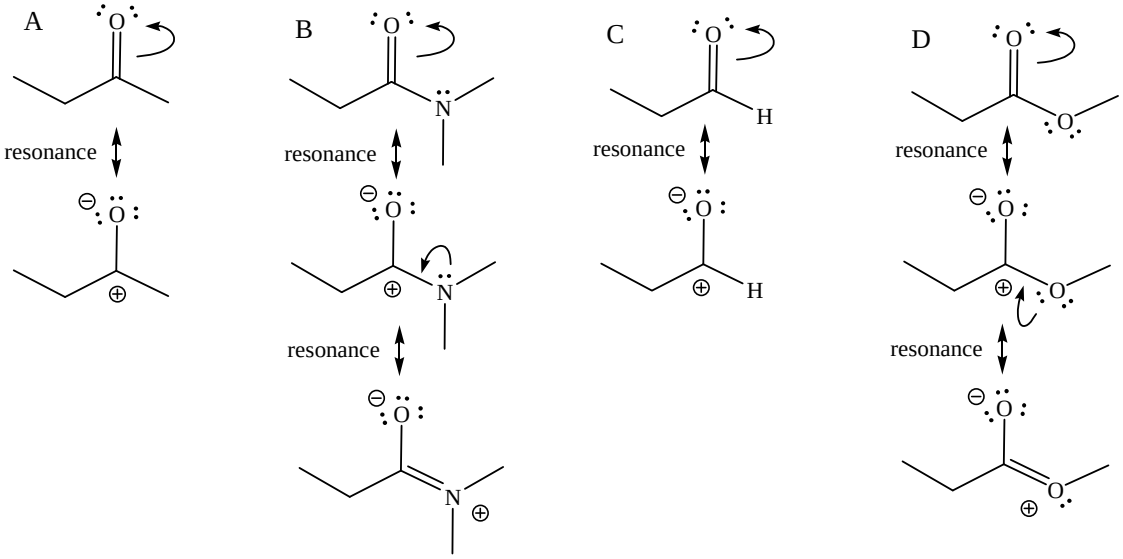


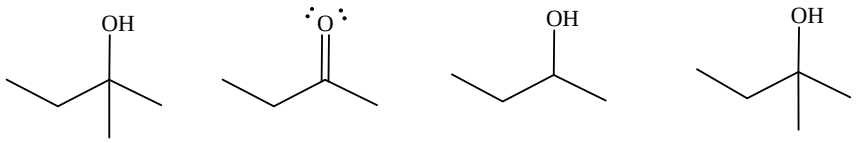
2-formyl-3-pentyl-4-bromo-7-(2,2-dimethylcyclobutyl)hept-3Z-enyl 4S-mercapto-5-(4-ethyl-5-octylcyclodeca-2E,4Z-dienyl)-6,12-dioxo-7R-cyano-8-amido-9-propoxy-10-amino-11-hydroxydodec-8E-en-2-ynoate

5. What is the relative order of reactivity of the following functional groups? Explain your answers. Predict the expected product when reacted with an appropriate amount of methyl lithium, followed by normal workup. (20 pts)



The relative reactivity is decided on the basis of δ+ charge on the carbonyl carbon. The aldehyde carbon has the largest δ+ charge. It only has one "R" group, while the ketone has two "R" groups. The R groups are inductively donating and help spread out the δ+ away from the carbonyl carbon (can also argue hyperconjugation). Also, the ketone has two R groups making the tetrahedral intermediate more crowded, and slower reacting. Both the ester and the amide have a third resonance structure (better than the second resonance structure). This moves the δ+ off the carbon and on to the heteroatom (N > O), which reduces the reactivity of the ester and amide. Since nitrogen is less electronegative than oxygen, it is better at donating its electron density and reduces the δ+ most of all and is least reactive.
Order of reactivity = C > A > D > B.

Products after reaction with CH_3Li, workup.



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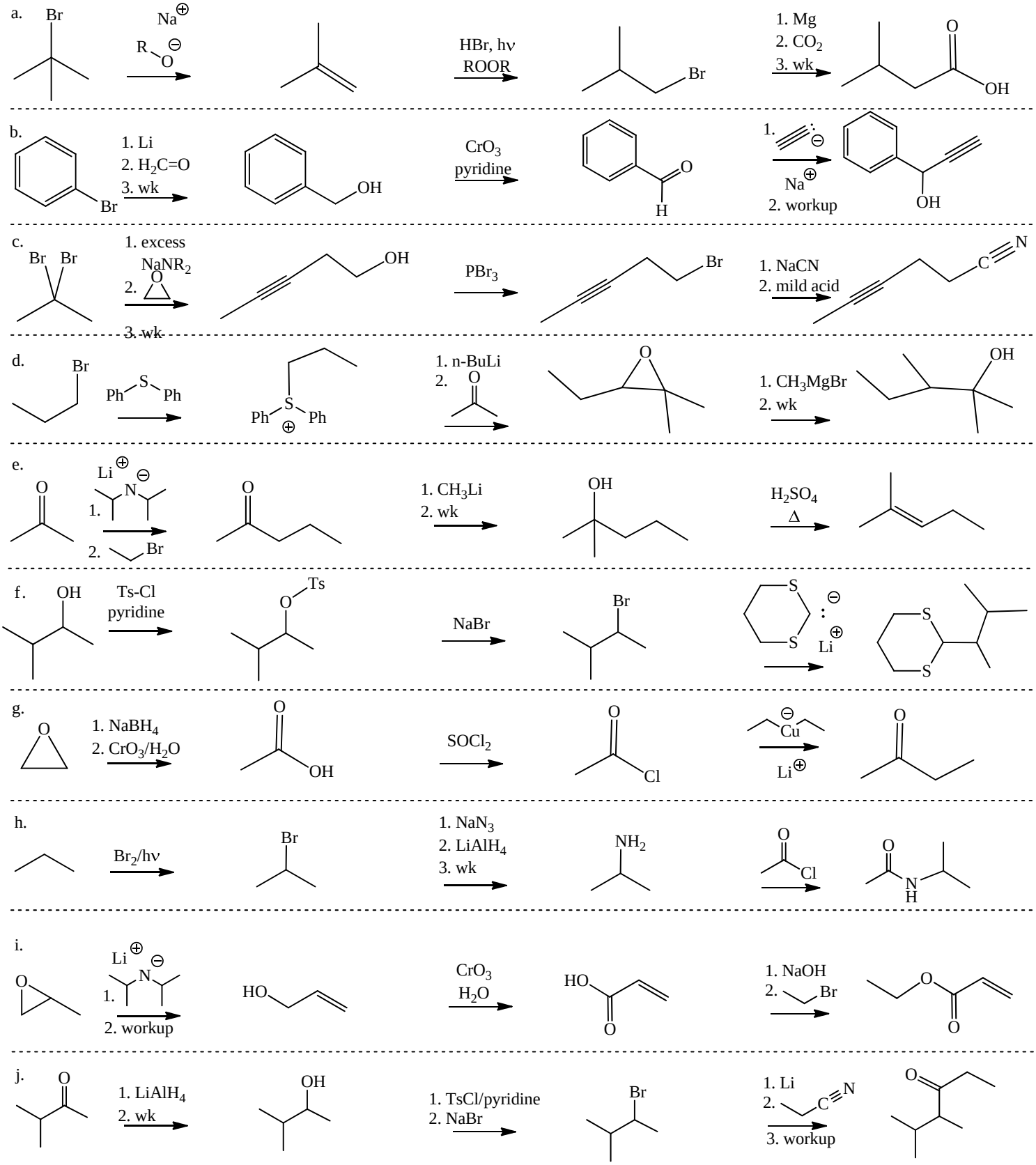

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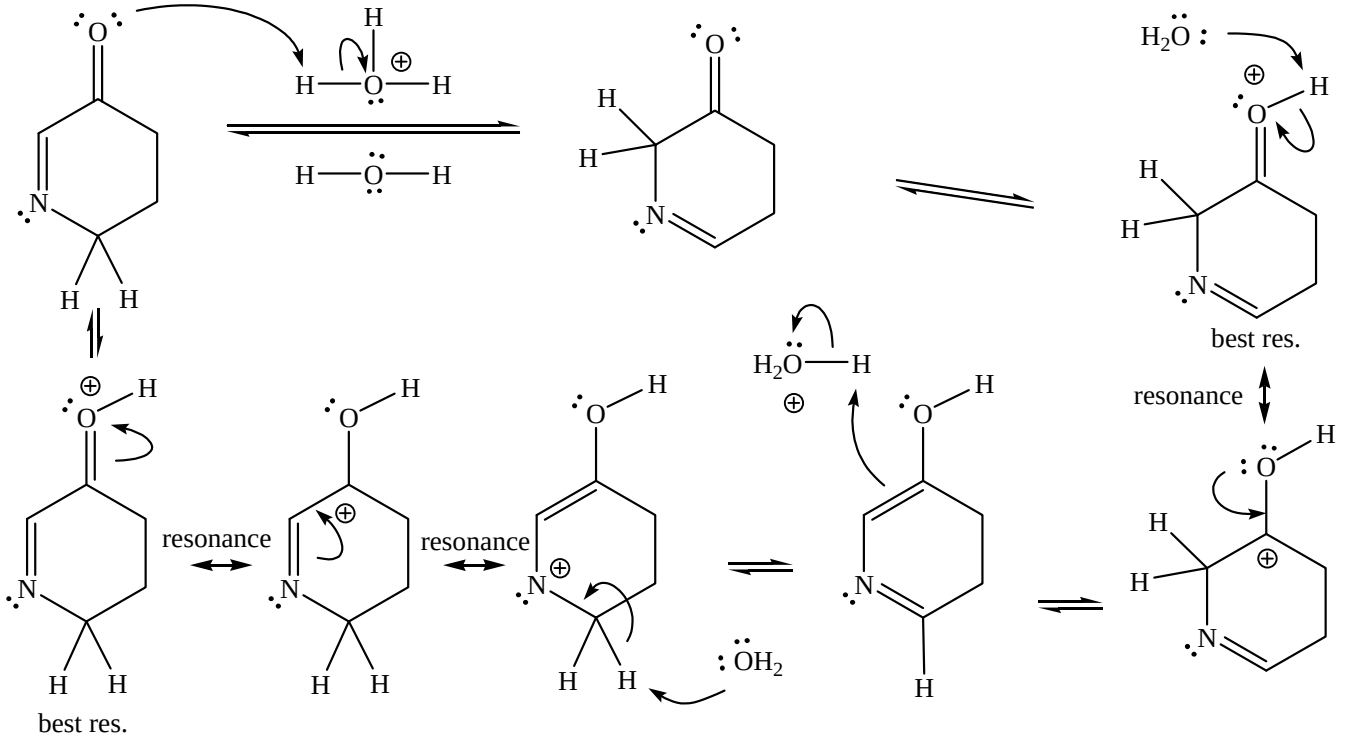

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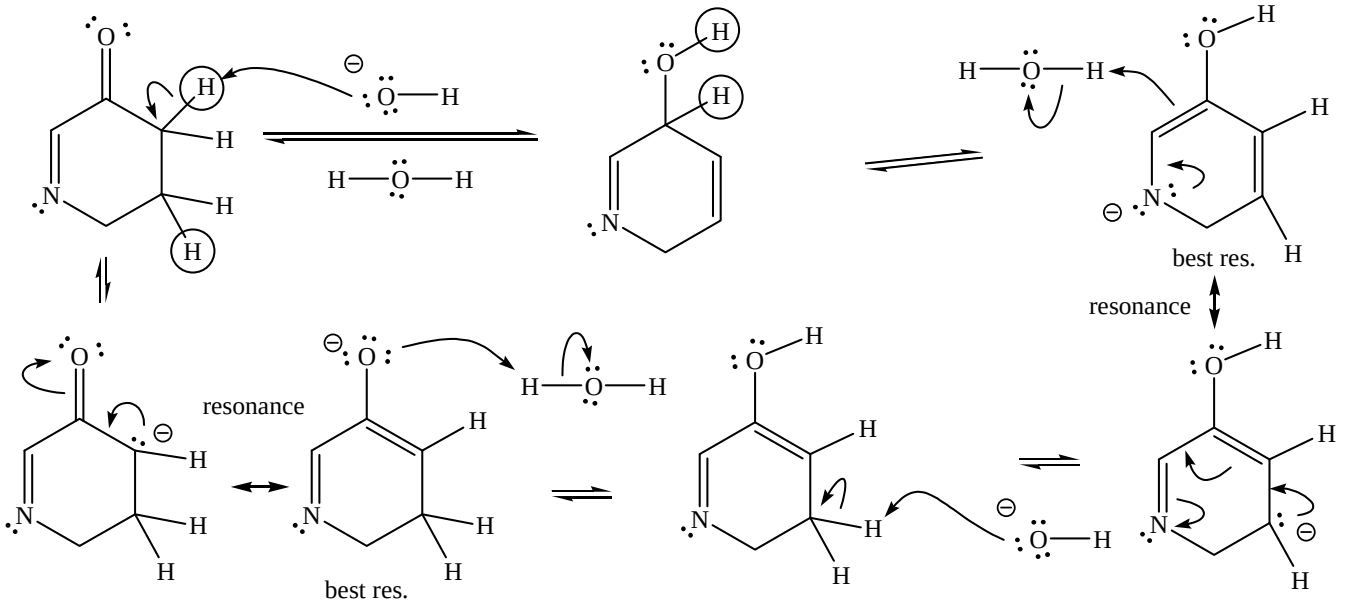

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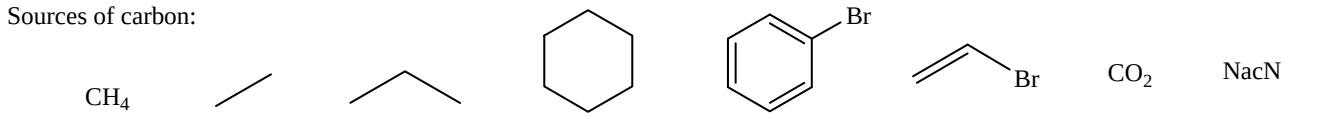
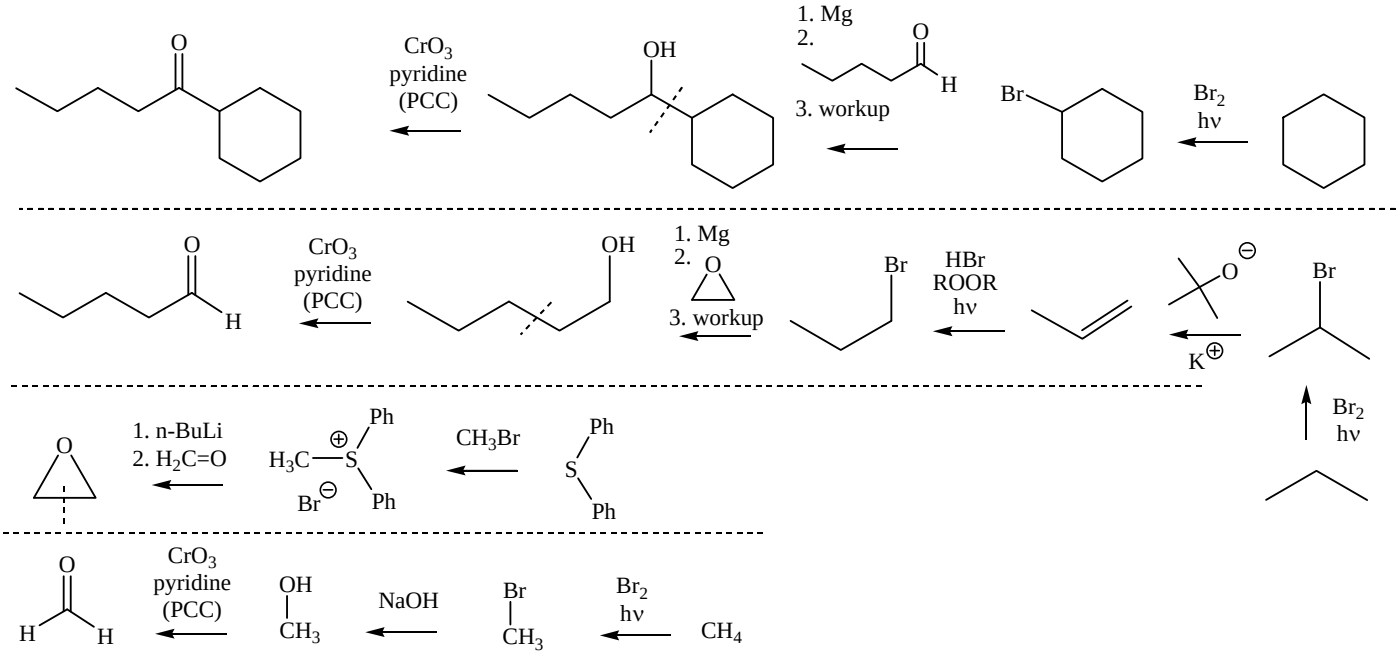


a.



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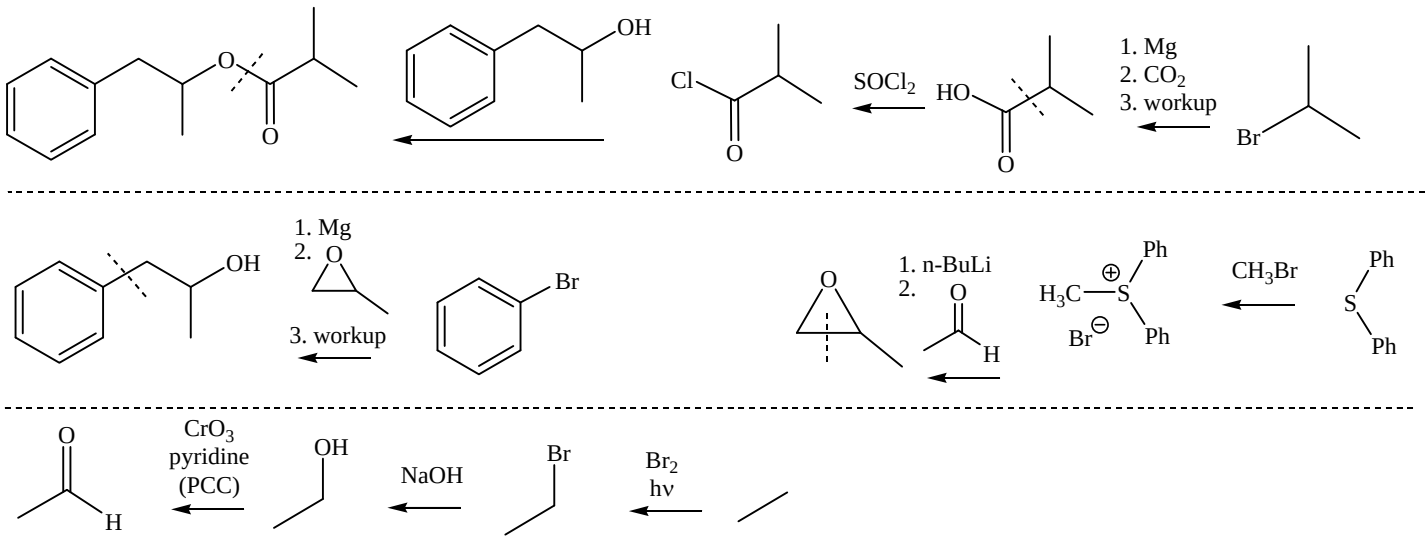

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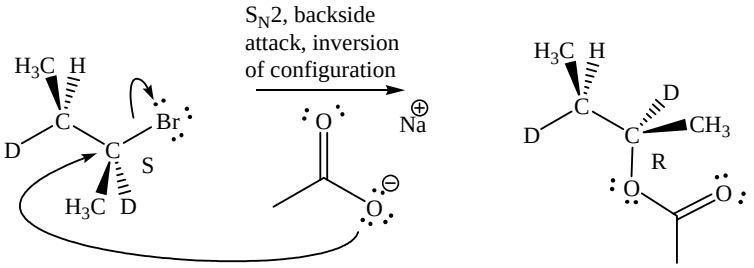
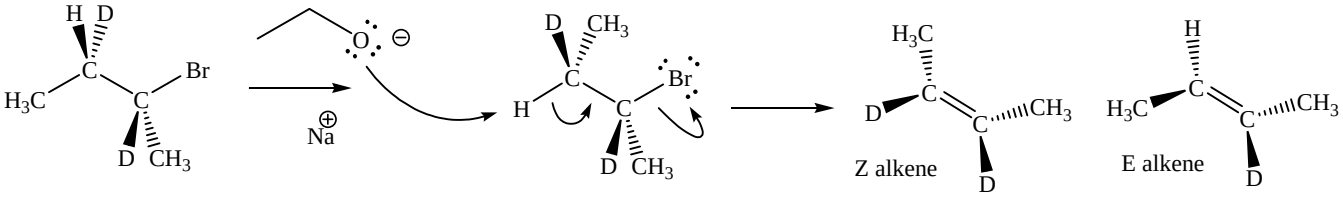
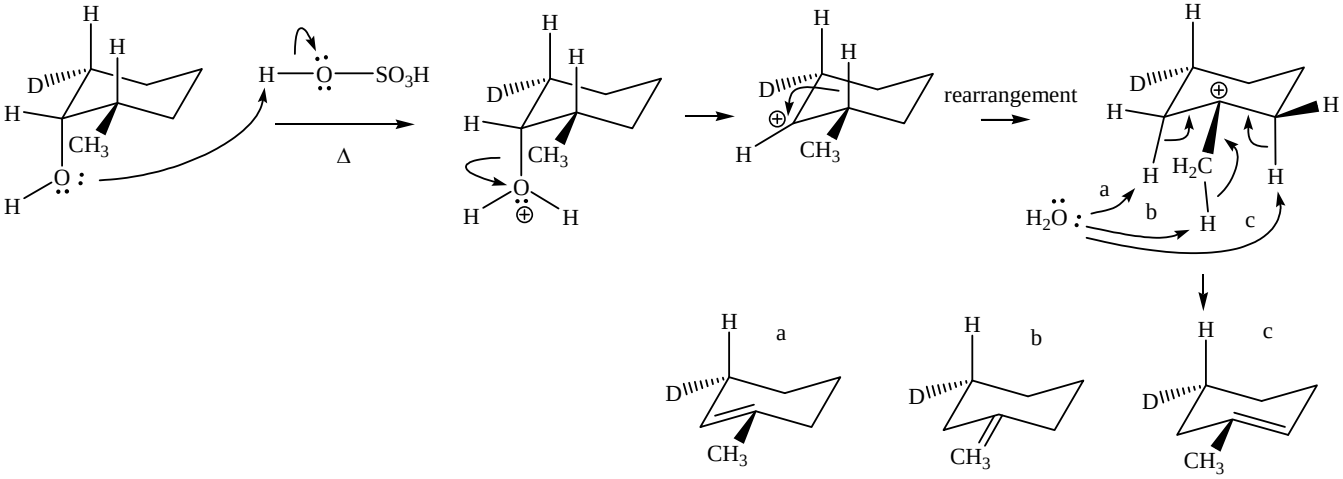


b. (7 pts)



E2, rotate H or D to anti position

c. (10 pts)



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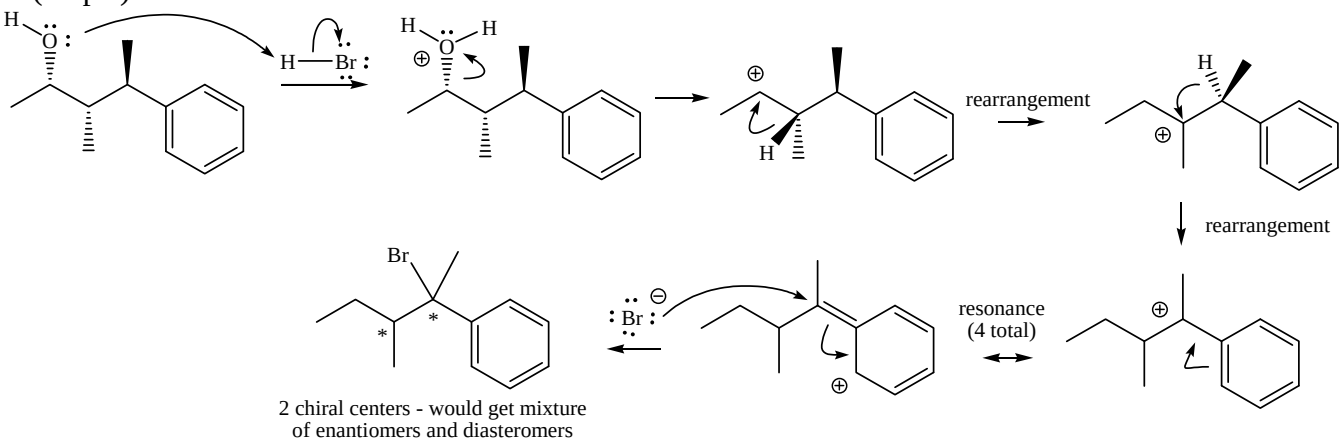
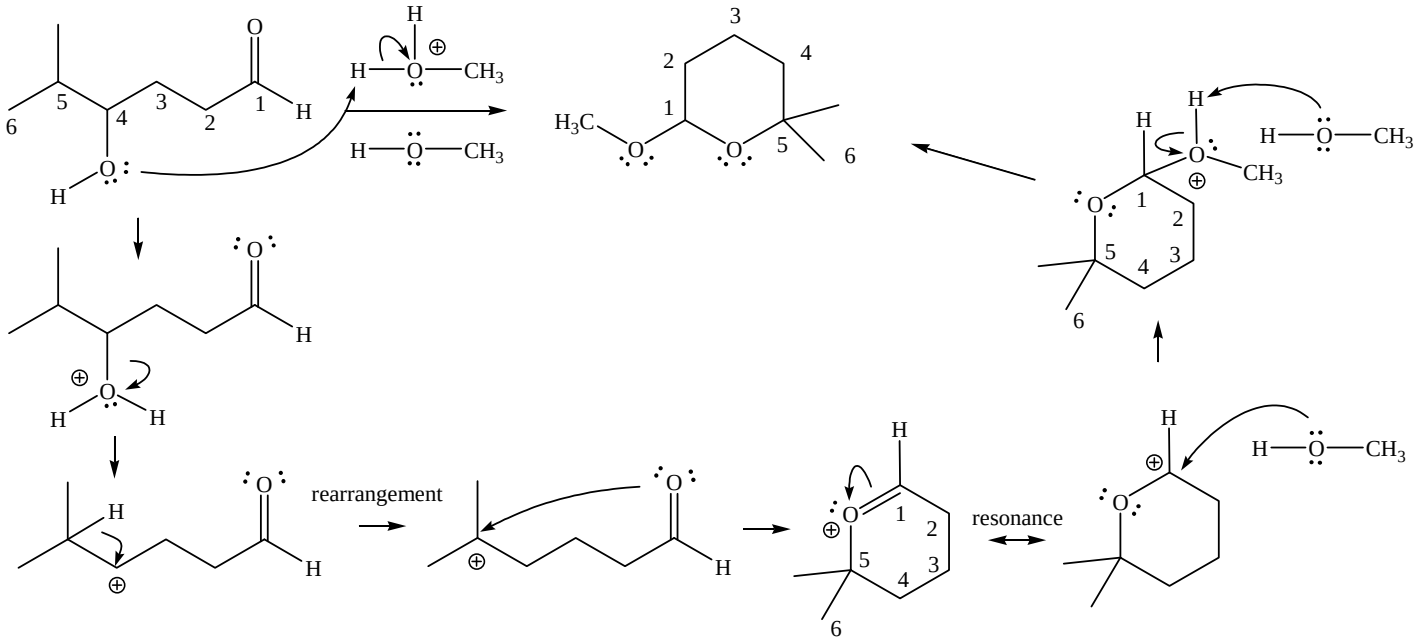


2 chiral centers - would get mixture
of enantiomers and diasteromers

7. a. Write a complete mechanism for each of the following reactions. Be careful where you begin. It might help if you number the carbons to see where changes have occurred. (15 pts each)



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